Interaction between Surfactant and Poly(*N*-vinylcaprolactam) Microgels

Yibing Gao, Steve C. F. Au-Yeung, and Chi Wu*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

Received November 12, 1998; Revised Manuscript Received March 2, 1999

ABSTRACT: Narrowly distributed spherical poly(*N*-vinylcaprolactam) (PNVC) microgels were prepared by precipitation polymerization in water. The effect of both anionic (sodium dodecyl sulfate, SDS) and cationic (*N*-dodecylpyridinium bromide, DPB) surfactants on the swelling and shrinking of the microgels were investigated by laser light scattering (LLS). Our results showed that the microgels gradually shrank to the collapsed state when the temperature increased from 20 to ∼38 °C. The addition of anionic surfactant caused an extra swelling of the microgels and shifted the collapsing temperature higher, whereas the addition of cationic surfactant has different effects on the swelling and shrinking of the microgels prepared by using different initiators, depending on whether the decomposed fragments of the initiator are ionic or neutral. Our results clearly showed that the ionic groups introduced into polymer gels from the initiators should be taken into consideration in the study of the surfactant/gel interaction.

Introduction

Recently, water-soluble nonionic polymers and their hydrogels have attracted much attention due to their scientific and technological importance. The interaction between hydrogels and surfactant as one of the focused points has been extensively studied.[1−9] It was found that some hydrogels could effectively concentrate surfactant molecules inside the gel networks and underwent a large volume change when the temperature increased. The adsorption of surfactant molecules into a gel network could also induce an extra swelling. In general, the addition of surfactant increases the volume change temperature. It has been envisioned that the swelling/shrinking properties of such gel/surfactant complexes could be useful in certain applications, such as the effective absorption of organic dyes, the immobilization of enzymes, and the controlled release of chemicals.[10−13]

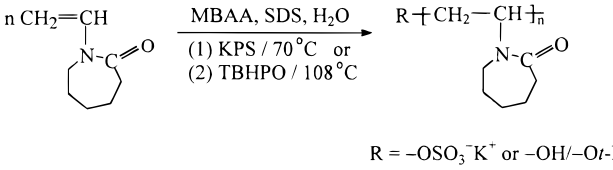
Thermosensitive poly(*N*-isopropylacrylamide)(PNIPAM) gel is one of the mostly studied hydrogels,[14−16] but some of the results were controversial. For example, the addition of anionic or cationic surfactant into a bulk PNIPAM gel led to a discontinuous volume phase transition,[2−5,17] whereas the PNIPAM microgels showed a continuous volume change even in the presence of surfactant.[18−22] The interaction between the hydrophobic backbone of polymer chain and the hydrocarbon tail of surfactant was attributed to the extra swelling and the shift of the transition temperature. Our previous study of the PNIPAM microgels showed that, besides the hydrophobic interaction, the side groups (−CONHCH-$(CH_3)_2$) attached to the chain backbone also had an influence on the swelling of the PNIPAM gels.[22] More studies on the interaction between the hydrogel network and surfactant molecules are certainly needed to clarify these controversial problems.

In this study, poly(*N*-vinylcaprolactam) (PNVC) was chosen as a model system not only because its hydrogel has a swelling and shrinking temperature near the body temperature but also due to its biocompatibility.[23−26] In comparison with poly(*N*-isopropylacrylamide), poly(*N*-vinylcaprolactam) has a heptagonal side group. A similar polymer, poly(vinylpyrrolidone), and its interaction with surfactant have been studied, but it has a phase transition temperature much higher than the body temperature.[27−30] To study the effects of only the ionic head of surfactant, we intentionally chose two different kinds of surfactant with an identical hydrocarbon tail; namely, anionic sodium dodecyl sulfate (SDS) and cationic *N*-dodecylpyridinium bromide (DPB).

