N-Vinylcaprolactam based Bulk and Microgels: Synthesis, Structural Formation and Characterization by Dynamic Light Scattering

DISSERTATION

For the academic degree
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From
DC Volodymyr B. Boyko
Born on 8. November 1978 in Kalush, Ukraine

Referees:
1. Prof. Dr. rer. nat. habil. Karl-Friedrich Arndt
2. Prof. Dr. rer. nat. habil. Erik Geissler
3. PD Dr. rer. nat. habil. Martin Helmstedt

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To my parents
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<tr>
<td>φ</td>
<td>volume fraction</td>
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<tr>
<td>wt.-%</td>
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<td>glass transition temperature</td>
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<tr>
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<td>temperature of phase separation</td>
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<td>$\theta$</td>
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<td>$R_g$</td>
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<tr>
<td>$\Gamma$</td>
<td>first cumulant</td>
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<tr>
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<tr>
<td>$\eta_0$</td>
<td>viscosity of solvent</td>
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<tr>
<td>PD.I</td>
<td>polydispersity index</td>
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<tr>
<td>$C$</td>
<td>concentration</td>
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<td>rotation diffusion coefficient</td>
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<tr>
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<tr>
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<td>styrene</td>
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<tr>
<td>PEGMA</td>
<td>$\omega$-hydroxy poly(ethylene glycol methacrylate)</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>AAEM</td>
<td>acetoacetoxyethyl methacrylate</td>
</tr>
<tr>
<td>HEMA</td>
<td>hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>AMA</td>
<td>allyl methacrylate</td>
</tr>
<tr>
<td>AMPA</td>
<td>2,2'-azobis(2-methylpropyramidine) dihydrochloride</td>
</tr>
<tr>
<td>CP</td>
<td>$N$-Vinylcaprolactam/ $N$-Vinylpyrrolidone</td>
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1. Introduction and the Aim of the Work.

Cross-linked polymers (polymer networks) are an important class of materials. Network formation occurs usually via polymerization of bi- and multifunctional monomers. However, it does not necessarily require covalent bond formation. Network can be formed by cross-linking of polymer chains by the secondary forces such as hydrogen bonding or coulombic interaction. FLORY [1] has proposed to subdivide networks into four classes:

- Well ordered lamellar structures (soap gels, phospholipids and clays)
- Covalently bonded networks, completely disordered
- Networks formed through physical aggregation (crystallization, complexation, helix formation), predominantly disordered (natural thermoreversible networks)
- Particulate, disordered structures (globular and fibrillar protein gels)

When a polymer network is in contact with a liquid, the network starts to swell due to the thermodynamic compatibility of the polymer chains and solvent. As result, gel is formed. Gels consist of a large liquid fraction and a very small polymer component. There is no universal definition of the term “gel” up to now and according to different authors [2-4] gel can be defined as:

- Swollen matter with three dimensional network structure that are insoluble in any solvent
- The gel is the soft, solid-like material of two or more components, one of which is liquid, present in substantial quantity
- A substantially diluted system which exhibits no steady state flow

With respect of the size of gels there are microgels and macrogels. When concentration of monomers or initial polymer is large enough gels fill whole volume and called macrogels or bulk gels. These bulk gels consist of one huge macromolecule formed by connection of polymer chains via cross-linking.

In diluted solution, the distance between different molecules is too large for the formation of the long range intermolecular cross-linking. This leads to formation of microgels. Microgels consist of one or several macromolecules in which each of the polymers holds cross-linked unit. It makes them fundamentally different from polymer solution (sol) in which macromolecules are homogeneously dissolved in the solvent. The microgels can be prepared with a narrow particle size distribution in the submicron size range.

When water is the swelling agent for gel it is called hydrogel. In the recent years, the unique physical properties of synthetic hydrogels have been exploited in number of the interesting
and novel applications. Because hydrogels have the capacity to contain a large volume of the solvent in the swollen state, they have been used in the variety of superabsorbent materials. Separation and filtration devices for small ions and large molecular weight macromolecules have been fabricated from these materials. Porous hydrogels have been prepared for three-dimensional cellular scaffoldings, soft contact lenses and artificial lenses. The application of hydrogels in medicine, agriculture, food preparation, cosmetic industry continues to grow [5 - 10].

Certain hydrogels are sensitive to the change of the external condition (temperature, pH etc.). As result of this sensitivity they can pass through the swollen to the shrunken state after some critical point. When the temperature is the stimuli, this point is called lower critical solution temperature (LCST). Special interest is focused on the hydrogels based on polymers, which have LCST near the temperature of the human body. The temperature-responsive nature of these polymers leads to a variety of biological applications. Hydrogels made from these polymers have been considered as drug delivery devices, materials for tissue engineering and materials for preventing surgical adhesion [11]. Phenomena of the thermo-sensitivity was intensively studied using as model poly(\(N\)-isopropylacrylamide) (NIPAM) as polymer or as cross-linked systems. Poly(vinyl methyl ether) (PVME) is also considered as material for preparation of the networks with the similar properties.

Poly(\(N\)-vinylcaprolactam) (PVCL) is the polymer from the group water-soluble poly(\(N\)-vinylamides) (PVAm). The properties of PVAm are intensively studied and summarized in several books and reviews [12-15]. Between PVAm there are several polymers with the LCST in water in the range of 32-80°C. Thermo-sensitivity of PVCL was observed in 1957 by SHOSTAKOVSKI et al. [16]. PVCL has LCST in the physiological range of around 32°C. It is biocompatible and materials based on this polymer can be potentially used in biomedical application. This polymer and its thermo-sensitive properties were relatively well studied but despite its long history the first hydrogel based on PVCL was reported only in 1996 [17]. This fact promises a wide field for synthesis and study of the novel cross-linked systems based on PVCL with different size and properties.

Due to its small size (0.05-1\(\mu\)m) microgels reacts on the change of environment during some microseconds instead several hours for hydrogels with dimension of several mm. This makes them attractive for investigation. The study of environment responsible microgels gives the advantage to investigate the same well-defined object in different conformational state (swollen, shrunken and aggregated states). The microgel is the interesting object not only from point of view of application but also from theoretical point of view. Due to the presence
of cross-links its properties in solution differ from these of polymer in solution, even from hyperbranched one. Static and dynamic light scattering methods, especially dynamic light scattering (DLS), are very convenient techniques for measuring swelling of microgels. The first DLS data for polyNIPAm microgels as functions of temperature and electrolyte concentration were published by Pelton et al. [18]. However, in the most cases DLS is used only for determination of hydrodynamic radius at the single angle of observation, which not always gives correct information. Light scattering methods, especially combination of dynamic and static light scattering, can give not only size but more information about microgel conformation and internal structure.

The light scattering, especially DLS, is the interesting method not only for characterization of microgels or even bulk gels but it can be also considered as nondestructive method for evaluation of the gel point. According to recent work of Shibayama [19], there are no systematic studies on real time and nondestructive gel point determination in the literature. The well-known rheological method of determination of the gel point was developed by Winter [20]. Up to now, this method was not applied for radical cross-linking polymerization. Radical reaction is relatively fast. It is difficult, when not impossible, to stop reaction at the desired point. That is why, in situ determination of the gel point should be done. This kind of rheological measurements not often used in praxis. Since DLS is sometimes called micro-rheology, the relation between both methods should be observed during gelation. Shibayama pointed out, that the problem of comparison of the results obtained during gelation from DLS and rheology is not settled at all.

The aim of this work is the synthesis and characterization of networks based on homo- and copolymers of N-vinylcaprolactam. The dimension of gels will be varied in the nanometer (microgels) and millimeter (bulk gels) range. The characterization of these materials will be focused on investigation of both processes, phase transition of microgels and the monitoring of bulk network formation, by light scattering techniques. To achieve this aim the following facts should be taken into consideration.

- The important moment in preparation of the thermo-sensitive microgels is prevention of their aggregation during formation as reaction is carried out at a temperature above LCST and attractive forces between polymer chains are dominant. It is difficult to find the stabilizer, which is able to stabilize microgel dispersion and from other side does not affect properties of the microgel. Formation of PVCL microgel in presence of “neutral”, nonionic, stabilizer will be studied in this work. The thermo-sensitive properties of resulting microgel and its colloidal stability will be examined with DLS and the sedimentation method.
1. Introduction and the Aim of the Work

- The introducing of the reactive functional groups in the thermo-sensitive microgels is able to make the range of their application broader but, normally, comonomer with hydrophobic or hydrophilic nature influences the thermosensitive properties. This effect can be desired in the case of regulation of LCST or undesired when resulting microgel should keep the properties of the thermo-sensitive polymer. The core-shell morphology of the particle is able to separate the thermo-sensitivity and functionality in the same microgel. Microparticles based on VCL and acetoacetoxyethyl methacrylate (AAEM) or styrene will be prepared in this work. Their properties will be studied by light scattering and microscopical methods.

- The introducing of cross-linker should reduce the flexibility of polymer chains in microgel network. Some aspects of the internal dynamic of microgel based on PVCL and PVP in solution will be discussed in the terms of angular dependence in light scattering.

- The rate of radical cross-linking polymerization depends on the reactivity of monomers and functionality of cross-linker. The study of in situ formation of hydrogels by radical polymerization will be done in this work. Bulk gelation of PVCL hydrogel and copolymeric hydrogels based on PVCL and hydroxyethyl methacrylate (HEMA) will be studied by the DLS. The preparation and swelling properties of copolymeric hydrogel will be studied in details. Results obtained for VCL/HEMA hydrogels from DLS and rheology, will be compared and theoretical relation of both methods will be discussed.
2. Theoretical Background

2.1 Phenomenon of the Phase Transition.

2.1.1 Non-cross-linked Polymers.

The behavior of the polymer in solution is much more complex as behavior of substances with low molecular weight. The solubility of the polymer can be described by the usual Gibbs free energy of mixing function

$$\Delta G_M = \Delta H_M - T\Delta S_M$$

(2.1-1)

The polymer solution is often described by the mean field lattice model developed by FLORY and HUGGINS [21-24], where polymer segments and solvents molecules are distributed in lattice with \(N_g\) elements. Upon dissolution solvent-solvent (1-1) and polymer-polymer (2-2) interactions are broken and solvent-polymer interactions are created. The exchange energy for one pair can be calculated

$$\Delta u = u_{12} - 1/2(u_1 + u_2)$$

(2.1-2)

The enthalpy of mixing for the number of the contacts \(N_{12}\) between solvent with volume fraction \(\phi_1\) and polymer with volume fraction \(\phi_2\) in the lattice with the coordination number \(z\)

$$\Delta H_M = N_{12}\Delta u = N_g z\Delta u \phi_1 \phi_2$$

(2.1-3)

Using thermal energy, the dimensionless FLORY-HUGGINS interaction parameter \(\chi\) can be obtained

$$\chi = z\Delta u / kT$$

(2.1-4)

This parameter depends on concentration and temperature

$$\chi = \chi_0 + \chi_1 \phi_1^2 + \chi_2 \phi_2^2$$

(2.1-5)

$$\chi = \chi_S + \chi_H / T$$

(2.1-6)
2. Theoretical Background

with enthalpic and entropic components $\chi_H$ and $\chi_S$ respectively

$$\chi_H = \Delta h_i / (RT\phi_2^2) \quad (2.1-7)$$
$$\chi_S = \Delta s_i / (R\phi_2^2) \quad (2.1-8)$$

The total number of lattice sites $N_g$ can be extended to AVOGADRO number $N_A$ by

$$N_g = N_A n_1 / \phi_i \quad (2.1-9)$$

with $n_I$ moles solvent in the total mol $n$ of solution. Thus enthalpy of mixing $\Delta H_M$ can be rewritten

$$\Delta H_M = nRT\phi_i \phi_2 \quad (2.1-10)$$

Enthalpy of mixing is usually positive (unfavorable for mixing) in the case of nonpolar polymers and solvents without specific interaction. If $n_2$ polymer segments connected via polymerization degree $m_2$ are dissolved in $n_1$ solvent molecules the entropy of the both components is increased

$$\Delta S_M = nR[(\phi_2 / m_2)\ln \phi_2 + \phi_i \ln \phi_i] \quad (2.1-11)$$

Since the entropy of mixing is small and enthalpy is positive, the polymers are much less miscible with the solvents (i.e. less soluble) than small molecules. Using expressions for enthalpy and entropy of mixing, the GIBBS energy of mixing for polymer solution can be written as

$$\Delta G/nRT = \phi_i \ln \phi_i + (\phi_2 / m_2) \ln \phi_2 + \phi_i \phi_2 \chi \quad (2.1-12)$$

The form of this equation predicts nonsymmetrical curve of the phase diagram. This equation can be also used for describing of polymers, which have the LCST. This fact was indicated by DUŠEK and PRINS [25-28]
2. Theoretical Background

Fig. 2.1.1 Demixing patterns in binary polymer solutions for polymers with polymerization degree $m_2$, (a) type I, (b) type II, (c) type III; ○ critical point; □ limiting critical point; (---) spinodal curve; (—) binodal curve; $\theta$ - theta point. Schematically reproduced from reference [28].
When a solution of a linear polymer with very high molecular weight shows a partial miscibility, the liquid-liquid critical state usually occurs at very small polymer concentration. The latter tends to zero if the molecular weight goes to infinity (θ state). Indication of possible complications with respect to this generally accepted rule has been reported occasionally, and their origin could be related to a strong dependence of the interaction parameter on concentration. This feature has been the subject of a recent phenomenological analysis in which three types of limiting critical behavior could be distinguished. The above mentioned "classical" θ behavior (type I) is characterized by a limiting critical concentration \( \phi_{2L} = 0 \) for infinitely high molecular weight. Decreasing of the molecular weight shifts the critical concentration and critical point to higher values. With type II, a single off-zero limiting critical concentration, \( \phi_{2L} \neq 0 \), occurs at non-θ-condition. The critical point is mostly independent on chain length for this type. Type III is characterized by one zero limiting critical concentration and two off-zero limiting critical concentrations. The first critical point, located at the low polymer concentration, behaves in the classical FLORY-HUGGINS way. It is shifted to zero concentration and to the θ-temperature at the infinite chain length. The chain length does almost not influence the other critical points, at high polymer concentration. Three known polymers with the LCST in the range of 32-38°C, PVCL, PNIPAm and PVME, surprisingly have different types [26,28-29] (I, II and III respectively) of miscibility behavior. All three types of phase behavior are plotted schematically (Fig. 2.1.1). The phase diagrams consist of binodal and spinodal curves. The metastable region is between these curves and the one-phase system can exist in this region. Spinodal curves described phase separation region.

### 2.1.2. Cross-linked Systems.

The state of neutral hydrogels network immersed in a single solvent can be described by the same equations as for the solution of the polymer. Classically, now the free energy of a neutral hydrogels consists of the two terms, one for the mixing of the network and solvent and one due the elasticity of the network. The solvent and elastic components of the energy are given by the relations:

\[
\Delta G/nRT = \phi_1 \ln \phi_1 + G_N + \phi_2 \chi
\]  

(2.1-13)

\( G_N \) is the elastic contribution of the network. It is defined as
2. Theoretical Background

\[ G_N = \frac{\Delta \text{G}_0}{\text{nRT}} = (3A/2m_c)\Phi_0^{2/3} (\phi_2^{2/3} - \phi_2) + (B/m_c)\phi_2 \ln \phi_2 \]  

(2.1-14)

where \( \Phi_0 \) is the polymer fraction at the network formation, \( m_c \) – is the average degree of polymerization of the polymer chains between two cross-links.

It is useful to consider two important general consequences of cross-linking:

- The molecular weight of the polymer becomes infinite;
- The system cannot reach a state of infinite dilution.

Cross-linking of a system exhibiting type I limiting critical behavior makes the molecular weight infinite and for that reason critical point would tend to the zero limit, but this state cannot be reached due the impossibility of infinite dilution. The maximum degree of dilution is determined by degree of cross-linking and depends on temperature. Such systems therefore show a continuous transition from highly swollen state to smaller degree of swelling.

A linear polymer solution exhibiting type II limiting critical behavior will separate into two liquid phases at finite molecular weight, one of higher and the other of lower concentration. The latter phase concentration approaches zero when the temperature rose. This phenomenon is impossible if a molecular weight becomes infinite due to cross-linking and there must occurs a swelling curve for the pure solvent/swollen network equilibrium. The swelling curve will interfere with the miscibility gap, and this interference causes a three-phase equilibrium between the pure solvent phase and two swollen phases, one is highly swollen whereas the other is contracted. A three-phase equilibrium is nonvariant in binary system at a fixed pressure, hence the discontinuity in swelling behavior.

Linear type III systems are already characterized by a discontinuity due to the three-liquid-phase equilibrium. Cross-linking now prevents the left-hand miscibility gap from remaining in the \( \theta \) point at \( \phi_2 = 0 \) (at about 20°C) and forces the solvent/swollen network equilibrium curve to follow the usual swelling behavior below the three-phase temperature. It is important to note that the occurrence of discontinuous swelling behavior is not only determined by the values of interaction parameter \( \chi \), but also by the cross-link density. When the latter is too high \( (m_c \) is too small) there is no miscibility gap and the swelling curve shifts toward the polymer rich side of the diagram. The phase diagrams for all three types of miscibility behavior of the cross-linked polymers are shown in the Fig. 2.1.2. The curves in the diagrams are represented schematically.
Fig. 2.1.2 Phase diagrams of cross-linked systems based on polymers with a – I, b – II, c – III type miscibility behavior; ○ - critical point; (---) - spinodal curve; (—) - binodal curve. Schematically reproduced from reference [28].
2. Theoretical Background


2.2.1. Synthesis and Characterization of PVCL.

N-vinylcaprolactam (VCL) has a ring, which consists of seven carbon atoms (Fig. 2.2.1a). So, it cannot be of the flat conformation. It is well known [30], that the ring of the cycloheptane has the different forms of the conformations as "chair", “bath” and "twist bath". But the presence of the rigid double bond in the cycloheptene excludes a pseudo transformation ("chair" – "bath") and reduces the number of forms. Creation of the conformer "bath" is unprofitable due to repulsion of carbon atoms on the "nose of bath" and carbons of the double bonds. Most of favorable conformation for the cycloheptene is the "chair" conformation, which is also favorable for the 4-cyclohepten-1-on.

A seven-member ring of caprolactam includes the rigid amid part connected to the double bond therefore for this combination the "chair" conformation is the most of probable. This state was proved by theoretical and experimental investigations [31-32].

The PVCL has syndiotactic structure of the main chain [14]. This construction can be well understood after consideration of the structural occupation of molecules in cells of the crystal. Two molecules of VCL in the "chair" conformation create these cells by the packing of this "chairs" on "seat-on-seat" structure with oppositely directed "backs" (Fig. 2.2.2). In this structure double bounds are far from each other. Probably these structural associations are present in solution and near the growing radical. An associate of two monomers has relatively high volume. The reaction of double bonds of different associates will be mainly controlled by their position near end-radical of polymer chain (by the presence of sterical hindrances).

Fig. 2.2.1 Chemical structure of N-vinylcaprolactam (a) and its structure determined by quantum-chemical calculation (b) [32]
2. Theoretical Background

The polymerization of VCL is not so well and systematic studied as for \(N\)-vinylpyrrolidone. The VCL can be polymerized by radical mechanism in or without solvent. SOLOMON et al. [33-35] have studied the bulk polymerization of VCL in the presence of different initiators in nitrogen or in air atmosphere. It was a surprise, but polymerization not carries out in the presence of benzoyl and lauroyl peroxides, even in nitrogen atmosphere. tert-Butyl peroxide, cumene hydroxide, Trigonox A 75 were active only at elevated temperatures (80-100°C), and tert-butyl perbenzoate was only slightly active. The most effective initiator is 2,2'-azobisisobutyronitrile (AIBN). Using of AIBN in relatively low concentrations leads to the high conversions in the temperature range from 60° to 80°C. The reaction rate is proportional to \([I]^{0.5}\) and equation for the overall reaction rate is applicable:

\[
\nu = k [I]^{0.5}[M] \quad (2.2-1)
\]

where, \(\nu\) - rate of polymerization; \(k\) - constant of polymerization; \([I]\), \([M]\) – concentrations of initiator and monomer respectively. From experimental data, SOLOMON et al. have calculated \(k_{70} = 0.07; k_{75} = 0.12; k_{80} = 0.19 \text{ l/(mol·min)}\). The activation energy was 25 ± 2 kcal/mol. The molecular oxygen influences the reaction, not only by diminishing its rate, but also by diminishing the molecular weight of the polymer.

EISELE et al. [36] showed polymerization of VCL in benzene and water with AIBN (in latter case emulsifier was used). Redox initiating systems (\(\text{NaHSO}_2 + \text{tert}-\text{butyl peroxide, } \text{NH}_3+\text{H}_2\text{O}_2\)) were also tested. Polymers with molecular weight from \(2 \cdot 10^4\) g/mol to \(1 \cdot 10^6\) g/mol were obtained. Polymers with smaller molecular weights up to \(2 \cdot 10^4\) g/mol can be obtained in \(\text{iso}-\text{propanol}\) [29]. In this case the solvent plays a role of a chain transfer agent. Synthesis of PVCL with high molecular weight by \(\gamma\)-irradiation is also reported [37,38].
polymerization of vinylamides cannot be initiated by Na$_2$S$_2$O$_8$ in water, due to the more probable reaction of the oxidation of the ring [39].

Several authors have studied the behavior of PVCL in water by dynamic and static light scattering methods and showed scaling relation of the average radius of gyration and translation diffusion coefficient with the weight average molecular weight, but their results are different. According to EISELE [36] these scaling laws are

\[ \langle r^2 \rangle = 1.77 \cdot 10^{-18} M_w^{1.15} \]  \hspace{1cm} (2.2-2)

\[ D_z = 1 \cdot 10^{-4} M_w^{-0.52} \]  \hspace{1cm} (2.2-3)

and according to LAU [40] these relations are

\[ R_g = 2.94 \cdot 10^{-2} M_w^{0.54} \]  \hspace{1cm} (2.2-4)

\[ D_z = 7.93 \cdot 10^{-5} M_w^{-0.505} \]  \hspace{1cm} (2.2-5)

where \( R_g \) - average radius of gyration (\( R_g = \langle s^2 \rangle^{1/2} \)), \( D_z \) - translation diffusion coefficient, \( M_w \) – weight-average molecular weight.

Different values of refractive index increment \( dn/dc \) for determination of \( M_w \) were reported in these studies. The refractive index increment was in the range from 0.16 to 0.206 ml/g. EISELE [36] has also showed independence of \( dn/dc \) on laser wavelength for the PVCL.

The KUHN-MARK-HOUWINK equation for PVCL in water at 25°C [41]:

\[ \eta = 0.0105 M_\eta^{0.69} \]  \hspace{1cm} (2.2-6)

with \( \eta \) – intrinsic viscosity, cm$^3$/g, and \( M_\eta \) – viscosity -average molecular weight.

Molecular weight and molecular weight distribution of PVCL cannot be correctly determined using size exclusion chromatography in most of solvents due to the sorption on the column. However, the determination of molecular weight distribution in chloroform with added of LiCl using special type of the column is reported [32].

2.2.2 Thermal Behavior of PVCL in Water.

Temperature of the phase separation of PVCL (cloud point) strongly depends on the molecular weight of polymer. The strongest increase of the transition temperature happens for polymers with \( M_n < 5 \cdot 10^4 \) g/mol. In the range of \( 2 \cdot 10^5 - 5 \cdot 10^4 \) g/mol cloud point slightly
increases from 32.5°C to 35-36°C, in the range of $5\cdot10^4$ - $6\cdot10^3$ g/mol $T_{tr}$ increases strongly from 36°C to 51°C (Fig. 2.2.3) [42]. Concentration of the polymer with $M_n = 21\cdot10^3$ g/mol in water solution in the range from 0.4 to 40 wt.-% has no influence on this temperature and only in the higher concentration range this temperature increases [42]. Lau [40] showed for PVCL with $M_n = 1-2\cdot10^6$ g/mol that decrease of concentration of polymer from 1 to 0.01 g/l increases $T_{tr}$ from 30.7°C to 31.5°C. Tager et al.[43] showed for PVCL with $M_n = 5\cdot10^5$ g/mol the change of the cloud point from 32 to 34°C depending on the concentration of the polymer in solution. Meeussen et al. [42,43,44] estimated the phase diagrams for polymers with different molecular weights (Fig. 2.2.4).

In a case of PVCL with $M_n = 21\cdot10^3$ g/mol only one jump of the heat capacity in the range of 140-150°C can be seen ($T_g = 147^\circ$C; $\Delta c_p = 0.11$J/(g ·K)) [32]. The absence of a melting point characterizes PVCL as rigid-chain, amorphous polymer. Several authors [29,32,44] have studied interaction PVCL-water with dynamic scanning calorimetry. At lower water content $N = 8-10$ (molecules water per polymer chain) thermograms show the decrease in $T_g$ to $-17^\circ$C - $-38^\circ$C (Fig. 2.2.5), the glass-rubber transition shifted even to a negative range of the temperatures. At $N = 2.6-8.2$ associates of water make no any crystals, taking part in cooperative glassing of the homogenous PVCL-water system.

At $N = 8.2$, the so-called “cold crystallization” of water carries out. Water takes part in glass transition of the mixture and first exothermic effect of crystallization and than endothermic effect of the melting of water can be observed during heating. A common crystallization (nucleation and growth of crystals on formed nuclei) can be observed only at $N > 20$ (68 wt.-%) (Fig. 2.2.6).

**Fig. 2.2.3** Dependence of the cloud temperature of PVCL in water on $M_n$ of polymer [42].

**Fig. 2.2.4** Phase diagram PVCL-water for polymers with different molecular weight [29].
On the base their results Kirsh et al. [32] formulated the mechanism of PVCL-water interaction. In the presence of small amount of water, the polymer and water make polymer-hydrate complexes. Each of the dipoles of carbonyl groups is able to bind maximum two molecules of water directly (types 1 and 3 on the Fig. 2.2.7). Other water molecules can be gradually attached via hydrogen bridges with first water molecules (type 2). Probably, this structure is a main component of the first water shell in a polymer-water complex. Probability of existing of this structure is much higher then of molecules in chain structure on scheme (type 4). The increase of \( N \) leads to formation OF water associates from molecules that participate in hydrogen bonding with each other and with PVCL carbonyls. C=O dipoles polarize water molecules and affect a charge distribution on atoms of water molecules and the degree of hydrogen bonding between the water molecules. Finally, the amide C=O interaction with water favors general weakening of interaction forces in a PVCL-water system. As follows from the quantum-chemical calculations, the energy of hydrogen bond between C=O and H\(_2\)O is significantly weaker then that of hydrogen bonds between water molecules. A further increasing of amount of water leads to the formation of the second and third hydration shells near by macromolecules. Molecules of H\(_2\)O of these shells interact with dipoles of carbonyls indirectly by interaction with the first hydration shell of polymer hydrate complex. This leads to the change of charge density and may be to change of molecular angles of molecules of water. It induces the formation of defected ice structures of water. At least near 15-20 molecules of water near one caprolactam ring are involved in the formation of complex below the phase transition temperature.

It should be noted, that Meeussen et al. [29] made opposite conclusions based on practically same results of investigation of the freezing of water in the presence of PVCL.
The formation of stable complexes between water and the chain repeating units was not detected and crystallization of water vanished at 60% of PVCL as a consequence of interference of the crystallization process with the vitrification of the solution. Increasing of the temperature in the PVCL-water system leads to the partial dehydration of the water in third and fourth hydration shells. Bridge hydrogen bonds in the first hydration shell are broken at the phase transition temperature. In this case macromolecules pass to the unordered conformation state in comparison with stable state with water interaction. This leads to the formation of the contacts between unpolar parts of caprolactam rings (increased hydrophobic interaction). As result, polymer precipitates. Precipitate includes the large amount of water, which stays in polymer even at 90°C.
2. Theoretical Background

Fig. 2.2.8 (a) Amide I band of PVCL at 26 °C and GAUSSIAN components (centers: 1565 cm\(^{-1}\), 1588 cm\(^{-1}\), 1610 cm\(^{-1}\)). (b) Amide I band at 41.2 °C and four GAUSSIAN components (centers: 1565 cm\(^{-1}\), 1588 cm\(^{-1}\), 1610 cm\(^{-1}\), 1625 cm\(^{-1}\)). (c) Integrated areas of the amide I components of PVCL-M are plotted versus temperature. ● - 1565 cm\(^{-1}\); △ - 1588 cm\(^{-1}\); ▲ - 1610 cm\(^{-1}\); □ - 1625 cm\(^{-1}\). Reproduced from [45]

The interaction of the PVCL with water was also studied by using IR. MAEDA et al. [45, 46] reported the temperature induced shift of the amid I band in D\(_2\)O. This peak was treated using FOURIER self-deconvolution of the spectra, which enhance the position of individual components. The amide I band consists of three GAUSSIAN components centered at 1565 cm\(^{-1}\), 1588 cm\(^{-1}\) and 1610 cm\(^{-1}\) below \(T_r\) and four components 1565 cm\(^{-1}\), 1588 cm\(^{-1}\), 1610 cm\(^{-1}\) and 1625 cm\(^{-1}\) above \(T_r\) (Fig. 2.2.8). The areas of components at 1565 cm\(^{-1}\), 1588 cm\(^{-1}\), 1625 cm\(^{-1}\) increase with increasing temperature above \(T_r\), whereas the 1610 cm\(^{-1}\) band, which is dominant below \(T_r\), becomes weaker with increasing of the temperature. The reason of such amount of individual components is unclear. However one can guess hydrogen-bonding situation which give rise to each component. Because the maxima of the amid I band of neat solid PVCL and dissolved in chloroform is located at 1621 and 1626 cm\(^{-1}\) respectively, the 1625 cm\(^{-1}\) component was attributed to the amide group whose C=O group and nitrogen atom do not form hydrogen bond with water. Because the addition of methanol reduces the intensity of the 1588 cm\(^{-1}\) band, it was related to the amide group that forms at least one hydrogen bond with water. The component at 1610 cm\(^{-1}\) was also related to the amide group with hydrogen bonding with water.

LEBEDEV et al. [47] have studied the interaction of PVCL with water by small angle neutron scattering (SANS) and neutron spin echo (NSE) around the coil to globule transition. Inelastic neutron scattering of the PVCL solution near 32.5°C showed anomalies, which arise from memory effects and surface tension relaxation by segmental motions. The higher amplitude of
2. Theoretical Background

The molecular motion in globules is the sequence of hydrogen bonds of water, which are breaking under the action of neighboring amide groups. So water becomes a good lubricant for chain fragments in globular state. In the state of coils the more apparent structure of water diminishes the chain mobility. The SANS and NSE data support the concept of immense effect of water on PVCL glassing.

2.2.3 The Influence of Different Compounds on Behavior of PVCL in Water.

2.2.3.1 Salts.

A phenomenon of the influence of salts on the structure of water is widely known. Known are also examples of influences of different salts types on catalytical activity of enzymes, the coil-to-globule transition of fibril proteins (collagen, myosin, etc.) [15]. Influence of salts on phase separation of synthetic polymers in water (PVME, PNIPAm) [48,49] was also observed. In spite of the large amount of experimental material, the mechanism of this phenomenon is not clear, due to the complexity of processes, which carry out in the polymer chain, water solution and solvate shell of immersed molecules.

There is also an influence of adding of salts in water solution of PVCL on polymer-water interaction. Dependencies of changing of $T_{tr}$ in salt solution are reported [50]. It is possible to divide these influences in two groups in the range of salts concentration from 0 to 2-3 mol/l.

In the cases of NaClO$_4$, KCNS, KI and KBr, there are extreme dependencies of the $T_{tr}$ on the salt concentration $C_s$. Values of $T_{tr}$ in solution of KCNS, KI is much higher then in pure water. Maximum of the transition temperature was observed in 1-1.2 mol/l salt solution, 57.5°C for KCNS and 53°C for KI respectively ($T_{tr} = 38.6$°C for $C_s = 0$ mol/l). In the case of NaClO$_4$ this temperature is 49°C ($C_s = 0.2$-0.04 mol/l) and for KBr 39.8°C ($C_s = 0.3$ mol/l). Further increasing of concentration of NaClO$_4$ and KBr leads to the sharp decrease of the transition temperature. That means, that KSCN and KI are strong and NaClO$_4$ and KBr are weak stabilizing agents for PVCL–water complexes.

Another type of interaction is present in solutions of KF and LiCl. For these salts linear decrease of $T_{tr}$ with increasing of salts concentration was observed. Stabilizing influence of anions increase in the row:

$$\text{SO}_4^{2-} < \text{H}_2\text{PO}_4^- < \text{CO}_3^{2-} < \text{F}^- < \text{HO}^- < \text{HCOO}^- < \text{Cl}^- < \text{NO}_3^- < \text{Br}^- < \text{ClO}_4^- \approx \text{I}^- < \text{CNS}^-$$
Anion has more influence than cation and for cations with the same anion (Cl\(^-\))

\[
\text{NH}_4^+<\text{Li}^+<\text{Mg}^{2+}<\text{Ca}^{2+}\approx\text{Cs}^+<\text{K}^+=\text{Na}^+=\text{Rb}^+<\text{Ca}^{2+}
\]

But for ClO\(_4^-\) this dependence will be:

\[
\text{Na}^+<\text{NH}_4^+<\text{MgO}^{2+}
\]

Such different influences can be easily understood after consideration of interaction of salts with water. Associates with tetrahedral geometry exist in the water due to ability of water molecule to be either a donor or an acceptor of two protons [51]. It is known, that the presence of KI in solution increases the mobility of water. Water can have high degree of mobility in the salt solution only in the case of "weakening" of the system of hydrogen bonds. With other words, the number of hydrogen bonds per one molecule of water should decrease and, may be, amount of associates with free OH groups or "H fragments" should increase. The latter one increases the energy of interaction between “bridge molecules” with C=O dipoles and lead to the stabilization of the conformation state of polymer–water complex and as result increasing of \(T_{tr}\) should be observed. So adding of NaClO\(_4\), KCNS, KI destroys tetrahedral associates and increase the number of associates with "H fragments". In the case when LiCl or KF are added, decreasing of the mobility of the molecules of water can be attributed to the strong association of them near anions and cations of salts. Most of water molecules are involved in this association. Another part of water is polarized by the hydrated ions. Decreasing of the cloud temperature shows an increase of amount of high-associated molecules of water and partial dehydration of PVCL.

