Poly(*N*-vinylcaprolactam) Microgel Particles Grafted with Amphiphilic Chains

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ABSTRACT: Grafted temperature-sensitive poly(*N*-vinylcaprolactam), PVCL, microgel particles have been prepared. The grafting has been accomplished using an amphiphilic macromonomer consisting of a hydrocarbon segment and a poly(ethylene oxide), PEO, segment. The water-soluble amphiphilic macromonomer has been synthesized and utilized in two different cases. In the first case, the grafted particles were prepared using macromonomers as reactive emulgators in emulsion copolymerization. In the second case the PVCL particles were first synthesized in an emulsion stabilized with SDS, and then, the microgel particles swollen with monomers were postmodified with amphiphilic macromonomers. Properties of the grafted nanoparticles in water were investigated by static and dynamic light scattering, as well as by ^{1}H NMR relaxation and diffusion measurements. All the polymers show the LCST behavior typical to PVCL, and they collapse upon heating. For the particles prepared in one step in an emulsion stabilized by the macromonomer, the collapse was discontinuous and took place in a very narrow temperature range. When the particles were prepared in two steps, the grafts were observed to change the particle size as well as the critical temperature of the collapse. In the latter case the thermal transition was much more gradual than in the former one. This is probably due to a difference in the number of electric charges in the polymer particles, originating from the initiator and SDS.

Introduction

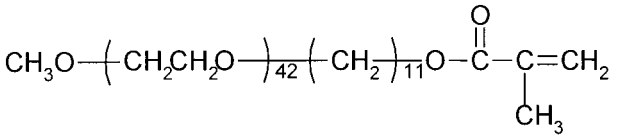
Thermally responsive latex particles composed of poly(*N*-isopropylacrylamide), PNIPA, have been successfully synthesized in aqueous emulsions or dispersions stabilized by a conventional surfactant sodium dodecyl sulfate, SDS.[1−3] In these syntheses, the water-soluble monomer, NIPA, has been polymerized at temperatures well above the lower critical solution temperature (LCST) of PNIPA. Properties of the product nanoparticles have been studied extensively. Recently, there has been a growing interest in another temperature-sensitive polymer, poly(*N*-vinylcaprolactam), PVCL.[4−6] Both PNIPA and PVCL have the lower critical solution temperature near body temperature, and consequently, they may find several biomedical applications.[7]

The shrinking or swelling of temperature-sensitive latex particles dispersed in water is an intraparticle phenomenon, but it is well-known that also interparticle aggregation takes place during the collapse transition. For various potential applications it is important to prevent the aggregation of the particles upon an increase in temperature. The aggregation is caused by the van der Waals attraction between the particles, and so it is necessary to provide repulsive interaction using either electrostatic or steric stabilization.[8] Very stable polymer dispersions have been synthesized using poly(ethylene oxide), PEO, as a stabilizing agent.[9] Owing to the biocompatibility of PEO, materials grafted with this polymer are also well-known in biotechnology.[10]

Several synthetic strategies may be applied to produce PEO grafted copolymers. Functionalized polymers can be postmodified with PEO,[11,12] but also, reactive PEO methacrylates have been used as macromonomers to synthesize grafted latices in dispersion polymerizations[13,14] and graft copolymers in solution polymerization.[11] In the latter case it needs to be taken in account that PEO may act as a chain transfer agent in radical polymerization.[12]

Recently, various amphiphilic PEO macromonomers have been used as reactive surfactants in dispersion[15−17] and emulsion polymerizations.[18,19] Using amphiphilic macromonomers, it is possible to synthesize grafted copolymers but also latices and microgels which are effectively sterically stabilized against flocculation.

In the present work an amphiphilic macromonomer has been synthesized that contains a hydrophilic PEO segment and a hydrophobic alkyl chain. A reactive methacrylate end group was introduced on the alkyl end. The macromonomer has the following structure.



When the macromonomer technique is used in emulsion polymerization, it is essential that the comonomer is more hydrophobic than the macromonomer. This is the main reason why this technique is not always possible to be applied in the synthesis of water-soluble polymers. *N*-Vinylcaprolactam is only slightly soluble in water, and therefore it should be a potential monomer in emulsion polymerization. PVCL starts to precipitate above 32 °C, and so, it is advantageous to synthesize the polymers at elevated temperatures.