Experimental Section

Materials. *N*-Vinylcaprolactam (NVC, courtesy of BASF) was recrystallized three times from its melt at the room temperature, and the resultant crystal was washed with cold methanol and dried under vacuum. *N*,*N*′-Methylenebisacrylamide (MBAA, from Aldrich) as a cross-linking agent was purified by recrystallization from methanol. Two different initiators, potassium persulfate (KPS, from Aldrich) and *tert*-butyl hydroperoxide (TBHPO, ∼80% in di-*tert*-butyl peroxide, from Riedel-de Haen), were used without further purification. Sodium dodecyl sulfate (SDS, from Aldrich) and *N*-dodecylpyridinium bromide (DPB, courtesy of Beijing University, China) were used as received.

Microgel Preparation. Narrowly distributed spherical poly(*N*-vinylcaprolactam) (PNVC) microgels were prepared in water by precipitation polymerization as follows: When using KPS as the initiator, into a 250 mL three-neck flask equipped with a reflux condenser, a thermometer, and a nitrogen-bubbling tube were added 1.066 g of NVC monomer, 0.0334 g of MBAA, 0.0169 g of SDS, and 35 mL of deionized water. The solution was magnetically stirred at ∼1000 rpm and bubbled



R = $-OSO_3^-K^+$ or –OH/–O*t*-Bu

with nitrogen gas for 2 h to remove the oxygen before the addition of 0.010 g of KPS dissolved in 5 mL of deionized water to initiate the polymerization. The reaction was carried out at 70 °C for about 20 h. Note that radicals generated by KPS are anionic so that each starting chain end has an anionic sulfate group and the resultant microgels were slightly negatively charged. In the case of using TBHPO as the initiator, after mixing 0.1224 g of ∼80% TBHPO solution with 1.071 g of NVC monomer, 0.0329 g of MBAA, 0.0179 g of SDS, and 40 mL of deionized water, the solution mixture was rapidly heated to a high temperature to start the polymerization. The reaction was carried out at 108 °C for 30 h. The resultant microgels were neutral. Hereafter, we denote the ionic and

10.1021/ma981756+ CCC: $18.00
Published on Web 05/01/1999

Table 1. Summary of Static and Dynamic LLS Results of the Swollen (at 25 °C) and Collapsed (at 40 °C) PNVC Microgels in Deionized Water[a]

sample	T, °C	dn/dC, mL g^{-1}	M_w, g mol^{-1}	A_2, mol mL g^{-2}	$\langle R_g \rangle$,nm	$\langle R_h \rangle$, nm	$\langle R_g \rangle/\langle R_h \rangle$	ρ, g cm^{-3}
i-PNVC	25.0	0.210	6.9×10^7	5.3×10^{-6}	90	115	0.78	0.02
	40.0	0.228	6.7×10^7	-5.2×10^{-5}	45	56	0.80	0.15
n-PNVC	25.0	0.212	6.7×10^7	5.3×10^{-6}	87	112	0.78	0.02
	40.0	0.232	6.4×10^7	-5.2×10^{-5}	43	55	0.78	0.15

[a] The relative errors: dn/dC, ±1%; M_w, ±5%; A_2, ±10%; $\langle R_g \rangle$, ±5%; $\langle R_h \rangle$, ±2%; $\langle R_g \rangle/\langle R_h \rangle$, ±7%; and ρ, ±8%.

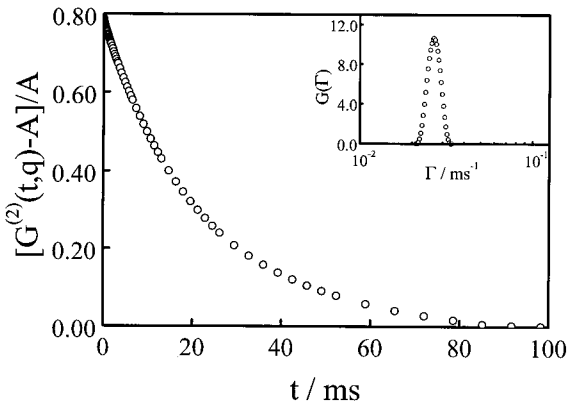


Figure 1. Typical intensity−intensity time correlation function $G^{(2)}(t,\theta)$ of the i-PNVC microgels in water at 16.0 °C. The inset shows its corresponding normalized line-width distribution $G(\Gamma)$ calculated from the Laplace inversion of $G^{(2)}(t,q)$.

