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ORIGINAL CONTRIBUTION

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Poly(*N*-vinylcaprolactam) microgels. Polymeric stabilization with poly(vinyl alcohol)

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Abstract Poly(vinyl alcohol), PVA, with different molecular weights, M_w, and degrees of hydrolysis has been used to study the steric stabilization of microgels based on poly(*N*-vinylcaprolactam). The stabilizer influences the particle size and stability, but has no influence on the thermal properties. The thermal behavior of microgels depends on the heating rate: slow heating leads to the formation of aggregates and fast heating to an intramolecular collapse. The aggregates showed an unusual angular dependence of the diffusion coefficient, which can be explained by the presence of probably an additional rotational diffusion.

Keywords *N*-vinylcaprolactam · Microgel particles · Thermosensitive behavior

Introduction

The interest in microgels has grown rapidly over the last 20 years because of their easy preparation and their potential uses in many industrial applications. Microgels are currently being investigated for their use as drug delivery systems, in chromatographic separation technology, as catalyst media, etc. [1, 2, 3].

Poly(*N*-isopropylacrylamide), PNIPAm, microgels (and their copolymers) are the most widely investigated systems [4, 5, 6, 7]. Microgels based on NIPAm are thermosensitive and they can swell or shrink in dependence on the temperature. In water at room temperature, microgel particles have a swollen conformation with water occupying the internal spaces within the microgel structure. During heating, the particles shrink, because the polymer–solvent interactions are dramatically reduced. The microgels form a hard sphere structure and the polymer chains are preferred to interact with each other. The swelling and shrinking of a polymer network can be generally attributed to a balance between the repulsion and attraction among functional groups attached to the network. This repulsion and attraction can arise from the combination of the four intermolecular forces: electrostatic, hydrophobic, van der Waals, and hydrogen bonding [8].

Poly(*N*-vinylcaprolactam) (PVCL) is a relatively new type of nonionic water-soluble polymer. It should be more biocompatible than PNIPAm [9], it can form complexes with organic compounds, it is resistant to hydrolysis, and its gel undergoes a continuous volume transition in the temperature range 25–36 °C. Up to now, only a few studies on PVCL microgels have been reported [10, 11, 12, 13], because its polymerization is much more complicated and its volume phase transition is not so sharp as for the PNIPAm microgels. If charged comonomers are incorporated in the PVCL network, they influence the sharpness and the temperature of its transition.

In this work we have investigated the dispersion polymerization of *N*-vinylcaprolactam (VCL) in the presence of *N*,*N*′-methylenbisacrylamide (MBA) in water. The field of dispersion polymerization attracted great interest mainly for producing dispersions of water-insoluble polymers, which sometimes form monodisperse particles [14]. 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 are adsorbed in a sufficient amount, they prevent agglomeration of the particles by the mechanism of attached steric stabilization. Some of the polymer stabilizers can also be grafted on the particle surface which makes the stabilization independent of adsorption. Another possibility to obtain stable dispersions is adding free polymer chains which are soluble in the dispersion medium. In this case particles are stabilized by the depletion mechanism [15].

We have carried out the dispersion polymerization of VCL in the presence of a cross-linker above its lower critical solution temperature (LCST) in water using poly(vinyl alcohol) (PVA) with different molecular weights and different degrees of hydrolysis as stabilizer. The thermal behavior of the obtained microgel was studied.

Experimental

Materials

VCL monomer (Aldrich) was purified by distillation under vacuum. PVAs (Wacker and Aldrich) with different molecular weights $M_w = 14{,}000$, 17,000, and 40,000 g/mol and a degree of hydrolysis of 88 or 99%, MBA cross-linker (Merck), and 2,2′-azobis(2-methylpropionamidine) initiator (AMPA, Aldrich) were used without further purification. Deionized water was used as the polymerization medium.

Sample preparation

Cross-linked PVCL particles were prepared in the following way: the proper amounts of monomer (2.09 g), cross-linker (from 0.06 to 0.12 g, and stabilizer (from 0.1 to 1.5 g) were dissolved in 145 g of deionized water and then placed into a double-wall glass reactor equipped with a stirrer and reflux condenser. After 1 h incubation at 70 °C and nitrogen purging, 0.05 g initiator dissolved in 5 g water was added with continuous stirring. The reaction was carried out for 8 h. The polymerization yield, determined gravimetrically, was around 80%. The microgel was then purified from unreacted species with extensive dialysis, using a Biomax 5 membrane (Millipore). The conditions of preparation of microgels are listed in Table 1.