### 2.2.3.2 Alcohols and Amides

Specificity of PVCL – water interaction is good to be seen in changing of \(T_{tr}\) in water-organic mixtures in comparison with pure water. Adding of good solvents for PVCL to the water has strong influence on solubility of polymer in water [52]. Most of alcohols are good solvents for PVCL but some of them in some proportion with water decrease the solvent quality and, as result, decrease the \(T_{tr}\). It is possible to find not only a dependence of \(T_{tr}\) on concentration but also on chemical nature of the alcohol in the row of aliphatic alcohols with different alkyl radicals (methanol, ethanol, \(n\)-propanol, \(iso\)-propanol,
2. Theoretical Background

tert-butanol). Methanol practically does not decrease the $T_N$ of PVCL, ethanol [53,54] and iso-propanol change this temperature to 28°C (14 vol.-%) and 17°C (10 mol.-%), respectively (Fig. 2.2.9-2.2.10). tert-Butanol and, in higher extent, $n$-propanol decrease $T_N$ to the values lower than 10 °C – 12 °C. They make the range of concentrations of alcohol in water, which are bad solvents for PVCL, considerably broader than for methanol or ethanol. In this row of alcohols, decreasing of $T_N$ can not be explained by decreasing of acidity of OH group because a most strong effect exists for alcohols with low $pK_a$. For alcohols one can consider that C=O of PVCL interact directly with the hydroxyl group via hydrogen bonding and their concentration increases near polymer chain. But the same effect of decreasing of $T_N$ can be seen after adding of polar acetonitrile which has not acidic hydrogen and can not built hydrogen bond with C=O group.

It was concluded [52], that acetonitrile interacts with caprolactam only via the hydrogen bonding with molecules of water which are polarized by the C=O group. Probably, the C≡N group interacts with proton of water, which occupies first hydration shell and does not create "bridge" hydrogen bonds. The hydroxyl group of the alcohol molecule can make hydrogen bonds either with oxygen atoms or protons of water near to the polymer chain (Fig. 2.2.11). These interactions lead to increase of alcohol concentration probably in second shell of water in surrounding of the PVCL. Decreasing of $T_N$ with an increasing of alkyl chain length of alcohol is connected with increasing of the hydrophobic interaction of the hydrocarbon parts of alcohol and of the partial dehydrated polymer. Introducing hydrophilic group in alcohol chain, for example –NH$_2$, leads to immobilization of additional water molecules via hydration of amine group.

Fig. 2.2.9 $T_N$ of PVCL ($M_w = 27 \cdot 10^3$ g/mol) in ethanol-water solution [53].

Fig. 2.2.10 $T_N$ of PVCL ($M_w = 56 \cdot 10^3$ g/mol) in alcohol-water solution [52].
As result, increasing of concentration of monoethanolamine to 15-20 mol-% leads to increase of $T_r$ to 45 °C. The same effect has urea. Properties of PVCL in water, which contains amides or glycols, were also studied [55]

### 2.2.3.3 Surfactants.

Interaction of PVCL the ionic surfactants [56, 57] can be divided in two groups: interaction before and after overlapping concentration $c^*$. Below the overlapping concentration, individual polymers coils form intermolecular aggregates in a pure aqueous solution upon heating. The addition of the ionic surfactant results in a slight decrease of the polymer size at the temperature below the phase transition temperature. The formation of the mixed chain-surfactant aggregates lead to the effective cross-linking between the different parts of the PVCL molecule, resulting in a decrease of the particle size. Besides, the increasing temperature does not lead to any intermolecular aggregation in this case, apparently due to the formation of the charged molecule-surfactant complexes. The phase transition temperature for these complexes increased. At lower surfactant concentration formation of intermolecular cross-links take place in addition to intramolecular ones. But upon heating this aggregates broke into individual particles. At high concentrations of the surfactant, the swelling of the polymer chain is observed, which is combined with the increase of amount of surfactant molecules penetrating the polymer coil. Mobile counterions (like Na$^+$ or Cl$^-$) migrate inside macromolecule. This leads to osmotic pressure, inducing a significant swelling of the complexes.

At polymer concentrations above $c^*$ the addition of the ionic surfactant to the polymer solution leads to an increase of the polymer size at all surfactant concentrations. At high polymer concentrations mixed polymer- surfactant micelles were formed from the individual pieces of the macromolecule and the polymer units of the neighboring macromolecules. Apparently, this is due to the macromolecular aggregation. The size of aggregates is
increasing proportionally to the amount of the added surfactant due to the formation of the intramolecular cross-links by surfactant-polymer micelles.

### 2.2.3.4 Polyacids.

Poly(N-vinylamides) can form the complexes with polycarbon acids in diluted solution (5 wt.-%) at a pH when most of the carboxylic groups are in the nonionized state [58-60]. Two polymers, PVCL and polyacid, form the separate phase (1:1) and precipitate from water solution. At the same conditions, low-molecular acids have not such kind of influence on PVCL. Process of complex formation, probably, carries out in several steps. First, due to the intersegmental movement of flexible chains, an approach of some chain units very close to each other takes place. Simultaneously, water will be removed from the polymer – water complexes through the bicentric structure of the polymers chains. Then more bicentric structures are formed. These compact dense structures include a lot of macromolecules. An increasing of the ionization of the polyacid chain can induce the destruction of the polymer-polymer complex. As a result, the intermolecular electrostatic repulsion energy increases, which leads to an unwrapping of intermolecular globules. The complex of PVCL with poly(methacrylic acid) (PMAA) is the most stable among the poly-N-amide-polycarbon acid complexes. Its decomposition was observed at the degree of ionization of the PMAA of \( \alpha = 0.6 \). Assuming that direct hydrogen bonds between the COOH groups of the polyacid and C=O group of PVCL were formed and existing of sterical hindrances, much more stable complex PVMA-PAA should be observed. Such complex exists, but it decomposes at the ionization of ionization of the polyacrylic acid of \( \alpha = 0.1 \). Proposed mechanism [15] for polymer-polymer interactions is the same as interaction between PVCL and low-molecular compounds. This complexation is carried out due to formation of a cooperative network of hydrogen bonds involving polarized molecules of water, forming complete bridges between COOH and C=O (Fig. 2.2.12). In this case sterical hindrances became negligible.

Laser light scattering and differential scanning calorimetry measurements have been performed for aqueous solutions of thermo-sensitive linear copolymers of \( N \)-vinylcaprolactam and methacrylic acid of different composition [61,62]. It was shown that the copolymers undergo a phase transition upon heating in neutral and basic solutions. The enthalpy of the phase transition sharply decreases with the increasing of methacrylic acid fraction, as shown by differential scanning calorimetry.
The copolymers demonstrate pH-sensitive properties as well: intermacromolecular aggregation takes place in acidic media. FTIR spectroscopy measurements showed that the aggregation is result of formation of insoluble macromolecular complexes. The mechanism of the complexation inside of the copolymer is the same as in the mixtures of homopolymers of poly(N-vinylcaprolactam) with poly(methacrylic acid). In weak acidic media there are narrow pH intervals close to pH of aggregation in which thermo-sensitive properties of the copolymers diminish considerably and the scattering intensity from the solutions at high temperatures is much less than at basic pH. Besides, under these conditions the enthalpy of phase transition decreases significantly.

2.2.4 Copolymers on PVCL Basis

The most studied VCL-copolymer is the PVCL-co-vinyl acetate (VAc) system [53,63,64]. Introducing of hydrophobic groups of VAc in the copolymer results in a decrease in $T_{tr}$, e.g. a copolymer with 66 mol-% VAc precipitate from water solution at 5 ºC. The hydrolysis of PVCL-VAc gives copolymers with OH (vinyl alcohol (VA) units) groups (PVCL-co-VA) [53]. For these copolymers the dependence of $T_{tr}$ on the copolymer composition is also unusual: with increasing of VA content up to 50 mol.-% the transition temperature decreases from 33 ºC (100% PVCL) to 25 ºC. Further decreasing of the PVCL content to 13 mol-% increases $T_{tr}$ to 52 ºC (Fig. 2.2.13). The minimum the curve of thermo-precipitation corresponds to an equimolar composition, which shows the possibility of hydrogen bond formation between OH and C=O groups by intramolecular association. Infrared spectroscopy of these copolymers showed the shift of $\nu_{C=O}$ of the caprolactam ring from 1630 cm$^{-1}$ (15 mol.-% VA) to 1580 cm$^{-1}$ (87 mol.-% VA).
This shift is an evidence for the hydrogen bonding between the groups of different nature. Adding of free PVA in solution does not change the properties of PVCL.

Thermo-sensitive graft copolymers based on PVCL backbone and either hydrophilic poly(tetrahydrofuran) PTHF or poly(ethyleneoxide) PEO were synthesized [65-67]. The amphiphilic PVCL-g-PTHF copolymers were evaluated as thermo responsive emulsifiers. Their solubility decreases with increasing of the hydrophobic PTHF content. For PVCL-g-PEO in the aqueous solutions, a decrease of $T_r$ was found with increasing content of PEO grafts. However, above the certain amount of PEO the $T_r$ increases slightly again.

Introducing hydrophilic groups in copolymer, for example $N$-vinylpyrrolidone (VP) [64,68], leads to an increase of $T_r$ from 33°C to 80°C (66 mol.-% VP). The same effect has $N$-vinyl-$N$-acetamide (VMA) [53] (Fig. 2.2.13). Transition from PVP to VP-VCL copolymers profoundly affects the complexation ability of the copolymers in aqueous solutions. The copolymers have highest complexation ability than PVP and PVCL homopolymers [69]. The higher complexation ability is observed with 10-15 mol-% content of VP. The VP units influence the main chain structure and form sequences which can act as "hinges" in the formation of intramolecular structures. All these structural changes favor the packing of the nonpolar groups of the VCL into compact structure with high local density.

The syntheses of VCL copolymers with vinylamine and allylamine are reported [70]. The temperature behavior in water is not shown, and only a decrease of experimental $pK_a$ values in comparing to the calculated ones is discussed.
Copolymerisation of VCL with maleic anhydride (MA) carries out via charge-transfer complex, monomers polymerize with coloration even in the absence of initiator [71]. Thermo-sensitivity of obtained copolymers is not reported, but from copolymerization constants ($r_{VCL} = 0.006$, $r_{MA} = 0.17$) one can conclude that these copolymers are hydrophilic. The thermo-sensitivity of copolymers of VCL with vinylimidazol (VI) and their complexation ability with Cu$^{2+}$ were examined [72-75]. As vinylimidazol moiety introduces hydrophilicity into the macromolecule and its charge depends on pH. The $T_r$ increases with increasing of VI content and its ionization. Thus, copolymers VI/VCL 5/95 (mol/mol) and 10/90 (mol/mol) precipitated at pH 8 (nonionized system) at around 35°C. The cloud point for the copolymer 25/75 (mol/mol) is shifted slightly to a higher temperature with increasing the imidazol content. It is 60°C for the copolymer 50/50 (mol/mol). The decreasing of pH increases the ionization of the polymer chain. As a result thermo-precipitation occurs at higher temperatures. Compositions 25/75 (mol/mol) and 50/50 (mol/mol) do not precipitate up to 80°C at pH 6 and 8. It has been shown in a computer experiment [76] that the coil–globule transition in “protein-like” copolymers induced by the attraction of hydrophobic units should occur at higher temperatures to give a more closely packed globule than in the case of random hydrophobic-polar copolymers. This is due to the memory effect: the hydrophobic core that exists in the fixed conformation is mainly reproduced upon the secondary coiling caused by the attraction of hydrophobic units. During the copolymerization of a mixture of hydrophobic and hydrophilic monomers in water at a temperature above LCST, the macromolecule would start to contract. After it reached the required length, a core enriched with the hydrophobic PVCL units is formed. The hydrophilic segments of VI would be mainly concentrated at the periphery of the core. In other words, macromolecules of this type should display features of the “protein-like” spatial packing of hydrophobic and hydrophilic sequences of polymer chains. LOZINSKY et al. [75] have studied detailed the copolymerization of VCL with VI at temperatures below and above the LCST of the PVCL. It was shown that nonprecipitating copolymer fractions obtained from products of copolymerization of the VCL and VI at initial monomer ratios of 85/15 (mol/mol) and 90/10 (mol/mol) can be identified as protein-like copolymers.

2.2.5 Cross-linked Systems on PVCL Basis

It is important to note, that there are several differences between macrogels and microgels. Microgels have much larger interfacial areas than macrogels due to their respective sizes and
microgels have an ability to flow (in the dispersed phase). Thermo-sensitive microgels are synthesized above their LCST in order to produce stable, monodisperse particles via free-radical polymerization. Due to the radial gradient in the cross-linking density they have more heterogeneities [77]. Despite the differences, macrogels and microgels should show similar trends upon changes of the external conditions.

The preparation of macrogels based on PVCL has some peculiarities. Due to the pure solubility of VCL in water and sensitivity of caprolactam ring to oxidation, it cannot be polymerized with the most useful method in water with the redox initiator Na$_2$S$_2$O$_8$ – $N,N',N'^{-}$-tetramethylethylenediamine (TEMED). MAKHAeva et al. [17,78] have synthesized PVCL hydrogels in ethanol-water mixture in the presence of $N,N$-methylenebisacrylamide (MBA) with AIBN. Using DSC analysis two successive cooperative transitions of PVCL hydrogel were detected. The low-temperature transition (31.5°C) seems to be connected with microsegregation phenomena resulting in the creation of hydrophobic domains or micelles in the gel. It was shown, that the high-temperature phase transition (37.6°C) is probably connected with a volume phase transition of the gels. Swelling of obtained hydrogel in water in presence of organic additives and surfactants was examined. Cross-linked PVCL shows similar behavior as linear polymer in pure water and in water with organic additives.

Two- and three-dimensional phase diagrams have been constructed for thermo-sensitive PVCL-PEO aqueous systems [79]. Both, the solution and the block copolymer networks have been investigated to study the effect of the copolymer content and cross-linking density on their phase separation temperatures. Introducing the hydrophilic PEO into an aqueous solution of PVCL decreases its $T_{tr}$. This suggests, that the strength of the hydrogen bonds within the PVCL-water system is weakened by the introduction of PEO which also interacting with water. It was found, that the influence of PEO on the weakly cross-linked networks is comparable with that of PVCL-PEO-H$_2$O solutions. The presence of the cross-links is the major importance for the explanation of the $T_{tr}$ location for networks with a higher degree of cross-linking. This leads to the model of an irregular water distribution in these swollen networks.

A new type of thermo-sensitive hydrogels has been developed from organic/inorganic hybrid materials using the sol-gel technology [80]. PVCL has been incorporated in these materials because of its thermo-responsive properties. The synthesis of the hybrid hydrogels was achieved by the in situ formation of an inorganic silica phase in the presence of an aqueous solution of high molecular weight PVCL. This methodology results in the preparation of micro-heterogeneous systems in which silica particles of nanometer dimensions act as
physical cross-links for the PVCL molecules. Hydrogen bonds between the remaining non-condensed silanol groups and the PVCL carbonyl functions, together with physical entanglements, are responsible for the strong interactions between the organic and inorganic phases. The response of the reinforced hybrid hydrogels to temperature becomes less pronounced for increasing silica fractions.

The effect of the amount of positive and negative charges on the swelling and the mechanical behavior of PVCL gels, obtained by irradiation of VCL in an ethanol-water mixture in the presence of 3,3’-(ethane-1,1-diyl)bis(1-vinyl-2-pyrrolidone) as a cross-linker, was studied [81,82]. When incorporated in a network, charges have a strong influence on volume phase transition of the PVCL gel. As it can be seen from Fig. 2.2.14, even a small amount of charge shifts the $T_{tr}$ to a higher region. In a first approximation, the swelling of hydrogels can be described by the theory of polyelectrolyte networks in which repulsion of the charges on the chain was considered.

According to this theory and with FLORY-HUGGINS interaction parameter $\chi = 0.522$ calculated for uncharged PVCL network swollen in water, no jumpwise change in volume with increasing temperature should be observed. The same effects were examined for copolymer networks of PVCL with PVP [83]. For all copolymers, a continuous transition was found; the transition temperature increases with increasing of VP and ammonium salt content. The decrease in swelling with heating is accompanied by an increase in the equilibrium modulus, so that mechanical behavior is predominantly determined by swelling.

The same copolymers with a higher PVP content showed a first-order phase transition in water-acetone mixtures.

![Figure 2.2.14](image_url)

**Fig. 2.2.14** Influence of the $T_{tr}$ of the PVCL network on the amount of incorporated charge [81,82].
2. Theoretical Background

The extent of the collapse and critical acetone concentration in the mixture slightly increase with increasing of content of VCL and the ammonium salt in the gels.

The thermal behavior in water of PVCL microgels with and without the presence of anionic and cationic surfactants was studied [84]. The surfactant-free microgels continuously shrunk as the temperature increased, reaching the fully collapsed state at \( \sim 38^\circ C \). The addition of a small amount of surfactant led to additional swelling and a higher temperature of the collapse. The effect of surfactant can be partially attributed to the micelle formation inside the microgel network.

Thermo-sensitive PVCL nanoparticles coated with short PEO segments grafts have been successively prepared using the macromonomer techniques [85,86]. Either particles prepared in SDS emulsion have been coated with the macromonomer, or the graft copolymerization has been done in one step in an emulsion, stabilized by the amphiphilic monomer. In the former case, the collapse transition of particles occurs in a wide temperature range. In the latter case, a discontinuous transition is observed. The colloidal stability of obtained microgels is studied. Thermally responsive particles where prepared by the emulsion polymerization of VCL [86]. By varying of the chemical nature of the initiators and surfactants, particles with different types and degrees of stabilization were obtained. The use of an anionic initiator or an anionic surfactant led to the electrostatically stabilized particles as it was confirmed by the capillary electrophoretic measurements of zeta potentials of the PVCL particles. All the product particles showed thermal behavior which is typical of PVCL, but sterically stabilized ones were superior in the stability against added electrolytes.

The copolymerization of a few molar percent of ionic sodium acrylate (NaA) into the PVCL microgel slightly rose its volume phase transition temperature and increased the extent of its swelling [87-90]. The collapse of PVCL chains forces the COO\(^-\) groups to stay on the periphery. The intramicrogel complexation between Ca\(^{2+}\) and these groups leads to the shrinking of microgels, but the interparticle complexation induces the aggregation. The aggregation temperature depends on ionic comonomer content. A comparison of linear copolymer chains and spherical microgels showed, that the aggregation of linear chains is more profound then that of spherical microgels, presumably because the competition between inter- and intrachain complexation leads to less aggregation. The association of the linear chains was gradually changed from reaction limited to the diffusion limited process, reflected in the change of the fractal dimension of resulting aggregates from 2.5 to 1.6. The complexation of obtained microgels with gelatin was studied.
2.2.6 Application of PVCL

It is well known, that the catalytic activity of enzymes is sharply decreasing with increasing of the solution temperature and in the presence of different denaturizing agents in water. PVCL can be used as a protein carrier in the polymer matrix with chemically bonded protein [91] or it can be used as one of the separate components in alginate based gel particles [92,93]. This gives the possibility to a strong increase resisting of enzymes to thermo-deactivation. Conjugates of PVCL with enzymes can be precipitated after heating and easily removed from solution. This procedure can be repeated several times without a loss of catalytical activity. A water layer, which forms a network of hydrogen bonds, connects the polymer and the protein to each other. This layer is stable to heating up to 60-70°C. PVCL also prevents denaturation of the proteins in the presence of organic compounds such as dimethylformamide, glycerin and acetonitrile. PVCL macromolecules near to protein molecules can also influence the conformation of protein molecules. Heating induces the shrinking of PVCL with a sharp slowing down of mobility of the molecules. PVCL macromolecules are slowing down the mobility of proteins and create a skeleton around it, which becomes more and more rigid with heating and prevents denaturizing. The effect of thermo-precipitation of the PVCL with the conjugate from the reaction medium was used for immobilization and removing of trypsin [94].

The possible use of PVCL microgels as drug carriers was studied [95]. The more hydrophilic drug (nadolol) caused PVCL to swell less and collapse at much lower temperatures then the more lipophilic drugs (propranolol and tacrine). Both, propranolol and tacrine caused the polymer particles to swell considerably, and the collapse occurred in a comparatively narrow range. In the presence of the microgels, the release of drugs through the cellulose membrane at 40°C was smaller then at 20°C. The release of drugs in absence of PVCL at 20°C does not differ strongly as in the case of microgel – drug systems.

The PVCL can be used as a matrix for producing solid pharmaceutical and cosmetic preparations with controlled release of active ingredients [96]. It can be also used as the additive in oil-in-water nanoemulsion for the thickening of the composition [97], as the matrix in the colloidal dispersion of the biologically active compounds [98]. PVCL and its copolymers with VP are known under the trademarks Luvicap® and Luvitec®. These products can be used in coating, in producing of clays, paper, textile etc [99]. PVCL is one from the polymers, which are able to kinetically suppress hydrate crystallization [100]. This attribute is of significant commercial importance to the oil and gas industry.
3. Analytical Methods

3.1 Static Light Scattering

When electromagnetic wave contacts with the atom or molecule, oscillation of the electrons of the outer shell will be induced. Resulting shift of the charge or the centre of charge induces the dipole moment, which is the starting point of the scattered light. The scattering theory of pure liquids and macromolecular solution goes back to the SMOLUCHOWSKY, EINSTEIN [101] and DEBYE [102], and it usually referred to as “fluctuation theory”.

In the case of large macromolecules, single macromolecule possesses several scattering centers and its scattering intensity is angular dependent. Usually scattering intensity decreases with increasing of the angle of observation $\theta$. There is a phase shift of scattered waves from different scattering elements, which is represented by the scattering vector

$$q = (4\pi / \lambda) \sin(\theta / 2)$$

The fluctuation of the scattered intensity induced by intramolecular interference can be described through the scattering function $P(q)$ (form factor) which is defined as ratio of scattered intensities at the angle $\theta$ (interference) and $\theta = 0$ (without interference)

$$P(q) = \frac{I(q)}{I(q = 0)} = \frac{1}{N^2} \sum_i \sum_j \frac{\sin(qr_{ij})}{qr_{ij}}$$

with $r_{ij}$ distance between different scattering centers of single macromolecule. In concentrated solution intramolecular interference should be also taken into account. Resulting angular dependence is described by structure factor $S(q, c)$

$$S(q, c) = n \sum_l \sum_m \left( \sum_j \sum_k \frac{\sin(qr_{jk}^{lm})}{qr_{jk}^{lm}} \right)$$

with $l$ and $m$ as two different macromolecules and $j$, $k$ its segments. $r_{jk}^{lm}$ is defined as a difference between $j^{th}$ chain section of macromolecule $l$ and $k^{th}$ section of macromolecule $m$.

Only for the solutions of the homogenous spheres the apparent particle scattering factor can be factorized into contributions of particle and interparticle scattering as follows
3. Analytical Methods

Fig. 3.1.1 The form factor $P(q)$ versus $qR_g$ (a) and KRATKY plot (b) for the sphere (●), monodisperse coil (▲) and star (□).

$$S(q,c) = S'(q,c)P(q)$$ (3.1-4)

$S'(q,c)$ is the structure factor which carries information about the art of particle arrangement in space and is related to the centre of mass. For $qr_{ij} << 1$ the formfactor can be expressed by simple equation

$$P(q) = 1 - \frac{1}{3}q^2 \langle r^2 \rangle \quad \text{or} \quad P(q)^{-1} = 1 + \frac{1}{3}q^2 \langle r^2 \rangle$$ (3.1-5,6)

with $\langle r^2 \rangle$ as average square value of the radius of gyration ($R_g = \sqrt{\langle r^2 \rangle}$). In this case $qr_{ij}$ is independent on macromolecule geometry and angular dependency of scattering intensity is proportional to the $\sin(\theta/2)$ and no deductions with respect to the particle size can be done. For large macromolecules one must obtain extrapolation of measured intensity to $\theta = 0$ and dimension of macromolecule can be determined from the form of angular dependency. The scattering functions for different polymer conformations are shown in the **Fig. 3.1.1a**

<table>
<thead>
<tr>
<th>Table 3.1.1 The scattering functions and asymptotic behavior for various polymer architectures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scattering function</strong></td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Coil [103]</td>
</tr>
<tr>
<td>Sphere [104]</td>
</tr>
<tr>
<td>Star with number of rays $f$ [105]</td>
</tr>
<tr>
<td>Globular particles [106]</td>
</tr>
</tbody>
</table>
3. Analytical Methods

Usually, the so-called KRATKY plot \( P(q)(qR_g)^2 \) versus \( qR_g \) is used for increasing of the difference between scattering functions for polymers with different architecture (Fig. 3.1.1b). For \( qR_g \gg 1 \) scattering function has asymptotic behavior and can be rewritten in the simplified form (Table 3.1.1) (it should be noted that for hard sphere asymptotic behavior overlies sinusoidal function).

Using “single contact approximation” ZIMM [107] has proposed equation, which valid for all types shape of the macromolecule.

\[
\frac{Kc}{R_g} = \frac{1}{M_w P(q)} + 2A_2c + 3A_3c^2 \ldots \quad (3.1-7)
\]

\[
\Delta R_g = \Delta\left(\frac{I(\theta)}{I_0}\right) - 2 = R_{\theta(\text{solution})} - R_{\theta(\text{solvent})} \quad (3.1-8)
\]

\[
K = (4\pi^2 / \lambda_0^4)N_A n_0^2 (\partial n / \partial c)_T^2 \quad (3.1-9)
\]

with \( K \) as contrast factor (no scattering at zero refractive index increment \( (\partial n / \partial c)_T = 0 \) ); \( \Delta R_g \) – RAYLEIGH ratio \( (\Delta R_g \equiv R_g) \); \( I(\theta) \) - scattering intensity at the scattering angle \( \theta \); \( I_0 \) – primary light intensity; \( r \) – distance from scattering volume to detector; \( \lambda_0 \) – light wave length in vacuum; \( N_A \) – AVOGADRO number; \( n_0 \) – refractive index of solvent; \( c \) - concentration of polymer in solution; \( A_2 \) and \( A_3 \) – viral coefficients for the correction of deviation of the osmotic pressure from VAN’T HOFF equation. Taking into account the polydispersity of the macromolecules, the following relation holds

\[
\frac{Kc}{R_g} = \frac{1}{M_w} \left[ 1 + \frac{1}{3} (qR_g)^2 \ldots \right] + 2A_2 c + 3A_3 c^2 + \ldots \quad (3.1-10)
\]

Normally, third viral coefficient is much smaller then second one, so term \( 3A_3c^2 \) can be ignored. Usually eq. (3.1-10) can be evaluated by the method proposed by ZIMM [108]. In this method \( Kc/R_g \) should be plotted versus \( q^2 \). WESSLAU [109] has proposed to use a GUINIER diagram for spherical objects. In this method ln(\( Kc/R_g \)) should be plotted versus \( q^2 \). In this case an upward bend observed in ZIMM diagram will be transformed in linear form that simplifies the process of extrapolation. In the case of strong concentration dependency the \( 3A_3c^2 \) component of eq. (3.1-10) cannot be neglected. To solve this problem, a BERRY [110] diagram can be used. In this case \( \sqrt{Kc/R_g} \) should be plotted versus \( \sin(\theta/2) \).
3. Analytical Methods

3.2 Dynamic Light Scattering

3.2.1 General Properties of the Time Correlation Function

Due to the Brownian motion of the scattering particles, a shift of the frequency of the scattering light $\Delta \omega$ occurs in analogy to the well-known Doppler effect of acoustic waves. The Lorentzian spectrum $P(\omega)$ (Fig. 3.2.1) of this shift can be described by equation

$$P(\omega) = \langle I \rangle \frac{\Delta \omega / \pi}{(\omega - \omega_0)^2 + (\Delta \omega)^2}$$

(3.2-1)

Lorentzian spectrum can be expressed in the terms of electrical field correlation function $g'(t)$ using mathematical theorems formulated by Wiener and Khintschin

$$P(\omega) = \int g'_1(t) \exp(i \omega t) dt$$

(3.2-2)

$$g'_1(t) = \frac{\langle E^*(q,0)E(q,t) \rangle}{\langle E^*(q,0)E(q,0) \rangle}$$

(3.2-3)

$$g'_1(t) = \exp(-\Delta \omega t) = \exp(-\Gamma t) = \exp(-Dq^2t)$$

(3.2-4)

In the praxis, time fluctuation of intensity can be measured (Fig. 3.2.2). The motions, which give rise to light scattering fluctuations, are of different origin depending on whether condensed one-component systems or solutions are considered. In one-component systems (melt, simple liquid or gas) it is the density fluctuation while in solution concentration fluctuations contribute in addition.

Fig. 3.2.1 Schematic plot the frequency shift of the scattered light.
These fluctuations are not fully independent of each other but are correlated. The correlation results from motions within the system and can be described by the time correlation function (TCF) of the scattered intensity

\[ g_2(t) = \frac{\langle I(0)I(t) \rangle}{\langle I(\infty) \rangle^2} \]  

(3.2-5)

\( g_2(t) \) is connected with electrical field correlation function via SIEGERT [111] relation

\[ g_2(t) = A +Bg_1^2(t) \]  

(3.2-6)

where \( A \) is a measured baseline and \( B < 1 \) is the coherence factor, which depends on the quality of the instrumental set-up. In the simplest case time correlation function measured from time fluctuation can be represented by simple exponentional function

\[ g_2(t) - 1 = \exp(-2\Gamma t) \]  

(3.2-7)

with \( \Gamma \) as first cumulant. \( \Gamma \) is defined as initial slope of the logarithmic TCF at \( t = 0 \)

\[ \Gamma = -\partial \ln(g_1(q,t))/\partial t \]  

(3.2-8)

Field correlation function can be also expressed via static \( S(q,c) \) and dynamic \( S(q,c,t) \) structure factors

Fig. 3.2.2 Typical scattered light intensity fluctuations (a) and its time correlation function (b).
3. Analytical Methods

\[ g_1(t) = \frac{S(q,c,t)}{S(q,c)} \] (3.2-9)

Similar factorization as in static light scattering (eq. (3.1-4)) can be also be used as an approximation for the dynamic structure factor \( S(q,c,t) \) such that

\[ g_1(t) = \frac{P(q,t)S'(q,c,t)}{P(q)S'(q,c)} \] (3.2-10)

3.2.2 Behavior of Special Polymer Structures.

3.2.2.1 Hard Sphere.

Monodisperse and homogeneous hard sphere is an example for a structure with highest symmetry. There is no shape in time. Only the rotation around the center of mass could affect the particle scattering factor but the final result remains indistinguishable from initial state (Fig 3.2.3). Thus, we have \( P(q,t) = P(q) \) and

\[ g_1(t) = \frac{S'(q,c,t)}{S'(q,c)} \] (3.2-11)

In sufficient diluted solution, the theory predicts the absence of angular dependence of diffusion coefficient even for particles, which display a very strong angular dependency in static light scattering (only translation diffusion coefficient \( D_z \) can be measured).

\[ D_z = \Gamma / q^2 \] (3.2-12)

It should be noted, that for polydisperse hard spheres TCF becomes angular dependent if the particle scattering factors \( P_j(q) \) deviates from unity [112].

![Translation](Translation.png) ![Rotation](Rotation.png)

**Fig. 3.2.3** Types of motion of a hard sphere; (●) is the centre of mass.
3.2.2.2 Flexible Chain.

For flexible chain, as it is shown in Fig. 3.2.4, there will be a translation motion of the centre of mass and a change of the shape with the time because of internal segment fluctuations. These become clearly noticeable for an observer traveling with the centre of mass. Theory can separate the motion of the mass centre from those relative to the center of mass. The center of mass follows the same diffusion equation as that for hard sphere. For the internal motion with respect to the centre of mass a normal mode analysis has to be made. PECORA [113] started with the spring-bead model and solved the set of equations of motions by means of the WANG-UHLENBECK [114] equation and obtained the general solution with some approximation

\[
g_1(t) = \exp(-D_z^2 t) \left[ P_0 q + \sum_j P_j(q) \exp(-b_j t / \tau_1) \right]
\]  \hspace{1cm} (3.2-13)

\[\Gamma_0 = D_z^2 q \hspace{1cm} \Gamma_j = b_j / \tau_1 \] \hspace{1cm} (3.2-14,15)

where \( \tau_1 = 2R_g / \pi^2 D_z \) is the slowest internal relaxation time. The prefactors \( b_j \) depend on the polymer architecture and on the type of relaxation processes, i.e., whether these are coupled with hydrodynamic interaction (ZIMM model) [115] or not (ROUSE model) [116].

The first exponential function corresponds to the translation diffusion and the other to internal modes of motion. The decay constants of the internal motion do not contain the angular dependent factor \( q^2 \), which is characteristic of translation motion, and the FOURIER transform must be for this reason \( q^2 \) independent. This fact is decisive criterium by which internal motions can be distinguished from translation diffusion.

![Translation and Change in Shape](image)

**Fig. 3.2.4** Types of motion of a flexible chain; (●) is the centre of mass.
3. Analytical Methods

3.2.3 Concentration and Angular Dependence of Diffusion Coefficient.

As it was already mentioned above, for different architectures two different cases could be present: only translation motion or translation motion with several internal modes. Internal modes have much faster relaxation times than given by the diffusive translation motion of the center of mass and this motion becomes increasingly faster with increasing size of domains. Hence, the superimposed internal relaxation spectra must cause an increase \( \Gamma(q) \) as the scattering angle \( q \) is increased. For values \( q R_g < 2 \) this effect can be calculated for flexible chain segments by rigorous perturbation theory which resulted in following dependence of apparent diffusion coefficient \( D_{app} \) [117]

\[
D_{app}(q,c) = D_z (1 + k_D c)(1 + CR_g^2 q^2 - ...)
\]  

(3.2-16)

The first bracket in the eq. (3.2-16) describes the concentration dependence, which often is well represented by a linear dependence

\[
D_{app}(c) = D_z (1 + k_D c)
\]

(3.2-17)

with \( k_D \) as a coefficient that depends on the second virial coefficient as well as on concentration dependence of hydrodynamic friction. The coefficient \( C \) is determined by the longest internal motion with respect to the center of mass. \( C \) was calculated for various molecular architectures and proved to be a valuable guide for estimating of different types of architectures.

