Water-Soluble Complexes Formed by Poly(2-vinylpyridinium)-*block*-poly(ethylene oxide) and Poly(sodium methacrylate)-*block*-poly(ethylene oxide) Copolymers

Jean-François Gohy,[†,§] Sunil K. Varshney,[‡] and Robert Jérôme*[,†]

Center for Education and Research on Macromolecules (CERM)—Institute of Chemistry B6,
University of Liège, Sart-Tilman, B-4000 Liège, Belgium, and Polymer Source, 771 Lajoie Street,
Dorval, PQ H9P 1G7 Canada

Received November 30, 2000; Revised Manuscript Received February 1, 2001

ABSTRACT: Formation of interpolyelectrolyte complexes (IPEC) by mixing protonated poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (P2VP-*b*-PEO) with neutralized poly(methacrylic acid)-*block*-poly(ethylene oxide) (PMAA-*b*-PEO) has been investigated in water. It was observed that (i) IPEC are formed in a limited pH range, which is controlled by the degree of ionization of the PMAA and P2VP blocks; (ii) IPEC self-assemble to form the core of monodisperse spherical micelles surrounded by a corona of PEO blocks; (iii) IPEC are salt-sensitive, falling apart above a critical salt concentration; (iv) IPEC are not observed at high pH, but micelles are formed by the P2VP-*b*-PEO copolymers, which contain an uncharged P2VP core surrounded by a PEO corona; (v) IPEC are not observed at low pH, but the PMAA-*b*-PEO diblocks aggregate into micelles, the core of which is formed by a hydrogen-bonded complex between PMAA and PEO; and (vi) these PMAA-*b*-PEO micelles, which are temperature-sensitive, show a complete reorganization of the micellar core above a critical temperature.

Introduction

Self-association of diblock copolymers dissolved in a selective solvent of one constituent is well documented in the scientific literature.[1] Micelles are formed that consist of a core containing the insoluble blocks surrounded by a shell of the solvated blocks. The behavior of amphiphilic copolymers in water, including micellization, is of great interest because of potential in various applications, such as electrosteric stabilization of latex particles[2] and of pigment dispersion in waterborne paints.[3] Micelles in aqueous media have also been considered for use as drug carriers.[4] Recently, micelles of various shapes have been observed in water, which range from spherical micelles to vesicles, tubules, and complex superaggregates.[5]

Micellization in water has been extensively studied for a series of amphiphilic copolymers consisting of polystyrene,[6−8] poly(methyl methacrylate),[9] and poly(propylene oxide)[10] as a hydrophobic block and a water-soluble polyanionic (e.g., sodium polymethacrylate[6]), polycationic (e.g., protonated poly[(dimethylamino)ethyl methacrylate[9]]), or neutral block (e.g., PEO[7,10,11]).

Moreover, there are examples in the scientific literature of micellar cores formed in water by oppositely charged blocks. At least, one of these blocks is attached to a water-soluble nonionic block. The mutual electrostatic interactions of the polycationic and polyanionic blocks form insoluble interpolyelectrolyte complexes (IPEC). This strategy was recently worked out by several research groups.[12] For instance, Kataoka et al. showed that chain length recognition takes place in mixtures of fully ionized poly(ethylene oxide)-*block*-poly(α,β-aspartic acid and poly(ethylene oxide)-*block*-poly(L-lysine) diblocks, because the oppositely charged blocks of the same length associate into supramolecular assemblies.[13] However, none of these studies paid much attention to the degree of ionization of the interacting blocks. IPEC were indeed formed by fully ionized oppositely charged blocks. In this paper, IPEC formation will be investigated in mixtures of poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (P2VP-*b*-PEO) and poly(methacrylic acid-*block*-poly(ethylene oxide) (PMAA-*b*-PEO) diblock copolymers. The influence of the degree of ionization of the P2VP and PMAA blocks will be studied by changing systematically the pH of the aqueous solution. The influence of the ionic strength on the IPEC stability will be also investigated. Finally, the effect of temperature will be considered. The purpose is to show that the P2VP-*b*-PEO/PMAA-*b*-PEO mixtures are versatile micellar systems, which can respond to several stimuli, i.e., pH, temperature and ionic strength.