In the present investigation, cross-linked nanoparticles of PVCL have been prepared. PVCL is a polymer closely resembling poly(*N*-isopropylacrylamide) which shows the LCST in water around 32 °C. For the first time, the macromonomer technique has been applied to produce PVCL particles grafted with PEO derivatives. The PEO-containing maromonomer has been used

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either as a reactive surfactant in emulsion polymerization or as an agent with which preformed PVCL particles have been coated.

Because the optimization of the reaction conditions is essential for a successful emulsion polymerization, some of the reactions have been conducted in two different types of reactors. The particles prepared in various ways show distinct differences in their thermal behavior. The main differences in the polymers are suggested to owe to differences in the widths of the particle size distributions, on one hand, and on the charge densities of the particles, on the other. The charges in the particles originate from the initiator, potassium persulfate, and the emulgator, SDS.

Experimental Section

Materials. 1. Materials for the Synthesis of the Macromonomer. Poly(ethylene glycol)$_{42}$ monomethyl ether (M_w = 1900 g/mol), methacryloyl chloride, and 3,4-dihydro-2*H*-pyran were purchased from Fluka and 11-bromoundecanol from Aldrich. Methacryloyl chloride was distilled before the synthesis, and the other reagents were used as received.

2. Materials for the Polymerizations. *N*-Vinylcaprolactam, VCL (Polysciences Ltd.), *N*,*N*-methylenebis(acrylamide) (Electran), potassium persulfate, KPS, (Merck, p.a.), and sodium dodecyl sulfate, SDS (Fluka), were used without further purification. Water which was used as a solvent was purified with Elgastat UHQ-PS.

Syntheses. 1. Macromonomers. The PEO-containing macromonomer was synthesized from 11-bromoundecanol, poly(ethylene oxide)$_{42}$ monomethyl ether, and methacryloyl chloride using the method reported by Liu et al.[20] First, the hydroxyl group in 11-bromoundecanol (0.09 mol) was protected with 3,4-dihydro-2*H*-pyran (0.32 mol). Then, the protected 11-bromoundecanol (0.03 mol) was connected to the hydroxyl end group of poly(ethylene oxide)$_{42}$ monomethyl ether (0.015 mol) using the Williamson reaction. The protective group was removed by acid hydrolysis, and finally, a reactive methacrylate end group was introduced to the ω-methoxy poly(ethylene oxide)$_{42}$ undecanol (0.01 mol) using methacryloyl chloride (0.05 mol). The macromonomer was purified by precipitating from chloroform with ether. The pure product was dried in a vacuum and stored at −18 °C in darkness.

The macromonomer was characterized by ^{1}H NMR using chloroform as a reference substance. δ (ppm): 6.1 (1H, HC═C, trans), 5.6 (1H, HC═C, cis), 4.1 (2H, CH_2O), 3.6 (168H, $(CH_2CH_2O)_{42}$), 3.5 (2H $(OCH_2(CH_2)_9)$, 3.4 (3H, OCH_3), 2.0 (3H, CH_3C═C), 1.3−1.7 (18H $(CH_2)_9$).

2. PVCL Latex E1. Emulsion polymerization of VCL was carried out with magnetic stirring in a 100 mL one-neck reactor, using a method similar to that by Gao et al.[21] The mixture of 429 mg of VCL, 13.4 mg of *N*,*N*-methylenebis(acrylamide), 68 mg of SDS, and 12 mL of water was stirred for 2 h under a nitrogen flow. The reaction mixture was heated to 70 °C, and the polymerization was initiated by adding 2 mL of aqueous KPS solution (2 g/L) through the septum. The solution turned slightly opaque during the polymerization. The reaction was stopped after 22 h, and the polymer was purified by dialyzing against purified water for 7 days. The yield was 17 wt %.

3. PVCL Latex E2. Another batch of the latex was prepared using the same ratio of the reagents as with E1, conducting the polymerization at 70 °C in a double-wall 500 mL reactor equipped with a mechanical stirrer. The reaction mixture was stirred (400 rpm) with a Teflon blade made to match the round-bottom of the reactor. The yield was similar to that in the previous polymerization, but the particle size distribution was much narrower, as will be shown later in the text.