Angular dependency of apparent diffusion coefficient can be also expressed in the terms of the static structure factor [117,118]

\[
D_{app}(q) = D_z P(q)^\mu
\]

(3.2-18)

This means that the transition from initial to asymptotic behavior in dynamic and static light scattering occurs in the same \( q \) range and progress in a similar manner. It was already mentioned in Chapter 3.1 that in static light scattering the \( q \)-dependence is determined by the structure and polydispersity of the system. The described behavior according to eq. (3.2-18) seems to imply that, at least for the length scale probed by light scattering, these structure and
polydispersity characteristics have a similar influence on the $q$-dependence in dynamic light scattering. However, the meaning of the exponent $\mu$ remains to be evaluated.

A comparison of eq. (3.2-16) with eq. (3.1-10) in static light scattering reveals a close similarity. Thus in DLS first cumulant data can be plotted in a similar manner as a Zimm plot for the static measurements and parameters $C$, $k_D$ and $D_z$ can be obtained.

### 3.2.4 $\rho$ – Parameter

Additionally to the already considered $C$ parameter there is another one, which is much stronger structure-dependent, the so-called $\rho$ – parameter [117,119]. It can be measured by the combination of static and dynamic light scattering from

$$\rho = \frac{R_g}{R_h} \tag{3.2-19}$$

where $R_h$ is hydrodynamic effective radius which can be obtained from the translation diffusion coefficient by the STOKES-EINSTEIN relationship

$$R_h = \frac{kT}{6\pi\eta_0D_z} \tag{3.2-20}$$

$\rho$ – Parameter was calculated for different architectures and also for the polydisperse ones. These results can are listed in Table 3.2. As it can be seen, polydispersity increases $\rho$ value and oppositely branching decreases it.

**Table 3.2 The $\rho$ and $C$ parameters for various polymer architectures.**

<table>
<thead>
<tr>
<th>Architecture</th>
<th>$\rho$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random coil, monodisperse [117,120]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0- condition good solvent</td>
<td>1.50</td>
<td>0.173</td>
</tr>
<tr>
<td>Random coil, polydisperse [117,120]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0- condition good solvent</td>
<td>1.73</td>
<td>0.2</td>
</tr>
<tr>
<td>Regular star, polydisperse [117,120]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0- condition, $f = 4$</td>
<td>1.33</td>
<td>0.148</td>
</tr>
<tr>
<td>0- condition, $f &gt;&gt; 1$</td>
<td>1.079</td>
<td>0.098</td>
</tr>
<tr>
<td>Regular branched model [121] (soft sphere)</td>
<td>0.977</td>
<td>-</td>
</tr>
<tr>
<td>Homogeneous sphere [122]</td>
<td>0.778</td>
<td>0</td>
</tr>
</tbody>
</table>
3. Analytic Methods

3.2.5 Asymptotic Behavior in the DLS.

If the macromolecules have dimensions larger than \( qR_g \approx 5 \) then the TCF is no longer significantly influenced by the translation diffusion but is solely determined by internal modes of motion and the specific relaxation spectrum. Furthermore, the PECORA approximation for the individual processes is no longer valid and full \textit{Wang-Uhlenbeck} equation has to be used. \textit{De Gennes} [122], \textit{Dubois-Violette} and \textit{De Gennes} [123] considered the asymptotic behavior of large macromolecules at sufficiently large \( q \) values. Under these conditions several closed expressions were derived:

- For \textit{Rouse} [116] model (no hydrodynamic interaction)

\[
g_1(q,t) = \int_0^\infty du \exp \left[ -u - \sqrt{\Gamma} g(u / \sqrt{\Gamma}) \right] \exp \left( \frac{2}{\sqrt{\pi}} \right) \sqrt{\Gamma} t \right)
\]

\[
g(u) = \frac{2}{\pi} \int_0^\infty dx \frac{\cos(x \vartheta)}{x^2} \left[ 1 - \exp(-x^2) \right]
\]

\[
\Gamma_1 = \frac{kT}{12 \zeta_0} a^2 q^4
\]

\[
\Gamma / q^2 \rightarrow (kT / \eta_0) (a^2 q^4 / 12) \text{ for } R_g^2 q^2 \gg 1
\]

\( a \) - bond length, \( \zeta_0 \) – monomer friction coefficient, \( \eta_0 \) – viscosity of solvent

- For \textit{Zimm} [115] model (strong hydrodynamic interaction)

\[
g_1(q,t) = \int_0^\infty du \exp \left[ -u - (\Gamma t)^{2/3} h(u / (\Gamma t)^{2/3}) \right] \exp \left( -1.35(\Gamma t)^{2/3} \right)
\]

\[
h(u) = \frac{2}{\pi} \int_0^\infty dx \frac{\cos(x \vartheta)}{x^2} \left[ 1 - \exp(-x^{3/2} / \sqrt{2}) \right]
\]

\[
\Gamma_1 = \frac{kT}{6 \pi \eta_0} q^3
\]

\[
\Gamma / q^2 \rightarrow (kT / \eta_0) (q / 6 \pi) \text{ for } R_g^2 q^2 \gg 1
\]

3.2.6 Data Analysis in Dynamic Light Scattering

In the case of presence of several components in decay rate \( \Gamma \) the field correlation function \( g_1(t) \) is a weighted sum of individual contributions and can be written as
3. Analytical Methods

\[ g_1(t) = \int w(\Gamma) e^{-\Gamma t} d\Gamma \quad (3.2-29) \]

where \( w(\Gamma) \) is a continuous distribution function of decay rates \( \Gamma \). \( g_1(t) \) and \( w(\Gamma) \) are related by a Laplace transformation. Most of methods solve problem of inverting the Laplace transformation in order to obtain distribution function of decay rates from the measured intensity correlation function \( g_2(t) \) which is connected with \( g_1(t) \) via Siegert relation, other methods have deal with modeling of \( g_1(t) \) in a form different from Laplace transformation. There are a lot of different methods of data analysis obtained in DLS, which are good described in the literature [124].

3.2.6.1 Non-Laplace-transform Types of Data Analysis.

3.2.6.1.1 Cumulants (Simple Fit)

A method of cumulants was introduced by KoppeL [125]. The starting point is the observation of the formal correspondence between the field correlation function \( g_1(t) \) and moment-generating function \( M(-t, \Gamma) \)

\[ M(-t, \Gamma) \equiv \langle e^{-\Gamma t} \rangle = \int w(\Gamma) e^{-\Gamma t} d\Gamma = g_1(t) \quad (3.2-30) \]

where \( \langle \rangle \) denotes the average. The logarithm of moment-generating function \( M(-t, \Gamma) \) i.e. the logarithm of the field correlation function \( g_1(t) \), is the cumulant-generating function \( K(-t, \Gamma) \)

\[ \ln(g_1(t)) = M(-t, \Gamma) = K(-t, \Gamma) = \sum k_m(\Gamma)(-t)^m / m! \quad (3.2-31) \]

where \( k_m(\Gamma) \) is the \( m^{th} \) cumulant and can be expressed as a function of the central moments

\[ \mu_m = \int_{\Gamma_0}^\infty w(\Gamma_0)(\Gamma - \Gamma_0)^m d\Gamma \quad (3.2-32) \]

The first three cumulants are equal to the first three moments, which leads to
3. Analytic Methods

\[ g_1(t) = \exp(-\Gamma_0 t + (1/2!)\mu_2 t^2 - (1/3!)\mu_3 t^3) \]  \hspace{1cm} (3.2-33)

with the first cumulant \( \Gamma_0 \). In the praxis, \( \log(g_1(t)) \) is fitted to a polynomial of second, exceptionally of third order, which yields the coefficients of equation (3.2-33). The second cumulant is the measure of the width of the distribution \( \Gamma \), and hence of effective polydispersity, of the relative presence of several components. For unimodal distribution of slightly polydisperse polymers in solution, the following relation has been derived [126]:

\[ PD.I = \frac{\mu_2}{\Gamma^2} \approx \frac{(M_z / M_w - 1)}{4} \]  \hspace{1cm} (3.2-34)

which is valid with approximation \( M_z / M_w \leq 1.25 \).

The method of cumulants is very sensitive to the correct value of the baseline; this is especially true for \( \mu_2 \). It is also clear that for wide and complex correlation function this method is useless.

3.2.6.1.2 Williams-Watts Formula

In this method [127] the field correlation function is approximated by expression

\[ g_1(t) = \exp((-t / \tau_w)^\gamma) \]  \hspace{1cm} (3.2-35)

which is also called as stretched exponential function (here the simplest stretched exponential function is considered, in the case of polymodal distribution more complex form can be used) and it belongs to so called nonlinear analysis group. The parameter \( \tau_w \) localizes the position of the relaxation peak and \( \gamma \) its width. For \( \gamma = 1 \) equation (3.2-35) is represents single-exponential function; as \( \gamma \) decreases, the width of the peak increases.

3.2.6.2 General Inverse LAPLACE Transformation (GILT) Methods.

3.2.6.2.1 CONTIN (Constrained Regularization)

The regularization method was created by Tikhonov [128] and has been encoded in a very popular and widely used program CONTIN (CONTinuous INversion) by Provencher [129].
3. Analytical Methods

The solution of GILT problem is obtained by minimizing the function

$$\chi^2(\alpha) = \sum_i (1/\sigma_i^2)\left[ g_i - \int K(t,\Gamma)w(\Gamma)d\Gamma \right]^2 + \alpha \| \zeta w(\Gamma) \|^2$$  \hspace{1cm} (3.2-36)

with respect to the function $w(\Gamma)$; $\alpha$ is so called regularization parameter and $\zeta$ is an operator which usually taken to be the second derivative.

The value of $\alpha$ controls the strength of the regularization; $\alpha = 0$ or very small will be equivalent to a bare non-negative least squares method, whereas the larger $\alpha$ the more penalized are solutions with many peaks. CONTIN usually presents a progression of solutions with increasing of $\alpha$. The optimum of $\alpha$ should be large enough to do regularization effectively but small enough as not to oversmooth the true features of the solution. That is why, one should be careful during interpretation of CONTIN output (especially width in the terms of polydispersity!) and should not accept automatically chosen solution as being the closest to reality. It should be checked, whether the result is robust to small changes in $\alpha$. If it so, the chances are that it is real.

3.3 Rheological Properties of Liquid and Solids.

Mechanical spectroscopy is important method for the investigation of the properties of the liquid and solid materials. During the network formation material comes from the liquid to the solid state so it is important to consider some characteristics of the liquids and solids. One important characteristics of the liquid is the viscosity $\eta$ and for the liquid

$$\eta = \frac{\sigma}{(dv/dt)}$$  \hspace{1cm} (3.3-1)

with $\sigma$ as stress and $dv/dt$ as velocity gradient of different liquid layers. When some stress will be applied to concentrated polymer solution or melt some shear $\gamma$ will be produced and this shear will sharply increase with time. After that, the velocity rate $dv/dt$ decreases and tends to zero, polymer creep. The viscosity curve becomes flatter with decreasing of shear rate and the polymer solution shows Newtonian behavior with a constant viscosity. This region at low shear rates is called the terminal relaxation zone or the first Newtonian plateau. The constant viscosity in this range is called the zero-shear viscosity $\eta_0$ [3,130].
For a direct observation of the polymer relaxation, one may impose a small step shear strain $\gamma_0$ on samples while measuring the shear stress response $\tau_{12}(t)$ as a function of time. The result is the shear stress relaxation function

$$G(t) = \frac{\tau_{12}}{\gamma_0}$$  \hspace{1cm} (3.3-2)

also called relaxation modulus [3]. The concept of a relaxation modulus applies to liquids as well as to solids. The solid state manifests itself in a finite value of the relaxation modulus at long times, the so-called equilibrium modulus

$$G_e = \lim_{t \to \infty} G(t)$$  \hspace{1cm} (3.3-3)

The linear viscoelastic behavior of liquid and solid materials in general is often defined by the relaxation time spectrum $H(\lambda)$ [3], which will be abbreviated as “spectrum” in the following. The transient part of the relaxation modulus as used above is the LAPLACE transform of the relaxation time spectrum $H(\lambda)$.

$$G(t) = G_e + \int_0^{\lambda_{\text{max}}} H(\lambda)e^{-t/\lambda} \frac{d\lambda}{\lambda}$$  \hspace{1cm} (3.3-4)

The spectrum is non-negative function, which exists in the range of relaxation times $0 < \lambda \leq \lambda_{\text{max}}$. An important material property is the longest relaxation time $\lambda_{\text{max}}$ beyond which the spectrum is equal to 0. The spectrum cannot be measured directly [3].

In a frequently used experiment, the sample is subjected to oscillatory shear at small amplitude $\gamma_0$. Applying a sinusoidal shear strain $\gamma(t)$ with an angular frequency $\omega$

$$\gamma(t) = \gamma_0 \sin(\omega t)$$  \hspace{1cm} (3.3-5)

it is possible to determining the resulting shear stress

$$\tau_{21}(t) = G'(\omega)\gamma_0 \sin(\omega t) + G''(\omega)\gamma_0 \cos(\omega t)$$  \hspace{1cm} (3.3-6)
with \( G'(\omega) \) and \( G''(\omega) \) as storage and loss moduli. These moduli are defined as [3]

\[
G'(\omega) = G_e + \omega \int_0^\infty [G(t) - G_e] \sin(\omega t) dt 
\]

(3.3-7)

\[
G'(\omega) = \omega \int_0^\infty G(t) \cos(\omega t) dt 
\]

(3.3-8)

The storage modulus is defined as the stress in the phase with the strain in a sinusoidal shear deformation divided by the strain. It is a measure of the energy stored and recovered per cycle. The loss modulus is defined as the stress 90° out of phase with the strain divided by the strain. It is the measure of the energy dissipated or lost as the heat per cycle of the sinusoidal deformation. Often the term loss tangent is used

\[
\tan \delta(\omega) = \frac{G''(\omega)}{G'(\omega)} 
\]

(3.3-9)
4. Experimental Results

I. Thermo-sensitive Microparticles Based on Poly(N-Vinylcaprolactam)


4.1.1 Introduction.

Thermo-responsive aqueous colloidal microgels form an interesting subject of polymer colloids - the gels have properties in common with water-soluble polymers, water-swollen macro gels, and water-insoluble latex particles. Like water-soluble polymers, the properties of microgels depend upon the balance of polymer-polymer vs. polymer-water interactions. Like macroscopic aqueous gels, colloidal microgels are characterized by a degree of swelling, an average cross-link density and characteristic time constants for swelling and shrinking. Like hydrophobic polymer colloids, colloidal microgels can be prepared to have monodisperse particle size distributions; microgels can be characterized by standard colloidal techniques including electrophoresis, dynamic light scattering, rheology and electron microscopy. Microgels can be flocculated by salt or flocculant addition.

The fundamental requirement for the formation of thermo-sensitive microgel is that the polymerization in water should be carried out at the temperatures above LCST [131]. Under these conditions the water-soluble monomer reacts to give insoluble polymer. Sometimes this procedure is called “precipitation polymerization”. The PNIPAm particles can be prepared by a method analogous to the surfactant-free polymerization of styrene, which results in polymer particles stabilized by sulfate surface charge groups originating from the potassium persulfate initiator [132]. Another example of the preparation of the thermo-sensitive microgel in stabilizer-free condition is irradiation of diluted solution of PVME above LCST [133]. The microgel formation is result of intra- or intermolecular cross-linking of collapsed polymer chains in this case. But generally, it is difficult to prepare particles by stabilizer-free conditions. Using of the ionic surfactants for stabilization from other side introduce some difficulties because surfactant binds to the polymer and it is difficult to remove it [131].

The dispersion polymerization normally uses a medium, in which the monomer, the initiator and also an external polymer stabilizer are soluble. The polymer, in contrast, is insoluble in the medium, and therefore it separates out from the reaction mixture. Polymer stabilizers adsorb on
the surface of the polymer particles. When they were adsorbed in a sufficient amount, they prevent agglomeration of the particles by the mechanism of the attached steric stabilization. Some of the polymers also can be grafted on the particle surface and making the stabilization independent on the adsorption. Another possibility to obtain stable dispersion is adding of free polymer chains which are good soluble in dispersion medium. In this case particles are stabilized by the depletion mechanism [134].

The best steric stabilizers are amphiphilic block or graft copolymers [134]. One of the comonomers should generate a homopolymer block that is nominally insoluble in the dispersion medium whereas the other should polymerize to form a polymer that is soluble in the dispersion medium. Random copolymers are usually less active as steric stabilizers than block or graft copolymers although under certain conditions they are able to confer enhanced steric stabilization. Homopolymers are also able to impart steric stabilization but their effect is not comparable with stability produced by amphiphilic copolymers. Anchoring of the homopolymer however can be effective if the surfaces of the colloidal particles contains the sites with which homopolymer can interact specifically. It must be argued in support of the case for homopolymeric steric stabilizers that one of the most effective and industrially most important steric stabilizers for aqueous dispersions is poly(vinyl alcohol). It should be also remembered, that this polymer is commonly prepared industrially by alcoholysis of poly(vinyl acetate) and it is usually only partly hydrolyzed (of order 88% or higher). Therefore it is a copolymer of poly(vinyl alcohol) and poly(vinyl acetate), often with considerable block character.

It is possible to prepare the PVCL by grafting of polyethylenoxide using macromonomer technique [85,86]. However, resulting microgel had low difference between swollen and shrunken state, i.e. thermo-sensitive properties were strongly influenced by the stabilizer. The possibility of stabilization of PVCL microgel by poly(vinyl alcohol) with different molecular weight and hydrolysis degree was studied.

### 4.1.2 Synthesis of the PVCL Microgels.

The influence of the type of stabilizer and its concentration on the stability of PVCL microgel is summarized in the Table 4.1.1. The PVA with high molecular weight does not stabilize PVCL microgel dispersion during preparation. Decreasing of the molecular weight to 17,000 g/mol gives possibility to obtain stable dispersion only when stabilizer does not contain vinyl acetate groups. Besides, obtained dispersions were stable only several days.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVA $^{(a)}$</th>
<th>PVA, g/l</th>
<th>Stability</th>
<th>$R_h$, nm</th>
<th>PD.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14,000-99</td>
<td>10</td>
<td>+</td>
<td>182</td>
<td>0.127</td>
</tr>
<tr>
<td>2</td>
<td>14,000-99</td>
<td>8.3</td>
<td>+</td>
<td>186</td>
<td>0.126</td>
</tr>
<tr>
<td>3</td>
<td>14,000-99</td>
<td>6.7</td>
<td>+</td>
<td>192</td>
<td>0.124</td>
</tr>
<tr>
<td>4</td>
<td>14,000-99</td>
<td>5</td>
<td>+</td>
<td>228</td>
<td>0.146</td>
</tr>
<tr>
<td>5</td>
<td>14,000-99</td>
<td>3.3</td>
<td>+</td>
<td>260</td>
<td>0.134</td>
</tr>
<tr>
<td>6</td>
<td>14,000-99</td>
<td>1.7</td>
<td>+</td>
<td>287</td>
<td>0.159</td>
</tr>
<tr>
<td>7</td>
<td>14,000-99</td>
<td>5</td>
<td>*</td>
<td>249</td>
<td>0.129</td>
</tr>
<tr>
<td>8</td>
<td>14,000-99</td>
<td>5</td>
<td>*</td>
<td>293</td>
<td>0.164</td>
</tr>
<tr>
<td>9</td>
<td>17,000-99</td>
<td>0.67</td>
<td>+</td>
<td>280</td>
<td>0.143</td>
</tr>
<tr>
<td>10</td>
<td>17,000-99</td>
<td>1.33</td>
<td>*</td>
<td>328</td>
<td>0.191</td>
</tr>
<tr>
<td>11</td>
<td>17,000-99</td>
<td>3.3</td>
<td>*</td>
<td>Floccules</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>17,000-99</td>
<td>2.33</td>
<td>*</td>
<td>Floccules</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>17,000-88</td>
<td>0.67</td>
<td>**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>17,000-88</td>
<td>2.33</td>
<td>**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>40,000-99</td>
<td>1.33</td>
<td>**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>40,000-88</td>
<td>1.33</td>
<td>**</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^{(a)}$- dispersion is stable for an infinitely long time $^{**}$- unstable dispersion
* - precipitation of the dispersion after some days $^{(b)}$- PVA type: $M_w$ g/mol – degree of hydrolysis

The stability of PVCL microgels increases with a decreasing of the molecular weight and a decreasing degree of hydrolysis of stabilizer. Polymeric stabilization of the microgel dispersion differs from attached steric stabilization of water insoluble polymers (styrene, butylmethacrylate). These polymers are more stable in the presence of high molecular PVA with a relatively low degree of hydrolysis [135] due to the adsorption of hydrophobic non-hydrolyzed parts of polymer chain. In the case of PVCL microgels, adsorption is weak and thus free polymer chains can play an important role in stabilization. It is also evident, that a lower amount of PVA with high molecular weight is required to maintain the stability of the system. But further increase of PVA concentration results in the destabilization of the colloidal system. This effect is well known [134] as the transition sequence instability $\rightarrow$ stability $\rightarrow$ instability. That means, that some concentration of stabilizer is not enough to make a stable dispersion, its increasing leads to polymeric stabilization and its further increasing induces the depletion flocculation. The dependence of the microgel size on the PVA concentration is shown in Fig. 4.1.1. With increasing PVA concentration the hydrodynamic radius decreased linearly from 290 nm to 190 nm, but after a concentration of around 7 g/l, the stabilizer had no influence on the particle size. This indicates that free PVA chains have influence on the nucleation of the microgel but mechanism of this influence is not fully clear.

**Fig. 4.1.1** Dependence of the hydrodynamic radius \( R_h \) on the PVA (\( M_w = 14,000 \text{ g/mol} \), degree of hydrolysis - 99\%) concentration \( C_{PVA} \) at 15°C.

There is no influence of the reaction rate (e. g. temperature, initiator) on the particle size, but an increasing cross-linking degree leads to a decrease in the stability and to an increase in the particle size. One explanation is that, at the polymerization temperature, MBA residues in polymer network tended to increase water solubility of PVCL-MBA copolymer. Increasing solubility means an increased critical length for oligomer phase separation to form precursor particles. This should lead to a lower number of larger precursor particles, which in turn, lead to lower concentration of larger primary (colloidally stable) particles [136].

4.1.3 Thermal Behavior of PVCL Microgels in Water.

The thermal behavior of selected microgels prepared in the presence of PVA in water is shown in **Fig. 4.1.2**. Thermal behavior of microgels strongly depends on type of the heating regime. In the first case microgel dispersion was measured by stepwise direct heating (slow heating procedure, s.h.). In this case there was a continuous decrease in the hydrodynamic radii up to 30°C and a sharp increase in size of the particles at around 32°C. This increase of size indicates the aggregation of the individual particles. The aggregation point did not depend on the microgel and the stabilizer concentrations and can be taken as the critical aggregation temperature (CAT). This point is close to the reported LCST for PVCL and it means that, like in the case of the linear PVCL, PVA does influenced the LCST.

Quite different thermal behavior was observed, when the samples were quickly heated to 50°C (dispersion at ambient temperature was immersed in a bath at the temperature of 50°C) and then step-by-step cooled (fast heating procedure, f.h.). In contrast to the first case, no aggregation was observed and the temperature dependence was usual for thermo-sensitive microgels (the form of swelling-deswelling curve can be described by the BOLTZMAN sigmoidal model). It can be also seen, that high concentration of PVA slightly decreases the swelling of the microgel.

In the swollen state and in the case of individually shrunken PVCL particles (measured after fast heating) independence of measured diffusion coefficient $D_{\text{app}}$ on the angle $\theta$ of observation was observed. That means that only translation diffusion can be detected. Contrary, the diffusion coefficients for the aggregates were strongly angle dependent (Fig. 4.1.3a). This dependency was completely opposite to those predicted by the theory for the coil, stars or particles with spherical shape [137], where the diffusion coefficients increase (instead of a decrease) with decreasing observation angle or at least are independent on the angle of observation. In the case of a pure diffusive behavior (only translation mode) the relaxation rate $\Gamma$ can be extrapolated to the origin [138] (dashed line in Fig. 4.1.3b). In the case of PVCL aggregates the line intersects the $\Gamma$ axis. This intersection shows probably the presence of a rotational diffusion, which can result from the non-spherical shape of the aggregates.

Fig. 4.1.3 (a) - Dependence of the diffusion coefficient \(D\) on scattering vector \(q^2\) for at different temperatures. (b) - Dependence of the measured relaxation rate \(\Gamma\) on scattering vector \(q^2\): dashed lines – pure translation mode in the cases of intraparticle collapsed or swollen microgel; solid line – linear fit of the experimental data which show complex diffusive behavior. The sample was prepared at 1.67 g/l of PVA (\(M_w = 14,000\) g/mol, degree of hydrolysis - 99%), \(C_{PVCL} = 0.127\) g/l.

There are several models that can predict hydrodynamic radius of non-spherically shaped particles with irregular structure (anisotropically shaped fractal clusters) [139]. The first model developed for the fractal clusters and it models clusters as uniformly porous sphere. The procedure is based on the calculation the hydrodynamic radius from the drag force experienced by a porous sphere moving at a given velocity which is obtained by solving the Stokes equation to describe the fluid motion outside the sphere, coupled with Brinkman’s equation for the fluid motion inside the sphere. For this, the permeability of the sphere should be known. The porous sphere model provides reliable results only for large clusters with a size of primary particles much smaller than that of the cluster, so that the effect of individual particles can be neglected.

The second approach is based on description of the effects of different spheres, which form the cluster, on hydrodynamic behavior of the cluster [139]. It was done on the basis of Kirkwood–Riseman theory. In this framework, the force, acting on every sphere in the aggregate is the sum of the drug force, acting on the individual sphere if it was alone, and the force arising from hydrodynamic disturbances, created by the presence of the other particles. This model has been successfully applied to Monte Carlo generated clusters. However, it is difficult to use this model in praxis because method requires detailed information about the aggregate structure, the exact position of the all particles in cluster.

For interpretation of the results obtained from DLS a model for the elliptical particles was used. This model was used for the characterization of aggregates of cellulose in \(N\)-
methylmorpholin-N-oxid/monohydrate [140]. PERRIN [141-143] has developed a hydrodynamic model of molecular rotation motion. This theory assumes that the macromolecule can be treated as a macroscopic particle immersed in continuum fluid. It furthermore assumes “stick boundary conditions”, which postulate that at the surface of the macromolecule (particle) the solvent velocity is zero relative to the particle velocity. For an ellipsoid of revolution of major semiaxis $a$ and minor semiaxis $b$. PERRIN has shown that rotation diffusion coefficient is described by

$$\theta_{\text{Rot}} = \frac{3kT}{16\pi\eta a^3} \left\{ \frac{(2 - p)G(p) - 1}{(1 - p^2)^2} \right\}$$

(4.1-1)

where $p$ is the axial ratio $p = b/a$ and $G(p)$ is the function of the axial ratio which for prolate ellipsoids, $p < 1$, has the form

$$G(p) = (1 - p^2)^{1/2} \ln \left\{ \frac{(1 - p^2)^{1/2} + 1}{p} \right\}$$

(4.1-2)

and for oblate ellipsoids (plates) $p > 1$, has the form

$$G(p) = (1 - p^2)^{1/2} p \arctan(p^2 - 1)^{1/2}$$

(4.1-3)

This should be compared with to the result for the sticky sphere of radius $a_{eq}$

$$\theta_{\text{Rot}} = \frac{kT}{8\pi\eta a_{eq}^3}$$

(4.1-4)

PERRIN also determined the translation diffusion coefficient for ellipsoidal molecules

$$D_{\text{Trans}} = \frac{kT}{6\pi\eta a} G(p)$$

(4.1-5)

Results of DLS measurements can be expressed as [144]

\[ S(q,t) = N\beta^2 \exp[-(q^2 D_{\text{Trans}} + 6\theta_{\text{Rot}})t] \]  

(4.1-6)

where \( N \) is the number of molecules in the scattered volume and \( \beta \) is the optical anisotropy of a molecule, i.e. the difference between the polarizabilities parallel and perpendicular to the symmetry axis. The first cumulant in this case is equal to

\[ \Gamma(q) = q^2 D_{\text{Trans}} + 6\theta_{\text{Rot}} \]  

(4.1-7)

As result one can measure the translation and rotation diffusion coefficients. Combining equations (4.1.1) and (4.1.5) one obtain

\[ \frac{\theta_{\text{Rot}}}{D_{\text{Trans}}} = \frac{(kT)^2}{40.5(\pi \eta)^3} \left\{ \frac{(2 - p)G(p) - 1}{(1 - p^2)G^3(p)} \right\} \]  

(4.1-8)

As result, the semiaxis \( a \) and \( b \), radius of the equivalent sphere can be calculated. These values are listed in Table 4.1.2. Calculated values for \( p \) slightly differ from 1 of sphere. The experimental results can be described by the mathematical model of oblate ellipsoid (none of solution can be found from the model of prolate ellipsoid).

Usually a decrease of concentration should reduce probability of aggregation. In the case of PVCL microgel in the presence of PVA decrease of concentration has no strong influence on the dimension of the aggregates. However, extremely diluted dispersion shows only translation diffusion at the earlier stages of aggregation. Decrease of ellipsoid size during heating can be easily explained by both intraparticle collapse and formation of a more dense structure by increasing of intraparticle interaction. The aggregation number is low (calculated as the ratio of radius of equal sphere and hydrodynamic radius of the individual particle measured in fast heating regime)- clusters consist on 2-3 individual spheres.

So, diffusion for the aggregates observed for PVCL aggregates is the average value of the pure translation and an additional rotation diffusive mode. This leads to the unreasonable values of the hydrodynamic radii calculated from the extrapolated diffusion coefficients and STOKES-EINSTEIN equation. Different diffusion coefficients can be easily separated only after extrapolation of the measured relaxation rate to zero angle. Surprisingly, it is difficult to find the observation of this phenomenon in publications concerning the aggregation of macromolecules or microgels.

Table 4.1.2 Parameters calculated for PVCL aggregates assuming their elliptical shape.

<table>
<thead>
<tr>
<th>$C_{PVCL}$, g/l</th>
<th>$T$, °C</th>
<th>$D_{trans}$, cm$^2$/s</th>
<th>$\theta_{rots}$, s$^{-1}$</th>
<th>$a$, nm</th>
<th>$b$, nm</th>
<th>$p$</th>
<th>$a_{eq}$, nm</th>
<th>$N_{agg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.127</td>
<td>32</td>
<td>$1.91 \times 10^{-9}$</td>
<td>3.77</td>
<td>563</td>
<td>652</td>
<td>1.16</td>
<td>429</td>
<td>2.5</td>
</tr>
<tr>
<td>0.127</td>
<td>35</td>
<td>$4.3 \times 10^{-9}$</td>
<td>6.18</td>
<td>372</td>
<td>458</td>
<td>1.23</td>
<td>372</td>
<td>2.4</td>
</tr>
<tr>
<td>0.127</td>
<td>38</td>
<td>$3.94 \times 10^{-9}$</td>
<td>7.88</td>
<td>407</td>
<td>490</td>
<td>1.203</td>
<td>350</td>
<td>2.4</td>
</tr>
<tr>
<td>0.0127</td>
<td>32</td>
<td>$6.87 \times 10^{-9}$</td>
<td>0</td>
<td>433</td>
<td>433</td>
<td>1</td>
<td>433</td>
<td>2.5</td>
</tr>
<tr>
<td>0.0127</td>
<td>38</td>
<td>$9.03 \times 10^{-9}$</td>
<td>6.39</td>
<td>376</td>
<td>500</td>
<td>1.33</td>
<td>318</td>
<td>2.2</td>
</tr>
</tbody>
</table>

There are a lot of publications about aggregation and its kinetic studied by photon correlation spectroscopy, but in most cases only results at the observation angle of 90° were reported. According to the results observed here, one should be careful during discussion of the number of aggregation and the fractal dimension of the aggregates (fractal dimension smaller as 3 shows irregular shape and thus effect of rotation can not be neglected!) on the base of hydrodynamic radii measured only at single angle.

The effect of the heating rate on the particles size distribution of the microgels is shown in Fig. 4.1.4. The particle size distribution for microgels obtained in the presence of PVA is broad. Due to relative strong dilution (concentration is at least one order smaller as usual for polymer solution) PVA peak is not observable. During step-by-step heating to 32°C, aggregation occurred and the peak-maximum of the hydrodynamic radius distribution is shifted to a higher value. The size of the aggregates was checked after annealing of the sample for several hours. Only a single exponential time correlation function and a monomodal relaxation time distribution were observed in all cases (Fig. 4.1.4).

Fig. 4.1.4 Changing of the TCF (a) and hydrodynamic radius (b) relaxation time distribution for PVCL microgel particles at the observation angle of $\theta = 60°$ in the swollen state and after direct heating (s.h.) and step-by-step cooling (f.h.); sample was prepared at presence 1.67 g/l of PVA ($M_w = 14,000$ g/mol, degree of hydrolysis –99%); $C_{PVCL} = 0.127$ g/l
That means, that the process of aggregation was already completed. After fast heating to 50°C and step-by-step cooling, the peak-maximum is shifted to a smaller value as expected for thermo-sensitive microgels. The effect of heating rate on the thermal behavior in water was observed for thermo-sensitive copolymers based on NIPAm [145,146] and was considered as a consequence of competition between interparticle interaction and intraparticle coil-to-globule transition. Up to 31°C the solvent quality for PVCL chains decrease, but the Van der Waals attractive forces, are still low and the PVCL chains on the microgel surface are involved with PVA in the sterical stabilization. Water became a bad solvent at 32°C and the Van der Waals attractive forces subsequently increased. At the same time, the electrostatic repulsion slightly increases as the charge density increases (remaining initiator groups) when the particles shrink. PVCL chains shrink and all individual particles aggregating because attractive (Van der Waals and hydrophobic interaction) forces are now dominating. In this case, only PVA is stabilizer for the microgel, but probably this stabilizing effect is not strong enough to prevent aggregation but strong enough to prevent complete precipitation. During slow heating the colloidal particles were in the metastable state. Microgels particles are not yet fully collapsed, so individual particle have more chances to undergo the interparticle aggregation.