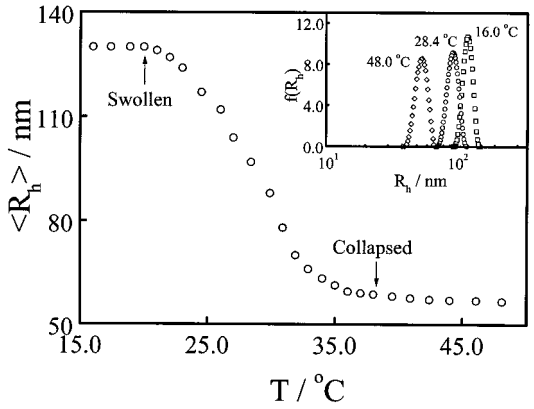


Figure 2. Temperature dependence of the average hydrodynamic radius $\langle R_h \rangle$ of the i-PNVC microgels in water. The inset shows the corresponding hydrodynamic radius distributions $f(R_h)$ of the i-PNVC microgels in water.

neutral microgels prepared by using KPS and TBHPO as i-PNVC and n-PNVC, respectively. The unreacted chemicals and surfactant were removed by a three-cycle centrifugation (Sigma 2K15 ultracentrifuge) at 15 400 rpm and 40 °C, decantation, and redispersion in deionized water. The resultant microgel dispersions were diluted with deionized water to $\sim 6 \times 10^{-6}$ g/mL before the laser light scattering measurements.

Laser Light Scattering (LLS). A commercial LLS spectrometer (ALV/SP-150) equipped with an ALV-5000 digital time correlator and a ADALS solid-state laser (DPY425II, output power $\approx$ 400 mW at $\lambda_0 = 532$ nm) was used. The incident beam was vertically polarized with respect to the scattering plane. In static LLS, for a dilute solution and at a relatively small scattering angle θ, the angular dependence of the excess absolute time-averaged scattered light intensity, known as the excess Rayleigh ratio, $R_{vv}(\theta)$, is a function of the weight-average molar mass M_w, the second virial coefficient A_2, and the mean square root of the z-averaged radius of gyration of the polymer chain $\langle R_g^2 \rangle^{1/2}$ (or written as $\langle R_g \rangle$).[31] After measuring $R_{vv}(\theta)$ at a series of concentration C and scattering angle θ, we were able to determine M_w, $\langle R_g \rangle$, and A_2 from a Zimm plot which incorporates angular and concentration extrapolation on a single grid. In dynamic LLS, the intensity−intensity time correlation function $G^{(2)}(t,\theta)$ in the self-beating mode was measured. For a polydisperse sample, the Laplace inversion of $G^{(2)}(t,\theta)$ can lead to a line-width distribution $G(\Gamma)$,[32,33] where Γ is a function of both θ and C. For a diffusive relaxation, Γ can be related to the translational diffusion coefficient D as $\Gamma = Dq^2$ at $C \rightarrow 0$ and $q \rightarrow 0$, where $q = (4\pi n/\lambda_0) \sin(\theta/2)$ with n and λ_0 being the solvent refractive index and the wavelength of light in a vacuum, respectively.[34]

Results and Discussion

Figure 1 shows a typical measured intensity−intensity time correlation function for the i-PNVC microgels in water at 16.0 °C, where the polymer concentration was so dilute ($C \sim 6 \times 10^{-6}$ g/mL) that the concentration correction was not necessary. The normalized characteristic line-width distribution $G(\Gamma)$ (the inset in Figure 1) clearly shows that the i-PNVC microgels are narrowly distributed. $G(\Gamma)$ can be transformed into a translational diffusion coefficient distribution $G(D)$ or a hydrodynamic radius distribution $f(R_h)$ by using $\Gamma = Dq^2$ or the Stokes−Einstein equation, $D = k_B T/(6\pi\eta R_h)$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