Experimental Section

Polymer Synthesis. The diblock copolymers were synthesized by sequential living anionic polymerization of the rigorously purified monomers under an argon atmosphere in dry tetrahydrofuran (THF). Diphenylmethylpotassium (DMP) was used to initiate the polymerization of 2-vinylpyridine (2VP) or *tert*-butyl methacrylate (tBMA) at −78 °C. Thirty minutes later, an aliquot was picked out from the reactor for analysis by size exclusion chromatography (SEC). Ethylene oxide (EO) was then added, and the temperature was raised to 35 °C for 24 h. Polymerization was stopped by addition of methanol, and the P2VP-*b*-PEO or PMAA-*b*-PEO copolymer was recovered by precipitation in hexane and dried in vacuo at 40 °C for 48 h. For the P2VP-*b*-PEO sample, the polymerization was carried out with 0.0015 mol of DMP, 0.06 mol of 2VP, and 0.3 mol of EO in 1 L of THF. For the PMAA-*b*-PEO, the amounts of reagents were 0.0018 mol of DMP, 0.04 mol of tBMA, and 0.33 mol of EO in 1 L of THF. The PtBMA blocks were then

---

[†] University of Liège.

[‡] Polymer Source.

[§] J.-F. Gohy is "Chargé de Recherches" by the Belgian National Fund for Scientific Research (F.N.R.S.)

* To whom correspondence should be addressed.

10.1021/ma0020483 CCC: $20.00

converted into PMAA by hydrolysis in 200 mL of a 5/1 (v/v) dioxane/HCl mixture. Two diblocks were synthesized, and they will be designated as P2VP(41)-*b*-PEO(204) ($M_w/M_n = 1.05$) and PMAA(21)-*b*-PEO(177) ($M_w/M_n = 1.8$), where the number in parentheses indicates the degree of polymerization of each block. SEC was carried out with a Varian liquid chromatograph equipped with a refractive index detector and calibrated by polystyrene standards. Three columns from Supelco (G6000-4000-2000 HXL) were eluted by THF added with 2 vol % triethylamine.

Preparation of the Solutions. Aqueous solutions were prepared by direct dissolution of known amounts of solid samples in glass vessels containing pH- and ionic strength-adjusted water. pH was controlled by a 0.05 mol/L phosphate buffer. NaCl was used to adjust the ionic strength, when required. In all the experiments, bidistilled water was used and filtered through 0.2 μm filters. The 2VP/MAA molar ratio was kept equal to 1 and the copolymer concentration to 1 g/L in all the experiments.

Light Scattering. Dynamic light scattering (DLS) was measured with a Brookhaven Instruments Corp. DLS apparatus that consisted of a BI-200 goniometer, a BI-2030 digital correlator, and an Ar ion laser (LEXEL Lasers; wavelength = 488 nm). A refractive index matching bath of filtered decalin surrounded the scattering cell, and the temperature was controlled at 25 °C. Prior to sample loading, the appropriate glass vessel was soaked overnight in sulfochromic solution, thoroughly cleaned by bidistilled water, and dried in a vacuum oven.

The scattering angle was 90°, and the second-order correlation function $G_2(t)$ was measured. In the case of a single-exponential decay, $G_2(t)$ can be expressed by eq 1:

$$G_2(t) = B[1 + \beta \exp(-2\Gamma t)] = B[1 + \beta|G_1(t)|^2] \qquad (1)$$

where B is the baseline, β is an optical constant that depends on the instrument, Γ is the decay rate for the process, t is time, and $G_1(t)$ is the first-order correlation function, which was analyzed by the method of the cumulants:

$$G_1(t) = \exp[-\Gamma_1 t + (\Gamma_2/2)t^2 - (\Gamma_3/3!)t^3 + ...] \qquad (2)$$

where Γ_i is the ith cumulant. The polydispersity index (PDI) of the micellar aggregates was estimated from the Γ_2/Γ_1^2 ratio. The Z-average diffusion coefficient over the whole set of aggregates was calculated from the first cumulant

$$\Gamma_1 = Dq^2 \qquad (3)$$

where D is the translation diffusion coefficient and q is the absolute value of the scattering vector

$$q = [4\pi n \sin(\theta/2)]/\lambda \qquad (4)$$

n is the refractive index of the solvent, θ is the diffusion angle, and λ is the wavelength of the incident light.

The diffusion coefficient extrapolated to zero concentration (D_0) for spherical particles is related to the hydrodynamic radius, R_h, by the Stokes–Einstein equation:

$$D_0 = k_B T/6\pi\eta R_h \qquad (5)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent.

Results and Discussion

The micelles formed by mixtures of the PMAA(21)-*b*-PEO(177) and the P2VP(41)-*b*-PEO(204) diblocks were analyzed by dynamic light scattering. The evolution of the system was monitored as a function of pH, ionic strength, and temperature.