Instrumentation and characterization

Dynamic light scattering

A commercial laser light scattering (LLS) 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 22 mW and wavelength 632.8 nm) as the light source.

In dynamic LLS, the intensity–intensity–time correlation function $g_2(q,t)$ in the self-beating mode was measured and can be expressed by the Siegert relation

$$g_2(q,t) = A\left(1 + \beta|g_1(q,t)|^2\right)$$

where t is the decay time, A is a measured baseline, β is the coherence factor, $g_1(q,t)$ is the normalized first-order electric field–time correlation function and $g_1(q,t)$ is related to the measured relaxation rate Γ

$$g_1(q,t) = \exp(-\Gamma t) = \int G(\Gamma)\exp(-\Gamma t)d\Gamma$$

A line-width distribution $G(\Gamma)$ can be obtained from the Laplace inversion of $g_1(t)$ (CONTIN procedure). For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D at $q \to 0$ and $c \to 0$ by

Table 1 Chemical composition and the stability of PVCL microgel particles

Sample	PVA[a]	PVA, g	MBA, g	Stability	R_h, nm (15 °C)	PDI
1	14,000, 99	1.5	0.03	+	182	0.127
2	14,000, 99	1.25	0.03	+	186	0.126
3	14,000, 99	1	0.03	+	192	0.124
4	14,000, 99	0.75	0.03	+	228	0.146
5	14,000, 99	0.5	0.03	+	260	0.134
6	14,000, 99	0.25	0.03	+	287	0.159
7	14,000, 99	0.75	0.06	+	249	0.129
8	14,000, 99	0.75	0.09	*	293	0.164
9	17,000, 99	0.1	0.03	+	280	0.143
10	17,000, 99	0.2	0.03	*	328	0.191
11	17,000, 99	0.5	0.03	*	Floccules	–
12	17,000, 99	0.35	0.03	*	Floccules	–
13	17,000, 88	0.1	0.03	**	–	–
14	17,000, 88	0.35	0.03	**	–	–
15	40,000, 99	0.2	0.03	**	–	–
16	40,000, 88	0.2	0.03	**	–	–

+ dispersion is stable for an infinitely long time

* precipitation of the dispersion in some days

** unstable dispersion

[a] PVA type: M_w, degree of hydrolysis

$D = \Gamma/q^2$

or a hydrodynamic radius R_h given by

$R_h = k_B T/(6\pi\eta D)$

with q, k_B, T, and η being scattering vector, the Boltzmann constant, absolute temperature, and solvent viscosity, respectively. All dynamic LLS experiments were carried out at angles $\theta = 30–140°$. The concentration of the microgel in water was about 1.5×10^{-4} g/ml. Microgel solutions were filtered using 5-μm nylon filters. Typically, the sample in a 10-mm test tube was immersed in a toluene bath and thermostated within an error of ±0.1 °C.

The polydispersity index, PDI, was calculated from $\mathrm{PDI} = \mu_2/\Gamma^2$, where μ_2 is the second moment of the second-order fitting in the cumulated analysis.

Stability measurements

The stability measurements were performed with a separation analyzer LUMiFuge 114 (L.U.M. GmbH, Germany). Measurements were made in glass cuvettes at an acceleration velocity of 2,000 rpm for 60 min.

Results and discussion

Stability and particle size

It can be seen from Table 1 that the stability of PVCL microgels increases with decreasing molecular weight and decreasing degree of hydrolysis. Polymeric stabilization of the microgel dispersion differs from attached steric stabilization of water-insoluble polymers (styrene, butyl methacrylate). These polymers are more stable in the presence of high molecular weight PVA with a relatively low degree of hydrolysis [16], due to the adsorption of hydrophobic nonhydrolyzed 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 [15] as the transition sequence: instability → stability → instability. This means that some concentration of stabilizer is not enough to make a stable dispersion, its increase leads to polymeric stabilization, and its further increase induces depletion flocculation.

The dependence of the microgel size on the PVA concentration is shown in Fig. 1. With increasing PVA concentration the size decreased linearly from 290 to 190 nm, but after a concentration of around 7 g/l, the stabilizer had no influence on the particle size.