Figure 2 shows the temperature dependence of the average hydrodynamic radius $\langle R_h \rangle$ for the i-PNVC microgels in water, where $\langle R_h \rangle$ is defined as $\int_0^\infty f(R_h)\, R_h\, dR_h$. The inset in Figure 2 shows that there was little change in the distribution, except that the peak position clearly indicates that the i-PNVC microgels gradually shrank to the collapsed state when the temperature increased from 20 to 38 °C. At $T \sim 20$ °C, the swelling of the i-PNVC microgel reached its maximum. $\langle R_h \rangle$ decreases more than ~2 times when the temperature increases from 16 to 36 °C, corresponding to a hydrodynamic volume decrease of ~13 times. The shrinking of the i-PNVC microgel is continuous, similar to that of the PNVC bulk gels.[1] Moreover, the i-PNVC microgel and bulk gel have a similar collapsing temperature.

Table 1 summarizes the LLS results of the i-PNVC and n-PNVC microgels in both the swollen and collapsed states, where M_w, $\langle R_g \rangle$, and A_2 were calculated from Zimm plot. The values of M_w are nearly constant, indicating that the microgels are stable even in the collapsed state and there was no interparticle aggregation. As expected, A_2 changed from positive in the swollen state to negative in the collapsed state. The ratios of $\langle R_g \rangle/\langle R_h \rangle$ in the swollen and collapsed states are very close to $(3/5)^{1/2}$, a value predicted for a uniform and nondraining sphere. The chain density (ρ) of the PNVC microgel network was estimated from a combination of the static and dynamic LLS results, i.e., $M_w = N_A[(4\pi/3)\langle R_h \rangle^3]\rho$. On the basis of the changes in $\langle R_h \rangle$ and ρ, we knew that ~90% of water entrapped inside the swollen microgel network was expelled out during the collapsing process.

Figure 3 shows the temperature dependence of the average hydrodynamic radius $\langle R_h \rangle$ of the i-PNVC mi-

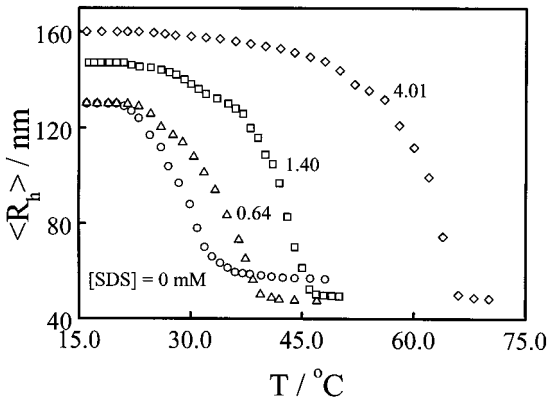


Figure 3. Effect of adding different amounts of anionic surfactant SDS on the swelling and shrinking of the i-PNVC microgels in water.

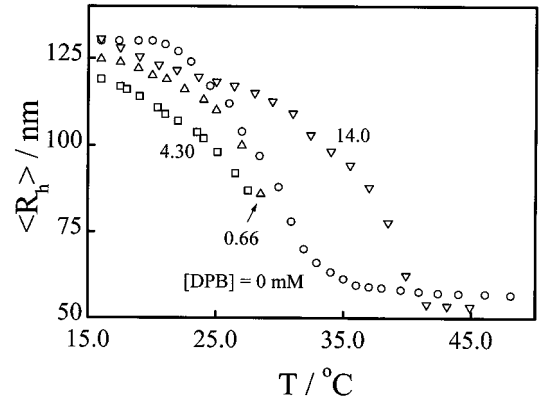


Figure 4. Effect of adding different amounts of cationic surfactant DPB on the swelling and shrinking of the i-PNVC microgels in water.