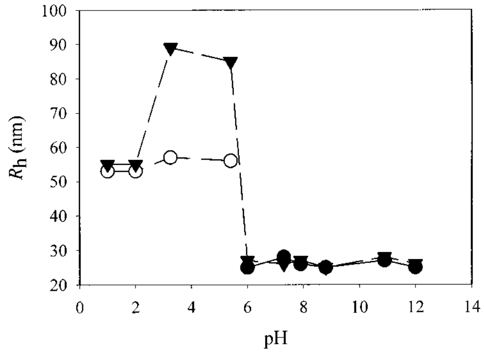

Figure 1. R_h vs pH for the PMAA(21)-*b*-PEO(177) copolymer (open circles), P2VP(41)-*b*-PEO(204) (black circles), and PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture (black triangles).

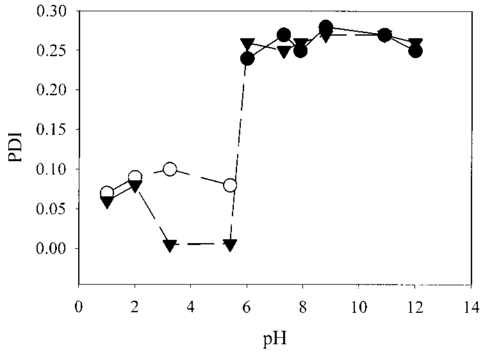

Figure 2. PDI vs pH for the PMAA(21)-*b*-PEO(177) copolymer (open circles), P2VP(41)-*b*-PEO(204) (black circles), and PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture (black triangles).

Effect of pH on the Association Behavior. Figure 1 shows the evolution of R_h as a function of pH for the PMAA(21)-*b*-PEO(177) and the P2VP(41)-*b*-PEO(204) diblocks and for their stoichiometric mixture, i.e., the 2VP/MAA molar ratio equal to 1. How the PDI changes with pH is shown in Figure 2. From these experimental observations, it is clear that the PMAA(21)-*b*-PEO(177) diblock forms micelles with $R_h \approx 55$ nm and PDI ≈ 0.08 at pH < 6, whereas the P2VP(41)-*b*-PEO(204) forms smaller micelles with $R_h \approx 25$ nm and PDI ≈ 0.25 at pH $\geq$ 6.1. The pH-dependent micellization of the P2VP(41)-*b*-PEO(204) was discussed in detail elsewhere.[12e,14] The mixture of these two diblocks shows the same behavior as the PMAA(21)-*b*-PEO(177) at pH $\leq$ 2, and the micelles formed at pH $\geq$ 6.1 are essentially the same as the ones observed for the P2VP(41)-*b*-PEO(204) diblock. At 2 < pH < 6.1, a novel type of micelles with $R_h \approx 85$ nm and PDI = 0.005 is however observed. This behavior can be rationalized as follows: At pH $\leq$ 2, the P2VP block is protonated, and the P2VP(41)-*b*-PEO(204) diblocks exist as free chains in water, whereas the PMAA(21)-*b*-PEO(177) diblock forms micelles. At pH $\geq$ 6.1, the reverse situation is observed; i.e., the PMAA block is ionized, and essentially free chains of PMAA(21)-*b*-PEO(177) exist in solution. In parallel, the hydrophobic nonprotonated P2VP blocks aggregate into micelles. Finally, at 2 < pH < 6.1, both PMAA and P2VP blocks are at least partially ionized, and IPEC's are formed which self-assemble into the core of micelles stabilized by the PEO blocks. Figure 3 is a schematic picture of the evolution of the micellar structure as a function of pH. The very low PDI of the IPEC micelles must be noted, in complete agreement with previously reported data.[12,13] However, R_h of the IPEC micelles was considerably lower (ca. 15 nm) in a

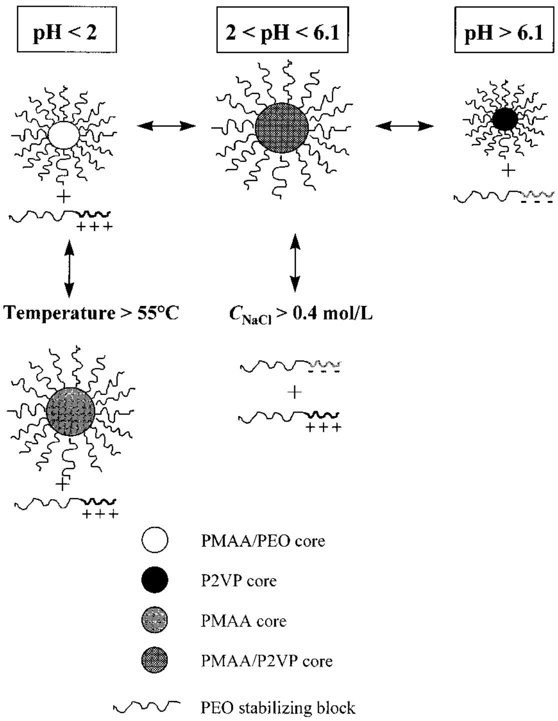

Figure 3. Schematic picture of the evolution of the PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) micellar system as a function of pH, ionic strength, and temperature.