4. Direct Emulsion Copolymerization: E3. The direct emulsion polymerization of VCL with the reactive macroemulgator was also carried out using magnetic stirring and a 100 mL reactor. The mixture of 1654 g of VCL, 52 mg of *N*,*N*-methylenebis(acrylamide), 182 mg of PEO macromonomer, and 57 mL of water was stirred for 2 h under a nitrogen flow. The temperature was raised to 60 °C, and the polymerization was initiated by adding 5 mL of aqueous KPS solution (10 g/L) through the septum. Polymerization was stopped after 22 h, and the solution was dialyzed for 7 days. After the dialysis the solution was slightly opaque, and there were no precipitates. The yield was 20 wt %.

Table 1. Summary of the Grafting Reactions

sample	V (mL)	c_{E1}(g/L)[a]	m_{KPS} (mg)	T(°C)	t (h)
E1-g1	50	70	0.5	50	2
E1-g2	50	70	2.7	50	3.5
E2-g	200	0.13	2.7	50	3.5

[a] The concentration of the microgel E1 or E2.

5. Postmodification of E1 Latex: E1-g(1) and E1-g(2). Grafting of the PVCL latex E1 was carried out in 100 mL reactors with magnetic stirring. Two 5.0 mL samples of the latex E1 (c = 1.3 g/L) were diluted to 50 mL with water, and 50 mg of the macromonomer was added. The solutions were stirred at 400 rpm for 2 h with a nitrogen purge to remove oxygen. Then, the solutions were heated to 50 °C, and different amounts of KPS were added to start the grafting reaction. After the grafting, the solutions were purified by dialysis for 1 week. The amounts of KPS and abbreviations for the polymers are shown in Table 1.

6. Postmodification of E2 Latex: E2-g. The latex E2 was grafted with the macromonomer using the same reaction conditions as described above for the grafting of E1.

Measurements. 1. Laser Light Scattering. Static light scattering (SLS) and dynamic light scattering (DLS) measurements were performed using a Brookhaven Instruments BI-200SM goniometer and a BI-9000AT digital correlator. A laser (LEXEL 85, 1W) operating at 514,5 nm wavelength was used as a light source. Time correlation functions were analyzed with a Laplace inversion program CONTIN. The SLS data were treated using Zimm's double-extrapolation method. The DLS measurements were performed with a scattering angle 90°. A Wyatt/Optilab 903 interferometer was used to measure the dn/dc values at λ = 514.5 nm. When measuring LCSTs, the heating rate was 5 °C/min.

2. ^{1}H NMR Relaxation and Diffusion Measurements. The experiments were carried out with a Varian ^{UNITY}INOVA spectrometer operating at 300 MHz for protons, equipped with a gradient probe and temperature controller by Varian Inc. Measurements were made heating the sample from room temperature to 50 °C with heating steps of 5 °C.

The relaxation times T_1 were measured by a standard inversion−recovery pulse sequence, typically using 30 values of τ and a recycle time $>5T_1$. For the pulsed field gradient (PFG) diffusion measurements, a stimulated echo sequence[22] with a delay time Δ = 11 ms between the first and the last 90° pulse was applied. Typically, 30 spectra were recorded over linearly incremented gradient strengths of 0−65 G/cm. The diffusion coefficient, D, was calculated from the slope of the signal intensity versus the gradient strength, obtained with a regression fit of the raw data. The instrument was calibrated by measuring the diffusion coefficient of pure water.

Results and Discussion

Determination of the Critical Micelle Concentration. When using amphiphilic macromonomers, the detailed knowledge of their solution properties in water is naturally of essential importance. The most important characteristic is the critical micelle concentration, cmc. Light scattering was used to measure the cmc of the macromonomer in an aqueous solution. The scattered light intensity increases sharply when the amphiphilic macromonomers start to form micelles, as may be seen in Figure 1. The cmc is 0.25 g/L at 20 °C.