There is no influence of the reaction rate (e.g., temperature, initiator) on the particle size, but an increasing degree of cross-linking 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 the polymer network tend to increase the water solubility of VCL–MBA copolymer. Increased 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 leads to a lower concentration of larger primary (colloidally stable) particles [17].

Thermal behavior

The thermal behavior of microgels (samples 2, 4, 6) in water is shown in Fig. 2. There is a continuous decrease in the diameter up to 30 °C and a sharp increase in size of the particles to 900–1200 nm at around 32 °C (slow heating procedure, s.h.). The aggregation point did not depend on the microgel and stabilizer concentrations, and can be taken as the critical aggregation temperature (CAT). This point is close to the reported LCST for PVCL [18]. Quite different thermal behavior was observed when the samples were quickly heated to 50 °C (immersed in a bath at the temperature of 50 °C) and then cooled step-by-step (fast heating procedure, f.h.). In contrast to the first case, no aggregation was observed and the temperature dependence was usual for thermosensitive microgels. It can also be seen that a high concentration of PVA slightly decreases the swelling of the microgel.

A nondiffusive behavior D of the microgels (independence of translational diffusion coefficient from the angle θ of observation) was observed in the cases of

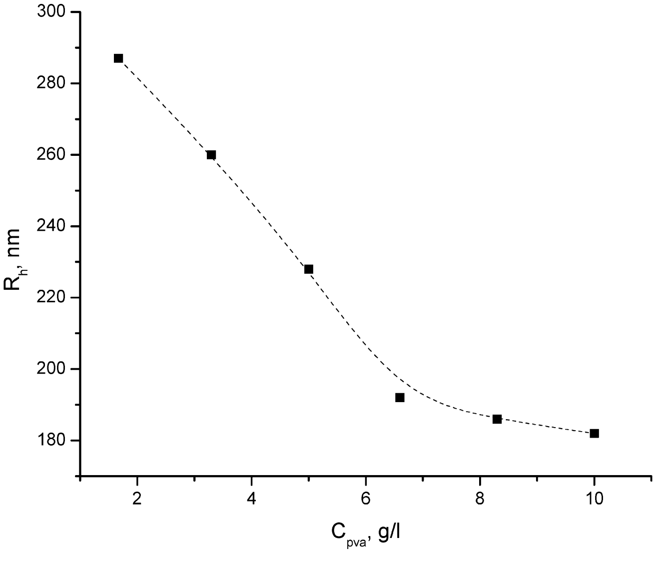

Fig. 1 Dependence of the hydrodynamic radius R_h on the PVA ($M_W = 1{,}400$ g/mol, degree of hydrolysis 99%) concentration C_{PVA} at 15 °C

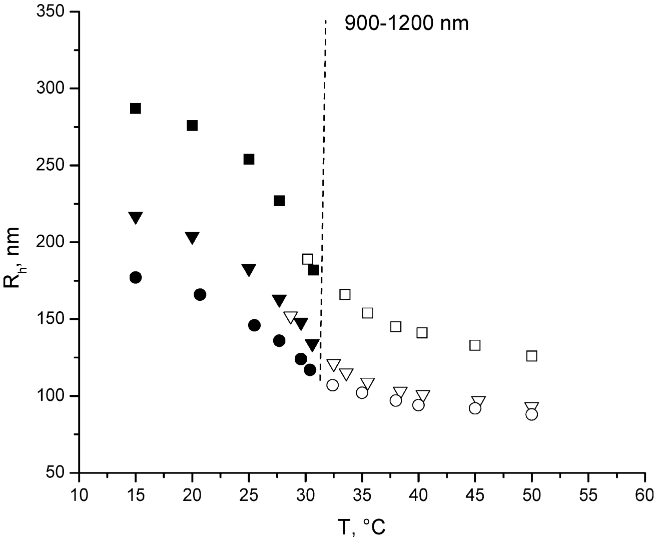

Fig. 2 Temperature dependence of the hydrodynamic radius R_h. *Filled symbols*–direct heating, *open symbols*–cooling after fast heating; *quadrates*–sample 6, *triangles*–sample 4, *circles*–sample 2