previous study[13] compared to the size observed in this study (ca. 85 nm), although the degree of polymerization of the self-assembling blocks was quite comparable in the two investigations. This difference originates from the chain length recognition which drives the IPEC formation. According to Kataoka et al., only the oppositely charged blocks of the same degree of polymerization are able to self-assemble with formation of well-defined, dense, and very monodisperse IPEC micelles.[13] In the present study, although the degree of polymerization of the self-assembling blocks is quite different, i.e., 41 for the P2VP block and 21 for the PMAA block, IPEC micelles are formed. This apparent contradiction can however be rationalized by considering the actual degree of ionization of the blocks involved. Actually, Kataoka et al. mixed identical molar amounts of completely ionized negatively and positively charged species, attached to chains of the same degree of polymerization. In this study, the ionization of both the P2VP and PMAA blocks is controlled by the pH of the buffered aqueous solution. Figure 4 shows how the concentration of the ionized 2VP and MAA units depends on the pH. These curves were calculated on the assumption that the pK_a's of P2VP and PMAA are independent of the degree of ionization, which is not exactly true. From Figure 4, a pH is reached where the concentrations of the positively charged 2VP units and the negatively charged MAA units are equal. This critical pH roughly corresponds to the midpoint of the narrow pH range, in which IPEC micelles are observed (Figure 1). It is now clear that the chain length recognition claimed by Kataoka is only operative when each monomer unit is completely charged. Actually, charged blocks of unmatched length can self-assemble with formation of IPEC micelles, provided that the number of positive and negative charges is nearly equal. However, the self-assemblies probably have a lower density and a bigger aggregation number compared to the counterparts formed by completely charged blocks of the same degree of polymerization. The size of the IPEC micelles in this study (R_h = 85 nm) is ca. 6 times larger than the value reported by Kataoka (R_h = 15 nm), although the unimers have comparable length in both the studies.

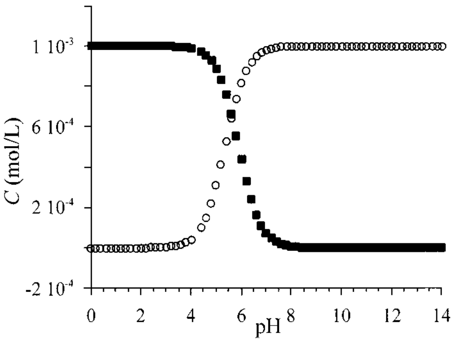

Figure 4. Theoretical dependence of the concentration of ionized P2VP (black squares) and PMAA (open circles) on pH (calculated for initial P2VP and PMAA concentrations of 10^{-3} mol/L).

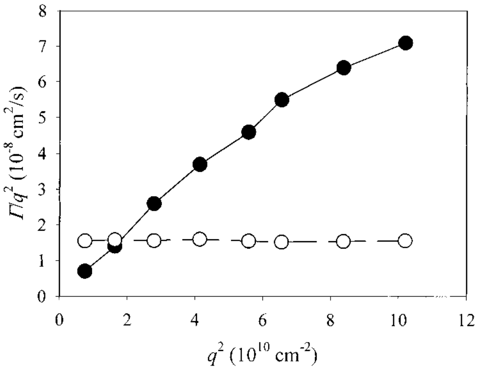

Figure 5. Γ/q^2 as a function of q^2 for the PMAA(21)-*b*-PEO(177) diblock at pH = 1 (open circles) and the P2VP(41)-*b*-PEO(204) diblock at pH = 9 (black circles).