At the temperature of 50°C, which is well above the LCST of the particles, shrinking is fast and the charge density increases rapidly at the particle-water interface, which in turn means the colloidal stability should increase. The presence of PVA also prevents formation of the aggregates. Both processes, slow heating and fast heating, are reversible. The aggregates will dissociate in individual swollen particles or individual particles will swell after cooling. The heating and long-time incubations of concentrated microgel dispersion at temperatures above 32 °C lead to an irreversible coagulation. This process is possibly can be explained by the fact that in the aggregated state particles are touched to each other. Under these circumstances the Brownian collision stresses the stabilizer molecules, which endeavor to escape from the stress zone. This effect can be affected either by desorption from the particle surface or by the lateral movement over the particle surface (more probable in the case of PVCL microgel) away from the stress zone. However, microgel can be dried and redispersed again without the presence of sufficient amount of the coagulum. This is an important consequence of the thermodynamic stability of sterically stabilized dispersions. Recently, Everett and Stageman have demonstrated the spontaneous redispersion of freeze-dried poly(methylmethacrylate) particles coated by poly(dimethylsiloxane) [147]. It should be noted, that PVA plays an important role in the stabilization of microgels during synthesis, it is difficult, when not impossible, to obtain PVCL microgel in stabilizer free conditions. The preparation of the stable microgel dispersion
was also unsuccessful in the presence of poly(oxylene) block copolymers with different hydrophobic-hydrophilic balance.

### 4.1.4 Colloidal Stability.

Colloidal stability of the microgels was checked as a function of concentration of an added electrolyte (NaCl). Independently on the PVA concentration, all samples were completely stable up to 0.7 M of NaCl at 25°C, and at higher salt concentrations precipitation was observed. It should be noted, that an electrolyte, when it is present in solution, not only decreases the repulsion between particles due to the screening of charges on the surface, but also strongly decreases the solubility of poly-N-vinylcaprolactam in water. It was shown [50], that the reducing influence of NaCl on LCST of PVCL is 10 K·l/mol. That means, at some electrolyte concentration water is not any more good solvent for PVCL. At high temperatures (fast heating) in electrolyte solutions, microgels are also unstable due to the charges screening effect. All this facts only confirm the conclusions that at 25°C the particles are stable as a result of (i) a HAMAKER constant similar to that of the solvent because the particles are swollen with water and (ii) a sterical barrier (hydrated PVCL chains and PVA chains in solution). At the slow heating aggregation occurs, that means an increase of the stickiness of the particles because of (i) an increase of attractive potential (the HAMAKER constant is higher due to the expelling of water from particles), (ii) decrease of sterical repulsion (for PVCL it can be even attractive under bad solvent condition) and (iii) the thermal energy increases the probability of collision. At the fast heating electrical repulsion became dominate and microgel remains stable.

### 4.1.5 Conclusions.

From the results mentioned above, it can be concluded, that PVA stabilization of PVCL microgel dispersion differs from attached stabilization of insoluble polymers due to the weak adsorption of hydrophobic part of stabilizer on the PVCL chains. Increasing of the molecular weight of PVA and its concentration lead to the depletion flocculation through the transition sequence instability $\rightarrow$ stability $\rightarrow$ instability. Decreasing of the molecular weight of PVA and increasing of its concentration give possibility to reduce (to some extend) particle size. There is no influence of the stabilizer quantity on transition temperature of PVCL, but the stabilizer, when its concentration is high, decreases the swelling of the microgels.
The stability of the microgels at room temperature is a cooperative effect of free PVA chains in solution and free PVCL chains on the particle surface. After heating, PVCL chains shrink and microgels aggregate due to a not sufficient stabilization by PVA. Diffusive behavior for these aggregates is the average value of translation and rotation diffusions. During fast heating to the temperature above LCST, immobilization of the remaining charged initiator groups on the surface occurs and the colloidal stability increases. The thermal behavior of the PVCL microgel dispersion is summarized in the Fig. 4.1.5. The stability of microgels toward electrolyte is not dependent on the PVA concentration. Aggregation effects at $C_{NaCl} > 0.7$ M appear as the result of screening of initiator charges and the reduced solubility of PVCL chains.
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

4.2.1 Introduction

In the recent years, increasing attention has been focused on the preparation and characterization of microgels containing thermo-sensitive polymers and some functional groups [131]. The swellability of a microgel depends on the type of microgel, its affinity to the solvent, which in turn is dependent on monomer (and/or comonomer) composition/concentration, as well as degree of cross-linking. The nature of monomers used in preparation of the microgels will determine overall properties of the final product. The addition of the monomers with different functionalities to the microgel can create particles with a wide range of different properties and gives possibility to broader the range of their application. However, introducing of the monomer with hydrophobic or hydrophilic nature influence the thermo-sensitivity. Only a few syntheses of microgels with different functional groups based on N-vinylcaprolactam were reported [85-90]. In this part the colloidal and temperature behavior of a novel system based on N-vinylcaprolactam and hydrophobic comonomer acetoacetoxyethyl methacrylate (AAEM) were studied. Microgels were prepared by the precipitation polymerization under surfactant-free conditions. The acetoacetate functional group of the AAEM can react in a wide range of post modification reactions: reactions with amines, aldehydes, chelation, Michael reaction, etc. [148]. Therefore, obtained microgels can be interesting object for application in medicine or in metal separation. The chemical structure of VCL/AAEM co-polymer is presented in Fig. 4.2.1.

![Chemical structure of VCL/AAEM copolymer.](image)

Fig. 4.2.1 Chemical structure of VCL/AAEM copolymer.
4.2.2. Characterization of VCL/AAEM Microgels

4.2.2.1 IR Spectroscopy

Incorporation of AAEM in microgel was checked with IR spectroscopy. Typical IR spectrum for copolymer microgel is shown in Fig. 4.2.2. Major changes can be observed in region 1500 – 1800 cm\(^{-1}\). Characteristic signals for PVCL (amide band I at 1623 cm\(^{-1}\)) [15] and for PAAEM (C=O band at 1745 cm\(^{-1}\)) are marked with arrows. It should be noted, that the signal for PAAEM consists of the vibrations of both ester and ketone carbonyls, which cannot be completely discriminated in this case. Additionally, quantitative characterization of microgel composition by IR is difficult due to the presence of amide groups of cross-linker. However it is can be noted that with increasing of AAEM content in the monomer mixture the altitude of the carbonyl band increases and altitude of amide band decreases that indicate the change of microgel composition.

![IR Spectra](image)

**Fig. 4.2.2** (a) – IR spectra of VCL/AAEM copolymer microgel prepared at the molar monomer ratio 97.5/2.5; (b) – signals for carbonyls of VCL and AAEM as a function of monomer mixture composition: (–) – 98.75/1.25; (–) – 95/5; (–)– 90/10.

4.2.2.2 Elemental Analysis.

It is well known [12,15], that copolymerization of \(N\)-vinyl monomers with methacrylic ones is far from ideal due to the large difference in reactivity. Besides, faster consumption of acrylic cross-linker should lead to formation of some noncross-linked polymers based mostly on the PVCL. So, incorporated amounts of AAEM presented in microgels are higher than it is taken in the starting monomer mixture (Fig. 4.2.3).
4.2 Thermosensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

Elemental analysis is not an exact method for determination of composition of polymers based on N-vinyl lactams [12] but this method gives possibility to follow the changes in composition induced by the changes in the monomer mixture. The reaction mixture is very complex and microgel is hygroscopic, so elementary analysis does not reflect its real composition.

4.2.2.3 Thermal Analysis.

Incorporation of AAEM units \( T_g^{PAAEM} = 18 \, ^\circ\text{C} \) [148]) in copolymer should lead to a decreasing of the glass transition temperature of the network to lower values than for pure PVCL. For PVCL it was shown, that absorbed water strongly influences \( T_g \) determination and a maximal value of 147°C is reported [32]. It is also known that water cannot be easily removed from PVCL and the value of 191 °C measured in this work therefore appears more exact and acceptable because measurements were done after incubation of the microgel at 225°C. Surprisingly, two different \( T_g \) values were observed for copolymeric VCL/AAEM microgels. This fact indicates the phase separation inside of microgel. Taken into account different reactivity of comonomers and assuming the radial composition gradient one can expect that internal part of spherical microgel reached by PAAEM chains and periphery by PVCL. Thus first observed \( T_g \) of 187 °C (Fig. 4.2.4) correspond to the glass transition of PVCL.
4.2 Thermosensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

![Graph showing heat flow vs. temperature](image)

**Fig. 4.2.4** Glass transition temperature for VCL/AAEM microgel (15.2 mol-% of AAEM).

Second one is much higher as for PAAEM but probably this temperature corresponds to the terpolymer of complex composition based on PVCL, PAAEM and PMBA. The TGA measurements indicated that VCL/AAEM copolymers are thermally stable in nitrogen atmosphere up to 300 °C.

### 4.2.2.4 Scanning Electron Microscopy

Scanning electron microscopy images for sample with 4.8 mol-% AAEM are shown in **Fig. 4.2.5**. It is difficult to obtain good pictures for microgels with this method probably due to a strong influence of water on glass-transition of polymer chains. This influence cannot be avoided even with freeze-drying. In general, freeze-drying did little damage and some types of microgels were more susceptible than others. It was found, that it is impossible to remove completely the bound water from microgels by freeze-drying [149]. It is also found, that positively charged particles have tendency to form aggregates during drying [150]. It is possible to recognize that the individual particles are relatively uniform in size. Situation is totally different when the microgel was filled by the hydrophobic polypyrrole. In this case polypyrrole acts as hard skeleton, which gives not possibility for PVCL to make film and it avoid aggregation – polypyrrole is negatively charged. From images of the filled microgels it is clear that VCL/AAEM microgels are monodisperse. The present nonuniformity of the surface is the result of polypyrrole inclusions. The preparation and investigation of properties of such filled microgels can be read elsewhere [151].
4.2.3 Thermal Behavior of VCL/AAEM Microgel in Water.

4.2.3.1 Static Light Scattering

Static light scattering was performed for the measurements of radius of gyration, $R_g$, at different temperatures. Fig. 4.2.6 represents typical GUINIER plots for the same microgel at room and elevated temperature. The straight nature of angular dependence shows the spherical shape of the particles. Due to the strong dilution (concentration is of order $10^{-1}$-$10^{-2}$ g/l), concentration dependence of $R_g$ is practically absent and can be neglected within the error of 2-4%. Second viral coefficient $A_2$ is very small (three order lower than those for polymer in solution) and positive - around $2.3 \cdot 10^{-7}$mol·cm$^3$/g$^2$ at 25°C and $1.3 \cdot 10^{-7}$mol·cm$^3$/g$^2$ at 50°C.

![GUINIER plots for VCL/AAEM microgel (6.7 mol-% of AAEM) at a - 25°C, b - 50°C](image)
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

That means that the overall interactions between particles are repulsive. One can expect that $A_2$ should be negative at the temperature above the LCST of PVCL as a polymer in bad solvent. However, in this case $A_2$ characterizes the interaction between microgel particles as colloid entities and not those of the polymer segments, which govern the swelling [152]. An extra force, repulsive in nature, must act between particles in water at elevated temperature. Since microgel surface should be slightly charged due to the presence of the rests of initiator, electrical interactions can account for the repulsion and for the positive second virial coefficient. Additional sterical repulsion between PVCL chains at room temperature is also present.

The scattering light intensity shows very strong dependency on the scattered angle in the case of microgel. This angular dependence gives opportunity for the analysis of the shape (structure) of the microgel particles. In Fig. 4.2.7 the experimentally determined $P(q)$ functions for microgel in swollen and collapsed state are collected and plotted in the KRATKY plot with theoretical curves for different shapes of polymer chains. It is clear, that at both, room and elevated, temperatures VCL/AAEM microgels shows behavior of the globular particles. Experimentally obtained scattering functions are in a good agreement with calculated theoretically GUINIER approximation for globular particles. It is well known, that the KRATKY plot is very sensitive to the polydispersity and such agreement with the theory at 25°C can be explained by low polydispersity of obtained particles and as it was shown that scanning electron microscopy experiments confirms this conclusion.

![Fig. 4.2.7 KRATKY plots for VCL/AAEM microgel (6.7 mol.-% of AAEM) at 25°C and 50°C](image-url)

Fig. 4.2.7 KRATKY plots for VCL/AAEM microgel (6.7 mol.-% of AAEM) at 25°C and 50°C
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GUINIER approximation is valid only in the range \( qR_g < 3 \). In the case of larger \( qR_g \) values the situation becomes more complicated and scattering function cannot be easily predicted for microgels. KUNZ and BURCHARD [153] have used radial density distribution to describe results of SLS. For objects with spherical symmetry, the particle scattering factor can be calculated from the radial density distribution \( g(r) \) by the FOURIER transformation as follows

\[
P(q) = \left[ \frac{\int r^2 g(r) \frac{\sin(qr)}{qr} dr}{\int r^2 g(r) dr} \right]^2
\]

(4.2-1)

The radial density distribution can be calculated but this procedure requires knowledge of three independent parameters, which determines fraction of the core, shape of the distribution and the maximum of gamma distribution. It is difficult to obtain these parameters experimentally and different assumption should be done before eq. (4.2-1) will give result, which fits measured scattering function. This model was successfully used for describing of the static light scattering results measured for poly(methylmethacrylate) microgel [153]. VAGRA et al. [154] have reported that the shape of reciprocal scattering function \( P(q)^{-1} \) for NIPAm microgels in the range of \( qR_g \) between 0 and 4 strongly depends on cross-linking degree. The resulting reciprocal scattering functions, were found in between \( P(q)^{-1} \) of sphere and coil. They have tried to introduce spherical density distribution in equation of scattering function but universal model was not obtained.

STIEGER and RICHTERING [155] have reported that for NIPAm microgels below LCST fitting of intensity profile with a model expression of the form factor for homogenous sphere with box shaped radial scattering length density distribution did not describe experimental data. However the form factor of a sphere with a scattering length distribution that gradually decreases at the sphere interface following half-GAUSSIAN distribution fitted experimental dates very well for all temperatures. Unfortunately, details are still not published and cannot be used in this work. It seems that the question of the universal model in static light scattering for microgels is still opened and requires further investigations.

At elevated temperatures the microgel behavior should tend to the hard sphere behavior due to the collapse of PVCL chains and formation of compact structure. The reason of the deviation of experimental results from predicted is not fully clear and will be checked by dynamic light scattering.
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

The behavior of radius of gyration for different VCL/AAEM microgels at the different temperatures is summarized in Fig. 4.2.8. It is known, that in the case of spherical objects \( R_g \) carries the information about the internal structure [153]. It is clear from the \( R_g \) values presented in Fig. 4.2.8 that increasing of AAEM concentration increases hydrophobicity of the core and makes the internal “core” more dense and compact. This leads to the decreasing of the thermo-sensitivity of the core and transition temperature shifted to 23-25 °C. Some of measured \( R_g \) values in Fig. 4.2.8 are apparent (static light scattering was measured at the concentration of \( 1 \cdot 10^{-5} \) g/ml) but, as it was shown previously, due to a weak concentration dependence of \( R_g \) for VCL/AAEM microgel, these values are close, when not equal, to these, extrapolated to \( c \rightarrow 0 \). The same simplification (measurements at single extremely diluted concentration for determination of \( R_g \)) is often used for microgels investigation [156,157].

4.2.3.2 Dynamic Light Scattering.

The concentration and angular dependency was measured for VCL/AAEM microgels at room temperature. As in the case of SLS, no any concentration dependency was observed for apparent diffusion coefficient. The absence of the angular dependence of the apparent diffusion coefficient was also observed (Fig. 4.2.9).
That means that both concentration dependence of hydrodynamic friction and longest internal mode of segmental motion with respect to the center of mass can be neglected and diffusion coefficient will be equal to the translation diffusion of the particles center of mass. However the angular dependency was observed in the cases of PVAc [121], PBMA [158] and PS [159] microgels with comparable size in good solvents (the laser wave length was also nearly the same). Especially slightly cross-linked chains on the periphery should have faster relaxation times than given by the diffusion center of mass. For chains in good solvent with sufficient large $qR_g$ (at least $> 2$) internal motion should be observable. Several of the internal modes can be suppressed, this may be a result of reduced internal flexibility of the subchains due the branching, but could be also a result of the constraints of the fixed ends in a network, which would suppress a number of modes that are possible in the freely moving linear chain. From other side, in the microgel the characteristic length is the chain length between cross-links and it can be simply to short to observe internal motion. Probably all these reasons have contribution.

The particle size of VCL/AAEM microgels was measured at different temperatures. Fig. 4.2.10a represents temperature dependencies of hydrodynamic radii for microgels with different AAEM content.
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

For all samples the broad continuous decrease of hydrodynamic radius was detected, and transition temperature was slightly shifted to ~28 °C (was measured as inflection point) in comparison to reported 32 °C for PVCL. This fact together with results of static light scattering and measurements of glass transition temperature leads to the conclusion that VCL/AAEM microgels have a core-shell structure. It is worth mentioning the polymerization mechanism in present system to summarize the experimental results presented above. Microgel particle formation occurs by homogenous nucleation, which is known sometimes to give latex dispersions with a narrow particle size distribution [160]. At the first stage, a water-soluble cationic radical initiates mainly a water-soluble (in present concentrations) AAEM and MBA monomers which then grows in solution until they reach a critical chain length after which the growing chain precipitates to become a colloidally unstable “precursor particle”. The precursor particles follow one of two competing processes. Either they deposit onto an existing colloidal stable polymer particle or they aggregate with other precursor particles until they form a particle sufficiently large to be colloidal stable. These stable particles create nuclei for PVCL growing chains. Particle grow occurs up to consumption of the pedant double bounds, which should be available on the particle/water interface due to more hydrophilic character of MBA [131], and further reaction leads only to physical anchoring of the hydrophobic chains. Besides, cross-links can be formed even without involving of double bonds of the cross-linker.

The self-cross-linking of PNIPAM during polymerization above LCST due to the chain transfer reaction is known phenomena [136,161,162]. At the polymerization temperature of 70 °C which is far above the LCST, the growing PVCL microgel particles are colloidally

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Fig. 4.2.10 Average hydrodynamic radius (a) and swelling degree (b) as a function of the temperature; ○ - 4.3 mol.-% of AAEM, ■ – 6.7 mol.-% of AAEM, △ – 15.2 mol.-% of AAEM.
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

stabilized by electrostatic stabilization originating from charged groups introduced by the cationic initiator. Microgel is only slightly positively charged in the swollen state but in collapsed state the area of surface is increased.

It can be supposed that resulting particles have a core-shell structure due to fast consumption of high reactive AAEM on the first stage of reaction. Only in this case the absence of influence of the hydrophobic monomer on the thermal behavior of copolymeric microgel can be expected. Similar structure was observed for copolymer microgels of NIPAM with hydrophobic vinyl laurate [163]. The shell consists mainly of covalently bonded PVCL chains, which in swollen state at low temperatures sterically stabilize microgels. As result, concentration of AAEM only slight influences size of formed particles but regulates degree of swelling and thus size at the temperature below LCST (Fig. 4.2.10b).

The particles size distributions for the sample with 6.7 mol-% AAEM at different temperatures are shown in Fig. 4.2.11. Heating of the microgel dispersion does not influence polydispersity of particles size distribution so only intraparticle collapse is observed and interparticle hydrophobic aggregation is not present. Note, that the hydrodynamic radius distributions, obtained by transformation with the CONTIN program, were always found to be symmetric in the logarithmic scale. This symmetry in the logarithmic scale possibly may be an effect of the LAPLACE inversion procedure, which requires some smoothing of the experimental data and this may cause a broader distribution than actually present [164]. In any case, the particles size distribution for VCL/AAEM microgel is much more narrow than for PVCL microgel prepared in the presence of PVA.

![Fig. 4.2.11 Hydrodynamic radius distribution (6.7 mol-% AAEM) as a function of the temperature at the observation angle \( \theta = 90^\circ \).](image)

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The relative distribution width $\mu_2/\Gamma^2$ obtained from cumulant analysis was small. The values $M_L/M_w$ for PVCL/AAEM microgels were estimated as 1.06-1.08 using the relation (3.2-34) and no clear dependence was observed. These values confirm the conclusion about relatively narrow particle size distribution.

4.2.3.3 Combined SLS and DLS

It is well known that the ratio $\rho = R_g/R_h$ reflects the conformation of a polymer chain or the density distribution of a particle and thus gives valuable information about the internal structure of microgels. Fig. 4.2.12 shows the $\rho$-parameter as function of the temperature calculated from experimental $R_g$ and $R_h$ data presented in Fig. 4.2.8 and 4.2.10. It is useful to consider this ratio because the influence of molar mass dependencies can be neglected. At room temperature $\rho$-parameter value is much smaller as value for the hard sphere. Typical $\rho$ values for microgels in the range 0.3-0.6 have been reported [153,158]. That means that particles become more transient in the outer region. It also indicates the heterogeneous swelling of the whole particle. These values are smaller as the minimal value of 0.775 for hard sphere, which can be theoretically calculated. Any attempt to include hydrodynamic interaction according to OSEEN [165] leads to values larger then a hard sphere in any of the models. But this phenomenon can be understood when one will take into account radial symmetry of microgel and the radial density function $g(r)$. Assuming that a hydrodynamic radius is the outer radius one can obtain homogenous density distribution in the case of compact sphere (microgel in collapsed state).

![Graph showing temperature dependence of $\rho$ parameter for VCL/AAEM microgels.

Fig. 4.2.12 Temperature dependence of $\rho$ parameter of the VCL/AAEM microgels;
○ - 4.3 mol.-% of AAEM, ■ – 6.7 mol.-% of AAEM, ▼ – 15.2 mol.-% of AAEM.](attachment:fig4212.png)
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Fig. 4.2.13 Calculated radial density distribution $g(r)$ for VCL/AAEM microgel (6.7 mol.-% of AAEM) at (a) 20 and (b) 50°C

In the swollen state imperfection in cross-linking density (core is usually more dense) leads to decreasing density at the particles surface, the core is covered by the dangling chains that increase the hydrodynamic radius but they have small influence on the radius of gyration and $\rho$-parameter is smaller than the value for hard sphere. The radial density distribution calculated for the microgel in swollen state and collapsed state are shown in the Fig. 4.2.13. These distributions were calculated assuming the homogenous structure of the core and shifted to the core surface gamma distribution of the shell. The density distribution of the shell is described by the gamma function in this case (see the reference [153] for details). In reality the situation can be more complicated [153].

Fig 4.2.12 shows that at the lower temperatures state particles are swollen and at the elevated temperatures mobility of PVCL chains decreases. As result, a compact structure without internal motion is formed and microgel exhibits hard sphere behavior. Up to now there are only a few observations [166] of the transition from “soft” to “hard” sphere for thermo-sensitive microgels. Microgels with $\rho$ value higher as 0.775 in the swollen state are also reported in the literature. The decrease of this parameter to 0.65 with heating or even the presence of minimum of $\rho$ was shown for such kind of microgels [167]. As it was shown from results of SLS and DLS, only using these methods simultaneously gives complete information about conformational changes of the internal structure of microgels based on PVCL in the absence of hydrophilic comonomers.
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4.2.4 Thermal Behavior of AAEM/VCL Microgels in Water-Alcohol Mixtures.

For investigation of the influence of the alcohol on the dimension, the VCL/AAEM microgel was diluted by the different alcohol-water mixtures and the hydrodynamic radius was measured by DLS. **Fig. 4.2.14** shows the hydrodynamic radii of the microgel sample measured in solutions, which contain different amounts of methanol or ethanol (measurements were made at 20 °C). **Fig. 4.2.14** indicates that PAAEM particles are not sensitive to the addition of alcohol and \( R_h \) value is nearly constant in broad alcohol concentration range. This indicates that AAEM-rich microgel core must be nearly not influenced by presence of alcohol molecules. For VCL/AAEM particles both for methanol and ethanol systems the opposite effect was observed: decrease of \( R_h \) up to ~ 15 mol.-% of ethanol and ~ 20 mol.-% of methanol in solution (partial collapse of VCL-rich shell) and then increase of the \( R_h \) with further increase of alcohol in solution (swelling of VCL-rich shell). The influence of iso-propanol and n-propanol in water is more pronounced but measurements were unsuccessful due to the lack of stability. This behavior of VCL/AAEM microgels may be explained after consideration of a hydration-dehydration of polymer chains caused by the presence of solvent molecules with hydrophobic groups. To understand this effect, it is necessary to analyze the fact that the so-called structure of liquid water, produced by an extensive network of hydrogen-bonded molecules, is certainly modified by changes in temperature or pressure, and by the addition of ionic or non-ionic solvents [168].

**Fig. 4.2.14** Hydrodynamic radius of microgel as a function of binary solvent composition (T=20 °C);
- VCL/AAEM in methanol (6.7 mol.-% of AAEM), ● - VCL/AAEM in ethanol (6.7 mol.-% of AAEM); ■ - PAAEM in ethanol.
When a small amount of a low polarity organic solvent is added to water, cages of water molecules surround these solute molecules, this phenomenon being known as hydrophobic hydration. The shape of this hydration shell depends on the molecular structure of the solvent molecule. This shell is stabilized by the hydrogen bonds formed among water molecules in a configuration different from that in pure water. The low polarity molecules are also called “structure-makers” due to their ability to increase relaxation time of ‘clusters’ of water molecules. In this case the solute-water interactions are poor and solute does not destroy water structure, but enhance its stability. Alcohols and ketones are examples of structure-makers, while compounds like DMSO, glycerol are considered to be “structure-breakers” because their favorable interactions with water decrease stability of the hydrogen-bonded water structure [168]. But the referred “structure promotion” is limited to the capability of water to hydrate certain amounts of solvent molecules, beyond which the so-called hydrophobic interaction may be prevalent, ultimately leading to phase separation. A more hydrophobic solute demands a larger number of water molecules to hydrate it and is more likely to cause rupture of its hydration shell.

In pure water the PVCL chains are highly hydrated, and this leads to swelling of gel. This indicates that formation of hydrogen bonds between C=O group of VCL units and water molecules is favorable. Addition of alcohol molecules in water-rich solutions results probably in mobilization of water molecules to participate in hydration structure. However, as the concentration of organic solvent further increases, the hydration shells around solvent molecules are broken or, in other words, the amount of solvent is large enough to avoid its complete hydration. Then “free” solvent molecules can interact with PVCL chains. It seems, that this hydrophobic interaction predominate thermodynamically over the formation of hydrogen bonds between C=O groups of PVCL and OH of alcohol and on this stage addition of alcohol increases $T_m$ and the VCL-rich shell starts to swell rapidly. The investigated system remains stable at different alcohol concentrations and no aggregation effects were detected.

The minimum in $R_h$ – $C_{ethanol}$ diagram in Fig. 4.2.14 correlates with the minimum in the phase diagram of linear PVCL in water-ethanol mixture reported by KIRSH et al. [53] (compare with Fig. 2.2.9).

From experimental data presented in Fig. 4.2.14, it is possible to conclude that VCL/AAEM microgels will lose their thermo-sensitivity in binary alcohol-water solutions when alcohol concentration is higher as indicated by minimum in Fig. 4.2.14. Experimental results confirm this hypothesis. Fig. 4.2.15 presents the hydrodynamic radii of VCL/AAEM microgels as a function of the temperature measured in different alcohol-water solutions.
4.2 Thermosensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

**Fig. 4.2.15** Hydrodynamic radius of VCL/AAEM microgel (6.7 mol.-% of AAEM) in different ethanol-water (a) and methanol-water (b) mixtures as a function of temperature

**Fig. 4.2.15** indicates that VCL/AAEM microgels possess thermo-sensitive properties in water and alcohol-water mixtures up to the certain alcohol concentration. At higher alcohol contents the VCL rich shell of the microgels swells and this leads to the change of particle dimensions. With increasing of alcohol concentration phase transition became broader and disappears in the mixture, which is good solvent for whole temperature range. It should be noted, that the microgel never riches fully collapsed state in the presence of alcohol even at elevated temperatures probably due to hydrophobic interaction between polymer and alcohol. This interaction is stronger than in the case of microgels, based on more hydrophilic N-isopropylacrylamide, which have size in collapsed state in mixture lower than in water [169,170].

### 4.2.5 Investigation of Colloid Stability by Sedimentation

The sedimentation of VCL/AAEM dispersions was investigated by a method developed by **Lerche et al.** [171]. An optoelectronic sensor system integrated in special centrifuge allows to detect spatial and temporal changes of light transmittance during the rotation. In contrast to other approaches [172] the local transmittance is determined over the entire sample length simultaneously. Throughout the measurement, transmittance profiles are recorded and sedimentation process can be depicted as a time course of the relative position of the boundary between supernatant and sediment (resolution better than 100 µm) or of the transmittance averaged over the entire or a chosen part of the sample length. On the basis of the obtained data the sedimentation constants, the packing density, etc., can be derived.
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

![Diagram](image)

**Fig. 4.2.16** The front of sedimentation (a) of the VCL/AAEM microgel (15.2 mol-% AAEM) and sedimentation curves (b) for the microgels with different AAEM content.

The typical transmittance profile of sedimentation process for VCL/AAEM microgel in **Fig. 4.2.16a** shows continuous decrease in sediment height due to compression of the sediment. In this case the transmittance profiles were recorded every 10 sec and every 100th measurement is shown. **Fig 4.2.16a** shows that a sedimentation fronts move parallel to the cuvettes bottom. The transmittance profiles can be transformed into transmittance-time curves. The transmittance increases with centrifugation time since particles move to the bottom of the cell. **Fig. 4.2.16b** presents transmittance-time curves for VCL/AAEM particles prepared at different compositions. The slope of the sedimentation curves indicates that particles, which contain high AAEM amounts, precipitate faster if to compare with particles containing less AAEM.

The calculated sedimentation rates from the slopes of transmittance-time curves are summarized in **Fig. 4.2.17**. The sedimentation rate increases nearly in linear order with increasing AAEM content in particle structure. The sedimentation rate \( v \) for particles in diluted system can be defined as

\[
 v = \frac{2r^2 \Delta \rho f}{9 \eta} \quad (4.2-2)
\]

where \( r \) - is particle radius; \( \Delta \rho \) - is density difference; \( f \) – is centrifugal force; and \( \eta \) - is the viscosity of medium. Centrifugal force is defined as

\[
 f = \omega R^2 \quad (4.2-3)
\]
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

Fig. 4.2.17 Hydrodynamic radius of microgels (■) and sedimentation rate (○) as a function of AAEM content (T = 20°C).

with \( \omega \) – is rate of rotation, \( R \) – is radius of the rotor of centrifuge. Since the viscosity of the medium and centrifugal force are constant for all microgels, the sedimentation rate can be influenced by particle size or density difference between particles and medium. The sedimentation rate is more sensitive to the change of the particle radius than to the change of density. The values of average hydrodynamic radius measured by DLS for different microgels decrease gradually with increasing AAEM content. The analysis of equation (4.2-2) with respect to the experimental data presented in Fig. 4.2.17 shows that particles with smaller size are less stable. This effect cannot be explained only by increasing of \( \Delta \rho \) values due to the incorporation of AAEM units. The equation (4.2-2) does not include the effect of particles deformation under centrifugal forces. It was developed for rigid spherical particles of the same composition.

It should be noted, that AAEM improves the stability of VCL chains in water, and when no AAEM is used in reaction, coagulation of particles during polymerization process. Also, VCL/AAEM particles are quite stable (determined sedimentation rates are low). From this point of view, AAEM cannot be treated like component, which reduces the stability of the particles. It is supposed, that AAEM induces some additional cross-linking in the microgel particles and due to its higher reactivity particle heterogeneity increases at higher concentrations. In other words, the composition and the internal structure of particles are changed due to the incorporation of AAEM units.
4.2.6 Rheology

It is well known, that the viscosity of hard-sphere suspensions depends only on the volume fraction of the particles. This concept can also be used for the microgels. The viscosity of VCL/AAEM 2.2 wt.-% dispersion was measured over several decades at different temperatures. As it shown in Fig. 4.2.18, even at the studied concentration microgel suspension does not show shear thinning. That means, that the experimental volume fraction $\phi$ is lower than critical volume fraction $\phi^*$. In this case the shear forces on particles and suspension presents a liquid like behavior and rheology is governed mainly by the Brownian motion. Unfortunately, it was impossible to concentrate the microgel suspension to a concentration with $\phi > \phi^*$. In this case suspension presents solid like behavior and shear thinning should be observed [173]. At higher concentrations the microgel dispersion lost colloidal stability due to increasing interparticle forces (particles are densely packed and can come “in contact”).

The viscosity of microgel dispersion at the shear rate of 39.8 $s^{-1}$ was taken for calculation of the relative viscosity. Obtained data were used for calculation of the volume fraction of microgel using the expression given by Thomas [174]

$$\eta_{rel} = 1 + 2.5\phi + 10.05\phi^2 + 0.00273\exp(16.6\phi) \quad (4.2-4)$$

The volume fraction of microgel dispersion decreased during heating from 10 to 35 °C (Fig 4.2.19).

Fig. 4.2.18 Temperature dependence of the shear viscosity of VCL/AAEM microgel (15.2 mol-% AAEM)

Fig. 4.2.19 The volume fraction calculated from eq. (4.2-4) for VCL/AAEM microgel (15.2 mol-% AAEM) as function of temperature
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

LOWE et al. [175] have concluded that decrease of viscosity can be directly related to the progressive decrease in hydrodynamic volume of the particles and results obtained in this work confirm this conclusion.

The reduced viscosity, $\eta_{\text{red}}$, is defined as $\eta_{\text{red}} = (\eta_{\text{rel}} - 1)/c$ with $c$ as concentration expressed in g/dl. It can be seen that reduced viscosity decreases with increasing the temperature and reaches the plateau at a temperature, which is close to the LCST of PVCL. The results for microgel dispersion and for linear polymer differ slightly: the reduced viscosity decreased in 2.3 and 2.6 times, respectively, at the heating from 10 to 30°C. The decrease in viscosity is more progressive for PVCL. This can be explained by the presence of “inert” AAEM in the microgel. However, the presence of AAEM only slightly influences the properties of PVCL on the surface and its critical point.