crogels in the presence of different amounts of SDS. Note that the SDS concentrations used were well below the critical micelle concentration (cmc = 8.3 mM at 25 °C). It is clear that the addition of SDS leads to an additional swelling of the i-PNVC microgels at low temperatures and shifts the collapsing temperature higher. This is consistent with what we observed in previous NMR and light scattering studies for the PNIPAM microgel/SDS systems,[22] wherein the NMR relaxation times (T_1 and T_2) of each proton of the surfactant molecule were measured, and the values below and above its cmc, and also with and without the microgels, were compared. We concluded the formation of micelles inside the microgel even the surfactant concentration is lower than its cmc. The additional swelling of the PNIPAM microgels was attributed to the repulsion between the negatively charged SDS micelles formed inside the microgel network.[35] Figure 3 also shows that, at the collapsing limit, the i-PNVC microgels in the presence of SDS are slightly smaller than the surfactant-free i-PNVC microgels. We will discuss this difference later.

Figure 4 shows the temperature dependence of the average hydrodynamic radius $\langle R_h \rangle$ of the i-PNVC microgels in the presence of different amounts of cationic surfactant DPB. At the temperatures lower than 18 °C, the addition of DPB actually resulted in a slight shrinking of the i-PNVC microgels, instead of the swelling shown in Figure 3. Moreover, Figure 4 shows that the shrinking temperature in the presence of cationic DPB is lower. It should be stated that the microgels started to aggregate before reaching the fully

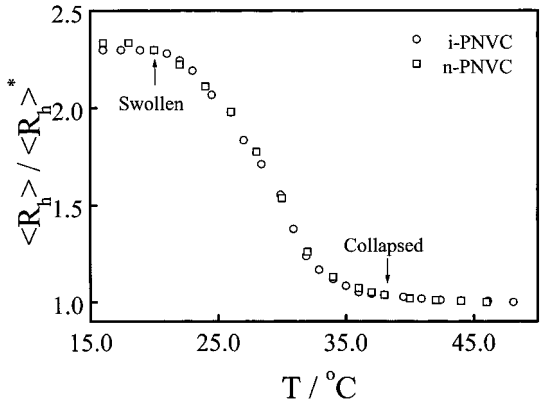


Figure 5. Temperature dependence of the swelling of both the i-PNVC and n-PNVC microgels in water, where $\langle R_h \rangle^*$ is the hydrodynamic radius at the collapsing limit.

collapsed state. This can be attributed to the neutralization of the slightly negatively charged i-PNVC microgels when a small amount of cationic DPB molecules was added. The neutralization makes the microgel network more hydrophobic, easier to shrink, and unstable at higher temperatures. However, when the DPB concentration was higher than its cmc (~12 mM at 25 °C), no shrinking of the microgels was observed at 16.0 °C, but the collapsing temperature was shifted higher and the microgels became stable at higher temperatures. This could be attributed to the association of DPB on the surface of the microgels, presumably a surfactant film, which prevents or reduces the interparticle aggregation. Once again, in the presence of surfactant, the microgels in the collapsed state are smaller than the surfactant-free microgels. One of the reasonable explanations might be due to the remaining of a trace amount of surfactant molecules inside the microgel network even in the collapsed state, and it is this trace amount of surfactant molecules that made the microgel network relatively more hydrophobic so that it could collapse more.

Figures 3 and 4 reveal that the addition of SDS and DPB into the i-PNVC microgel dispersion has very similar effects on the microgel swelling and shrinking behavior as in the case of the PNIPAM microgel dispersion.[22,35] This has been attributed to the negative charges introduced on the microgel network by KPS in the initiation of the polymerization; namely, the adsorption of anionic surfactant SDS molecules increases the repulsion, so that there is an additional swelling of the microgel network, whereas the adsorption of cationic surfactant DPB molecules neutralizes the negative charge and makes the microgel more hydrophobic. To check this point, we synthesized the PNVC microgels by using *tert*-butyl hydroperoxide (TBHPO) as the initiator so that the microgel network became neutral.