The shape of the IPEC micelles has also been estimated by DLS. Figure 5 shows the dependence of the diffusion coefficient on the detection angle for the PMAA(21)-*b*-PEO(177) and P2VP(41)-*b*-PEO(204) diblocks, Γ/q^2 being plotted against q^2. In the case of spherical particles, the rotational motion is not detectable, and Γ/q^2 is independent of q^2.[15] This situation is clearly observed for the PMAA(21)-*b*-PEO(177) diblock at pH = 1. In sharp contrast, Γ/q^2 increases with q^2 for the P2VP(41)-*b*-PEO(204) diblock at pH = 9. The same analysis has been carried out for the PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture as a function of pH (Figure 6). It is clear that the morphological characteristic features of this mixture are quite comparable to the PMAA(21)-*b*-PEO(177) diblock at pH $\leq$ 2 and to the P2VP(41)-*b*-PEO(204) diblock at pH $\geq$ 6.1. The IPEC micelles, which dominate at pH = 4, are spherical, in agreement with previously reported data.[12]

Effect of Temperature on the Association Behavior at Low pH. The effect of temperature on the micellization features has also been examined. A strong effect is observed at low pH, as shown by the data reported in Figure 7. A similar behavior is observed for the PMAA(21)-*b*-PEO(177) diblock in aqueous solution at low pH. This observation indicates that the temperature effect is specific to this diblock. Indeed, the diffused intensity sharply increases at ca. 40 °C whereas a parallel increase in R_h is reported. The increase in

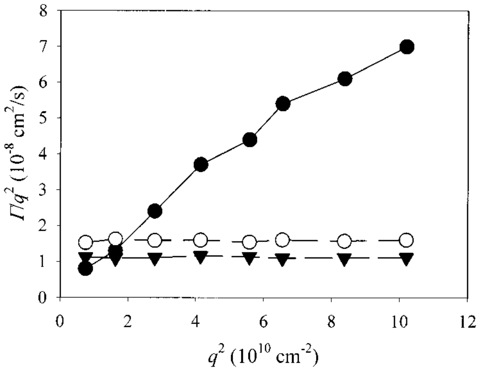

Figure 6. Γ/q^2 as a function of q^2 for the PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture at pH = 1 (open circles), pH = 4 (black triangles), and pH = 9 (black circles).

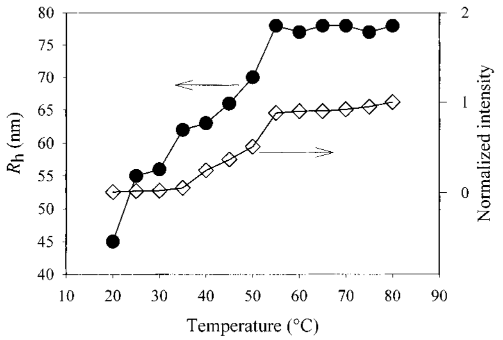

Figure 7. Normalized intensity and R_h as a function temperature for the PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture at pH = 1.

the scattered intensity is so important that the originally clear solution turns opalescent. Although this macroscopic observation might be interpreted as a cloud point, no insoluble material is observed, and R_h of the micelles goes on increasing. At temperatures higher than 55 °C, the normalized intensity and R_h do not change anymore (Figure 7). The origin of this sharp increase in scattered intensity must be found in the formation of a new type of micelles. The increase in micellar size and a change in the refractive index increment from the micellar core to the solvent could contribute to increase the scattered intensity. This reorganization of the micellar structure would start at ca. 40 °C and be complete at ca. 55 °C. On the basis of these experimental observations, the following model emerges for the structure of micelles formed at low pH by the PMAA(21)-*b*-PEO(177) diblock at different temperatures. At low temperature, micelles are formed, although it is well-known that nonionized PMAA is water-soluble and has an hypercoiled conformation as result of the intramolecular hydrogen bonding of the MAA units.[16] However, PMAA and PEO form a hydrogen-bonded complex in water at low pH.[17,18] Since these two polymers are part of the same copolymer and the composition of the PMAA(21)-*b*-PEO(177) is highly asymmetric, this complexation by hydrogen bonding can occur and leave PEO chain segments uncomplexed, as sketched in Figure 8. In a further step, the intramolecular complexes can self-assemble into a micellar core, stabilized by a corona of uncomplexed PEO segments. Hydrogen-bonded complexes have been recently used to create micelles in toluene.[19] This micellization is quite similar to the formation of micelles driven by interpolyelectrolyte complexation. To our best knowledge, this paper is the first report on hydrogen bonding as a means to trigger micellization in water. This effect has been confirmed by adding urea to an aqueous solution of the PMAA(21)-*b*-PEO(177) diblock. Urea is an excellent competitor in processes based on hydrogen bonding. For instance, it is frequently used to denaturate proteins. The PMAA(21)-*b*-PEO(177) micelles are dissociated by urea (concentration = 1 g/L), which is in line with the key role of the hydrogen bonds in the micellization process. The covalent bonding of the PMAA and PEO blocks is also a prerequisite for successful micellization, because no micelle is formed upon mixing PMAA and PEO homopolymers; merely an increase in the solution viscosity is observed, as reported elsewhere.[17]