4.2.7 The Modification of VCL/AAEM Microgels

The postmodification of the polymer is a very complicated process, which requires special condition (elevated temperature, special solvent etc.). But sometimes the monomers with certain functional groups are not suitable for introduction into polymers for two reasons:

- chemical changes in conditions of polymerization can occur.
- the functional group can create undesirable effect on process of polymerization.
In the case of the thermo-sensitive microgel, introduction of hydrophilic comonomers increases transition temperature of growing oligomer, which can lead to pure control of particle size or to absence of precipitation on the earlier stage. As was already concluded, that copolymerization of VCL with AAEM gives particles with core-shell structure with acetoacetic functionalities on the surface of core. It is well known, that such functional groups can easily react with compounds with at least one amine group at ambient temperature by the following reactions:

\[
\begin{align*}
\text{O} & \text{O} \quad \text{CH}_2 \quad \text{C} \quad \text{O} \\
& \quad \text{CH}_3 + \text{H}_2\text{N} \left(\text{CH}_2\right)_n \text{R} & \quad \text{O} \\
\end{align*}
\]

The first reaction is reversible and can be used for protection of acetoacetic groups, which can hydrolyze in water especially at thermal ageing. This hydrolysis proceeds almost at any value pH value and gives acetoacetic acid, which in turn decomposes on acetone and carbon dioxide. Interaction with formation of enamine usually proceeds quickly. The rate of this reaction grows with temperature. Basically, enamine formation proceeds to the end for 8 hours at room temperature. Primary amines (tert-butilamine) and arylamines (aniline) are usually less suitable due to the sterical hindrances and incomplete formation of enamine.

![Fig. 4.2.20](image) The hydrodynamic radius of the VCL/AAEM microgel (15.2 mol-% AAEM) treated by different amines as a function of temperature
4.2 Thermo-sensitivePoly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

Several diamines were used for modification of the AAEM/VCL microgel. Reactions were carried out at room temperature, so no any sterical difficulties due the presence of PVCL shell were expected. Several fold excess of amine was taken for complete consumption of acetoacetic groups. Results of the treatment are summarized in Fig. 4.2.20. The introducing of hydroxyl groups leads to decrease of the phase transition temperature of microgel. This effect can be easily understood using results of investigations of copolymer of VCL with vinyl alcohol. The hydroxyl group interacts with amide group of caprolactam ring and reduces hydration of the polymer. It is reasonable to assume the same specific interaction of the PVCL with amine group and it confirmed for microgel treated with dimethylethylendiamine (asym.) and hexandiamine. In the latter case, the swelling degree of the microgel decreased due to, probably an additional cross-linking.

4.2.8 Conclusions

Thermo-sensitive microgels based on VCL and AAEM have been prepared under surfactant free conditions. Incorporation of hydrophobic comonomer influences stability of obtained particles. From one side it reduces the stability, as was shown by the sedimentation study, but from other side it makes preparation of stable dispersion under surfactant free conditions possible.

The results obtained from SLS showed hydrophobic internal structure with weak thermo-sensitive properties. The angular dependence of VCL/AAEM microgels in SLS at room and elevated temperatures showed the behavior of globular particles. Experimentally obtained scattering functions were in a good agreement with that calculated theoretically.

DLS experiments showed the same transition temperature for all microgels independently on composition. The presences of internal part with low thermo-sensitivity and highly thermo-sensitive outer part of the particle evident the core-shell structure of microgel. This morphology is result of the fast consumption of the more reactive methacrylic monomer. Transition temperature of the PVCL-rich shell is shifted to ~28 °C in comparison to reported 32 °C for pure PVCL. The decrease in size of microgel during heating was followed by the decrease of the viscosity of dispersion and the volume fraction of the microgel in dispersion. The VCL/AAEM ratio determines the size of microgels below LCST due to regulation of cross-linking (swelling), but only influences slightly size of collapsed particles i.e. the size of the particles during formation. The absence of the angular dependence of the apparent
4.2 Thermo-sensitive Poly(N-Vinylcaprolactam/Acetoacetoxyethyl Methacrylate) Microgels

diffusion coefficient was observed for all VCL/AAEM microgels in swollen and collapsed state, that means reduced internal mobility induced by the cross-linking.

Combining results obtained from SLS and DLS show the change of conformation from “swollen” soft sphere to compact shrunken “hard sphere”. Thus it was shown, that from results of combined SLS and DLS one could obtain not only the size of macromolecules but also the information about the internal structure and the conformational changes induced by the change of environment.

The swelling degree and the transition temperature of microgel can be easily regulated by the composition of the dispersion medium. The thermo-sensitivity of microgel dispersed in water-alcohol mixture is determined only by the properties of PVCL. The transition temperature decreased with increasing of the alcohol content and with it further decreases gradually disappeared. The behavior of PVCL based microgel was differing from that of microgels based on PNIPAm, a higher swelling degree in the collapsed state were observed for all alcohol-water concentrations comparing with pure water.

Finally, the possibility of reaction of functional groups of the microgel with the compounds, which contain at least one amine group, was demonstrated. Obtained microgels had a reduced swelling degree and a lower transition temperature comparing with initial microgel due to specific interaction of VCL units with immobilized functionalities.
4.3 Internal Dynamics in the Diluted Microgel Dispersions.

4.3.1 Introduction

The theory of the dynamics of a GAUSSIAN coil in dilute solution in the free-draining limit was developed by ROUSE [116] and was later put in the more convenient form by ZIMM [115]. ZIMM in addition to the free draining case also treated the case with hydrodynamic interactions.

The relative contributions of the translation motion and different internal modes depend on the product of the scattering vector, \( q \), and the radius of gyration of polymer, \( R_g \). When \( qR_g \ll 1 \), the translation motion is the dominant contribution, and the time correlation function (TCF) is predicted to decay as a single exponential function. As \( qR_g \) becomes larger, the various internal modes begin additionally to contribute in the correlation function and the correlation function becomes to be multiexponential. In the limit of \( qR_g \gg 1 \), the contribution from translation is small and the resulting correlation function is best expressed by the function given by DU-BOIS-VIOLETTE and DE GENNES [122,123].

The dynamic structure factor data for flexible chain has a complex form of

\[
S(q,t) = \exp[-Dq^2t] \sum_{n=1}^{\infty} S_n(q,t)
\]

where \( S(q,t) \), \( \exp[-Dq^2t] \) are DLS relaxation modes in the form predicted by PECORA and SORLIE [176] for the free-draining model of flexible coil. Considering the effect of hydrodynamic interactions PERICO et al. [177] calculated the spectral distribution of the light scattered from flexible polymer coils in solution on the basis of bead - spring model in the non-free-draining limit. They found that the effect of the internal motions became more pronounced in the case of presence of hydrodynamic interaction comparing with free-draining case. At \( qR_g \geq 1 \), \( S(q,t) \) depends only on five decay rates, coming up from the pure translation mode and four principal intramolecular terms.

\[
S(q,t) = S_1(q) \exp[-Dq^2t] + S_2(q) \exp[-(Dq^2 + 2/\tau_1)/t] + S_3(q) \exp[-(Dq^2 + 1/\tau_2)/t] + S_4(q) \exp[-(Dq^2 + 4/\tau_1)/t] + S_5(q) \exp[-(Dq^2 + 2/\tau_2)/t] + ...
\]

(4.3-2)
with the intensity factor $S_n(q)$ which is $qR_g$ dependent. $\tau_n$ is the relaxation time of the $n^{th}$ internal mode, which is twice the ZIMM normal mode relaxation time. It should be noted, that each relaxation mode has a characteristic line width (or decay rate), for example, for 4th relaxation mode $[Dq^2 + 4/\tau_1]$ is characteristic decay rate and relaxation time comes from the first internal mode $\tau_1$. In particular five decay rates are described by only two, additional to the translation motion, internal modes (i.e. maximum 3 peaks can be observed) [178].

PERICO et al. [181] have also calculated the numerical values of intensity factors $S_n(q)$ of five relaxation rates at the values of $(qR_g)^2$ from 1 to 10 in the non-draining limit. On the basis of the ZIMM model

$$\Gamma_n = \frac{1}{\tau_n} = \frac{0.293RT\lambda_n}{M[\eta]\eta_0} \quad (4.3-3)$$

where $R$, $T$, $M$, $\eta_0$ and $[\eta]$ are the gas constant, absolute temperature, the polymer molecular weight, the solvent viscosity and the intrinsic viscosity of polymer respectively. $\lambda_n$ represent the eigenvalues in the ZIMM model which are available from the literature [179].

CHU et al. [178] have studied internal motions of polystyrene in toluene and have discussed results in terms of the theory described above. Wu [180] has concluded on the basis of results of CHU and his own results obtained from diluted solution of polystyrene in the toluene that internal motions associated rather with $2\Gamma_2$ than with $\Gamma_1$ and $4\Gamma_2$. That means that the ability of DLS to measure certain internal modes is somehow related to the observation length scale $1/q$. In other words, there are some internal motions which are more favorable from energetic point of view and they cannot be observed in certain range of $qR_g$. Wu has observed same results in the case of highmolecular PNIPAm at 15°C [181]. The internal motion of PNIPAm microgel at the same temperature was briefly discussed in the same publication.

Up to now, internal motions in microgel network were not discussed in details. Microgel cannot be infinitely flexible due to cross-linking points and probably it should exhibit a restoring force to bending. It should also exhibit to some extend hydrodynamic interactions.

In most of publications, concerning microgels, angular dependence of apparent diffusion coefficient either is neglected (measurements were done only at a fixed angle of observation) or at least is not described. Some detailed publications on other hand used information from angular dependence just for calculation of diffusion coefficient, $D_z$, without consideration of internal dynamics.
The systems, described previously in Chapters 4.1-4.2, did not show any internal motion and only translation diffusion was observed in all cases. The one possible reason is that the size of these microgel was not large enough to observe internal motion.

In this part, the dynamics of narrowly distributed spherical thermo-sensitive microgel based on a copolymer of N-vinylcaprolactam (VCL) and N-vinylpyrrolidone (VP) (Fig. 4.3.1) was studied by DLS over a wide range of scattering angles and at different temperatures.

### 4.3.2 The Object of Investigation.

Copolymerization of VCL with VP in the presence of N,N′-methylenebisacrylamide (MBA) as cross-linker above the LCST of PVCL gives some advantages. Due to its hydrophilic nature, PVP units can stabilize microgel particles by the steric mechanism due to immobilization of PVP on the surface and an increase of the repulsive forces [182]. On the other hand, at the polymerization temperature, MBA and VP in polymer network tend to increase water solubility of VCL-MBA-PVP copolymer. Increase solubility means an increased critical length for oligomer phase separation to form precursor particles. This should lead to a lower number of larger particles. At lower concentrations in the reaction recipe (2.5 – 10 mol.-%) the quantity of VP is not enough to stabilize PVCL microgel. Dispersions were stable only for several days after preparation. Increase of VP content to 20 mol-% leads to dispersions, which are stable for an infinitely long time (at least more than one year). Main properties of the VCL/VP (CP) microgel prepared in the presence of 20 mol-% of VP are listed in the Table 4.3.1 (see below for details).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_g ), nm</th>
<th>( R_h ), nm</th>
<th>( \rho )</th>
<th>( M_L/M_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>236</td>
<td>371</td>
<td>0.63</td>
<td>1.11</td>
</tr>
</tbody>
</table>

**Table 4.3.1.** Main characteristics of the CP microgel determined by SLS and DLS at 15°C

![Chemical structure of VCL/VP (CP) copolymer](image)

**Fig. 4.3.1** Chemical structure of VCL/VP (CP) copolymer
4.3 Internal Dynamics in the Diluted Microgel Dispersions.

4.3.3 Angular Dependence of N-Vinylcaprolactam/ N-Vinylpyrrolidone Microgel Determined by the CONTIN Analysis.

Only one relaxation time was observed in DLS at the angle of observation of 30° at 15°C (Fig. 4.3.2a). That means that only translation diffusion is present. The contributions of internal motions to the spectral distribution are insignificant, so that $D_{app}$ approaches the $z$-average translation diffusion coefficient $D_z$ when $q \to 0$. The values of relative width $\mu_z / \Gamma^2$ (determined from cumulant analysis) are very small (0.0275) which indicates, that microgel used in this study is relatively narrow distributed.

Fig. 4.3.2b shows the CONTIN analysis at the angle of observation 46°. Two peaks were observed at this angle ($qR_g \approx 2.4$). The peak at the higher relaxation time should be attributed to the translation motion and the second one corresponds to internal motion and it contributes only 0.5% to the scattering intensity.

![Fig. 4.3.2](image)

Fig. 4.3.2 The relaxation time distributions obtained for CP microgel ($C = 0.185$ g/l) at 15°C at different angles of observation: a - 30°, b - 46°, c - 80°, d - 106°.
With increasing angle of observation (decreasing of the value $1/q$ and increasing of $qR_g$) the peak related to the translation motion shifts to lower time values. As predicted by the theory, the contribution of first internal motion with decay rate $[Dq^2 + 2/\tau_1]$ increases and its position stays more or less constant. Note, that with increasing of contribution of the first internal mode, CONTIN strongly shifts position of translation term and it leads to higher values of translation diffusion coefficient than observed in single exponential range.

This fact is also illustrated in Fig. 4.3.3. Theoretically, the first cumulant $\Gamma(q)$ should be proportional to the $q^2$. Good agreement with the theory is observed only in the region $a$ where the internal mode contribution is insignificant and where the error in translation diffusion does not exceed 1%. In the region $b$ deviation of the calculated diffusion coefficient becomes significant. This fact, which can be explained by the nature of CONTIN, was also pointed out in the reference [178]. For polystyrene [178] and well-studied DNA fragment [176], it was possible to generate correlation functions using equations (4.3-2,3). Adding of a small amount of GAUSSIAN noise (0.1%) to such simulated correlation functions gave results close to experimentally observed curves. That means that CONTIN includes noise in calculation of the real signals, and peaks are moved out from their real position and sometimes it is difficult to understand if they really exist. Investigations of the bimodal mixtures of microscopically studied monodisperse latexes showed that CONTIN analysis gives usually incorrect information about size of components in the mixture [183].

![Fig. 4.3.3](image)

Fig. 4.3.3 The angular dependence of the slowest relaxation time ($\Gamma$) observed at 15°C; the solid line represents theoretically predicted angular dependence for particles of same size when only translation diffusion is present.
In the case of microgel, it is not possible to simulate correlation functions due to the fact that in the microgel internal motions should involve only a part of network and equation (4.3-3) is valid only for linear flexible polymer chain [177]. Assuming the portion of network as isolated and diffusive one, its translational diffusion coefficient should be faster than translational diffusion coefficient of the whole microgel [181]. This fact is schematically illustrated in the Fig. 4.3.4. Whole network has contributions of both components in $R_g$ and $D_z$ but the segmental mobility is the same as of polymer chain with the smaller size. Only the angular dependence of diffusion coefficient $D_i^{\text{eff}}$ of polymer chains with $R_g^{\text{eff}}$ can be measured because the effective diffusion coefficient $D_z^{\text{eff}}$ represents the translational diffusion of the part without segmental motion, i.e. it is independent on the angle of observation. These values cannot be determined, so all TCFs generated by eq. (4.3-2,3) will correspond to noncross-linked polymer with the equal radius of gyration and will not include influence of cross-linking and branching.

Fig. 4.3.2c shows relaxation time distribution at the angle observation of 80° ($qR_g \approx 4$). Instead of the two peaks observed before, three relaxation times can be observed. The contribution of translational diffusion in this case is 95.2 % of intensity; the first internal term contributes 4.4 % and peak that, according to CHU, should be the fourth internal term (the fifth term in eq.(4.3-2)) $[Dq^2 + 2/\tau_z]$ contributes around 0.4 %. It should be noted that only one relaxation time additionally to the translation one was observed for PNIPAm microgel.

CHU was able to separate all three components only after simulation; during experiment translation term and first relaxation term were included in the single broad distribution. In the case of microgel studied here resolution between components is very clear due to high value of translation term.
The range, where all three components were observed are marked in the **Fig. 4.3.3** as region *c*. Angular dependencies of the relaxation times, which correspond to internal motions, are summarized in **Fig. 4.3.5**, which indicates that both terms are nondiffusive (extrapolation to the \( q = 0 \) is impossible) and can not correspond to impurities. At the angles higher than 98°, values of translation diffusion became unreasonable (results are not shown in **Fig. 4.3.3**). This is probably because at very high angles the sampling times are very short and thus the number of photons per sampling time and resulting signal-to-noise ratio are relatively low. However, as it shown in **Fig. 4.3.2d**, at the angle of 106° contributions of translation and relaxation terms are 83%, 10.4% and 6.6% respectively and resolution between all components is still acceptable. Opposite is usual for polymer in solution: the difference between translation relaxation time and relaxation times of internal modes is much more smaller and a single broad distribution can be observed at the higher angles of observation.

**4.3.4 Angular Dependence of N-Vinylcaprolactam/N-Vinylpyrrolidone Microgel Determined by the Cumulant Analysis.**

PECORA et al. [176] have shown that first cumulant analysis like as the CONTIN analysis leads a systematical error for the multiexponential time correlation function. This is because of the relation of the first cumulant to the average of the inverse relaxation time and thus a peak with the faster relaxation will have a large effect on the first cumulant.
4.3 Internal Dynamics in the Diluted Microgel Dispersions.

However, TRAPPE et al. [184] have pointed out that the determination of $\Gamma(q)$ on the TCFs obtained in single $\tau$ mode is more accurate than on TCFs obtained in multi $\tau$ mode, since for the initial part of correlation function more data are produced in the single $\tau$ mode. As it was shown above, CONTIN analysis does not give correct relaxation time values at higher $q$ values. The possibility to use first cumulant was tested.

**Fig. 4.3.6** shows angular dependence of the normalized diffusion coefficient $D_{\text{app}}/D_z$ obtained in the range of 30-98°. At low angles ($qR_g < 2.4$) a constant value of diffusion coefficient was observed. This value was in good agreement with those obtained from CONTIN analysis in region $a$. Such constant range was also observed in the case of the NIPAm microgel [181]. After that, $D_{\text{app}}/D_z$ exponential increases with increasing of the $qR_g$ value ($2.4 < qR_g < 4.2$).

The dependence of $D_{\text{app}}/D_z$ for microgels can be predicted on the basis of model for the regularly branched polymers. Poly(vinyl acetate) (PVAc) microgels swollen in methanol showed agreement with this model. For regularly branched polymers with infinitely large number of branching generations theory predicts [121]

$$\frac{D_{\text{app}}}{D_z} = 1 + \frac{1}{15} qR_g \exp[0.0933(qR_g)^2]$$  \hspace{1cm} (4.3-4)

The number of branching generations for the CP microgel is approximately $N = 7$ as determined from static light scattering (**Fig. 4.3.7a**)

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4.3 Internal Dynamics in the Diluted Microgel Dispersions.

In this case equation (4.3-4) cannot be used for comparison with experimental dates. Unfortunately, mathematical description of the angular dependence for regularly branched polymer with 7 branching shells is not given in original reference [121]. Furthermore, in this work the way of mathematical simulation is not deeply described and it was not possible to calculate the theoretical curve. However, regularly branched model predicts stronger angular dependence of the $D_{\text{app}}/D_z$ for the $N = 6$ (see Fig. 5a in the original publication [121]) than obtained for CP microgel and with increasing of $N$ this dependence should also increase. This deviation is probably the result of more complicated structure of the microgel than the idealized structure of regularly branched polymer (cross-linking is not included in this model). The disagreement between experimentally determined $\rho = 0.63$ and theoretically predicted $\rho = 0.977$ appears from the same reason, as value $\rho < 0.775$ can not be calculated by any of existing models. Thus regularly branched model can be used for the characterization of the microgel only with some limitations.

Angular dependence of the normalized diffusion coefficient shows power law behavior in the range $qR_g > 4.2$. The asymptotic power low behavior $D_{\text{app}}(q) \sim q^n [\Gamma(q) \sim q^{n+2}]$ has been predicted with the exponent of $n = 1$ for chains with strong hydrodynamic interactions (ZIMM limit) and $n = 2$ for fully screened hydrodynamic interactions (ROUSE limit). Linear dependence $D_{\text{app}}(q) \sim q^{1.05}$ was reported for cross-linked polystyrene stars (c-PS-star) system [184], for copolymer of styrene and divinylbenzene [185] and for DNA fragment

![Fig. 4.3.7](image)

**Fig. 4.3.7** (a) - KRATKY plot of CP microgel at 15°C; (-----) – GUINIER approximation for globular particles, (-----) – plateau values for regularly branched polymers with 6 and 8 shells; (b)- regularly branched polymer with four branching shells [121]
4.3 Internal Dynamics in the Diluted Microgel Dispersions.

[176]. In contrast \( n = 0.8 \) was found for cross-linked polycyanurates (c-PCyan), cross-linked polyester (c-Pest) systems [184]. The value of \( n = 0.96 \pm 0.05 \) is in good agreement with value predicted for ZIMM limit. In the terms of the first cumulant the power law is \( \Gamma(q) \sim q^{2.96} \). Note, that regularly branched model predicts no universal asymptotic behavior for regularly branched polymer and for number of generations \( N > 10 \) a maximum in the angular dependence of the normalized diffusion coefficient should be expected.

The reciprocal scattering function \( P(q)z^{-1} \) shows power law behavior at \( qR_g > 3.2 \) with the exponent \( n' = 5.26 \) (Fig. 4.3.8). The scattering curve should decrease in the asymptotic range with the power of 4, i.e \( P(q)z^{-1} \sim q^4 \), for the particles with existing internal surface [186]. The reason of higher exponent is not clear and additional experiments in the range of higher \( qR_g \) values should be done to clarify this phenomenon.

Experimental values do not show the scaling behavior predicted in equation (3.2-18) in the whole \( q \) range. The relation between the of \( D_{app}/D_z \) and \( P(q) \) has nonlinear form in the double logarithmic coordinates. The deviation is a result of the shift of the transition to the asymptotic region to higher values of \( qR_g \) in the dynamic light scattering. For polymer coil in solution, the asymptotic range should be observed at \( qR_g > 3 \). The reason of the shift in DLS can be explained by the complicated structure of the microgel. As it was already mentioned above, the angular dependence of microgel is described by the angular dependence of effective diffusion coefficient \( D_{1 eff} \) of polymer chains with \( R_{g1} \).

![Fig. 4.3.8](image)

**Fig. 4.3.8** The reciprocal scattering function \( P(q)^{-1} \) versus \( qR_g \) for the CP microgel at 15°C; (---) – experimentally observed power law; (--__) – theoretical power law for the particles with existing internal surface.
In reality, the situation is more complicated because the part of network, which shows internal motions, is not independent. Exponent $\mu$ in the case of validity equation (3.2-18) can be defined as the ratio between the exponents $n$ and $n'$ calculated from dynamic and static light scattering in the asymptotic range. This method gives the value 0.183. The $\mu$ value is smaller than values observed for branched polymers (0.4-0.55 [118]).

Probably, dynamic light scattering is more sensitive to the change in the structure (appearance of cross-linked chains). The static light scattering predicts the angular dependence for all architectures including the hard sphere. The last one has not the angular dependence in the dynamic light scattering and this disagreement is compensated by the $\mu = 0$ in the equation (3.2-18). For all other architectures angular dependence for small $qR_g$ values can be described by equation (3.2-16) with $C$ as the structure sensitive coefficient. Evidently, a decrease in $C$ parameter indicates a decrease of the internal segmental mobility. The $C$ coefficient is the initial slope in the plot of $D_{app}/D_z$ versus $(qR_g)^2$. Such plot for CP microgel is shown in the Fig. 4.3.9. The normalized diffusion coefficient of microgel in Fig. 4.3.9 has an upturn at low $(qR_g)^2$ with a nearly linear behavior at large $(qR_g)^2$. For polymer a linear behavior at the low $(qR_g)^2$ with an upturn at large $(qR_g)^2$ was observed. Due to this difference in behavior between polymer and microgel the equation (3.2-16) is not valid for microgel.

The absolute values of reduced cumulant $\Gamma^*(q)$ at high values proved to be a sensitive measure of the internal mobility, and the information about internal structure of polymers can be deduced from these values. $\Gamma^*(q)$ is defined as [184]
\[ \Gamma^*(q) = \frac{\Gamma(q) \eta}{q^3 kT} \]  

(4.3-5)

where \(k\), \(T\), \(\eta\) are the BOLTZMAN constant, absolute temperature and the solvent viscosity respectively. It is dimensionless value, but includes no polymer specific normalization. For linear chains \(\Gamma^*(q)\) is just the prefactor of the \(q^3\) dependence of \(\Gamma(q)\) in asymptotic range. \(\Gamma^*(q)\) should reach a constant value of \(\Gamma^*(\infty)\) in the case of ZIMM limit with \(q^3\) dependence of the first cumulant. In contrast, increase of \(\Gamma^*(q)\) is predicted in asymptotic range for ROUSE limit (\(\Gamma(q) \sim q^4\) in this case, so \(q\) term will not disappear from equation (4.3-5)). Up to now, ROUSE behavior was observed by DLS only in semidiluted polymer solution [187].

As it shown in Fig. 4.3.10, \(\Gamma^*(\infty)\) is reached at \(qR_h \approx 7\) (\(qR_g \approx 4.2\)). In the case of c-Pcyan and c-Pest-chain systems the power law \(\Gamma(q) \sim q^{2.8}\) was observed. A plateau value was not observed in studied \(qR_h\) range for these systems. For c-PS-star system the power law \(\Gamma(q) \sim q^3\) was observed. The plateau value \(\Gamma^*(\infty) \approx 0.062\) was observed in this case (this value was measured for the polymer coil in good solvent). In the case of NIPAm microgel, a very low value of \(\Gamma^*(\infty) = 0.013\) was obtained and this value is comparable with those obtained in this work.

Usually, decreasing of the \(\Gamma^*(q)\) value at constant \(q\) means an increase in the relaxation time (slowing down of segmental motions) for the polymer sections of the same segmental length.

**Fig. 4.3.10** (●) - the reduced cumulant \(\Gamma^*(q)\) versus \(qR_h\) for CP microgel (\(C = 0.185\) g/l) at 15°C; (--) - experimental value of the \(\Gamma^*(\infty)\); (----) – value of the \(\Gamma^*(\infty)\) for NIPAm microgel [181], (---) – experimental value of the \(\Gamma^*(\infty)\) for the flexible polymer chain in the good solvent, (—) – theoretically predicted dependence of the reduced cumulant for hard sphere.
4.3 Internal Dynamics in the Diluted Microgel Dispersions.

This slowing down is equal to a loss in flexibility. Galinsky and Burchard [187] have concluded that branching introduces strong perturbations to the simple spring-bead model of linear chains, instead of being connected by only two springs to neighbor, the ends of segment in the branched structure are actually connected by three or four springs and these springs should have an effect on internal mobility. So, the branching or cross-linking should alter Zimm relaxation spectrum. This effect is small for long segments between branching points, but may become significant when the branching density is high.

In the case of microgel good agreement with Zimm theory is observed but the plateau value is much lower than predicted for the flexible chains. There are several reasons for such behavior. The microgel is monodisperse on the macro level (particles are more or less of the same size) but there are strong inhomogeneities (surface layer is less cross-linked and one can expect long dangling chains on the surface) on the micro level. As a consequence of this polydispersity inside of the microgel, \( \rho \)-parameter is smaller than value of 0.775 for compact hard sphere. For polymer chain (also for branched one), internal motions start to contribute at \( qR_g \approx 1 \) or in other words when the observation length scale is \( 1/q \sim R_g \). In the case of microgel the internal motions are determined by the sections of the clusters, which include branching, and cross-linking points. Taking into account the radial gradient of cross-linking density, one can expect that there are short sections between cross-linking points with fully suppressed internal mobility in the microgel network or their size is simply too short for observation of the internal mobility. That’s why, whole microgel particle cannot undergo collective volume fluctuations or the internal motions, while the less cross-linked branched clusters can undergo collective volume fluctuations to show the internal motions. So at the length scale \( 1/q \sim R_g \) internal motions of these small clusters are hidden by the translation motion of whole microgel sphere. Internal motions can be observed only when length scale of observation is comparable with the size of clusters (\( R_g/2.4 \) in the studied case). The presence of “inactive” segments leads to weak angular dependence of \( D_{app} \) and decrease of \( \Gamma^*(\infty) \) value. But the general dynamic of polymer chains with the observable internal motions differs not from those, predicted for linear flexible chains with hydrodynamic interaction in diluted solution and value of exponent close to \( n = 1 \) can be observed (in semidiluted solution hydrodynamic interaction can be screened and exponent will be close to 2). However, the cross-linked structures will never reach the plateau value obtained for linear or slightly branched systems (it is confirmed also by results of Wu [181]) as it was assumed in reference [184]. Branching/cross-linking density will determine this value (lower than for linear
chains). Unfortunately, the presence of power law for NIPAm microgel [181] was not discussed. This discussion could more clarify this problem. 

AKCASU et al. [188] found that asymptotic equations for the TCF follow the remarkable scaling law

\[ g_1(q,t) = \exp(f[t/t^*]) \]  (4.3-6)

This expression has for very long delay times the asymptotic form of a stretched exponential function

\[ g_1(q,t) \rightarrow b \exp(-\alpha(t/t^*)^\beta) \]  (4.3-7)

with exponents of \( \beta = 2/3 \) for nondrained chains (ZIMM limit) and \( \beta = 1/2 \) for ROUSE limit and with \( t^* \) as a characteristic time. However, such universal behavior is obtained only in the asymptotic range, i.e. when \( qR_g >> 1 \), at least larger than 4.

AKCASU et al. [190] developed a method for the interpretation of DLS experiments in terms of the first cumulant over the full range from \( qR_g << 1 \) to \( qR_g >> 1 \).

**Fig. 4.3.11** Plot of logarithmic field correlation function \( g_1(q,t) \) versus the scaled time \( \Gamma(q)t \) at angles of observation of (□) - 30° and (●) – 98° for CP microgel (\( C = 0.185 \) g/l) at 15°C. Solid lines – shape functions predicted for linear chains in asymptotic range in ZIMM and ROUSE limits [188], dot line – single exponential limit. The inset shows plot of logarithm of \( -\ln [g_1(q,t)] \) versus logarithm of \( \Gamma(q)t \) for the long time tail of correlation function at \( \theta = 98^\circ \) (○), solid line – linear fit of experimental data.
TRAPPE et al. showed [184] that such kind of analysis can be also applied for the branched systems and hypothetically this analysis can be used also for the microgels.

As it was expected, TCFs in range $q R_g < 2.4$ have single exponential form like in the case of linear polymers for $q R_g < 1$ ($\Gamma(q) \sim q^2$, $\beta = 1$). From cumulant analysis described above, one can expect that in asymptotic range the shape function should be stretched exponential with $\beta$ close to 0.66. As it is shown in Fig. 4.3.11 experimental value of 0.65 is obtained, but the experimental shape function does not correspond to those, predicted by the theory. As the $\beta$ value corresponds to the theoretical one, experimental shape function cannot be in transition region between single exponential and theoretically predicted one. The nature of this deviation should probably be the same as for the decrease of plateau value of $\Gamma^*$: only a part of whole microgel network undergoes internal motions and other part due high cross-linking density (too short segments between cross-links) has not contribution to internal motions. As in the case of cumulant $q^{2.96}$ dependence, observed value of $\beta = 0.65$ is in agreement with those predicted in ZIMM limit. On the other hand, cross-linking leads to disagreement of $\Gamma^*(\infty) = 0.01$ with experimental value of 0.062 for coil in the good solvent in the case of reduced cumulant and shift of the stretched exponential shape function comparing with that calculated by Akcasu.

**4.3.4 Thermal behavior of N-Vinylcaprolactam/ N-Vinylpyrrolidone Microgel.**

It is well known that PVCL has lower critical solution temperature (LCST) at ~32°C. Introducing of hydrophilic VP units in the copolymer network should increase this value if no specific interactions between VCL and VP units are present. Fig. 4.3.12 summarizes the thermal behavior of $R_g$, $R_h$ and their ratio $\rho$. Both, $R_g$ and $R_h$ continuously decrease with heating. At a temperature around 38 °C aggregation occurs. This point corresponds to the average transition temperature of the microgel and can be taken as critical aggregation temperature (CAT). This aggregation indicates that sterical stabilization by hydrophilic PVP chains is not enough to prevent interparticle hydrophobic interaction between collapsed PVCL segments. However, it should be noted that this aggregation is weak, even after several hours, both aggregated and nonaggregated form of microgel can be observed. Their relaxation times cannot be completely separated by CONTIN analysis in the whole range of angular dependence. This fact makes deeper investigation of the aggregation process rather complicated.
Temperature dependence of dimensionless $\rho$ value has typical form for thermo-sensitive microgels - at the temperatures close or above LCST it tends to reach value of 0.775 for compact hard sphere. Eventually, this value should not be reached in the case of CP microgel due to the presence of PVP hydrophilic chains on the surface even at higher temperatures. In this case this asymptotic value should be, probably, slightly lower as for hard sphere due to hair-like structure of resulting particles, but unfortunately this hypothesis cannot be experimentally proved.

Fig. 4.3.13 The normalized diffusion coefficient $D_{app}/D_z$ for the CP microgel ($C = 0.185$ g/l) as a function of the temperature: a - versus $qR_h$; b - versus $qR_g$. 

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4.3 Internal Dynamics in the Diluted Microgel Dispersions.