Table 1 shows that there is nearly no difference between the i-PNVC and n-PNVC microgels in terms of M_w, A_2, $\langle R_g \rangle$, and $\langle R_h \rangle$ in both the swollen and collapsed states. Figure 5 shows that the i-PNVC and n-PNVC microgels have a nearly identical swelling/shrinking behavior, where just for comparison $\langle R_h \rangle$ has been normalized by $\langle R_h \rangle^*$, the average hydrodynamic radius at the collapsing limit. It reveals that the introduction of a very small amount of negative charges on the i-PNVC microgel network has no effect on the swelling/shrinking behavior of the surfactant-free microgels.

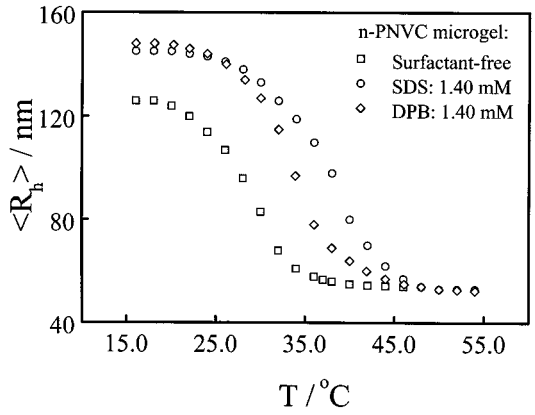


Figure 6. Effect of adding different surfactant on the swelling and shrinking of the n-PNVC microgels in water.

Figure 6 shows the effect of SDS and DPB on the swelling/shrinking of the n-PNVC microgels. As in the case of the i-PNVC microgel dispersion, the addition of SDS causes an additional swelling and shifts the collapsing temperature higher. However, it is interesting to see that when a small amount of DPB was added, instead of shrinking as in the case of the i-PNVC microgel dispersion, the n-PNVC microgels actually showed an additional swelling and a shift of the collapsing temperature to ~48 °C. Here, the n-PNVC microgel network is neutral so that there should be no neutralization when cationic DPB was added. The additional swelling indicates that DPB, just as SDS, could form micelles inside the n-PNVC microgel network even when its concentration is well below its cmc. The force driving surfactant into the n-PNVC microgel network should be the hydrophobic interaction between the microgel network and the hydrocarbon tail of surfactant. Figure 6 also shows that, in the presence of DPB, the n-PNVC microgels shrink at a lower temperature. This might be due to its higher cmc; i.e., the formation of the DPB micelles is relatively more difficult than that of the SDS micelles, or in other words, the breaking of the DPB micelles formed inside the microgel network as the temperature increases would be easier. In contrast to Figures 3 and 4, the n-PNVC microgels had the same size in the collapsed state no matter whether or what kind of surfactant was added, indicating that in the collapsed state no surfactant remained inside the n-PNVC microgels.

In summary, the study of the shrinking and swelling of poly(*N*-vinylcaprolactam) (PNVC) microgels with and without the presence of anionic or cationic surfactant showed the following: (i) The surfactant-free PNVC microgels continuously shrank as the temperature increased, reaching its fully collapsed state at ~38 °C. (ii) The addition of a small amount of anionic surfactant (SDS) led to an additional swelling of both the ionic i-PNVC and neutral n-PNVC microgels and a higher collapsing temperature, while the addition of a small amount of cationic surfactant (DPB) resulted in a slight shrinking of the i-PNVC microgels. The difference could be attributed to the neutralization of a small amount of anionic groups introduced onto the microgel network by the initiator. (iii) The effect of surfactant on the swelling and shrinking of the PNVC microgels can be partially attributed to the micelle formation inside the microgel network.

Acknowledgment. The financial support of the Research Grants Council of Hong Kong Government Earmarked Grant (CUHK 305/96P, 2160063) and the National Distinguished Young Investigator Fund (1996, A/C 29625410) are gratefully acknowdged.