The cmc measured using the scattered light intensity differs slightly from that reported by Liu et al.[20] for the same type of a macromonomer (0.14 g/L). In the latter

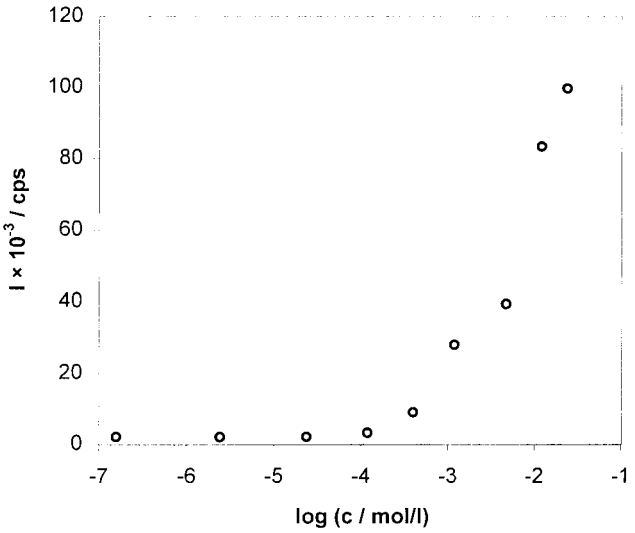

Figure 1. Dependence of the scattered light intensity on the concentration of the macromonomer. The intensity is given in counts of photons per second, cps.

case, the cmc was determined by surface tension measurements. The difference in cmc due to the method of determination may, however, be as high as 50%.[23] In all the polymerizations reported here, where the macromonomer was used (direct copolymerization E3 and the postmodified latices E1-g and E2-g), the macromonomer concentration was well above the critical. Because the measured value for cmc is fairly low, only a few of macromonomers homopolymerize in the aqueous solution phase.[24] The hydrophobic monomer, vinylcaprolactam, most probably diffuses into the hydrophobic cores of the micelles either before or during the polymerization. The macromonomer used in this work seems to be a proper choice for a reactive surfactant.

Thermosensitive Microgels. In general, the size distributions of the PVCL microgel particles synthesized in one step are monomodal and reasonably narrow. This is the case regardless of the choice of the emulgator, either SDS (E1, E2) or the macromonomer (E3). The distributions at 20 °C are shown in Figure 2. The size distributions remain monomodal also after the grafting conducted as a second step. It should be noted that, especially in the case where special attention was paid to the effective agitation of the reaction mixture during the polymerization of the PVCL particle, the size distributions before and after the grafting were considerably narrow (E2 and E2-g).

Thermal Behavior of the Particles. The sizes of the particles were measured against temperature by dynamic light scattering. The temperature dependence of the average hydrodynamic radius (R_h) of the polymer E1 and its grafted derivatives E1-g1 and E1-g2 is shown in Figure 3. It may be seen that the collapse of the grafted particles is smoother than that of pure PVCL latex E1. Also, grafted particles start to shrink at lower temperatures. This is contrary to the expectation but may indicate that the starting material E1 is further cross-linked during the grafting process. As was shown in Figure 2, polymer E1 has a broader size distribution than E2 and E3. This probably owes to the heterogeneity of cross-linking in E1. The structural heterogeneity of the E1 particles, as well as the suggested cross-linking during the grafting, may be the reason for slightly smaller sizes of E1-g particles compared to E1.