Fig. 4.3.13 shows that the angular dependencies of the normalized diffusion coefficient $D_{app}/D_z$ for the different temperatures build a master curve in the range of 15-30 °C in both, $qR_h$ and $qR_g$ coordinates. Further heating, however, leads to deviation, which cannot be explained only by the inaccuracy of measurements. The same effect can be observed in the terms of reduced cumulant (Fig. 4.3.14). Surprisingly, the values of the reduced cumulant for 35°C are higher than master curve for the range 15°-30°C. As it was mentioned above it means higher internal mobility, but one can expect decreasing internal mobility during heating of the thermo-sensitive microgel with LCST and this reducing of the internal motion should be expressed in reduced $\Gamma^*(\infty)$ value. This effect can probably be explained by the reorganization, which occurs in the microgel during heating due to its complicated composition. So far the temperature is below 32°C, all components of microgel are in the good solvent. As the temperature increases to value higher than 32°C, PVCL segments, which should be dominant in the microgel (due to the lower content of VP in reaction mixture polydispersity in composition can be present), tend to make a compact structure without internal motion. At the same time, the mobility of PVP segments stays constant at the faster translational diffusion $D_z$ of the whole network. The portion of translational diffusion $D_i^{\text{eff}}$ of segments, which shows internal motions increases. As result $D_z$ becomes closer to $D_i^{\text{eff}}$. In any case, deeper investigations with simpler system should be done to clarify this moment. All attempts to obtain pure PVCL microgel particles with the size large enough to show internal motions were unsuccessful.

![Graph showing reduced cumulant $\Gamma^*(q)$ versus $qR_h$ for CP microgel (C = 0.185 g/l) as a function of temperature; solid line – theoretically predicted dependence of the reduced cumulant for hard sphere.](image)

Fig. 4.3.14 The reduced cumulant $\Gamma^*(q)$ versus $qR_h$ for CP microgel (C = 0.185 g/l) as a function of temperature; solid line – theoretically predicted dependence of the reduced cumulant for hard sphere.
4.3 Internal Dynamics in the Diluted Microgel Dispersions.

4.3.5 Conclusions

Thermo-sensitive microgels based on N-vinylcaprolactam and N-vinylpyrrolidone were prepared under the surfactant-free condition. The presence of hydrophilic comonomer during polymerization leads to formation of a stable dispersion of large particles with narrow particle size distribution.

The DLS study showed that internal modes in microgel dispersion made a contribution at $qR_g > 2.4$ instead of $qR_g > 1$ for polymer coil in diluted solution. The additional motion to translational diffusion was observed in the range $2.4 < qR_g < 4$. Two internal motions and translation diffusion were observed at $qR_g > 4$. These modes are represented by the relaxation times $\tau_1$ and $\tau_2$ and $\tau_0$ respectively. However, precise determination of these values by CONTIN analysis is difficult due the influence of noise on the evaluation of multicomponent systems. As result, the position of one component influences the position of other components. These relaxation times cannot be predicted from the theory for polymer coil due to complicated structure of microgel.

Angular dependence of the normalized diffusion coefficient $D_{app}/D_z$ calculated by cumulant analysis shows power law behavior $D_{app}(q) \sim q^n$ at the $qR_g > 4.2$. The experimentally determined value of exponent $n = 0.96 \pm 0.05$ is in good agreement with value predicted for ZIMM limit for polymer chains with hydrodynamic interaction. That means that internal dynamic inside microgel particle is the same as in flexible polymer coil. The scattering function of the microgel obtained from SLS can be described, to some extent, by the regularly branched model. Angular dependence of the reciprocal form factor function obtained from SLS experiment shows power law behavior $P(q) \sim q^{n'}$ at the $qR_g > 3.2$ with the exponent $n' = 5.24$. The disagreement of appearance of the asymptotic behavior between DLS and SLS is result of nonuniformity of the microgel structure and the presence of rigid chains with strong reduced mobility.

The reduced first cumulant $\Gamma^*(q)$ reached a constant value $\Gamma^*(\infty) = 0.01$ at large $qR_g$. This plateau is much lower than experimental plateau value $\Gamma^*(\infty) = 0.062$ for linear chains. The absolute value of reduced cumulant is the sensitive measure of internal mobility and low plateau value additionally confirms the hypothesis of reduced mobility of cross-linked chains.

The shape function was calculated for cross-linked microgel. The shape function obtained for the microgel did not agree with calculated for flexible polymer chain but both function, experimental and calculated ones can be described by a stretched exponential function with exponent 0.66. This corresponds to ZIMM limit of hydrodynamic interaction.
The studied microgel has thermo-sensitive properties. The transition temperature of microgel was shifted to around 38°C due to the presence of hydrophilic segments. At the temperature 38°C weak aggregation occurs. This aggregation indicates that sterical stabilization by hydrophilic PVP chains is not enough to prevent completely interparticle hydrophobic interaction between collapsed PVCL segments. In the range of temperature 15°C – 30°C the angular dependence of normalized diffusion coefficient can be described by single master curve. Further heating leads to deviation from master curve. This is a result of accelerated segmental mobility as was shown by the reduced cumulant. The reason of such deviation is not completely clear but it can results from decreasing of size of rigid polymer segments without internal motion (shrunken PVCL segments) with the constant size of segments, which showed internal mobility (PVP reached segments). The interpretation of the experimental observation needs more tests using more extended theoretical calculations and the objects with more defined structure.
4.4 Preparation of Styrene/N-Vinylecaprolactam PEGMA-functionalized Latex Particles

4.4.1 Introduction

Emulsion polymerization is a well-known method for preparation of the latex polymers with defined structures. The synthesis of the core-shell particles usually does not lead to an ideal core-shell morphology with the complete phase separation. Depending on the compatibility of the two polymers and reaction conditions, the components in the interface can be mixed on the molecular level with continuous concentration gradient or microdomains can be formed. In the past decade, increasing attention has been paid to preparation and characterization of the thermosensitive polymer composite particles with hydrophobic core and hydrophilic shell. The first preparation of PNIPAM coated core-shell particles was reported by Pelton [189] who described both the one-shot surfactant-free preparation of polystyrene-PNIPAM gels and the grafting of PNIPAM onto existing latex particles. Duracher et al. [190,191] investigated the preparation and properties of cationic polystyrene-polyNIPAM core shell particles. Both cationic initiator and aminoethylmethacrylate introduced positively charged groups. The cationic monomer gave smaller particles, however a variety of particle morphologies were obtained, depending upon the polymerization conditions.

Many of the potential biotechnological applications of particles with a thermosensitive nature require the presence of reactive functional groups to act as coupling sites. Poly(ethylene oxide) macromonomers can be used as reactive stabilizer in preparation of well defined polymeric microspheres with hydroxyl groups on the surface. Pich et al. [192] have reported the preparation of polystyrene latex stabilized by ω-hydroxy poly(ethylene glycol methacrylate). The influence of PEGMA concentration on particles size and size distribution was studied.

The aim of the present study was incorporation of more hydrophilic co-monomer N-vinylecaprolactam into the reaction system. It is expected that incorporation of VCL in this particular system will result in formation of thermo-sensitive PST/PVCL particles with interesting properties.
4.4 Preparation of Styrene/N-Vinylecaprolactam PEGMA-functionalized Latex Particles

4.4.2. Particle Size and Morphology

Fig. 4.4.1 presents the average hydrodynamic radius of PST/PVCL particles prepared at different VCL contents in the monomer mixture. The weight ratio monomers/PEGMA was kept 2.5 or 5 wt.-%. Experimental data summarized in Fig. 4.4.1 indicate that when the VCL content in the monomer mixture increases the particle size increases nearly in a linear order. Probably in presence of VCL the critical chain length of the formed oligomers in aqueous phase is larger than that without VCL resulting, via homogeneous nucleation, in the formation of a smaller number of mature particles at constant PEGMA content. Particles prepared at similar monomer compositions but higher PEGMA content show considerably lower particle diameters. PEGMA showed some surface-active properties, however it surfactant properties are rather pure. The detailed kinetic investigations are necessary to investigate nucleation process in this system more in details.

PICH et al. [192] have found, that the diameter of PST particles can be varied from 200 to 600 nm by changing the PEGMA content in the system. Fig. 4.4.1 indicates that an additional effective possibility to vary the particle dimensions is addition of more hydrophilic co-monomer. As it is shown in Fig. 4.4.1, addition of VCL leads to an increase of the particle size without any change of the particle size distribution (PSD). When the VCL content in monomer mixture increases to the some extent, the particle size distribution becomes bimodal.

![Fig. 4.4.1](image)

**Fig. 4.4.1** The average hydrodynamic radius of VCL/ST latex as a function of VCL/ST wt.-% ratio in the monomers mixture; ● samples prepared at 2.5 wt.-% of PEGMA ○- samples prepared at 5 wt.-% of PEGMA.
Table 4.4.1 *Average particle radii of PST/PVCL particles prepared at 2.5 wt.-% PEGMA measured by DLS and SEM (ΔR = R_h – R_SEM)*

<table>
<thead>
<tr>
<th>VCL, wt.-%</th>
<th>$R_h$, nm</th>
<th>$R_{SEM}$, nm</th>
<th>ΔR, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>241</td>
<td>185</td>
<td>56</td>
</tr>
<tr>
<td>7.55</td>
<td>272</td>
<td>216</td>
<td>56</td>
</tr>
<tr>
<td>11.11</td>
<td>266</td>
<td>235</td>
<td>31</td>
</tr>
<tr>
<td>14.7</td>
<td>306</td>
<td>263</td>
<td>43</td>
</tr>
<tr>
<td>34.5</td>
<td>388</td>
<td>380</td>
<td>8</td>
</tr>
</tbody>
</table>

Dispersions prepared at 34.5 wt.-% of VCL in monomer mixture contain both large particles (experimental points are shown in Fig. 4.4.1) and small particles around 100-150 nm. The formation of the smaller particles at higher VCL contents can be explained by an enhanced amount of VCL dissolved in water and formation of higher number of nucleation sites in reaction medium in the very beginning of the polymerization process. Additionally, particle size measurements were performed with scanning electron microscopy (SEM). Experimental results presented in Table 4.4.1 are in good agreement with DLS measurements. ΔR-values in Table 4.4.1 were obtained as a difference between hydrodynamic radius and radius measured by SEM. Usually the ΔR-value calculated from DLS and microscopy measurements reflects the thickness of the hydrodynamic shell around the particle. Results presented in Table 4.4.1 indicate that the thickness of hydrodynamic layer decreases for higher VCL contents in latex particles. In the case of PS/PEGMA [192] the thickness of hydrodynamic layer was nearly independent on the PEGMA content grafted onto the particle surface. Furthermore, the table 4.4.1 indicates that incorporation of VCL causes the hydrodynamic shell to be less swollen and particle surface becomes harder. The particle size increases with the VCL amount and the particle size distribution becomes broader at a VCL content of 14.7 wt.-% and some small particles are formed. A dramatic increase of polydispersity at higher VCL contents is clearly to observe. Particles prepared without PEGMA (Fig. 4.4.2f) are much larger than analogues prepared at 2.5 wt.-% PEGMA (Fig. 4.4.2c) indicating that PEGMA provides efficient stabilization when grafted onto particle surface. Wu et al. [193] have reported that average surface area, which is occupied by PEO macromolecule, is the fundamental parameter for the control of the particle size. So adding of further macromonomers can stabilize more particle surface, which results in smaller particles. Note that the polymerization of ST or VCL separately under the studied conditions leads to coagulation during reaction. The absence of stabilizing effect of PVCL in the case of emulsion polymerization of ST was also reported [15].
4.4 Preparation of Styrene/N-Vinylcaprolactam PEGMA-functionalized Latex Particles

Fig. 4.4.2. SEM images of samples prepared at 2.5 wt.-% of PEGMA and different VCL contents: (a) no VCL; (b) 7.55 wt.-%; (c) 11.11 wt.-%; (d) 14.70 wt.-%; (e) 34.50 wt.-%; (f) 11.11 wt.-% (no PEGMA)

Fig. 4.4.3 SEM images (a) and AFM topography (b) and phase (c) images of particles prepared with 2.5 wt.-% PEGMA: 1st row 7.55 wt.-% VCL; 2nd row 14.7 wt.-% VCL
4.4 Preparation of Styrene/N-Vinylecaprolactam PEGMA-functionalized Latex Particles

SEM images presented in Fig. 4.4.2 show PST/PVCL particles prepared at different experimental conditions. At higher magnification it is good to see, that PST/PVCL particles prepared in presence of PEGMA have small inclusions on the surface. Fig. 4.4.3 shows SEM and atomic force microscopy (AFM) images of samples prepared with the constant PEGMA amount. Both SEM and AFM phase images of samples prepared with different VCL amounts show clearly that amount of inclusions and surface roughness increase with VCL content. For samples presented in Fig. 4.4.3 the shell layer seems to be constituted of small spherical patches of relatively regular size. It is thought, that the surface roughness in PST/PVCL particles reflects the polymerization mechanism, which occurs and results in the formation of a rich-PVCL shell layer.

4.4.3 Thermal Behavior of PST/PVCL Latex in Water.

Particle size measurements were performed at different temperatures. PST/PVCL particles prepared with persulfate initiator show dramatic decrease of the particle size at $T = 35 \, ^\circ\text{C}$. This temperature is close to the LCST of PVCL in water. Sample prepared with 14.7 wt.-% of VCL was heated up and then cooled. Fig. 4.4.4 indicates no hysteresis between heating and cooling runs. Sample prepared with 11.11 wt.-% of VCL shows similar behavior and particle size decreases in the same temperature range.

![Graph showing particle size measurements](image)

**Fig. 4.4.4** Average hydrodynamic radius as a function of the temperature: sample prepared with 14.7 wt.-% of VCL and persulfate ($\triangle$ – heating, $\blacktriangle$ – cooling); sample prepared with 11.11 wt.-% of VCL ($\square$ - persulfate initiator, $\bigcirc$ – azo-initiator); PEGMA 2.5 wt.-%
Contrary, sample, which was prepared with 2,2’-azobis(2-methylpropionamidine) dihydrochloride (AMPA) as initiator, shows much lower particle diameter and no thermal sensitivity if to compare with sample prepared at similar VCL content, but with persulfate as initiator. When azo-initiator was used, smaller particles were also obtained in PST/PEGMA system. Table 4.4.2 summarizes the particle size of obtained dispersions measured at 20 and 55°C. The shrinkage of the PST/PVCL particles at elevated temperatures is much higher in comparison to analogue PST/PEGMA particles due to the presence of temperature-sensitive PVCL on the surface.

The thermo-sensitivity of PST/PEGMA particles was reported by PICH et al. [192] and was explained by brush-like structure of the particle surface layer, which is formed during polymerization process. The rapid decrease of $R_h$ at elevated temperatures is related to the collapse of PEO segments and subsequent collapse of the swollen shell at nearly constant $R_g$. The thermal behavior of the particle shell is strongly influenced by the cross-linking effects, which can be controlled by PEGMA amount in the reaction mixture or by presence of additional cross-linking agents. The change of viscosity of dispersion was similar to the change of hydrodynamic radius with temperature. The decrease of the particle diameter becomes more significant in presence of PVCL. This trend can be observed from particles prepared with 2.5 and 5 wt.-% PEGMA.

Similarly to PST/PEGMA system, shrinkage of the PST/PVCL particles is more significant when lower PEGMA amounts were used in polymerization recipe. Presence of azo-initiator in reaction system leads to formation of smaller particles. Surprisingly no thermal sensitivity

### Table 4.4.2. Shrinkage of the particle size for PST/PVCL dispersions

<table>
<thead>
<tr>
<th>sample</th>
<th>VCL, wt.-%</th>
<th>PEGMA, wt.-%</th>
<th>Initiator type</th>
<th>$R_h^{20^\circ C}$, nm</th>
<th>$R_h^{55^\circ C}$, nm</th>
<th>$R_h^{55^\circ C}/R_h^{20^\circ C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>2.5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>241</td>
<td>159</td>
<td>0.66</td>
</tr>
<tr>
<td>1</td>
<td>7.55</td>
<td>2.5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>272</td>
<td>149</td>
<td>0.55</td>
</tr>
<tr>
<td>2</td>
<td>11.11</td>
<td>2.5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>266</td>
<td>132</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>14.70</td>
<td>2.5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>306</td>
<td>77</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>34.50</td>
<td>2.5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>11.11</td>
<td>-</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>690</td>
<td>538</td>
<td>0.78</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>162</td>
<td>97.5</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>7.53</td>
<td>5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>225</td>
<td>119</td>
<td>0.53</td>
</tr>
<tr>
<td>8</td>
<td>11.11</td>
<td>5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>236</td>
<td>117</td>
<td>0.45</td>
</tr>
<tr>
<td>9</td>
<td>14.66</td>
<td>5</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>248</td>
<td>96</td>
<td>0.39</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>2.5</td>
<td>AMPA</td>
<td>177</td>
<td>110</td>
<td>0.62</td>
</tr>
<tr>
<td>11</td>
<td>11.11</td>
<td>2.5</td>
<td>AMPA</td>
<td>156</td>
<td>146</td>
<td>0.94</td>
</tr>
</tbody>
</table>
was detected in case when 11.11 wt.-% of VCL was used in polymerization recipe. This phenomenon must be investigated in the future more carefully. It can be assumed that azo-initiator provides some additional cross-linking of the polymer chains, which reduces the thermal sensitivity of the formed particles.

### 4.4.4 Conclusions

It has been shown, that PST/PVCL polymeric particles can be prepared in presence of PEGMA. Particle size and particle size distribution of dispersions can be controlled by the VCL amount in the reaction mixture at constant PEGMA content. Increase of VCL amount leads to increase of particle size and particle size distribution due to the increase of the hydrophilicity of the particle surface. The surface roughness in PST/PVCL particles reflects the polymerization mechanism. It occurs and results in the formation of a PVCL rich shell layer.

The temperature sensitivity of obtained PST/PVCL dispersions increases dramatically with VCL amount used in the polymerization process. The heating and cooling runs indicate, that change of the particle size with temperature is completely reversible. Obtained particles were stable at elevated temperatures. No coagulation was observed.
II. Bulk Hydrogels Based on Poly(N-Vinylcaprolactam).

4.5 Investigation of Formation of PVCL Hydrogels by DLS.

4.5.1 Introduction

Gelation, i.e. the sol-gel transition of polymers is a very important branch of critical phenomena. The study of its kinetics is an attractive research problem to clarify the gel structure and the chemistry and physics of gelation. In polymer industry the determination of the gelation threshold is an important issue to control the mechanical properties of a gelling system. The in-situ dynamic light scattering technique is very suitable to study the gelation process without disturbing the gelling system. It is also worth mentioning, that the DLS method has the advantage to have access to shorter time scales than in-situ rheology. Compared with rheological methods, an in-situ (or a real time) determination of the gelation threshold by light scattering has been thought to be difficult because of the following reasons. Scattering signals in a gelling solution are dominated by interference between different clusters evolving by gelation. This interference conceals structural information on individual clusters. Hence, in order to investigate spatial correlation of concentration fluctuations, a scattering study has to be carried out on a diluted system. Experimental studies on sol–gel transition by light scattering [194], small-angle X-ray scattering [195] and small-angle neutron scattering [196] were done after terminating of gelation reaction, followed by dilution so as to observe single cluster scattering. Only a few studies were carried out on a reaction bath without dilution. KOBAYASHI [197] introduced a method, which uses speckles to detect the gelation point of a gelatin solution. He studied a mixture of gelatin with polystyrene latex spheres in water by static light scattering. The sample test tube was rotated during the experiment. When the sample reached the onset of gelation, strong speckles appeared. Speckles are dots of light scattered or reflected by a sample as non-zero cancellations of concentration (or density) fluctuations. ALLAIN et al. [198] used a similar method to detect the onset of gelation of acrylamide. Again, polystyrene micro-beads of submicrometer size were dispersed in the pregel solution. In both cases, it was assumed that polystyrene micro-beads are allowed to move freely if the mesh size of the medium is much larger than the size of the micro-beads, giving rise to a low scattered intensity. However, by gelation the system reaches the point at which the mesh size is reduced to become comparable to that of the micro-beads. At this point, the movement of micro-beads is frozen, resulting in a strong scattering as a speckle pattern.
4.5 Investigation of Formation of PVCL Hydrogels by DLS.

Wu et al. [199] also showed that speckles are a useful measure for an in situ detection of infinite network formation in epoxy resin. However, the physical implication of speckles was not extensively discussed. When an infinite network is formed, the polymer chains in the network lose their freedom to travel freely in the space and are arrested in a limited space. This results in non-cancellation of concentration fluctuations and emergence of position-dependent concentration fluctuations (i.e., frozen inhomogeneities). According to Shibayama [200] there are four types of the frozen inhomogeneities in gel state: spatial, topological, mobility and connectivity inhomogeneities (Fig. 4.5.1). The spatial inhomogeneities are nonrandom spatial variations of cross-link density in a gel, which result in anomalous scattering. The topological inhomogeneities represent defects of network, such as dangling chains, loops, chain entrapment, etc. These inhomogeneities affect the dynamics and swelling behavior of gels. Third, the connectivity inhomogeneities are dependent on cluster size, distribution, and architecture of polymer chains. These connectivity inhomogeneities govern the dynamics of the system and become significant at the sol–gel transition threshold as critical dynamics. The mobility inhomogeneities correspond to variations of local degree of mobility by introduction of cross-links. The mobility inhomogeneities are the reason why scattering speckle appears exclusively in gel state. In the case of the gel, the scattering intensity strongly fluctuates with sample position. Each speckle corresponds to time-average scattering intensity, $<I>_T$. On the other hand, an ensemble-average scattering intensity $<I>_E$ is obtained by taking an average over the sample positions. The inequality, i.e., $<I>_T \neq <I>_E$ is one of characteristic features of gels. A system in which the ergodic hypothesis does not hold is called a nonergodic system. So appearance of the speckles is the first indication of the liquid – solid (gel-sol) transition.

Dynamic light scattering from diluted pre-gel clusters yield valuable information. Adam et al. [201] observed on polyurethane clusters that below a certain concentration, the correlation function displays a stretched exponential form $\exp[-(t/\tau)^b]$ with $0.76 \geq b \geq 0.4$. 

![Fig. 4.5.1 Types of inhomogeneities in polymer gel [200]](Image)
Above the critical concentration, a power law behavior for the time correlation function (TCF) is revealed,

\[(g_2(t) - 1) \sim t^{-\mu} \quad g_1(t) \sim t^{-\beta}\]  

with \(0.9 \geq \mu \geq 0.5\) as reported by different authors [202]. These results suggest an analogy between the sol-gel transition and the glass transition, where the inverse of the concentration of polymer clusters plays the role of the temperature in a glass-forming system. NORISUYE et al. [203] have demonstrated that relaxation time distribution is a sensitive measure for the detection of the gelation threshold. In the gel mode scattering is represented by the single exponential function and it results in characteristic broadening of the relaxation time over several decades. This phenomenon can be also considered as indication of the gel-sol transition by DLS. Possibility to use all three discussed above indication (appearance of the speckles, power law and broadening of the relaxation time distribution) was studied for radical cross-linking polymerization of the \(N\)-vinylcaprolactam in the presence of \(3,3'-(\text{ethane}-1,1\text{-diyl})\text{bis}(1\text{-vinyl}-2\text{-pyrroldione})\) (BVP) as cross-linker (Fig. 4.5.2).

### 4.5.2 Study of the Efficiency of Cross-linking.

The BVP is often used for cross-linking of the VCL due to its similar structure that can give more or less homogenous network comparing with using of cross-linkers based on common methacrylic or acrylic double bonds (this problem will be discussed deeper in the Chapter 4.6). Disadvantage of this cross-linker is its insolubility in water. This can lead to the formation of hydrophobic domains when the hydrogel is swollen in water. The swelling properties of PVCL hydrogel are well studied [17,81-83] and will be not considered in this study. The concentration of cross-linker was taken in the range 0.25-2.5 mol.-%. This range of concentration is usually used for preparation of hydrogels with good mechanical properties.
4.5 Investigation of Formation of PVCL Hydrogels by DLS.

Fig. 4.5.3 The gel content as the function of cross-linker content in monomers mixture.

The efficiency of cross-linking was checked by the determination of the quantity of insoluble fraction (gel-sol analysis). Results of the gel-sol analysis are shown in Fig. 4.5.3. At the lowest concentrations of cross-linker the sol content is relatively high. With increasing of the cross-linker concentration gel content continuously increases to the constant value of ~90 wt.-%. This value is typical for the radical cross-linking polymerization and it shows high efficiency of BVP as cross-linker.

4.5.3 Investigation of Gelation by Monitoring of Viscosity

The time-depending measurements of zero shear viscosity $\eta_0$ were done to obtain some information about the rate of gelation of PVCL networks. Steady shear flow properties are sensitive indicators of the approaching gel point for the liquids near the liquid-solid transition. The zero shear viscosity growth with power law

$$\eta_0 \propto (p - p_c)^{-\zeta}$$

with critical exponent $\zeta$; $p$ is the extent of reaction and in the gel point it is equal $p_c$. The viscosity of the sol increases due to the diverging cluster size and proceeds to infinity at the gel point. Fig. 4.5.4 shows the results of the viscosity measurements during gelation for the selected samples.
4.5 Investigation of Formation of PVCL Hydrogels by DLS.

4.5.4 Investigation of Gelation Process by DLS

4.5.4.1 Change in the Scattered Intensity Profile.

In Fig. 4.5.5a-e the scattered intensity profiles for the pure polymerization process and the gelation process at an observation angle of 90° are shown. Several authors have reported that there is no angular dependence of the scattering profile during gelation so it is not necessary to measure whole angular spectra and an extrapolation to the zero angle is not needed [204]. In Fig. 4.5.5a no speckle patterns in the scattered intensity occurred on the polymerization of N-vinylcaprolactam without the cross-linker, indicating that here no gelation is taking place.
Fig. 4.5.5 Time dependence of the scattering intensity during polymerization of (a) – pure VCL, (b) – VCL in presence of 0.25 mol.-% BVP, (c) - VCL in presence of 0.5 mol.-% BVP, (d) - VCL in presence of 1 mol.-% BVP, (e) - VCL in presence of 2.5 mol.-% BVP. The arrows indicate the gelation threshold.

At the beginning the scattered intensity is very low as only monomer solution is present. After 20-25 min induction period the intensity increased as a result of a growth of polymer chains. Than the scattering intensity reached a maximum and after that it continuously decreased.
A plateau in the scattered intensity seems to be reached after 160 min reaction time in the case of the absence of cross-linker. The same behavior was observed by Norisuye et al. [204] for the radical polymerization of \( N \)-isopropylacrylamide at higher concentrations of monomer in solution. The maximum value of scattered intensity increases with increasing of the cross-linker concentration. Gradual decrease of intensity to the plateau value connected with increasing concentration of formed polymer to the value higher than so-called chain overlap concentration \( c^* \).

At a certain time of reaction in the presence of cross-linker (specially emphasized in the figures), the intensity began to show strong fluctuations, in other words, an appearance of frozen inhomogeneities by cross-links. This point corresponds to the gelation threshold. At this point, finite clusters start to connect each other. The cross-link effect seems to be still weak at this point. In each case, the occurrence of speckle patterns in the intensity monitored during the gelation corresponds to the gel point, this was also proved by a solubility test. With increasing concentration of the cross-linker the amplitude of the speckle patterns also increased. This can be explained by the fact that an increasing amount of cross-linker leads to the formation of much more polydisperse network clusters (frozen inhomogeneities). It is known [66], that 1-vinyl-2-pyrrolidone is more reactive than \( N \)-vinylcaprolactam, so one can expect more heterogeneities in the formed network due to the formation of spatial inhomogeneities. In the case of 0.25 mol.-% of cross-linker the amplitude of speckles is very low. The connectivity inhomogeneities probably dominate for this mixture.

The network formation by free-radical cross-linking copolymerization is determined by the peculiar polymerization behavior of pendant double bonds [205]. Their apparent reactivity is initially enhanced by cyclization, but decreased due to sterical hindrance (excluded volume) arising as a direct consequence of cyclization. Compact (microgel-like), internally cross-linked molecules with so-called instantaneous cross-link density are formed at the beginning of the polymerization. The pendant double bonds in the interior part of the microgel cannot take part in further polymerization and only the peripheral double bonds participate in the structure growth. Thus, gelation occurs by the chemical joining of these primary compact molecules (sometimes called as dendric growth) (Fig. 4.5.6) and macronetwork with so-called latent cross-link density is formed. Latent cross-link density is a function of primary clusters formation process (how many pedant bonds are available on the periphery) and clusters interconnection process (what fraction of the pedant double bond are consumed and cross-links points are formed). The amount of branching in the system depends on the amount of cross-linker and it defines the size and number of clusters.
Since the characteristic size of the network is the mesh size, which is much smaller than the cluster size, the scattered intensity is gradually suppressed compared to the peak intensity although the gelation continues. At this stage, a rearrangement of the chain conformation takes place (the stage, where strong fluctuations were observed). After this, the plateau stage after completion of the reaction should be observed. The gelation is still going on until “space filling” by poly(N-vinylcaprolactam) clusters attained. This means that the envelopes of the clusters fill the space. The behavior of scattering intensity observed for PVCL network formation differs from those reported in the work of Norisuye et al. [204] where a rapid decrease in the intensity after reaching maximum was observed. The observed behavior rather similar to those obtained on the polymerization of tetramethoxysilane (TMOS) [206] and on the sol-gel reaction of TMOS in the presence of organic monomer compounds (dimethylacrylamide, styrene) [206]. It should be also noted that Norisuye et al. [207] showed that in the case of gelation of some silica systems appearance of the power law does not correspond to the appearance of the speckles in the scattered intensity. But nevertheless, it is demonstrated, that monitoring of the light scattered intensity in all cases is quite sensitive to detect the gelation threshold for PVCL gelation.

### 4.5.4.2 Power Law Behavior of the Time Correlation Function.

In Fig. 4.5.7a-d the double-logarithmic plots of the time-intensity correlation functions \((g_2(t) - 1)\) versus the lag time \(t\) at several reaction times for different cross-linker concentrations are given.

Typical polymer solution dynamics in the time correlation functions \((g_2(t) - 1)\) after the induction period was always observed from the beginning of the reaction in all cases.

At the concentration of cross-linker 0.25 mol.-%, no clear power law between 30 and 60 min of reaction time was observed.
4.5 Investigation of Formation of PVCL Hydrogels by DLS.

Fig 4.5.7. Double-logarithmic plot of the time-intensity correlation functions \( g_2(t) - 1 \) versus the lag time \( t \) at several reaction times for polymerization of (a) – VCL in presence of 0.25 mol.-% BVP, (b) - VCL in presence of 0.5 mol.-% BVP, (c) - VCL in presence of 1 mol.-% BVP, (d) - VCL in presence of 2.5 mol.-% BVP. A linear fit (solid line) was applied to the data at gelation threshold. The arrows indicate the crossover between collective mode and cluster mode.

No change of the shape of the TCF was noticed during this time. The linear behavior from 0.1 to 10000 ms (Fig. 4.5.7a) was observed during whole reaction time after induction period was passed. The data points of the linear behavior were too noisy and seem not contain information about polymer. This measurement (VCL in presence 0.25 mol.-% BVP) was repeated for several times, but always the same behavior in the TCF was found. Thus power low behavior cannot be used for detection of the gel point in this case.

The decrease (see the arrows in the Fig. 4.5.7a-d) in the time correlation function in the region of 0.1 ms can be interpreted as a crossover from the collective diffusion mode (single-exponential behavior, caused by slightly cross-linked clusters and sol molecules) to the cluster mode (caused by formed larger connected gel clusters in a concentrated matrix). The
sharpness of this crossover increased with decreasing cross-linker content. The same observation was reported in ref. [203]. A suppression of the collective mode and the domination of a power law behavior at higher amounts of the cross-linker were explained by the fact that the degree of inhomogeneities increased and the polymer clusters plays more important role at the gel point.

After a certain reaction time, a power law behavior was found for the samples prepared with higher cross-linker concentration. This behavior was observed over three decades of lag time (Fig. 4.5.7b-d), indicating that the gel point was reached. Unfortunately, the long time tail of the correlation function was not sufficiently accessible on the experimental time scale due to the high reaction rate. Note that power law exist only a few ten seconds so not much experimental points are available, especially for slow relaxation times. The time of the power law observation corresponds to the appearance of the speckles in the case investigation of the scattering intensity.

The exponent $\mu$ discussed above (eq. 4.5-1) was determined for different samples. The obtained exponents are summarized in Table 4.5.1. It can be seen, that an increase of the amount of the cross-linker led to a higher value of the critical exponent. Maybe it is reasonable to assume, that there is a lower limit for the value of $\mu$ and at the conditions, which should lead to further decrease of this exponent, the power law behavior can not be observed, due to the very weak branching in the critical gel. The value 0.39 of the exponent for the sample prepared with 0.5 mol.-% of cross-linker is much smaller than up to now reported values. The increase in the exponent can be explained by the transition from a gel consisting of long slightly cross-linked chains (lower value of $\mu$) to a highly branched gel (higher value of $\mu$). Consequently, the amount of branching in the critical gel is responsible for the value of $\mu$.

<table>
<thead>
<tr>
<th>BVP, mol.-%</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>0.39</td>
</tr>
<tr>
<td>1</td>
<td>0.504</td>
</tr>
<tr>
<td>2.5</td>
<td>0.577</td>
</tr>
</tbody>
</table>
MARTIN et al.[208] reported, that gels showed a power-law behavior of the TCF even in the well-developed gel state. From this point of view, NORISUYE et al.[203] concluded, that a power law analysis is not relevant for chemically cross-linked gels prepared by a radical polymerization from a vinyl monomer solution studied in his work. TAKEDA et al.[209] showed for a radical cross-linking of NIPAm, that not in all cases a power law behavior was observed as an indication for the gelation threshold. The power law was only observed when using a defined “critical” monomer/cross-linker/solvent ratio in the studied concentration range of the cross-linker of 2.4...22 %. The same phenomena was reported for a poly(methylmethacrylate)/ethylene dimethacrylate gel system [210]. This type of gels prepared at certain ratio of components also showed power law in well-developed gel state. From other hand BURCHARD and LANG [211] have reported that in the case of gelation of polysaccharides power law exist only in the transition point between sol and gel state and with further development of the gel the power law has disappeared. The presence of a power law behavior as an indication for the gelation threshold seems not to be clear at all.

In the case of PVCL, after the gelation passing through the gel point power low disappears and the form of the TCF is more characteristic for gels. This transition from liquid to solid state is similar as observed for physically cross-linked gels. The presence of the power law was not observed in the case of PVCL hydrogels after complete network formation. The increase of the cross-linker content leads to the faster reaching of the gel point. This behavior may be explained in that way, that the amount of polymer chain clusters increases at the gelation threshold with increasing cross-linker amount and more pedant bonds on the periphery are available.