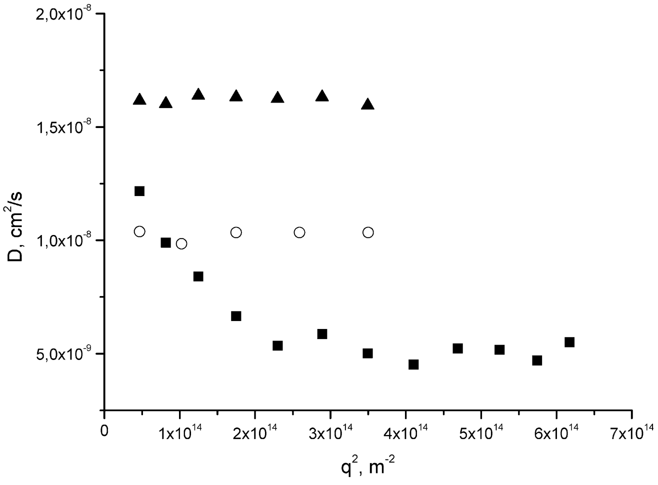

Fig. 3 Dependence of the diffusion coefficient D on scattering vector q^2 for sample 6 at different temperatures: *circles*–25 °C; *quadrates*–38 °C, slow heating; *triangles*–40 °C, fast heating

temperatures lower than the LCST and during the fast heating procedure. Conversely, the diffusion coefficients for the aggregates were strongly angle dependent (Fig. 3).

This dependency was completely contrary to those predicted by the theory [19], where the diffusion coefficients increase (instead of decrease) with decreasing observation angle. In the case of a pure diffusive behavior (translational mode only), the relaxation rate Γ can be extrapolated to the origin [20] (dotted line in Fig. 4). In our case, the line intersects the Γ axis at around 45 ms^{-1}. This intersection shows probably the presence of a rotational diffusion, which can result from the nonspherical shape of the aggregates. So, diffusion for the aggregates observed in our work is the average value of the pure translational mode and an additional rotational diffusive mode, which cannot be easily separated. This leads to the unreasonable values of the hydrodynamic radii calculated from the extrapolated diffusion coefficients.

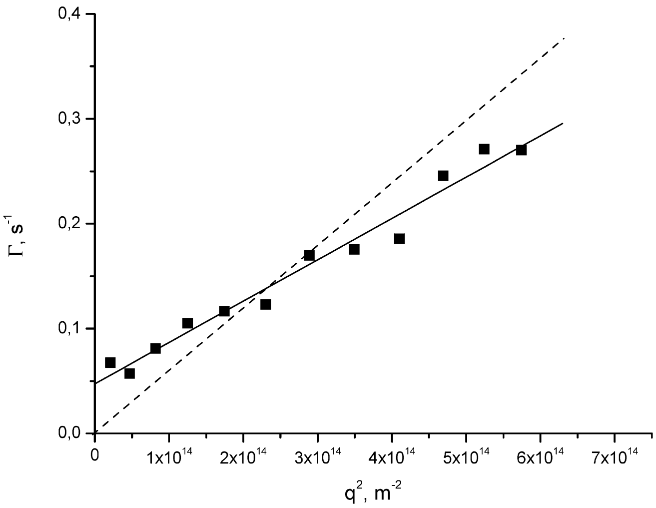

Fig. 4 Dependence of the measured relaxation rate Γon scattering vector q^2: *dotted line*–schematic presentation of the pure translational mode, predicted by the theory; *solid line*–linear fit of the experimental data

The effect of the heating rate on the particle size distribution of the microgels is shown in Fig. 5. During step-by-step heating to 32 °C, aggregation occurred and the peak maximum of the hydrodynamic radius distribution was shifted to a higher value. The size of the aggregates was checked after annealing of the sample for several hours. Only a monomodal size distribution was observed in all cases, which means that the process of aggregation was already completed. After fast heating to 50 °C and step-by-step cooling, the peak maximum was shifted to a smaller value, as expected for thermosensitive microgels. It should be noted that the hydrodynamic radius distributions, obtained by inverse Laplace transformation with the CONTIN program, were always found to be symmetric in the logarithmic scale. This symmetry may possibly be an effect of the Laplace inversion procedure, which requires some smoothing of the experimental data, and this may cause a much broader distribution than actually is present [21].