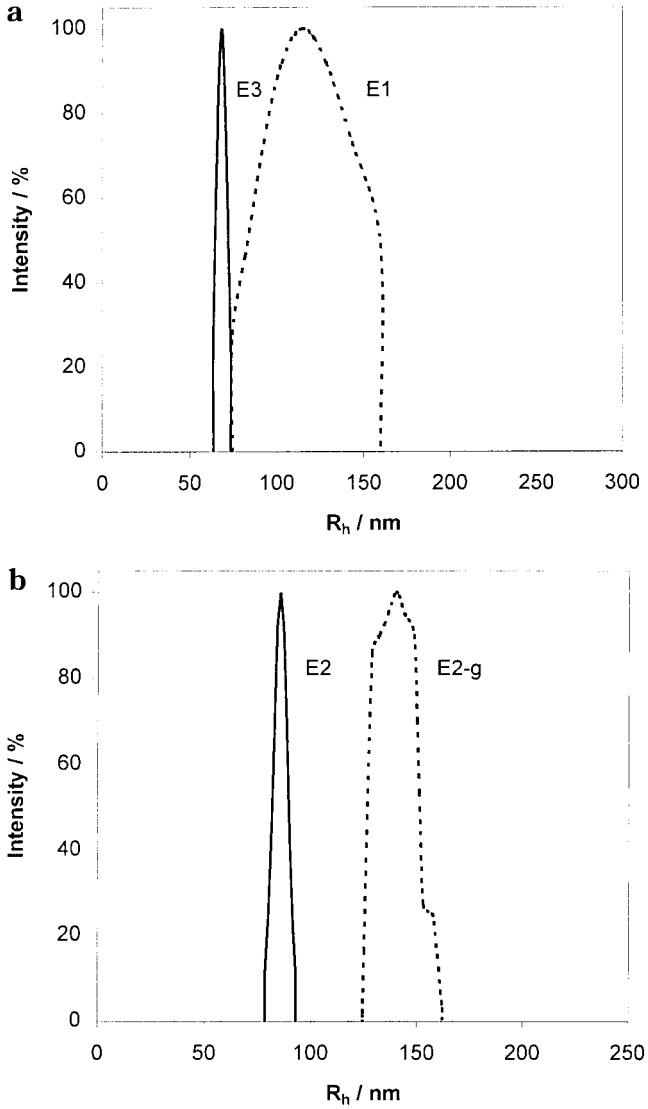

Figure 2. Size distributions of the PVCL particles in water at 20 °C: (a) latices E1 and E3; (b) latex E2 before and after the grafting.

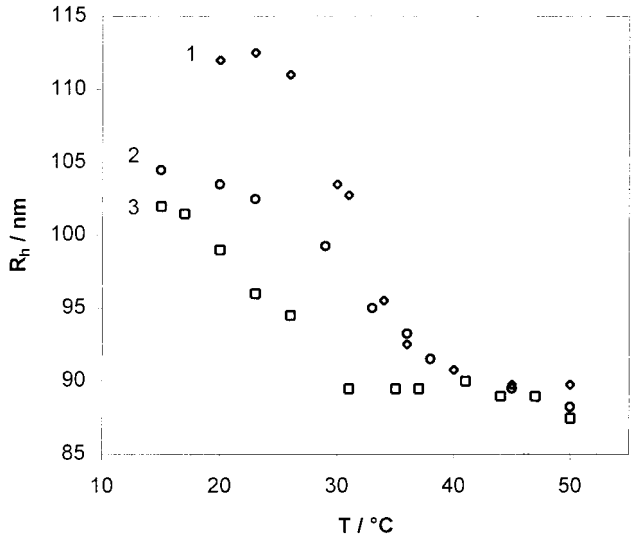

Figure 3. Temperature dependence of the PVCL microgel E1 (1) and the grafted derivates E1-g1 (2) and E1-g2 (3).

As may be seen from Figure 4, the particles E3 prepared in a direct emulsion polymerization are notice-

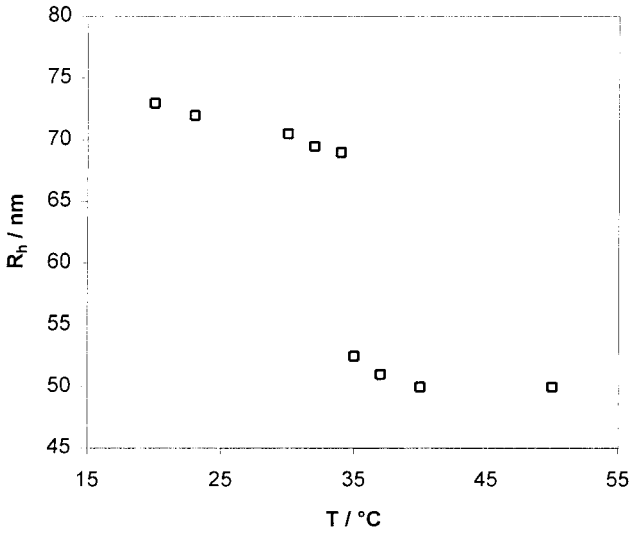

Figure 4. Dependence of the hydrodynamic radius of the grafted microgel E3 on the temperature.