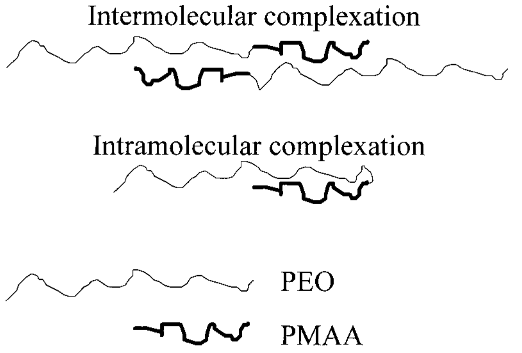

Figure 8. Schematic picture of the hydrogen-bonded complexes formed in water by the PMAA(21)-*b*-PEO(177) diblock at low pH and temperature.

Hydrogen bonds are temperature-sensitive, as exemplified by the denaturation of proteins exposed to higher temperatures. Therefore, the strong effect of temperature on the characteristic features of the micelles formed by the PMAA(21)-*b*-PEO(177) copolymer is not surprising. The stability of PMAA/PEO hydrogen-bonded complexes was studied elsewhere in a limited temperature range.[18] These complexes do not exist below 15 °C, and their stability is maximum at 40 °C. Unfortunately, no information was made available at temperatures higher than 40 °C, thus the critical temperature above which the hydrogen bonds are broken. From the data reported in Figure 7, this phenomenon would occur in the 40−55 °C range, although the micelles persist above 55 °C. This observation can be explained by a transition from micelles containing cores of hydrogen-bonded complexes to micelles in which the hydrophobic PMAA blocks form the core. This reorganization in the 40−55 °C range is consistent with the cloud-point temperature of ca. 50 °C characteristic of PMAA.[20] It can account for the increase in the micellar size upon increasing temperature, in agreement with the increased length of the PEO corona. A change in the aggregation number of the micelles cannot, however, be precluded. A larger difference in the refractive indexes of the aqueous solution and the hydrophobic PMAA core is also a possible contribution to the increase of diffused intensity.

All these experimental observations show that aggregation may be complex even in the case of a single diblock copolymer, such as the PMAA(21)-*b*-PEO(177) considered in this study.

Effect of Salt Concentration on the Association of IPEC. IPEC are sensitive to the ionic strength, falling apart above a critical salt concentration.[21] This dissociation was studied by Kabanov et al. for IPEC formed by PMAA-*b*-PEO diblocks and poly(*N*-ethyl-4-vinylpyridinium) polycations.[12d] The fluorescence intensity of pyrene at 363 nm was monitored as a function

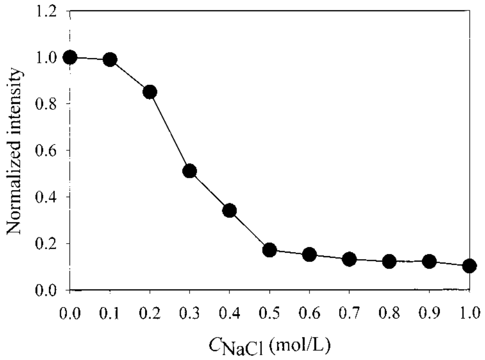

Figure 9. Normalized intensity as a function of NaCl concentration (mol/L) for the PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture at pH = 4.

of the NaCl concentration of an aqueous solution of the IPEC. A sharp drop in the fluorescence intensity was observed at a NaCl concentration of 0.35 mol/L. This behavior, which is not observed for a pyrene solution, was explained by the disintegration of the complex due to electrostatic screening.

Similarly, the laser intensity scattered by the PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture at pH = 5 sharply decreases upon NaCl addition (Figure 9). No micelle persists when the NaCl concentration exceeds 0.4 mol/L. The NaCl concentration needed to dissociate the IPEC in this study is in good agreement with the value reported by Kabanov et al.[12d] Figure 9 confirms that electrostatic interactions are the driving force to micellization for the PMAA(21)-*b*-PEO(177)/P2VP(41)-*b*-PEO(204) mixture at $2 < \mathrm{pH} < 6.1$.