Fig 4.5.8 Dependency of gelation time on the cross-linker concentration in monomers mixture.
This tendency is summarized in the Fig. 4.5.8. To avoid the influence of irreproducibility of the induction period, the time scale between the end of induction period and the gel point was taken as the gelation time. The gelation times (including induction period) do not coincide with those measured by the viscosity experiments. The reason of this disagreement is the different kinetic of gelation reaction. Intensive stirring was applied to the solution in the case of viscosity experiments. Contrary, dynamic light scattering measurements were done in the static condition and the diffusive processes determined the reaction rate. Thus these experimental cannot be compared directly.

4.5.4.3 Characteristic Broadening in the Relaxation Time Distribution Function.

The Fig. 4.5.9 shows the relaxation time distribution functions during the polymerization of the N-vinylcaprolactam without cross-linker and in presence of 1 mol.-% of BVP. In both cases, there are only monomodal relaxation time distributions in the range of relaxation time between 0.1 and 0.01 ms at the earlier stage of reaction. With longer reaction times the monomodal distributions are shifted to smaller relaxation times and the broadening in the relaxation time distribution functions becomes more important. The broadening is result of an increasing number of the growing clusters (or entanglements in the case of linear polymerization), which were formed above the overlap concentration c* in the reaction bath. With further reaction time, the penetration depth of the entangled chains became more important and the correlation length between two junction points becomes smaller. The peaks around 0.002 ms are due to an artifact by CONTIN and they are not related to any specific size of clusters.

**Fig. 4.5.9** Relaxation time distribution functions at several reaction times (a) -during the pure polymerization process, (b) - the cross-linking reaction of the VCL in presence of 1 mol.-% BVP.
At the certain time during cross-linking process, the concentration of the polymer clusters is high enough to induce the intermolecular cross-linking. At this stage several peaks with slow relaxation time appeared. This indicates the formation of large clusters of different size. For the same reaction times, no additional peaks were observed in the case of linear polymerization. At the reaction time, which corresponds to the gelation threshold, slow relaxation times tend to make one broad peak. But the clear characteristic broadening of relaxation time distribution, which NORISUYE et al. [203] observed for gelation of NIPAm was not observed. According to this publication, the peak was broadest around at the time, where the gelation threshold was located. After the gel point, the distribution became narrower again. For deeper investigation of this phenomenon a mathematical treatment of the autocorrelation function was done. TCF was split up into two independent parts: TCF of collective mode and TCF of cluster mode (GEN software was used, see [138] for details). A result of this manipulation is shown in Fig. 4.5.10. The gel point of the sample prepared with 1 mol.-% of cross-linker was reached at around 36 min after beginning of the reaction. This results from intensity experiments and observation of the power law. The relaxation time distribution, which corresponds to the gel mode, is too weak due to the strong signal of the collective mode and thus cannot be an exact evidence for the gel point. A broad relaxation time distribution was observed at gelation time but only after separation of the signals. This characteristic broadening must be observed in cases when power low is observed. The power law is the self-similar (fractal) and due to this self-similarity it should be described by a single relaxation time and the value of this relaxation time tends to infinity.

![Fig 4.5.10](image)

(a) Split of time correlation function at gelation threshold for VCL in the presence of 1 mol.-% BVP into: ▲ - collective TCF and ○ - cluster TCF versus lag time; inset the same in double logarithmic coordinates.

(b) Decay time distribution calculated from TCF of cluster mode.
Only at the gel point the relaxation time covers the whole range, where the power law can be observed. After further reaction time the broad distribution is separated in the several independent components. This effect is comparable with the narrowing observed by Norisuye [203].

### 4.5.5 Conclusions.

3,3’-(ethane-1,1-diyl)bis(1-vinyl-2-pyrrolidone) was used for cross-linking of VCL in ethanol solution by radical polymerization. The resulting sol content depends on cross-linker concentration and did not exceed the 30 wt.-% in studied concentration range (0.25-2.5 mol.-%). This indicates the high efficiency of cross-linking.

The network formation was investigated by dynamic light scattering. It was shown, that monitoring of the light scattered intensity in all cases is quite sensitive to detect the gelation threshold even in the presence of very low cross-linker concentration. The appearance of the speckles can be taken as gelation threshold and the amplitude of the speckles depends on cross-linker concentration.

The power law of TCF at the gel point is a sufficient but not a necessary condition for critical gelation. However, it can be observed in broad range of cross-linker concentration and random chosen monomers/solvent ratio, at least for VCL system. The power law disappeared after crossing the gel point and the “frozen” power law was not observed in well-developed gel state. The exponent calculated from power law depends on cross-linker concentration and can be attributed to the degree of branching. It was found that the time, required for gelation decreased with increasing of cross-linker concentration.

The relaxation time distribution cannot be used as a clear indication of the gel point in the case when collective mode is present in TCF due to the weak signal of the cluster mode.
4.6 Poly(N-Vinylcaprolactam-co-Hydroxyethyl Methacrylate) Hydrogels

4.6.1 Introduction

Recent advances in the preparation of three-dimensional structures with exact chain conformations, as well as tethering of functional groups, allow the preparation of promising new hydrogels. Meanwhile, intelligent hydrogels with pH- or temperature-sensitivity continue to be important materials in medical applications [212]. The importance of hydrogels in biomedical applications was first realized in the late 1950s with the development of poly(2-hydroxyethyl methacrylate) (PHEMA) gels as a soft contact lens material [213]. These PHEMA gels had a high water content at equilibrium and exhibited rubbery behavior and good biocompatibility, thus resembling natural tissues more closely than other synthetic materials. The copolymerization of HEMA and NIPAm yielded a thermo-sensitive hydrogel matrix with hydroxyl functionality [214-216]. The swelling behavior of the NIPAm/HEMA copolymeric gel was related to the gel structure, the surrounding temperature and swelling media. The application of these copolymeric hydrogels in enzymatic activity and release of low molecular substances were also tested [217].

The hydrogels based on the pure N-vinylcaprolactam were extensively studied during last several years. However the hydrogels with functional groups were not reported up to now. The novel hydrogel based on HEMA and VCL will be prepared in this work by radical cross-linking polymerization. The swelling properties in different solvents and thermo-sensitivity of obtained hydrogel will be studied. Dynamic light scattering and dynamic oscillation experiments will be used for study some aspects of copolymeric network formation.

4.6.2 Synthesis of VCL/HEMA Hydrogels.

The conditions of the hydrogels synthesis were chosen using experimental dates of the copolymerisation and cross-linking of the HEMA with homologue of the VCL – \(N\)-1-vinyl-2-pyrrolidone (VP). It was reported [218], that the difference in copolymerization constants between HEMA and VP is very high (\(r_H = 8.81\) and \(r_V = 0.097\)), so one can expect high heterogeneity in composition. Besides, using of 1.5% of the cross-linker with two same functionalities (ethyleneglycol dimethacrylate) led to very high content of non cross-linked soluble fraction. The sol consists mostly of products of the homopolymerization of VP [219]. That means that EGDMA undergoes a composition drift and both, methacrylic monomer and
dimethacrylic cross-linker are consumed totally at a fraction conversion around 0.5. Using of cross-linker with two “weak” functionalities (divinyl glycols) with low reactivity should lead to the same effect but in this case sol will contain mostly PHEMA. However it is dangerous to attempt to control cross-link structure only by the reactivity ratio of the monomers. It is essential to understand that, when divinyl monomers are incorporated in the polymer chains, only the potential candidates for cross-link points have been formed. Only after the pedant double bonds have been reacted, cross-links are generated for the first time. In other words, controlling of cross-links structure in the case of copolymerisation of vinyl and divinyl monomers requires balancing the following two processes: the timing of incorporation the divinyl monomers into the polymer and the timing of reaction of the incorporated pedant double bonds. Partly, using of the cross-linker with two different groups with different reactivity can solve this problem. So, allyl methacrylate (AMA) was used as cross-linker in the synthesis of the network based on VCL and HEMA (Fig. 4.6.1). In this case, it is expected, that at the earlier stage of reaction, HEMA will be react with the methacrylic unit of cross-linker. Probability of reaction of HEMA with allyl group of cross-linker is low and comparable with probability of reaction with VCL. As result, polymer chains with allyl pedant bonds are formed. Presence of such relatively stable pedant bonds increases probability incorporation of PVCL in network at the later stage of reaction. Note, that network formed from HEMA and VCL has two types of heterogeneities: heterogeneity in cross-linking density and heterogeneity in composition. Presence of the later one seems to be the single possibility to obtain network with more or less controlled presence of both components – HEMA and VCL.

The content of HEMA in the monomers mixture was varied in the range of 0-50 mol.-% to obtain thermo-sensitive network.

\[ \text{N-Vinylcaprolactam} \quad \text{Allyl methacrylate} \quad \text{Hydroxyethyl methacrylate} \]

**Fig. 4.6.1** The chemical structures of components of VCL/HEMA hydrogel.
Gel contents of obtained networks after preparation are shown in Fig. 4.6.2. In the case of pure VCL gel content is very low (around 35 wt.-%) due to, probably, formation of the highly cross-linked microdomains. These microseparated structures are the result of homopolymerization of cross-linker on the methacrylic bonds and macronetwork is formed by the interconnection of these micronetworks via the reaction of allyl bonds with VCL monomers or polymer radicals. Resulting PVCL hydrogel prepared in this way was turbid that evident existing of cross-linking heterogeneity. Sol content is much more lower in the case of cross-linking of HEMA by the AMA (< 25 wt.-%). In this case sol content is determined by the presence of unreacted pedant allyl bonds but this effect is compensated by the ability of HEMA to the self-cross-linking. In the case of copolymeric networks, gel content was in the range of 55-70 wt.-%. These values are still far from optimal gel content (around 90 wt.-%) which can be reached by the radical cross-linking polymerization. At increasing of cross-linker content (0.37 mol-% was used) can increase the gel content but it will decrease the mechanical stability of the hydrogel.

Element analysis was used for quantitative characterization of obtained hydrogels. It was already mentioned that elementary analysis is not exact method for determination of N-vinyl amides in copolymers but in the case of insoluble network it is the single way to obtain information about of composition. The presence of VCL in the hydrogel as a function of its content in the mixture of monomers is shown in Fig. 4.6.3. It is clear that the presence of cross-linker allow the presence of higher concentration of VCL in network that in a copolymer prepared from mixture of monomers with the same composition.
To confirm the copolymerization efficiency the glass transition temperature, $T_g$ was measured for samples prepared at different VCL/HEMA ratios (Fig. 4.6.4). The measured value for HEMA hydrogel was in the good agreement with reported 103 °C [219]. The problem of glass-transition of PVCL was already discussed in Chapter 4.2. The obtained value 190 °C seems to be acceptable. FOX equation (4.6-1) [220] and COUCHMAN equation (4.6-2) [221] were used to calculate the theoretical values of $T_g$ of copolymeric hydrogels:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4.6-1)$$

$$\ln T_g = w_1 \ln T_{g1} + w_2 \ln T_{g2} \quad (4.6-2)$$

Fig. 4.6.4 The glass transition of VCL/HEMA hydrogels as function of VCL content (wt-%).
where the $T_g$ is the glass transition temperature of the binary copolymer, $T_{g1}$ and $T_{g2}$ are the glass transition temperatures of PHEMA and PVCL, and $w_1$ and $w_2$ are the mass fractions of HEMA and VCL in copolymer. Both theoretically calculated and experimentally determined glass transition temperatures are compared in Fig 4.6.5. Experimental dates confirm the trend predicted by both models but no direct conclusion about advantage of one of them can be done due to not exact determination of the hydrogel composition.

Agreement of experimentally determined glass transition temperatures with models developed for homopolymers or statistical copolymers shows that heterogeneity in composition is not very high (two independent glass transitions should be detected in this case). All hydrogels were stable against heating; their decomposition temperatures (350-400°C in nitrogen atmosphere) are typical for thermally stable macromolecules and did not depend on composition.

### 4.6.3 Swelling Properties of VCL/HEMA Hydrogels.

#### 4.6.3.1 Swelling in Organic Solvents.

The solubility parameter is a basic thermodynamic property of polymers that is used extensively for predicting of miscibility of polymers in solvents. In general, HILDEBRAND [222] tried to correlate solubility with the cohesive properties of the solvents. In 1949 he
proposed the term of solubility parameter \( \delta \) which is connected with the cohesive energy \( E_{coh} \) via the molar volume \( V \)

\[
\delta = \left( \frac{E_{coh}}{V} \right)^{0.5}
\]

(4.6-3)

Main requirement for solubility of polymer in a solvent is the difference of their solubility parameters. It has to be small as possible because it plays a part in an expression for the thermodynamic interaction parameter \( \chi \)

\[
\chi \approx 0.34 + \frac{V_S}{RT} (\delta_1 - \delta_2)^2
\]

(4.6-4)

However, this requirement is not sufficient and there are combinations polymer – solvent with practically equal solubility parameters but not mutual soluble.

Experimental value of the solubility parameter for PVCL is not reported. For pure PHEMA \( \delta \) was determined experimentally by Davis et al. [223] in the range 29.0–30.1 \((J/cm^3)^{0.5}\). CAYKARA et al. [224] reported solubility parameter for PHEMA to be 26.86±0.10 \((J/cm^3)^{0.5}\). The solubility parameter of polymer can be determined experimentally from the swelling data of corresponding gel obtained in a series of solvents having a range of hydrogen bonding, dispersion and polarity. Results of measurements are summarized in Fig. 4.6.6.

**Fig. 4.6.6** Swelling of the VCL/HEMA hydrogels with different PVCL content (wt.-%) in solvents with different solubility parameters (see inset)
PHEMA hydrogel swell only in lower alcohols and slightly in water due to the presence of supramolecular ordering caused by its amphiphilic structure. Its experimentally determined solubility parameter $\delta = 27.5 \, (J/cm^3)^{0.5}$. This value is in a good agreement with those reported by CAYKARA. A PVCL network swells practically in all solvents with a maximum in chloroform (solubility parameter $\delta = 19 \, (J/cm^3)^{0.5}$). The swelling properties of PVCL gel in all solvents show its double polar and nonpolar nature, which is result of presence of polar amide group, nonpolar methylene ring and nonpolar main chain. Introducing of HEMA units in PVCL hydrogel leads to decreasing of swelling in all solvents and disappearing of the swelling properties in solvents with solubility parameter $\delta<18.6 \, (J/cm^3)^{0.5}$.

In HILDEBRAND equation only dispersion forces between structural units has been taken into account. For many polymers, especially water soluble, the cohesive energy also depends on the interaction between polar groups and on hydrogen bonding. Solubility for a nonionic water-soluble polymer is conferred through a balance between the hydrophilic nature of some polar portion, responsible for the polymer’s solubility in water, and a nonpolar portion, typically the backbone, which gives rise to hydrophobic interactions. The polymer’s solution properties are determined to a large degree by the balance between hydrophilic and hydrophobic interactions. In these cases the solubility parameter corresponds to the total cohesive energy. Formally, cohesive energy can be divided into three parts, corresponding with three types of the interaction forces.

$$E_{coh} = E_d + E_p + E_h$$  \hspace{1cm} (4.6-5)

with contribution of dispersion forces $E_d$, polar forces $E_p$ and hydrogen bonding $E_h$. The corresponding equation for solubility parameter is

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$  \hspace{1cm} (4.6-6)

Unfortunately values $\delta_d$, $\delta_p$, and $\delta_h$ can be not determined directly but can be predicted by the empirical methods which are based on structural groups contributions. The HOFTYZER-VAN KREVELLEN [227] method was used for calculation of theoretical solubility parameters for PVCL and PHEMA. Results of calculation are listed in the Table 4.6.1.
4.6 Poly(N-Vinylcaprolactam-co-Hydroxyethyl Methacrylate) Hydrogels

### Table 4.6.1 The solubility parameter and its components calculated for PVCL and PHEMA using HOFTYZER-VAN Krevelen structural method

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta_d$, (J·cm$^3$)$^{0.5}$</th>
<th>$\delta_p$, (J·cm$^3$)$^{0.5}$</th>
<th>$\delta_h$, (J·cm$^3$)$^{0.5}$</th>
<th>$\delta$, (J·cm$^3$)$^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVCL</td>
<td>16.09</td>
<td>9.4</td>
<td>4.75</td>
<td>19.23</td>
</tr>
<tr>
<td>HEMA</td>
<td>11.61</td>
<td>13.3</td>
<td>13.1</td>
<td>22.01</td>
</tr>
</tbody>
</table>

4.6.3.2 Swelling in the Mixed Solvents.

The swelling of VCL/HEMA hydrogels was measured in water-organic solvent. As organic solvents acetone and $n$-propanol were taken. The PVP, lower homologue of PVCL, undergoes the first order phase transition from soluble to insoluble state with the increasing of the concentration of acetone in water to the value higher than 75 vol.-% [225]. $n$-Propanol is the highest alcohol, which is miscible with water in whole concentration range. Pure PHEMA has the upper critical solution temperature in propanol solution at around 44°C [226]. From the results obtained in pure solvents it is clear that copolymeric hydrogels have not such critical point as they were swollen in $n$-propanol. VCL/HEMA gels showed decrease of swelling degree with increasing of $n$-propanol content in water from 0 to 20 vol.-% (Fig. 4.6.7a). These results are in a good agreement with results obtained for linear PVCL (compare with the Fig. 2.2.10). The reason for this decreasing is the cononsolvency phenomenon and this phenomenon was already discussed in the Chapter 4.2. With increasing of alcohol concentration the swelling degree increased to some constant value, which is determined by the HEMA content.

![Fig. 4.6.7 Swelling of the VCL/HEMA hydrogels with different PVCL content (wt.-%) in (a) – water- $n$-propanol mixtures, (b) - in water-acetone mixtures](image)
4.6 Poly(N-Vinylcaprolactam-co-Hydroxyethyl Methacrylate) Hydrogels

Pure PHEMA gel did not swell in n-propanol, as the temperature was lower as the UCST and very low swelling in water was observed. In the mixture swelling degree strongly increased due to the so-called effect of cosolvency. **Fig. 4.6.7b** shows swelling results obtained in water-acetone mixtures. Generally, increasing of the HEMA content in hydrogel decreased the degree of swelling and peak maximum for all copolymeric hydrogels was observed at the value around 60 vol.-% (maximum swelling for PHEMA hydrogel) comparing with the maximum for PVCL hydrogel at around 40 vol.-%. That means that affinity of HEMA units to the acetone-water units is stronger as for affinity of PVCL units and hence the swelling properties of PHEMA are dominant. Water-acetone mixture is a good solvent for copolymeric hydrogels in the whole concentration range at 20°C and better solvent than pure solvents. This effect is also result of cosolvency phenomenon. Mechanism for cosolvency can be explained on the example of interaction between water, PHEMA and n-propanol. The ternary system favors the formation of 1-2-3 (water-alcohol-polymer) 1-2 (water-alcohol), 1-3 (water-polymer), or 2-3 (alcohol-polymer) contacts. In a pure nonsolvent, the nonsolvent-polymer contacts are energetically unfavorable and the polymer cannot dissolve. Addition of another nonsolvent (or poor solvent) to this solution leads to the formation of increasing numbers of 1-2 contacts by forming a complex by intermolecular hydrogen bonding in the solution. In a cosolvent system, one can postulate the formation of 1-2-3 contacts on dissolution of the polymer in the solution that lowers the free energy of the system. **Fig. 4.6.8** is a schematic representation of the cosolvency mechanism of the HEMA polymer in the water-n-propanol mixture: the polar groups of water and n-propanol may associate with each other to present a nonpolar environment in which the methylene segments of the polymer can dissolve. On the other hand, the segments with hydroxyl group on the end may interact with the polar groups exposed on the alcohol-water complex.

![Fig. 4.6.8](image-url) The schematic representation of the cosolvency mechanism of the HEMA polymer in the water-n-propanol mixture.

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Therefore, the formation of 1-2-3 contacts will pull the polymer into solution and the cosolvent action can be explained qualitatively, that the introduction of a polymer chain into the binary solvent environment serves to bind the water-alcohol complex more strongly. Dissolution of the polymer will occur when a sufficient number of 1-2 contacts have formed in the vicinity of a polymer chain to allow it to be drawn into solution by the formation of sufficient 1-2-3 contacts. This leads to the observed phase behavior that polymer dissolves in a range of mixtures of two liquids. The maximum of solubility (swelling) will be observed in binary mixture with the highest energy of mixing (most thermodynamically unfavorable). As neither 1-3 nor 2-3 contacts are energetically favorable, any changes in the solvent composition that increases either component 1 or component 2 in the mixture will destroy the stability of 1-2-3 contacts. When the system can no longer maintain sufficient 1-2-3 contacts, phase separation takes place. In the case of HEMA hydrogel the cosolvency phenomenon occurs in the whole concentration range. The copolymeric hydrogel is much more complicated as both effects, cosolvency for HEMA units and cononsolvency for PVCL units, are present but the properties of PVCL in this case are dominant.

### 4.6.3.3 Swelling Behavior of VCL/HEMA Hydrogels in Water.

The effect of the temperature on the swelling ratio for obtained hydrogels with different PVCL content was measured. Results of the swelling measurements are shown in Fig. 4.6.9. Obtained curves were fitted with BOLTZMAN sigmoidal function and differentiated.

![Swelling properties of the VCL/HEMA hydrogels gels with different PVCL content (wt.-%) in water as function of temperature; arrow shows $T_v$ for PVCL.](image)

**Fig. 4.6.9** Swelling properties of the VCL/HEMA hydrogels gels with different PVCL content (wt.-%) in water as function of temperature; arrow shows $T_v$ for PVCL.
The minimum of the first differential (inset of Fig. 4.6.9) corresponds to the inflection point of the swelling curve. Note, that this point does not correspond to the $T_p$, in the case of bulk hydrogel and is taken as relative value to compare properties of hydrogel with different composition. The shape of the deswelling curve for pure PVCL gel is in good agreement with those reported by MAKHAeva and according to this reference [17] no hysteresis should be expected. Generally, increasing of HEMA content in the hydrogel leads to the decreasing of the swelling degree at all temperatures and the phase transition temperatures are shifted to lower temperature. The hydrogel with 44.9 wt.-% is still thermo-sensitive in the studied range but its swelling degree was changed only slightly. The shift of phase transition is the result of introduction of polymers segments with amphiphilic character – hydrophobic main chain and hydroxyl functionality. Additional hydrophobic groups increase entropy driven attraction between hydrophobic parts of chains. Hydrophilic hydroxyl additionally can interact with amide group of caprolactam via hydrogen bonding. This leads to intramolecular association and a reduced hydrophilic interaction with water. This kind of specific interaction is typical for copolymers of VCL with hydroxyl containing monomers.

### 4.6.3.4 Investigation of the Phase Transition by IR Spectroscopy.

The IR spectroscopy is a sensitive method for observation changes of polymer-water interaction. This method was used for investigation of the PVCL in $D_2O$ during the phase transition. So possibility to use this method for cross-linked polymers was studied. The hydrogel with highest PVCL content (86.7 wt.-%) was taken for investigation as it had comparable low mechanic stability in the swollen state and could be easily pressed into a thin film between CaF$_2$ crystals. The amide band I of PVCL was taken as the reference. Water shifts the position of this band from 1623 cm$^{-1}$ in the dried state to 1608 cm$^{-1}$ in the soluble (swollen) state. The temperature dependence of this band is shown in Fig. 4.6.10. Amide vibration becomes weaker and broader during heating. The curve-fitting method was used to obtain more information. The FOURIER self-deconvolution of the spectra was done for the determination of the number and the positions of the amide I components. This procedure enhances the positions of the individual components. After that, the amide I band was fitted with GAUSSIAN multi-peaks model and three different components were obtained (example is schematically shown in inset of Fig. 4.6.10). These components were centered at the 1610, 1589 and 1574 cm$^{-1}$ in the swollen state.
4.6 Poly(N-Vinylcaprolactam-co-Hydroxyethyl Methacrylate) Hydrogels

Fig. 4.6.10 The change of IR spectrum for VCL/HEMA hydrogel (86.7 wt.-% of PVCL) in D$_2$O as function of temperature; inset represents schematically the FOURIER self-deconvolution of the spectra with GAUSSIAN multi-peaks analysis.

These values are in a good agreement with 1610, 1588 and 1565 cm$^{-1}$ for linear PVCL in D$_2$O. MAEDA [45] has assigned 1610 cm$^{-1}$ and 1588 cm$^{-1}$ to amide groups, which form hydrogen bonds with water and amide groups, which form at least one hydrogen bond with water, respectively. The meaning of the band positioned at 1565 cm$^{-1}$ was not discussed and its nature is unclear. The relative areas of observed components of amide I are plotted versus temperature in the Fig. 4.6.11a.

Fig. 4.6.11 The change of relative area (a) and position (b) of the three components of amide band I ($\bullet$- 1610 cm$^{-1}$, $\diamond$-1589 cm$^{-1}$, $\blacklozenge$-1565 cm$^{-1}$) for VCL/HEMA hydrogel (86.7 wt.-% of PVCL) as function of temperature; in figure (a) the swelling curve for same sample is also shown ($\triangle$); dashed arrow represents onset of the phase transition (see text for details).
The areas of all components are more or less constant in the range 15-25°C. Further heating increases areas of components at 1589 cm\(^{-1}\), 1565 cm\(^{-1}\) and 1610 cm\(^{-1}\). The peak at 1610 cm\(^{-1}\), which is dominant at the temperature below \(T_{tr}\), becomes weaker. MAEDA has showed that onset of the changing in the areas corresponds to onset temperature of the endothermic peak in the DSC thermogram. The energetic effect of the phase transition for PVCL is very weak and this kind of DSC measurements can be performed only with very sensitive equipment. On other hand it is known that for hydrogels the onset in the endothermic peak of the phase transition corresponds to the offset of deswelling curve (see Fig. 4.6.9). The offset of deswelling curve for hydrogel with 86.7 wt.-% VCL coincides with the end of constant range for amide bands in IR spectroscopy so its real phase transition can be estimate as \(\sim 26°C\). Characteristically, the end of transition in IR corresponds to arriving the complete deswelling in swelling experiment. Note, that only 3 instead 4 components, reported by MAEDA for linear PVCL, were observed above \(T_{tr}\).

As the original broad band shifts its position, the positions of separated components are also shifted during heating procedure. Dependencies of the position for each band are summarized in the Fig. 4.6.11b. The component located at 1610 cm\(^{-1}\) in the swollen state shifts to 1620 cm\(^{-1}\). The latter value is close to the 1623 cm\(^{-1}\) for the pure amide band I for dried PVCL. So this shift can be attributed to complete dehydration of PVCL segments. The shift of around 40 cm\(^{-1}\) from higher to lower value was also observed by stepwise adding of small amount of water to the poly(vinylpyrrolidone). This dehydration is not complete for all PVCL segments and part of highly hydrated amide groups are transformed in groups with the lower degree of hydration. This results in increase of the area of the component at 1589 cm\(^{-1}\). Simultaneously, position of this component shifts to 1598 cm\(^{-1}\) that probably indicates the complex reorganization of hydrogen bonds.

**4.6.4 Investigation of Network Formation by the Dynamic Light Scattering.**

The principle of measurements of the gel point by dynamic light scattering was already discussed in Chapter 4.5. A constant content of the cross-linker was taken for preparation of the VCL/HEMA hydrogel and gelation process was studied for several VCL/HEMA monomer ratios. The appearance of speckle pattern and the power law behavior of TCF were monitored as criteria of gelation threshold. The gelation of VCL/HEMA mixture had the same peculiarities as the gelation of the pure VCL. In all cases, appearance of strong intensity fluctuations (Fig. 4.6.12a) was observed and this point corresponds to the gel point.
Fig. 4.6.12 The typical time dependency of scattered intensity for gelation of VCL/HEMA mixture (a), arrow shows gelation threshold; the TCFs observed at the gel point for monomer mixtures with different VCL content (b), arrow shows crossover between collective mode and cluster mode.

Fig. 4.6.12b shows the time-intensity correlation functions \(g_2(t)-1\) in a double-log plot against the delay time \(t\) for several monomer mixtures at the gel point at a scattering angle of 90°. The power law behavior was detected for all cases. The crossover between collective and cluster mode was more clear than in the case of gelation of VCL. The time required for reaching the gel state is much more longer in this case. It increases with increasing of the HEMA content. This slowing down can be easily explained on the basis of the mechanism of cross-linking, which was already discussed above. The cross-linker reacts with HEMA mostly on methacrylic bond with formation of the pedant allyl double bond. Reactivity of this bond is relatively low and this leads to the slow cross-linking. Increase of VCL content leads to the acceleration of gelation, as its reactivity is comparable with allyl group. Of course, described mechanism is approximate and it detailed study in terms of \(Q-e\) scheme should be done. The composition of the initial monomer mixture had a weak influence on the observed exponent of power law observed at the gel point. The dependence of the exponent on concentration has linear character (Fig. 4.6.13). The values of exponents are much higher than for PVCL hydrogels prepared in the presence of the cross-linker of comparable concentration. Probably, it indicates the higher degree of branching of VCL/HEMA hydrogels. It is well known [227] that HEMA has ability to self-cross-linking due to the chain transfer reaction of methylene group and at the constant cross-linker content branching degree will increase with increasing of HEMA content in the mixture. Experimental observation confirms this hypothesis and exponent of the power law linearly increases as HEMA content increases. Note, that the measurements of the power law are exact enough to be sure that the differences in the exponents are not in the experimental error range.
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Fig. 4.6.13 The time of gelation (■) and the exponent $\mu$ of power law of TCF observed at the gel point (○) as the function of HEMA content in monomers mixture.

There were no gels with power law in developed state, i.e. power law was observed only at the transition point between liquid and solid state. Time, during the shape of power law was relatively constant, was longer than for faster gelation of pure PVCL hydrogel. Calculating $g_1(t)$ from $(g_2(t)−1)$ values using the SIEGERT relation, $\beta$ values were obtained between 0.285 – 0.325, which are in good agreement with the value of 0.34 which was found for thermoreversibly gelling polysaccharide [211] and for trifunctional randomly branched polycyanurates [228].

Values for $\beta$ between 0.23-0.38 were reported on semi-dilute solutions of polyurethane clusters [201]. For a covalently cross-linked system of silica gels studied by MARTIN and WILCOXON [229] the corresponding exponent was 0.27. FANG et al. [210] found on the sol-gel transition on the poly(methyl methacrylate)/butyl acetate system a value of 0.34. A good agreement with the percolation model was noted in the last two cases. The values of exponents for VCL/HEMA hydrogels indicate the presence of highly branched clusters. The percolation theory can well describe the studied gelation process.

4.6.5 Investigation of Network Formation by the Dynamic Oscillation Experiments.

Due to the much longer gelation times of VCL/HEMA mixture in comparison with pure VCL it was reasonable to measure the gel point with help of the whole spectrum of rheological methods.
Steady shear flow measurements are sensitive indicators for the liquid near liquid-solid transition. The zero shear viscosity $\eta_0$ and equilibrium modulus $G_e$ grow with power laws [230]

$$\eta_0 \propto (p_c - p)^{-\nu} \text{ for sol, } p < p_c$$
$$G_e \propto (p - p_c)^z \text{ for gel, } p > p_c$$

having critical exponents $s$ and $z$; $p$ is the extent of reaction and in the gel point it is equal $p_c$. Very few experimental determinations of the values of the exponent $s$ and $z$ were published on the chemical gels [231]. As the longest relaxation time of the polymeric system diverges on the gel point, and it is necessary to wait until the system has relaxed to perform the measurements, no rheological measurements have been carry out in the near vicinity of the critical point. Because of this, determination of the exponent $s$ and $z$ is particularly difficult when measurements are performed in the reaction bath as the chemical reaction is proceeding. The cross-linking by the radical polymerization is much faster than most of studied by rheology cross-linking by polycondensation. It is difficult, when not impossible, to stop reaction in the desired point. That’s why, it is impossible to measure equilibrium modulus $G_e$ and resulting exponent $z$.

![Graph](image_url)

**Fig. 4.6.14** The time dependency of the absolute viscosity $\eta$ (■) and storage modulus $G'$ (○) measured during gelation reaction of VCL/HEMA mixture at the ratio 80/20 mol/mol. Dashed line indicates the gelation threshold.
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Taking into account relation \( G_e = G' \) at the frequency \( \omega^* \), which corresponds to the inverse of the longest relaxation time of the largest cluster [231], it was assumed, that scaling predicted for equilibrium modulus can be the same for storage modulus. From measurements of viscosity and storage modulus critical exponents (Fig. 4.6.14) \( s = 0.56 \pm 0.05 \) and \( z = 2.45 \pm 0.03 \) were calculated. Both the storage modulus \( G'(\omega) \) and loss modulus \( G''(\omega) \) obtained in the dynamic oscillatory shear experiments show power law over several frequency decades at the gel point

\[
G'(\omega) \sim G''(\omega) \sim \omega^s
\] (4.6-9)

This phenomenon was observed by Winter and Chambon [20]. Fig. 4.6.15 shows the storage and loss moduli as a function of angular frequency \( \omega \) for various reaction times. At 143 min the solution before the gel point tends to behave classically as a Newtonian liquid with \( G'(\omega) \sim \omega^{1.65} \) (theoretically \( G'(\omega) \sim \omega^2 \)), \( G''(\omega) \sim \omega^{0.97} \) (theoretically \( G''(\omega) \sim \omega^1 \)) [3]. After 157 min, both moduli appear to run parallel to each other over two decades, indicating that the gel point was reached. The following relations were calculated with a linear fit in a double-log plot:

\[
G'(\omega) \sim \omega^{0.773 \pm 0.011} \quad G''(\omega) \sim \omega^{0.736 \pm 0.002}
\]

After the gel point the storage modulus \( G' \) became larger than \( G'' \), the elastic portion became evident. The system now behaved as a visco-elastic solid.