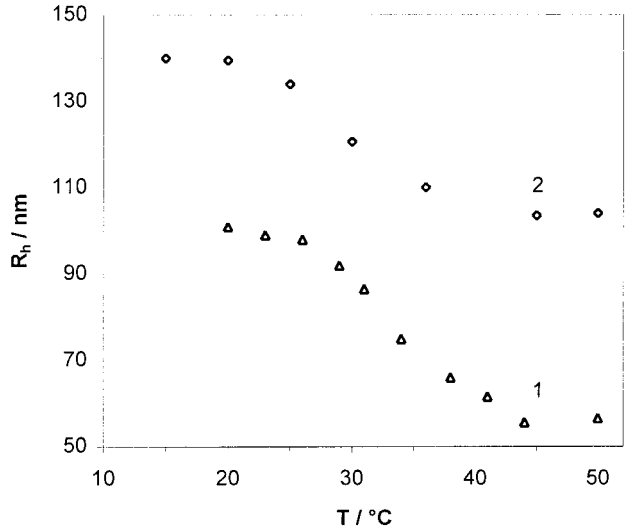

Figure 5. Temperature dependence of the PVCL microgels E2 (1) and the grafted derivate E2-g1 (2).

ably smaller than those prepared in two steps. The collapse transition shown in Figure 4 is sharp, taking place in the vicinity of 35 °C, though the change in the particle size is just moderate. It has been shown earlier that some of SDS always keeps absorbed onto the surface of the latex particles and may even be embedded inside the particles.[25] Thus, the smoothness of the collapse transition of the particles prepared using SDS (Figure 3) may well be attributed to the presence of negative charges of the sulfate groups inside and on the surface of the polymeric entities. An additional point that needs to be clarified in future work is the effect of the particle size on the collapse. Because diffusion of water out from the network structure is the process determining the rate of collapse, smaller particles are expected to compress faster than larger ones.

Also, the uniform spherical shape of the seed PVCL particle is an essential factor determining the properties of the grafted particle, as is clearly demonstrated in Figure 5. This figure shows the thermal behavior of the PVCL particles which were prepared using SDS as an emulsifier, but with a much more effective stirring than a plain magnetic stirrer, i.e., the polymer E2. As was noted already, E2 has a very narrow size distribution.

Table 2. Summary of the Light Scattering Measurements

sample	T (°C)	M_w[a] (g/mol)	R_g (nm)	R_h (nm)	R_g/R_h	δ (g cm^{-3})
E2	20	2.0×10^7	115	86	1.3	0.013
	50	1.6×10^7	43	42	1.0	0.112
E3	20	6.4×10^6	57	73	0.8	0.007
	50	6.0×10^6	48	53	0.9	0.016

[a] Apparent molecular weight.

In this case, the grafting of the PVCL particles leads to a noticeable increase of the particle size. The collapse of the seed PVCL particle E2, as well as that of the grafted one, E2-g, is gradual. The broad transition is suggested to owe to anionic charges in the polymers. Because in every polymerization KPS, capable of producing anionic groups into the polymers, has been used as an initiator, it may be concluded that the choice between the anionic SDS and the electroneutral macromonomer is a critical factor determining the size and thermal behavior of the product particles. It is noteworthy that the temperature range of the thermal collapse of the particles is not affected by the amphiphilic grafts in E2-g.

Some characteristics of the particles have been measured by light scattering at temperatures below and above the LCST, and these are shown in Table 2. Samples chosen for these measurements were E2 (not grafted particles synthesized in a SDS emulsion) and E3 (grafted particles prepared in the macromonomer emulsion) because both of these had very narrow size distributions. An important parameter is the ratio R_g/R_h which is known to be sensitive to the shape of the particles. At room temperature R_g/R_h of the sample E2 is high, (1.3), close to the value typical for random coils. The corresponding value for E3 is close to that typical for hard spheres. Gao et al.[21] have obtained R_g/R_h equal to 0.78 for PVCL particles polymerized in a SDS emulsion. The difference may owe to differences in the molecular masses and cross-link densities between the polymers. For example, Schmid et al.[26] have studied poly(vinyl acetate), PVAc, microgel particles and observed that, with molecular masses of the order of 10^7 or lower, the ratio R_g/R_h is above the value expected for linear polydisperse chains. This indicates the branched structure of PVAc. With increasing conversion, very high molar masses are obtained, and suddenly R_g/R_h drops below the theoretical hard-sphere value (0.78).