Conclusions

In this paper, IPEC micelles have been formed by mixing PMAA-*b*-PEO and P2VP-*b*-PEO diblock copolymers, in a limited range of pH. These micelles consist of an IPEC core formed by the association of the PMAA and P2VP blocks surrounded by a corona of PEO blocks. They have a spherical shape, and they are larger and less dense than micelles formed by mixing fully ionized oppositely charged blocks of matched length. These observations confirm that IPEC are formed by the association of the same number of positively and negatively charged units in strong relation to the degree of ionization of P2VP and PMAA vs pH. The electrostatic interactions in IPEC can be screened by the addition of NaCl, and the micelles then fall apart.

At low pH, ionized P2VP-*b*-PEO free chains coexist with PMAA-*b*-PEO micelles, whose core is a PMAA/PEO hydrogen-bonded complex, and the corona is formed by the excess of the PEO chain segments. These micelles are temperature-sensitive since the hydrogen-bonded PMAA/PEO complex core is substituted by an hydrophobic PMAA core above 50 °C.

At high pH, ionized PMAA-*b*-PEO free chains coexist with P2VP-*b*-PEO micelles.

Acknowledgment. J.F.G. and R.J. are very much indebted to the “Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles” for financial support in the frame of the “Pôles d’Attraction Interuniversitaires: 4-11: Chimie Supramoléculaire et Catalyse Supramoléculaire”. J.F.G. acknowledges the European Science Foundation program SUPERNET.

References and Notes

(1) (a) Tuzar, Z.; Kratochvil, P. *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum Press: New York, 1993. (b) Chu, B. *Langmuir* **1995**, *11*, 414. (c) Alexandridis, P. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 490. (d) Selb, J.; Gallot, Y. In *Developments in Block Copolymers*; Goodman, I., Ed.; Elsevier: Amsterdam, 1985, Vol. 2, p 85. (e) Moffit, M.; Khougaz, K.; Eisenberg, A. *Acc. Chem. Res.* **1996**, *29*, 95.

(2) (a) Winzor, C. L.; Mrazek, Z.; Winnik, M. A.; Croucher, R. D.; Riess, D. *Eur. Polym. J.* **1994**, *30*, 121. (b) Leemans, L.; Fayt, R.; Teyssié, Ph.; de Jaeger, N. C. *Macromolecules* **1991**, *24*, 5922.

(3) Creutz, S.; Jérôme, R.; Kaptijn, G. M. P.; van der Wert, A. W.; Akkerman, J. M. *J. Coat. Technol.* **1998**, *70*, 41.

(4) (a)Yokoyama, M.; Inoue, S.; Kataoka, K.; Yui, N.; Sakurai, Y. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 431. (b) Yokoyama, M.; Okano, T.; Sakurai, Y.; Ekimoto, H.; Shibazaki, C.; Kataoka, K. *Cancer Res.* **1991**, *51*, 3229.

(5) (a) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728. (b) Discher, B. M.; Won, Y. Y.; Ege, D. S.; Lee, J. C. M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. *Science* **1999**, *284*, 1143. (c) Yu, K.; Eisenberg, A. *Macromolecules* **1998**, *31*, 3509. (d) Gohy, J.-F.; Creutz, S.; Garcia, M.; Mahltig, B.; Stamm, M.; Jérôme, R. *Macromolecules* **2000**, *33*, 6378.

(6) (a) Tuzar, Z.; Webber, S. E.; Ramireddy, C.; Munk, P. *Polym. Prepr.* **1991**, *32*, 525. (b) Cao, T.; Munk, P.; Ramireddy, C.; Tuzar, Z.; Webber, S. E. *Macromolecules* **1991**, *24*, 6300. (c) Kiserow, D.; Prochazka, K.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 461. (d) Prochazka, K.; Kiserow, D.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z. *Makromol. Chem., Macromol. Symp.* **1992**, *58*, 201. (e) Chan, J.; Fox, S.; Kiserow, D.; Ramireddy, C.; Munk, P.; Webber, S. E. *Macromolecules* **1993**, *26*, 7016. (f) Tian, M.; Qin, A.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z.; Prochazka, K. *Langmuir* **1993**, *9*, 1741. (g) Tuzar, Z.; Kratochvil, P.; Prochazka, K.; Munk, P. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2362.

(7) (a) Wilhem, M.; Zhao, C. L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J. L.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 1033. (b) Hruska, Z.; Piton, M.; Yekta, A.; Duhamel, J.; Winnik, M. A.; Riess, G.; Croucher, M. D. *Macromolecules* **1993**, *26*, 1825.