The effect of heating on the thermal behavior was observed for thermosensitive copolymers based on NIPAm [22, 23] 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 decreases, but the van der Waals attractive forces are still low and the PVCL

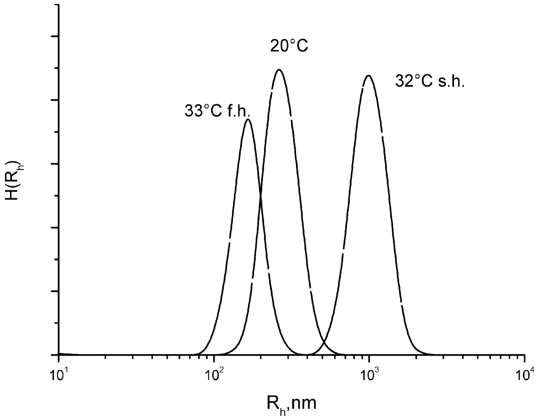

Fig. 5 Changing of the hydrodynamic radius distribution of PVCL microgel particles at the observation angle $\theta = 60°$ (sample 6) after direct heating (s.h.) and step-by-step cooling (f.h.)

chains on the microgel surface are involved with PVA in the steric stabilization. Water becomes a poor solvent at 32 °C and the van der Waals attractive forces subsequently increase. 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 aggregate because attractive (van der Waals and hydrophobic interaction) forces are now dominating. In this case, only PVA is a stabilizer for the microgel, but probably this stabilizing effect is not strong enough to prevent aggregation but enough to prevent complete precipitation. During slow heating the colloidal particles were in the metastable state. Microgel particles are not yet fully collapsed, so individual particles have more chance to undergo interparticle aggregation. At the temperature of 50 °C, which is well above the LCST of the particles, shrinking is fast and the charge density rapidly increases 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 completely reversible. The aggregates will dissociate in individual swollen particles or individual particles will swell after cooling. The effect of heating on the thermal behavior is summarized in Fig. 6.

It should be noted that PVA plays an important role in the stabilization of microgels during synthesis. It is difficult, if not impossible, to obtain PVCL microgels in stabilizer-free conditions. Besides, the heating and long incubation time of concentrated microgel dispersions at temperatures above 32 °C lead to an irreversible coagulation. This process is possibly induced by the slow diffusion of the stabilizer away from the stress zones, which were created by the close approach of the particles.

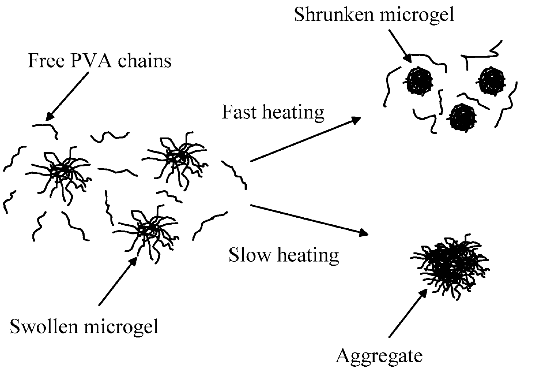

Fig. 6 Scheme of the volume phase transition of PVCL microgel particles in the presence of PVA during different heating regimes

Colloidal stability

The colloidal stability of the microgels was checked as a function of increasing concentration of an added electrolyte (NaCl). Independently of 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 electrolyte, when it is present in solution, not only decreases the repulsion between particles due to the screening of charges on the surface, but strongly decreases the solubility of PVCL in water. It was shown [24] that the reducing influence of NaCl on the LCST of PVCL is 10 K l/mol. This means that, at some electrolyte concentration, water is no longer a good solvent for PVCL. At high temperatures (fast heating) in electrolyte solutions, microgels are also unstable due to the charge screening effect.

Conclusions

From the results above, it can be concluded that PVA stabilization of PVCL microgel dispersions differs from attached stabilization of insoluble polymers due to the weak adsorption of the hydrophobic part of the stabilizer on the PVCL chains. Increasing the molecular weight of PVA leads to depletion flocculation through the transition sequence: instability → stability → instability. The particle size depends (to some extent) on the quantity of the stabilizer. There is no influence of the stabilizer quantity on the 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 insufficient stabilization by PVA. Diffusive behavior for these aggregates is the average value of translational and rotational diffusions.

During fast heating to a temperature above the LCST, immobilization of the remaining charged initiator groups on the surface occurs and the colloidal stability increases. The stability of microgels toward electrolyte is not dependent on the PVA concentration. Flocculation effects at $C_{NaCl} > 0.7$ M appear as the result of screening of initiator charges and the reduced solubility of PVCL chains.

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