The chain densities of the particles calculated using the relation $M_w = N_A[(4\pi/3)R_h^3]\rho$ are also given in Table 2. The density of the grafted particle E3 is especially low.

^{1}H NMR Relaxation and Diffusion Measurements. A typical ^{1}H spectrum of a grafted latex particle (E3) immersed in D_2O is shown in Figure 6. The chemical shifts differ from those given in experimental part, owing to a different solvent. Spectral lines that can be observed arise from the ethylene oxide protons in the graft chain.

The relaxation times T_1 of the CH_2 protons of the PEO component of the grafts were measured against temperature. With increasing temperature the relaxation time of all the samples increases. The relaxation profiles were found to fit well to a single exponential. Different samples behave quite similarly as is seen in Figure 7 where logarithmic relaxation times have been plotted against inverse absolute temperature. No significant change in the relaxation behavior could be observed in

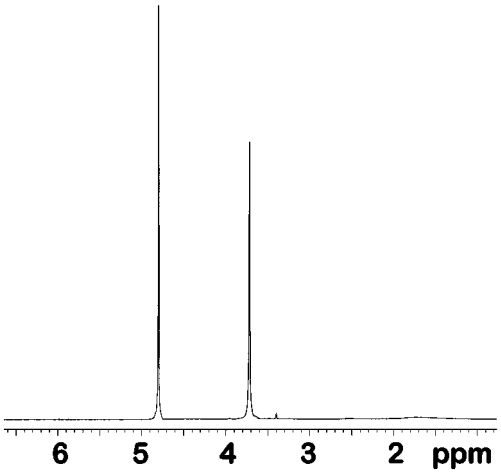

Figure 6. ^{1}H spectrum of a grafted latex particle immersed in D_2O.

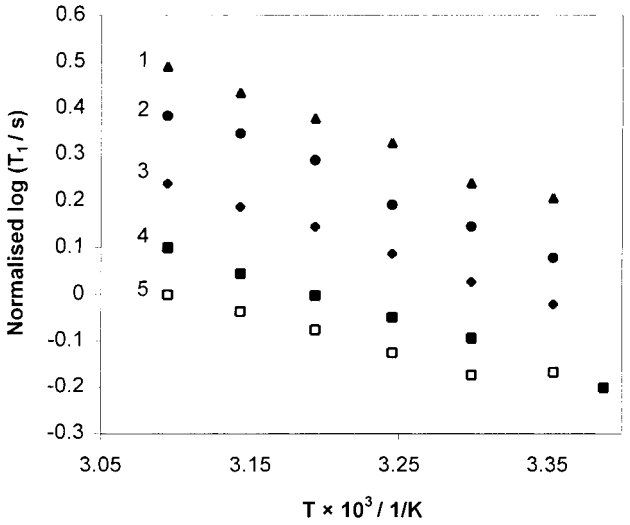

Figure 7. Normalized relaxation time T_1 of different samples: (1) E3, (2) E1, (3) micellar solution of the macromonomer, (4) E1-g2, and (5) E1-g1. For the normalization, see text.

any of the latices at the transition temperature around 35 °C. Note that in Figure 7 the straight line number 5 shows the real measured values of T_1. Other data series have been upshifted by adding 0.1 log(s). This means that all measured relaxation times fall into the same straight line, within an experimental error.

The relaxation rates of the PEO protons are of the same order of magnitude in all samples, in the entire temperature range studied. The dynamics of the PEO segment is not affected by the collapse of the PVCL particle, which implies that the grafts are in a brush conformation. It has been shown[27] that PEO macromonomers take a brush conformation on the surface of poly(butyl methacrylate) latex particles if the conversion in copolymerization is high enough. Recently, Sofia et al.[28] have studied the effect of PEO grafts on protein adsorption to a silicon surface. The critical factor was concluded to be the spacing between the grafts. Protein adsorption dropped to zero when the spacing became smaller than R_g of the graft, and the chains partially overlapped with each other.