Fig. 4.6.15 The time dependency of (a) the storage modulus \( G' \) (filled symbols) and the loss modulus \( G'' \) (open symbols) and (b) the loss tangent \( \tan \delta \) measured at different times during gelation reaction of VCL/HEMA mixture at the ratio 80/20 mol/mol; (---) - the gelation threshold.
The loss tangent \( \tan \delta \) was independent on frequency at the gel point as predicted by the theory. It was found to be around \( \tan \delta \approx 2.7 \). Computer simulations, using an analogy of gelation to resistor-superconductor networks (conjointly with percolation theory), gave \( n = 0.73 \) [231-233]. The ROUSE model, which assumes no hydrodynamic interactions between the polymeric clusters, predicts \( n = 0.66 \) [231,234]. MARTIN et al.[237] predicted, that \( n \) is between 0.66 and 1. Mean-field theory predicts \( n = 1 \) [235,236]. It appears, that there is no universal value of \( n \). Probably it is related to the specific nature of each gelling system. SCANLAN and WINTER [237] reported values between 0.19 and 0.92 on end-linked poly(dimethylsiloxane), RICHTER et al. [238] have reported an exponent of \( n = 0.2 \) for nematic crystalline network. The obtained exponent for VCL/HEMA system (average value \( n \approx 0.75 \)) is in agreement with the value of 0.73 predicted by the percolation theory. Percolation theory describes the random growth of molecular clusters on a \( d \)-dimensional lattice. It was suggested to possibly give a better description of gelation than the classical statistical methods since the mean-field assumptions (unlimited mobility and accessibility of all groups) are avoided. In contrast, immobility of all clusters is implied, which is unrealistic because of the translational diffusion of small clusters. The experimentally measured value of the exponent \( (n \approx 0.75) \) supports the assumption of a high degree of branching of the gel clusters.

From relation of storage modulus with equilibrium modulus \( G_\varepsilon = G' \) and from relation between loss modulus and zero-shear viscosity \( G'' = \omega \eta_s \) (both relations are valid at the frequency \( \omega^* \)) [231] comes relation between exponents \( n, s \) and \( z \)

\[
n = -\frac{z}{s + z} \quad (4.6-10)
\]

The exponent \( n = 0.81 \) calculated from this relation was close to those obtained experimentally. A deviation can be attributed to the error of \( s \) and \( z \) determination. Besides the equation (4.6-10) comes from assumption [239] of symmetry of the diverging of maximal relaxation time \( \lambda_{\text{max}} \)

\[
\lambda_{\text{max}} \propto \left\{ \begin{array}{l} (p_\varepsilon - p)^{-\alpha_-} \\ (p - p_c)^{-\alpha_+} \end{array} \right\} \quad (4.6-11)
\]

on the both sides of the gel point that means \( \alpha_- = \alpha_+ \). This symmetry is neither disproved nor confirmed experimentally.
The power law behavior, which possesses no characteristic relaxation time, is self-similar. This implies a self-similar (fractal) structure of the clusters forming the critical gel. Several different relationships between the critical exponent $n$ and the fractal dimension $d_f$ have been proposed recently. The fractal dimension $d_f$ of the polymer cluster is commonly defined by [230]

$$R_g \propto M^{1/d_f}$$  \hspace{1cm} (4.6-12)

where $R_g$ is the radius of gyration. $d_f$ can be related to the critical exponents (not valid for mean field theories). It results in a value of $d_f = 2.5$ for bond percolation on a 3-dimensional lattice. The fractal dimension of the BETHE lattice (FLORY-STOCKMAYER theory) is $d_f = 4$ [230], which leads to a physical discrepancy, since any value higher than 3 (dimensionality of the sample) results in the increasing of the cluster density with cluster size.

MUTHUKUMAR investigated [240] the behavior of monodisperse polymeric fractals following ROUSE chain dynamics, i.e. GAUSSIAN chains (excluded volume fully screened) with fully screened hydrodynamic interactions. It is well known that the excluded volume effect of a chain in dilute solution gets progressively screened to give the ideal dimension of the chain as the concentration is increased. The shrinkage of the size of the polymer with concentration increase is established even for branched polymers from neutron- and light scattering studies with different dilutions. Therefore, one should expect such screening of the excluded volume effect in a system where gelation is taking place. In the reaction bath where gelation is taking place, a family of clusters is present and the situation near the gel point is similar to a polymer melt as far as the screening of excluded volume is concerned. In this case exponent $n$ is given by

$$n = \frac{d}{\bar{d}_f + 2}$$  \hspace{1cm} (4.6-13)

with $\bar{d}_f$ as fractal dimension of the polymer if the excluded volume effect is fully screened.

MUTHUKUMAR [240] further investigated the effects of polydispersity, which are important for cross-linking systems. He used a hyperscaling relation from percolation theory to obtain his results. In the case of full screening of excluded volume he obtained
\[ n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \]  

(4.6-14)

A small change in the fractal dimension can lead to a significant change in \( n \), and therefore he concluded that \( n \) can take values between 0 and 1. Using the exponent \( n = 0.75 \) a fractal dimension of the VCL/HEMA gel clusters was estimated as \( d_f = 1.67 \).

### 4.6.6 The Relation Between Exponents Observed at the Gelation Threshold in Dynamic Light Scattering and Rheology.

Since DLS is sometimes called micro-rheology, the exponents \( \beta \) and \( \mu \) (equations 4.5-1,2) should be in relation with the viscoelastic exponent \( n \). The shear stress relaxation modulus \( G(t) \) at the gel point shows power law behavior \[ G(t) = St^{-n} \text{ for } \lambda_0 < t < \infty \]  

(4.6-15)

with \( S \) being the gel stiffness and \( t \) relaxation time. From other side for the dynamic structure factor \( S(q,t) \) and the time-dependent modulus \( G(t) \) an equation derived from DOI and Onuki [241] is valid

\[ g_1(q,t) \sim S(q,t) \cong \left( \frac{\xi_{ve}^2}{\Gamma_q \eta} \right) G(t) \]  

(4.6-16)

with \( \xi_{ve} \) as correlation length. That means there is a relation between the electric field correlation function and shear stress relaxation modulus. At the gelation threshold the following relation should be observed

\[ g_1(q,t) \sim S(q,t) \sim G(t) \sim G'(\omega) \sim G''(\omega) \sim t^{-n} \]  

(4.6-17)

This relation can be derived also from the work of Martin et al. [229]. According to this reference following relation is valid

\[ g_1(q,t) \sim S(q,t) \sim G(t) \sim t^{-d_f/(k+d_f)} \]  

(4.6-18)
As it can be seen, the critical exponent $\beta$ has the same physical origin as the power law behavior in the viscoelastic behavior at the gelation threshold and following relations should be valid

$$n = \beta = 0.5 \mu$$  \hspace{1cm} (4.6-19)

SHIBAYAMA and NORISUYE [200] pointed out, that this problem of comparison of the exponents $\mu$ and $n$ is not settled at all. Using time-resolved dynamic light scattering technique, NORISUYE et al. [206] found a power-law behavior in the time-intensity correlation function, $(g_2(q,t) - 1) \sim t^{n'-1}$, at the gelation threshold of silica gels under acidic ($n' \approx 0.5$) and basic ($n' \approx 0.73$) conditions. It easy to recognize that the relation $-\mu = n' - 1$ holds. TAKEDA et al. [209] investigated various radical cross-linked NIPAm gel samples with DLS and found $n' \approx 0.3$. In both references [206,209] the exponent $n'$ was identified with the exponent obtained from oscillatory shear experiments. However, no rheological experiments were performed.

For the hydrogel prepared with molar monomers ratio VCL/HEMA = 80/20 the exponents were determined as $\beta \approx 0.315$, $\mu \approx 0.61$ and $n \approx 0.75$. So equation (4.6-19) is not valid in this case. The difference cannot be the result of experimental error and cannot be explained at this moment. TAKATA et al. [242] considered the eq. (4.6-19) as not valid but no experiments were done to prove this hypothesis. More experimental studies on different systems and theoretical considerations are necessary to validate the relation between the two critical exponents of rheology and DLS or to find the real physical meaning of the exponents obtained in DLS.

### 4.6.7 Conclusions.

A novel thermo-sensitive hydrogel system based on VCL and HEMA was synthesized by radical cross-linking polymerization in ethanol using allyl methacrylate as cross-linker. The efficiency of cross-linking is low. Different functionalities of cross-linker play an important role in incorporation of both network components, which have a large difference in reactivity. The obtained hydrogels content 40 – 100 wt.-% of PVCL depending on VCL/HEMA ratio. The swelling experiments in solvents with different solubility parameter showed that the properties of both, PVCL and PHEMA components are present in hydrogel and cannot be described by the additivity principle. The independent contributions were also observed in the mixed solvents. The solubility parameter of PVCL was determined as 19 (J/cm$^3$)$^{0.5}$. This value is in agreement with a calculated one.
The thermo-sensitivity of copolymeric hydrogels was investigated by the swelling measurements and IR spectroscopy. Increasing of HEMA content in the hydrogel leads to the decreasing of the swelling degree at all temperatures and the phase transition temperatures are shifted to the lower temperature. It was shown that IR spectroscopy could be effective, but time consuming, method for determination of the phase transition temperature.

The VCL/HEMA network formation was investigated by dynamic light scattering and dynamic oscillation experiments. The formation of copolymeric network has the same peculiarities as formation of VCL gel in DLS. The strong intensity fluctuations were observed at the gel point and the power law was observed for the all studied VCL/HEMA mixtures. The exponent of power law was weakly dependent on VCL/HEMA ratio. The time required for gelation and exponent calculated from power law increased with increasing of HEMA content. The critical exponents $s$, $z$, $n$ and fractal dimension $d_f$ were calculated from dynamic oscillation experiments. The obtained values support the percolation model of the network formation. The critical exponents obtained by DLS and rheology were compared. The theoretically predicted equality between exponents $\beta$ and $n$ was not found, at least for this studied system.
5. Summary and Outlook

The light scattering methods were used for characterization of properties and formation of networks of different dimension, based on N-vinylcaprolactam. Formation of PVCL microgels in presence of PVA as stabilizer was studied. Decreasing of the molecular weight of PVA and increasing of its concentration allow to reduce (to some extend) particle size. There is no influence of the stabilizer quantity on transition temperature of PVCL, but the stabilizer, when its concentration is high, decreases the swelling of the microgels. Particle size strongly depends on heating rate: interparticle aggregation was observed during slow heating and intraparticle collapse during fast heating. In the swollen state and in the case of individually shrunken PVCL particles (measured after fast heating) the independence of measured diffusion coefficient on the angle of observation was found in DLS. That means that only translation diffusion can be detected. Contrary, the diffusion coefficients for the aggregates were strongly angle dependent. The aggregates showed an unusual angular dependence: the diffusion coefficient increases with decreasing of observation angle. This behavior shows probably the presence of a rotation diffusion, which can result from the non-spherical shape of the aggregates. This phenomenon was not discussed in the literature concerning with aggregation of the thermo-sensitive microgels. The systematic study of different systems, which are able to form stable aggregates of different size, is required to clarify and to characterize this phenomenon.

Thermo-sensitive microgels based on VCL and AAEM have been prepared under surfactant free conditions. The results obtained from SLS showed hydrophobic internal structure with weak thermo-sensitive properties. The angular dependence of VCL/AAEM microgels in SLS at room and elevated temperatures showed the behavior of globular particles. DLS experiments showed the same transition temperature for all microgels independently on composition. The presence of internal part with low thermo-sensitivity and highly thermo-sensitive outer part of the particle provide evidence of the core-shell structure of microgel. Transition temperature of the PVCL-rich shell is shifted to ~28 °C in comparison to reported 32 °C for pure PVCL. The absence of the angular dependence of the apparent diffusion coefficient was observed for all VCL/AAEM microgels in swollen and collapsed state that means that the internal mobility is reduced induced due to cross-linking. Combining results obtained from SLS and DLS show the change of conformation from “swollen” soft sphere to compact shrunken “hard sphere”. Thus it was shown, that from results of combined SLS and DLS one could obtain not only the size of macromolecules but also the information about the
internal structure and the conformational changes induced by the change of environment. Due to the presence of acetoacetate functional groups the microgels can be used in different applications.

Thermo-sensitive microgels based on N-vinylcaprolactam and N-vinylpyrrolidone were prepared under the surfactant-free condition. The presence of hydrophilic comonomer during polymerization leads to formation of a stable dispersion of large particles with narrow particle size distribution. The DLS study showed that internal modes in microgel dispersion made a contribution at $q R_g > 2.4$ instead of $q R_g > 1$ for polymer coil in diluted solution. The additional motion to translation diffusion was observed in the range $2.4 < q R_g < 4$. Two internal motions and translation diffusion were observed at $q R_g > 4$. Angular dependence of the normalized diffusion coefficient $D_{app}/D_z$ calculated by cumulant analysis shows power law behavior $D_{app}(q) \sim q^n$ at the $q R_g > 4.2$. The experimentally determined value of exponent $n = 0.96 \pm 0.05$ is in good agreement with the value predicted for ZIMM limit for polymer chains with hydrodynamic interaction. That means, that internal dynamic inside microgel particle is the same as in flexible polymer coil. Angular dependence of the reciprocal form factor function obtained from SLS experiment shows power law behavior $P(q) \sim q^{n'}$ at the $q R_g > 3.2$ with the exponent $n' = 5.24$. The scattering curve should decrease in the asymptotic range with the power of 4 for the particles with existing internal surface. The reason of higher exponent is not clear and additional experiments in the range of higher $q R_g$ values are necessary to clarify this phenomenon. The reduced first cumulant $\Gamma^*(q)$ reached a constant value $\Gamma^*(\infty) = 0.01$ at large $q R_g$. This plateau is much lower than the experimental plateau value $\Gamma^*(\infty) = 0.062$ for linear chains. This indicates that mobility of cross-linked chains is reduced. The shape function was calculated for cross-linked microgel. The shape of obtained function did not agree with the shape of function calculated for the flexible polymer chain. But, nevertheless, both functions, experimental and calculated ones, can be described by a stretched exponential function with exponent of 0.66. This corresponds to ZIMM limit of hydrodynamic interaction. The thermo-sensitive properties of CP microgel were studied. The transition temperature of microgel was shifted to around 38°C due to the presence of hydrophilic segments. At the temperature of 38°C weak aggregation occurs. In the range of temperature 15°C – 30°C the angular dependence of normalized diffusion coefficient can be described by single master curve. Further heating leads to deviation from master curve. This is a result of accelerated segmental mobility as was shown by the reduced cumulant. The reason of such deviation is not completely clear. The interpretation of experimental
observation needs more tests using more extended theoretical calculations and objects with more defined structures. There are two questions, which are still unanswered

- Should the master curve of angular dependence of the normalized diffusion coefficient be observed for the thermo-sensitive microgel, based only on thermo-sensitive homopolymer, in the whole temperature range?
- Will the plateau value $\Gamma^*(\infty)$ increase with heating for the particles based on thermo-sensitive polymer and hydrophilic polymer?

Model systems should be large enough to show the internal motion and stable in the whole temperature range.

PST/PVCL polymeric particles can be prepared in presence of PEGMA. Particle size and broader particle size distribution of dispersions can be controlled by the VCL amount in the reaction mixture at constant PEGMA content. Increase of VCL amount leads to increase of particle size and particle size distribution due to the increase of the hydrophilicity of the particle surface. The surface roughness in PST/PVCL particles reflects the polymerization mechanism and indicates their core-shell structure. It occurs and results in the formation of a PVCL rich shell layer. The temperature sensitivity of obtained PST/PVCL dispersions increases dramatically with VCL amount used in the polymerization process. The influence of initiator on the thermal properties of obtained particles was observed. The nature of this influence is not clear and must be investigated in the future more carefully.

3,3’-(ethane-1,1-diyl)bis(1-vinyl-2-pyrrolidone) was used as a cross-linker of VCL in ethanol solution by radical polymerization. The network formation was investigated by dynamic light scattering. It was shown, that monitoring of the light scattered intensity in all cases is quite sensitive to detect the gelation threshold even in the presence of very low cross-linker concentrations. The appearance of the speckles can be taken as gelation threshold and the intensity of the speckles depends on cross-linker concentration. The power law of TCF at the gel point, $(g^2(t) - 1) \sim t^{-\mu}$, is a sufficient but not a necessary condition for critical gelation. However, it can be observed in broad range of cross-linker concentration and random chosen monomers/solvent ratio, at least for VCL system. The power law disappeared after crossing the gel point and the “frozen” power law was not observed in well-developed gel state. The exponent calculated from power law depends on cross-linker concentration and can be attributed to the degree of branching. The relaxation time distribution cannot be used as a clear indication of the gel point in the case when collective mode is present in TCF due to the weak signal of the cluster mode.
The novel thermo-sensitive hydrogel system based on VCL and HEMA was synthesized by radical cross-linking polymerization in ethanol using allyl methacrylate as cross-linker. The VCL/HEMA network formation was investigated by dynamic light scattering and dynamic rheological experiments. The formation of copolymeric network has the same peculiarities as formation of VCL gel in DLS. The strong intensity fluctuations were observed at the gel point and the power law \( g_2(t) - 1 \sim t^{-\mu} \) was observed for the all studied VCL/HEMA mixtures. The exponent of power law was weakly dependent on VCL/HEMA ratio. The comparison of critical exponents obtained from DLS and rheology was done. The theoretically predicted equality between exponents from these methods was found as not valid at least for this studied system. Detailed investigations of this phenomenon are needed. A system, which gives possibility to stop reaction, should be found for this purpose. The investigations in the whole range of exponents, predicted for DLS and rheology, and deep theoretical consideration of results will help to understand the relation between these methods.

This work showed, that the dynamic light scattering is the unique method of characterization of polymers. It is useful for exploration of internal structures of objects with dimension around 100-1000 nm. Dynamic processes, such as cross-linking, can be monitored in the real time conditions. The advantage of DLS is the possibility to study the gelation process without disturbing the gelling system.

6.1 The Reagents.
The monomers \(N\)-vinylcaprolactam (VCL) (Aldrich, purity 99\%), \(N\)-vinylpyrrolidone (VP) (Aldrich, purity 99\%\+)
were purified by distillation under reduced pressure before use.
The monomers hydroxyethyl methacrylate (HEMA) (Aldrich, purity 97\%), acetoacetoxyethyl
methacrylate (AAEM) (Aldrich, purity 95\%), \(\omega\)-hydroxy poly(ethylene glycol methacrylate)
were taken without additional cleaning.
The cross-linkers \(N,N'\)-methylenebisacrylamide (MBA) (Aldrich, purity 97\%) and allyl
methacrylate (AMA) (Aldrich, purity 98\%) were used as received.
The initiators sodium peroxosulfate (Fluka), azobisisobutyronitril (AIBN) (Acros), 2,2’-
azobis(2-methylpropyonamidine) dihydrochloride (AMPA) were also used without additional
cleaning.
Poly(vinyl alcohol) with different molecular weights and hydrolysis degree (Wacker, Aldrich)
was used as stabilizer.

The cross-linker 3,3’-(ethane-1,1-diyl)bis(1-vinyl-2-pyrrolidone) (BVP) was prepared
according to the reference [243]. VP (250 ml) was mixed with the toluene (250 ml) in the
round-bottom flask equipped with stirrer and reflux condenser. Na (10 g) was added during 1
hour under stirring. The mixture was boiled under nitrogen atmosphere for 4.5 hours. After
that, reaction mixture was cooled overnight. The toluene was decanted and the fresh portion
of the toluene (300 ml) was added to the precipitate. The mixture was boiled for 1 hour,
cooled and the toluene was decanted. The toluene extracts were mixed and concentrated by
evaporation. The fivefold volume of water was added and the mixture was stirred for 1 hour.
Resulting precipitate was removed and purified by precipitation from cold ethanol. The yield
of BVP was 2.4\%, m.p. 121-121.5 °C.

6.3 Synthesis of PVCL Microgel Dispersions.
Cross-linked PVCL particles were prepared in the following way: 2.09 g of VCL, 0.06 g of
MBA (except samples 7 and 8 (Table 6.1) were prepared with 0.09 and 0.12 g, respectively)
and an appropriate amount of poly(vinyl alcohol) (Table 6.1) were dissolved in 145 g of
deonized water and than placed into double-wall glass reactor equipped with stirrer and
reflux condenser. After 1 hour of the incubation at 70°C and nitrogen purging, 0.05 g of AMPA dissolved in 5 g water was added under continuous stirring for initiation of the reaction. The reaction was carried out for 8 hours. The microgel was then purified from unreacted species with extensive dialysis, using a Biomax 5 membrane (Millipore).

### Table 6.1 The type and amount of PVA taken for the stabilization of PVCL microgel

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVA(^a)</th>
<th>PVA, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14,000-99</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>14,000-99</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td>14,000-99</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>14,000-99</td>
<td>0.75</td>
</tr>
<tr>
<td>5</td>
<td>14,000-99</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>14,000-99</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>14,000-99</td>
<td>0.75</td>
</tr>
<tr>
<td>8</td>
<td>14,000-99</td>
<td>0.75</td>
</tr>
<tr>
<td>9</td>
<td>17,000-99</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>17,000-99</td>
<td>0.2</td>
</tr>
<tr>
<td>11</td>
<td>17,000-99</td>
<td>0.5</td>
</tr>
<tr>
<td>12</td>
<td>17,000-99</td>
<td>0.35</td>
</tr>
<tr>
<td>13</td>
<td>17,000-88</td>
<td>0.1</td>
</tr>
<tr>
<td>14</td>
<td>17,000-88</td>
<td>0.35</td>
</tr>
<tr>
<td>15</td>
<td>40,000-99</td>
<td>0.2</td>
</tr>
<tr>
<td>16</td>
<td>40,000-88</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^a\) PVA type: \(M_w\) g/mol– degree of hydrolysis

#### 6.4 Synthesis of VCL/AAEM Microgel Dispersions.

Appropriate amounts of AAEM, VCL (see Table 6.2) and 0.06 MBA were added in 145 ml deionized water. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Solution of the monomers was placed into reactor and stirred for 1 h at 70°C with purging with nitrogen. After that, 5 ml water solution of initiator (5 g/l) was added under continuous stirring. The reaction was carried out for 8 hours. Polymer dispersions were freed from monomer and uncross-linked polymers by dialysis. Dispersions were dialyzed against water using Biomax 100 (Millipore) membrane.
6. Experimental Methods

### Table 6.2 Reaction recipe for preparation of VCL/AAEM microgels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>VCL, g</th>
<th>AAEM, g</th>
<th>AAEM*, mol-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.06</td>
<td>0.04</td>
<td>1.25</td>
</tr>
<tr>
<td>2</td>
<td>2.04</td>
<td>0.08</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>1.99</td>
<td>0.16</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>1.93</td>
<td>0.24</td>
<td>7.5</td>
</tr>
<tr>
<td>5</td>
<td>1.88</td>
<td>0.32</td>
<td>10</td>
</tr>
</tbody>
</table>

* - in VCL/AAEM monomers mixture

6.5 Synthesis of PST/PVCL Latex.

The appropriate amount of PEGMA was dissolved in 150 ml deionized water. The mixture of VCL and ST (Table 6.3) was added to the stirred solution. Obtained pre-emulsion was stirred for 1 h. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Pre-emulsion was placed into reactor and the 30 ml solution of 0.3 g of sodium peroxysulfate (except samples 10, 11 were the same quantity of AMPA was used as initiator) was added under continuous stirring. Temperature was raised up to 70 °C to start the polymerization process. Latexes were prepared at ca. 10 % solid content. Latexes were dialyzed against water using Biomax 100 (Millipore) membrane.

### Table 6.3 Reaction recipe for preparation of PST/PVCL latex.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ST, g</th>
<th>VCL, g</th>
<th>PEGMA, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.50</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>1</td>
<td>18.13</td>
<td>1.37</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>17.55</td>
<td>1.95</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>17.00</td>
<td>2.50</td>
<td>0.50</td>
</tr>
<tr>
<td>4</td>
<td>14.50</td>
<td>5.00</td>
<td>0.50</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>19.00</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>17.67</td>
<td>1.33</td>
<td>1.00</td>
</tr>
<tr>
<td>8</td>
<td>17.10</td>
<td>1.90</td>
<td>1.00</td>
</tr>
<tr>
<td>9</td>
<td>16.57</td>
<td>2.43</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td>19.50</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>11</td>
<td>17.55</td>
<td>1.95</td>
<td>0.50</td>
</tr>
</tbody>
</table>

6.6 Synthesis of VCL/VP Microgel Dispersions.

1.67 g of VCL, 0.38 g of VP and 0.06 MBA were dissolved in 145 ml of deionizer water. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Solution of the monomers was placed into reactor and stirred for 1 h at 70°C with
6. Experimental Methods

purging with nitrogen. After that, 5 ml water solution of AMPA (5 g/l) was added under continuous stirring for the initiating of reaction. Polymer dispersions were freed from monomer and uncross-linked polymers by dialysis. Latexes were dialyzed against water using Biomax 100 (Millipore) membrane.

6.7 Synthesis of PVCL Hydrogels.
The appropriate amounts of VCL, BVP (Table 6.4) and 60 mg of AIBN were dissolved in 14 ml ethanol and reaction mixture was bubbled with nitrogen for 30 min. Reaction was carried out in a 20 ml glass tube. The reaction mixture was heated to 60 °C and kept at this temperature for 24 hours. The hydrogels were removed from reaction vessels and dried in vacuum to the constant weight. Than the hydrogels were extracted with ethanol in Soxhlet apparatus for 72 h. After drying to constant weight, the gel content was determined as

\[ W_{gel} = \frac{m_s - m_e}{m_s} \times 100\% \] (6.7-1)

where \( m_s \) is the mass of the sample after synthesis and \( m_e \) is the mass of the sample after extraction.

Table 6.4. Reaction recipe for preparation of PVCL hydrogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>VCL, g</th>
<th>Cross-linker, mg</th>
<th>Cross-linker, mmol/mol *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>31</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>62</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>125</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>188</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>312</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* - mmol of cross-linker/mol of N-vinylcaprolactam

6.8 Synthesis of VCL/HEMA Hydrogels.
The appropriate amounts of VCL, HEMA (Table 6.5), 25 mg AMA and 60 mg of AIBN were dissolved in 14 ml ethanol and reaction mixture was bubbled with nitrogen for 30 min. Reaction was carried out in 20 ml glass tube. The reaction mixture was heated to 60 °C and kept at this temperature for 24 hours. The hydrogels were removed from reaction vessels and dried in vacuum to the constant weight. Than the hydrogels were extracted with ethanol in Soxhlet apparatus for 72 h. Gel content was determined from equation (6.7-1)
Table 6.5 Reaction recipe for preparation of VCL/HEMA hydrogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>VCL, g</th>
<th>HEMA, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH-1</td>
<td>6.5704</td>
<td>0.7209</td>
</tr>
<tr>
<td>CH-2</td>
<td>5.8398</td>
<td>1.4075</td>
</tr>
<tr>
<td>CH-3</td>
<td>5.1119</td>
<td>2.1090</td>
</tr>
<tr>
<td>CH-4</td>
<td>3.6487</td>
<td>3.5129</td>
</tr>
<tr>
<td>CH-5</td>
<td>0</td>
<td>7.0351</td>
</tr>
<tr>
<td>CH-6</td>
<td>7.2993</td>
<td>0</td>
</tr>
</tbody>
</table>

6.9 Determination of the Swelling Degree.
Swelling measurements were performed by direct weighing method. Dried gel samples (20-30 mg) were dipped into different solvents. The gels were kept in solution until constant mass values for swollen samples were determined (at least for 24 h). In the case of measurements of the temperature dependence the swollen sample was equilibrated for 8 hours at the each temperature. The swelling degree was calculated as

\[ Q = \frac{m_{sw}}{m_{dry}} \]  \hspace{1cm} (6.9-1)

Table 6.6 Solubility parameters \( \delta \) for different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \delta ), (J/cm(^3))(^{0.5} )</th>
<th>Hydrogen bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl-n-Butylketone</td>
<td>17</td>
<td>m</td>
</tr>
<tr>
<td>n-Butylacetate</td>
<td>17.4</td>
<td>m</td>
</tr>
<tr>
<td>Diethylketone</td>
<td>18</td>
<td>m</td>
</tr>
<tr>
<td>Xylene</td>
<td>18</td>
<td>p</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.2</td>
<td>p</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>18.6</td>
<td>m</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>18.6</td>
<td>m</td>
</tr>
<tr>
<td>Chloroform</td>
<td>19</td>
<td>p</td>
</tr>
<tr>
<td>Methylacetate</td>
<td>19.6</td>
<td>m</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.3</td>
<td>m</td>
</tr>
<tr>
<td>Hexanol</td>
<td>21.9</td>
<td>s</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>23.3</td>
<td>s</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>23.5</td>
<td>s</td>
</tr>
<tr>
<td>Propanol</td>
<td>24.3</td>
<td>s</td>
</tr>
<tr>
<td>Ethanol</td>
<td>26</td>
<td>s</td>
</tr>
<tr>
<td>Methanol</td>
<td>29.7</td>
<td>s</td>
</tr>
<tr>
<td>Water</td>
<td>47.9</td>
<td>s</td>
</tr>
</tbody>
</table>

Hydrogen bonding: p = poor; m = moderate; s = strong
where \( m_{\text{sw}} \) is the mass of the swollen sample and \( m_{\text{dry}} \) is the mass of dry sample. Swelling degree was taken as an average from 3 measurements. The solubility parameters for solvents were taken from the reference [244] (Table 6.6).

6.10 Static Light Scattering

The SLS measurements were made with FICA 50 with a helium-neon laser (wavelength of 632.8 nm). The measurements of microgel/latex dispersions were carried out at angles \( \theta = 15^\circ\text{-}120^\circ \). The concentration of the dispersions was in the range \( 1\cdot10^{-2}\text{-}2\cdot10^{-1} \) g/l. Dispersions were filtrated using 5 \( \mu \)m nylon filters. Typically, the sample in a 20 mm test tube was immersed in a dibutylphthalate bath and tempered within an error of \( \pm 0.1^\circ\text{C} \).

6.11 Dynamic Light Scattering

A commercial laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometer system ALV/CGS-8F S/N 025 was used with a helium-neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as the light source.

The measurements of microgel/latex dispersions were carried out at angles \( \theta = 30^\circ\text{-}120^\circ \). The concentration of the dispersions was in the range \( 1\cdot10^{-2}\text{-}2\cdot10^{-1} \) g/ml. Dispersions were filtrated using 5 \( \mu \)m nylon filters. Typically, the sample in a 10 mm test tube was immersed in a toluene bath and tempered within an error of \( \pm 0.1^\circ\text{C} \). The viscosity and refractive index data for water/alcohol mixtures were taken from the references [245, 246].

The online DLS gelation experiments were carried out at an angle of \( \theta = 90^\circ \) as a function of polymerization/cross-linking time. The solution was filtrated using a 0.2 \( \mu \)m nylon membrane filter. Typically, the sample in a test tube (diameter 10 mm, 3 ml reaction solution) was immersed in a toluene bath tempered within an error of \( \pm 0.1^\circ\text{C} \). This point was taken as the start of the reaction. In this type of DLS experiments two measuring modes were used. First, the scattered intensity was measured up to 3 hours to obtain the intensity profile. In the second one, the measurements for observation of the power law behavior in the TCF were done during the cross-linking process. The acquisition time of each run in the second mode was chosen as it was necessary to obtain enough data points, especially at longer delay times. The time window for observation of the transition between the solution and gel state through the critical gel point was approximately 2 min.
6.12 Rheological Measurements.

For rheology measurements of VCL gelation a PHYSICA MCR300 rheometer with a double gap system was used. The constant shear stress of 5 Pa was applied for measurements of viscosity during VCL gelation. 20 ml of the reaction mixture (Table 6.4) were taken for the measurement.

For rheology measurements of VCL/HEMA system a Fluids Spectrometer RFS 2 from Rheometric Scientific with a couette system (cup diameter: 34 mm, bob diameter: 32 mm, bob length: 33.3 mm) was used. Strains were applied in the range from 500 % (in the liquid state, at the beginning of the measurement to provide an accurate torque response) up to 20 % (around the gelation threshold to avoid a break down of the formed gel structure). The material was shown to behave linearly at these levels. 17 ml of the solution were taken for the measurement.

For rheology measurements of VCL/AAEM microgel a Fluids Spectrometer RFS 2 from Rheometric Scientific with a couette system (cup diameter: 34 mm, bob diameter: 32 mm, bob length: 33.3 mm) was used. Shear rates were applied in the range 1 - 1000 s\(^{-1}\). 17 ml of the solution were taken for the measurement.

6.13 Stability Measurements

Stability measurements were performed with separation analyzer LUMiFuge 114 (L.U.M. GmbH, Germany). Measurements were made in glass cuvettes at acceleration velocity 3000 rpm.

6.14 IR Spectroscopy.

The VCL/AAEM spectra were recorded with Mattson Instruments Research Series 1 FTIR spectrometer. Dried microgel samples were mixed with KBr and pressed in the form of tablet. The temperature dependence of spectrum for VCL/HEMA swollen in D\(_2\)O was measured with FTIR spectrometer Nic 210 (Nicolet) equipped with DTGS detector and Ge/KBr beam splitter. The swollen gel powder was pressed in the thin layer between two CaF\(_2\) crystals and the sample was placed in the tempered sample holder. 100 scans with resolution 0.5 cm\(^{-1}\) were done for each reference and sample measurement. The sample was equilibrated 15 min for each temperature.
6.15 Differential Scanning Calorimetry.
DSC measurements were made with Mettler TA 4000. TGA measurements were made with TGA 7 Perkin Elmer, Pyris-Software version 3.51. Before measurements the samples were dried in vacuum. The samples were analyzed in closed aluminium caps. The measurements were made at a heating rate of 5 °C/min in nitrogen atmosphere.

6.16 Scanning Electron Microscopy.
The measurements were made with Zeiss Gemini DSM 289 instrument with operating at 4 V. Diluted samples were placed on the previously cleaned aluminium supports. The samples were dried at room temperature for 24 hours and kept for vacuum for 6 hour.

6.17 Atomic Force Microscopy.
Measurements were made with Dimension 3100 (Digital Instruments Inc.) using the tapping mode regime (set point ratio 90%, integral gain 0.2, amplitude set point 0.7 V, scan rate 0.901 Hz). Samples were prepared by spin coating technique (2000 rpm, 10 min) on the previously cleaned glass supports.
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