(8) (a) Selb, J.; Gallot, Y. *Makromol. Chem.* **1980**, *181*, 809. (b) Selb, J.; Gallot, Y. *Makromol. Chem.* **1980**, *181*, 2605 (c) Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 1491. (d) Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 2523. (e) Biggs, S.; Vincent, B. *Colloid Polym. Sci.* **1992**, *270*, 563. (f) Gao, Z. S.; Varshney, S. K.; Wong, S.; Eisenberg, A. *Macromolecules* **1994**, *27*, 7923.

(9) (a) Baines, F. L.; Armes, S. P.; Billingham, N. C.; Tuzar, Z. *Macromolecules* **1996**, *29*, 8151. (b) Baines, F. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1996**, *29*, 3416 (c) Antoun, S.; Gohy, J. F.; Jérôme, R. *Polymer* **2001**, *42*, 3641.

(10) (a) Alexandridis, P.; Athanassiou, V.; Fukuda, S.; Hatton, T. A. *Langmuir* **1994**, *10*, 2604. (b) Yang, L.; Bedells, A. D.; Attwood, D.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1447. (c) Deng, Y.; Ding, J.; Stubbersfield, R. B.; Heatley, F.; Attwood, D.; Price, C.; Booth, C. *Polymer* **1992**, *33*, 1963. (d) Brown, W.; Schillen, K.; Almgren, M.; Hvidt, S.; Bahadur, P. *J. Phys. Chem.* **1991**, *95*, 1850. (e) Malmsten, M.; Lindman, B. *Macromolecules* **1992**, *25*, 5440. (f) Almgren, M.; Bahadur, P.; Jansson, M.; Li, P.; Brown, W.; Bahadur, A. *J. Colloid Interface Sci.* **1992**, *151*, 157. (g) Linse, P. *Macromolecules* **1993**, *26*, 4437. (h) Mortensen, K.; Brown, W. *Macromolecules* **1993**, *26*, 4128. (i) Almgren, M.; Brown, W.; Hvidt, S. *Colloid Polym. Sci.* **1995**, *273*, 2.

(11) (a) Bedells, A. D.; Arafeh, R. M.; Yang, Z.; Attwood, D.; Collet, J. H.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1235. (b) Luo, Y. Z.; Nicholas, C. V.; Attwood, D.; Collet, J. H.; Price, C.; Booth, C.; Chu, B.; Zhou, Z. K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 539. Nicholas, C. V.; Luo, Y. Z.; Deng, N. J.; Attwood, D.; Collet, J. H.; Price, C.; Booth, C. *Polymer* **1993**, *34*, 138.

(12) (a) Cohen Stuart, M. A.; Besseling, N. A. M.; Fokkink, R. G. *Langmuir* **1998**, *14*, 6846. (b) Harada, A.; Kataoka, K. *Macromolecules* **1998**, *31*, 288. (c) Harada, A.; Kataoka, K. *Langmuir* **1999**, *15*, 4208. (d) Kabanov, A. V.; Bronich, T. K.; Kabanov, V. A.; Yu, K.; Eisenberg, A. *Macromolecules* **1996**, *29*, 6797. (e) Gohy, J. F.; Varshney, S. K.; Antoun, S.; Jérôme, R. *Macromolecules* **2000**, *33*, 9298.

(13) Harada, A.; Kataoka, K. *Science* **1999**, *283*, 65.
(14) Martin, T. J.; Prochakza, K.; Munk, P.; Webber, S. E. *Macromolecules* **1996**, *29*, 6071.
(15) Xu, R.; Winnik, M. A.; Hallett, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 87.
(16) Anufriyeva, E. V.; Birshtein, T. M.; Nekrasova, T. N.; Ptitsyn, O. B.; Sheveleva, T. V. *J. Polym. Sci., Part C* **1968**, *16*, 3519.
(17) Bailey, F. E.; Lundberg, R. D.; Callard, R. W. *J. Polym. Sci., Part A* **1964**, *2*, 845.
(18) Bekturov, E. A.; Bimendina, L. A. *Adv. Polym. Sci.* **1981**, *41*, 99.
(19) Liu, S.; Zhu, H.; Zhao, H.; Jiang, M.; Wu, C. *Langmuir* **2000**, *16*, 3712.
(20) Eliassaf, J.; Silberberg, A. *Polymer* **1962**, *3*, 555.
(21) Kabanov, V. A.; Zezin, A. B.; Izumrudov, V. A.; Bronich, T. K.; Bakeev, K. N. *Macromol. Chem. Suppl.* **1985**, *13*, 137.

MA0020483