The diffusion coefficients of the CH_2 protons in the PEO part of the chain in different samples were measured with increasing temperature. The concentration of the samples was adjusted to 1.5 mg/mL. The

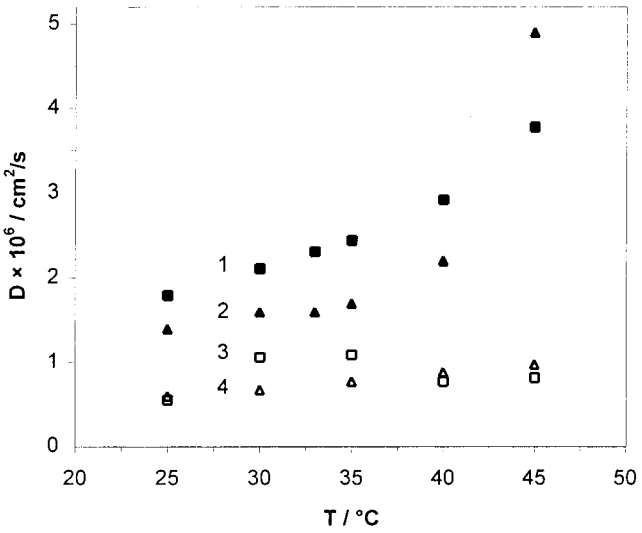

Figure 8. Diffusion coefficients of the samples: (1) E1-g2, (2) E1-g1, (3) mixture of E1 and the macromonomer, and (4) micellar solution of macromonomers.

diffusion coefficients are shown against temperature in Figure 8. It can be seen that, for the micellar solution of the macromonomer, the diffusion coefficient increases slightly with temperature as was expected. The diffusion coefficient of the CH_2 protons in the PEO segment in the macromonomer mixed with the latex E1 is of the same order of magnitude as that of the micelle. This probably indicates that macromonomers adsorbed on the particle surface tend to dissolve in the aqueous phase during the collapse transition.

For the grafts covalently bound to the latices E1-g(1) and E1-g(2) the temperature dependence is different; see Figure 8. Above the LCST of PVCL, a considerable increase in the diffusion coefficient is observed. The sudden increase may be attributed to the shrinking of the particle which leads to an increase in the rate of its translational diffusion and, consequently, also in the rate of diffusion of the grafts bound to the latex particle surface. The values of the diffusion coefficients above the LCST should be taken as apparent ones because the measurements were complicated by the heterogeneity of the collapsed samples and by turbulence in heated dispersions. The comparison between the mixture of a polymer particle and the macromonomer, on one hand, and the particles grafted with the macromonomer, on the other, does not necessarily rule out the possibility that the grafted latex samples also contain free macromonomers. However, the result shown in Figure 8 indicates that at least a considerable part of the macromonomers feel the changes in the sizes of the particles. In addition, it should be noted that the size distributions obtained by light scattering do not indicate the presence of micelles of the macromonomers.

Conclusions

Thermally sensitive PVCL nanoparticles coated with short grafts containing a PEO segment have been successfully prepared using macromonomer techniques. Either particles prepared in a SDS emulsion have been coated with the macromonomer, or the graft copolymerization has been conducted in one step in an emulsion stabilized with the amphiphilic macromonomer. In the former case, the collapse transition of the particles occurs in a wide temperature range. This is assumed to be due to the electric charges of SDS bound to the

particles. In the latter case, the particles have a spherical shape, and the thermal transition is discontinuous.

According to the ^{1}H NMR relaxation measurements, the grafts bound to the PVCL take a brush conformation at temperatures below and above the critical. Judging from the light scattering results and preliminary NMR diffusion measurements, all or at least the majority of the macromonomers are bound to the surfaces of the polymer particles.

The yields in the polymerization reactions were low, possibly owing to the known capability of the initiator, potassium persulfate, KPS, to hydrolyze the monomer vinylcaprolactam.[29] However, the particle size distributions were monomodal and narrow.

The stability of a latex is in general strongly dependent not only on the hydrophilic grafts on the particle surface but also on the charge density of the particle. Both the initiator, KPS, and the emulsifier, SDS, produce anionic charges on the polymer particles. In the future work these effects will be quantified.

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