References and Notes

(1) Makhaeva, E. E.; Le, M. T.; Starodoubtzev, S. G.; Khokhlov, A. R. *Macromol. Chem. Phys.* **1996,** *197*, 1973.
(2) Hua, Y.; Grainger, D. W. *Macromolecules* **1994**, *27*, 4554.
(3) Kokufuta, E.; Zhang, Y. Q.; Tanaka, T.; Mamada, A. *Macromolecules* **1993**, *26*, 1053.
(4) Kokufuta, E.; Nakaizumi, S. *Macromolecules* **1995**, *28*, 1704.
(5) Safranj, A.; Yoshida, M.; Omichi, H.; Katakai, R. *Langmuir* **1994**, *10*, 2954.
(6) Safranj, A.; Yoshida, M.; Omichi, H.; Katakai, R. *Langmuir* **1993**, *9*, 3338.
(7) Ishidao, T.; Akagi, M.; Sugimoto, H.; Iwai, Y.; Arai, Y. *Macromolecules* **1993**, *26*, 7361.
(8) Schild, H. G.; Tirrel, D. A. *Langmuir* **1991**, *7*, 665.
(9) Winnik, F. M.; Rinsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 912.
(10) Hoffman, A. S.; Afrassiabi, A.; Dong, L. C. *J. Controlled Release* **1986**, *4*, 213.
(11) Park, T. G.; Hoffman, A. S. *Appl. Biochem. Biotechnol.* **1988**, *19*, 1.
(12) Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *J. Membr. Sci.* **1991**, *64*, 283.
(13) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 162.
(14) Luan, C.-H.; Parker, T. M.; Prasad, K. U.; Urry, D. W. *Biopolymers* **1991**, *31*, 465.
(15) Wu, C.; Zhou, S. Q. *Macromolecules* **1995**, *28*, 5225.
(16) Wu, C.; Zhou, S. Q. *Macromolecules* **1995**, *28*, 8381.
(17) Saito, S.; Konno, M.; Inomata, H. *Adv. Polym. Sci.* **1993**, *109*, 207.
(18) Tam, K. C.; Ragaram, S.; Pelton, R. H. *Langmuir* **1994**, *10*, 418.
(19) Pelton, R. H.; Pelton, H. M.; Morphesis, A.; Rowell, R. L. *Langmuir* **1989**, *5*, 816.
(20) Brown, W.; Jianxi, Z. *Macromolecules* **1993**, *26*, 2711.
(21) Hidi, P.; Napper, D. H.; Sangster, D. E. *Macromolecules* **1995**, *28*, 6042.
(22) Wu, C.; Zhou, S. Q. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 1597.
(23) Pashin, I. I.; Kirsh, Yu. E.; Zubov, V. P.; Anisimova, T. V.; Kuzkina, I. F.; Voloshina, Ya. V. *Vysokomol. Soed* **1993**, *35*, 7, 788.
(24) Eisele, M.; Burchard, W. *Makromol. Chem.* **1990**, *191*, 1, 169.
(25) Shestyuk, S. F.; Galaev, I. Yu.; Savitskii, A. P.; Kirsh, Yu. E.; Berezin, I. V. *Biotechnologiya* **1987**, *3*, 2, 178.
(26) Kirsh, Yu. E.; Galaev, I. Yu.; Karaputadze, T. M.; Margolin, A. A.; Shvyadas, V. K. *Biotechnologiya* **1987**, *3*, 2, 184.
(27) Norwood, D. P.; Minatti, E.; Reed, W. F.; Corp. S. *Macromolecules* **1998**, *31*, 2957.
(28) Purcell, I. P.; Lu, J. R.; Thomas, R. K.; Howe, A. M.; Penfold, J. *Langmuir* **1998**, *14*, 1637.
(29) Chari, K.; Hossain, T. Z. *J. Phys. Chem.* **1991**, *95*, 3302.
(30) Fadnavis, N.; Engberts, J. B. *J. Am. Chem. Soc.* **1984** *106*, 2636.
(31) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(32) Pecora, R. *Dynamic Light Scattering*; Plenum Press: New York, 1976.
(33) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1991.
(34) Stockmayer, W. H.; Schmidt, M. *Pure Appl. Chem.* **1982**, *54*, 407.
(35) Gao, Y. B.; Au-Yeung, S. C. F.; Zhou, S. Q.; Wu, C. *J. Macromol. Sci., Phys.* **1997**, *B36*, 417.

MA981756+