A “Holy Trinity” of Micellar Aggregates in Aqueous Solution at Ambient Temperature: Unprecedented Self-Assembly Behavior from a Binary Mixture of a Neutral−Cationic Diblock Copolymer and an Anionic Polyelectrolyte

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ABSTRACT: Binary mixtures of a poly(ethylene oxide-*block*-2-(diethylamino)ethyl methacrylate) (PEO−PDEA) copolymer and poly(methacrylic acid) (PMAA) can form *three* types of micelles/aggregates in aqueous solution at ambient temperature, depending solely on the solution pH. Above pH 8.5, simple micelles are formed with hydrophobic PDEA cores and with the PEO chains located in the corona; the PMAA does not participate in micelle formation under these conditions. However, at pH 6−8.5, polyion complex micelles with charge-compensated PDEA/PMAA cores and PEO coronas are obtained. A third colloidal structure is formed below pH 3 due to hydrogen bonding between the PEO and PMAA chains. This remarkable reversible self-assembly behavior is unprecedented.

Introduction

The micellar self-assembly of AB diblock copolymers in selective solvents was first recognized almost 40 years ago.[1] In aqueous solution the driving force for micellization is usually the presence of a permanently hydrophobic block based on, say, polystyrene or poly(methyl methacrylate).[2,3] More recently, there has been increasing interest in the use of tunably hydrophobic blocks, since the resulting copolymers are stimuli-responsive.[4] However, this is not the only approach to micelle formation: Kataoka’s group,[5] Kabanov and co-workers,[6] and Gohy et al.[7] have each reported that polyion complexation between oppositely charged polyelectrolytes leads to ionic micelle cores. These polyion complexes offer some potential for biomedical applications, since synthetic cationic diblock copolymers can form compact supramolecular structures with the pendent anionic phosphate residues on DNA.[8] Such colloidal “packets” of DNA are small enough to be transported across cell membranes, which is a prerequisite for genetic engineering.

An alternative mechanism for achieving complexation between polymer chains is hydrogen bonding, which has recently received renewed attention. Scranton and co-workers have shown that high molecular weight statistical copolymers based on poly(methacrylic acid) (PMAA) and monomethoxy-capped poly(ethylene oxide) methacrylate can act as pH-responsive emulsifiers at low pH since hydrogen bonding occurs between the poly(ethylene oxide) side chains and the PMAA backbone, leading to hydrophobic patches.[9] Meijer’s group has shown that two homopolymers can form a hydrogen-bonded diblock copolymer in nonaqueous media if the end group of each homopolymer contains a sufficient number of hydrogen bond donor/acceptor sites.[10] More pertinent to this work, Jiang’s group has developed a novel route to polymeric micelles in aqueous media. A poly(styrene-*co*-methacrylic acid) statistical copolymer (MAA content varying from 4 to 13 mol %) formed a micelle core with a stabilizing corona of poly(*N*-vinylpyrrolidone) chains, with the latter binding to the MAA residues via hydrogen bonding.[11]

Within the past 5 years, the synthesis of so-called “schizophrenic” AB diblock copolymers has been described. Here both the A block and the B block are stimuli-responsive; hence this new class of copolymer surfactants is capable of forming two types of micellar structures in aqueous solution.[12] Recent examples include a purely pH-responsive diblock copolymer reported by Liu and Armes[13] and purely thermoresponsive diblock copolymers reported by both Laschewsky and co-workers and Weaver et al.[14]

Herein we describe the remarkable reversible self-assembly behavior of a binary mixture of a neutral−cationic diblock copolymer and a simple anionic polyelectrolyte at room temperature (see Figure 1). Judicious adjustment of the solution pH leads to the formation of a “holy trinity” of micellar/colloidal aggregates due to hydrophobic forces, polyion complexation, and hydrogen bonding; as far as we are aware, such complex self-assembly behavior in aqueous solution is unprecedented.[15] This is also the first example of a homopolymer being used to produce “schizophrenic” behavior in a diblock copolymer.

Experimental Section

Materials. Monohydroxy-capped poly(ethylene oxide) (PEO−OH; $M_n = 5000$; $M_w/M_n = 1.10$) was kindly donated by Cognis Performance Chemicals (Hythe, UK). 2-(Diethylamino)ethyl methacrylate (DEA) was purchased from Aldrich, and its

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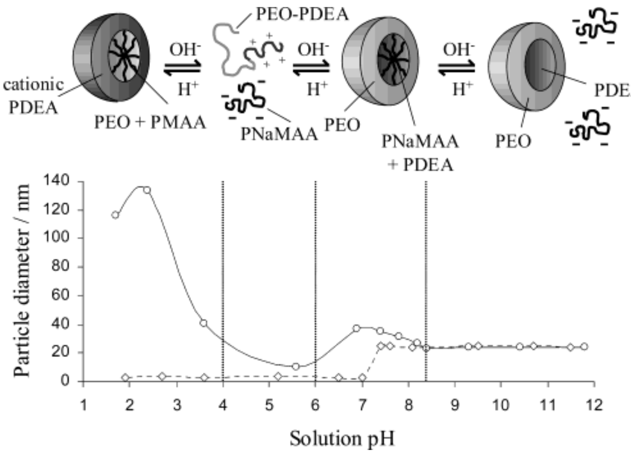

Figure 1. Variation of intensity-average particle diameter with solution pH for a 1:1 binary mixture of $PEO_{113}-PDEA_{50}$ and PMAA as determined by dynamic light scattering studies at 20 °C (○, $PEO_{113}-PDEA_{50}$ with PNaMAA; ◇, $PEO_{113}-PDEA_{50}$ alone). A schematic representation of the three types of aggregates that are formed is also depicted. The vertical dotted lines correspond to the approximate phase boundaries between the micelles/colloidal aggregates and unimer states.

inhibitor was removed by treatment with a basic alumina column prior to use. Sodium 4-styrenesulfonate (NaStS), Cu(I)Br, 2,2′-bipyridine (bpy), and isopropyl alcohol (IPA) were also obtained from Aldrich and were used as received. Deionized, doubly distilled water was used in all experiments. Poly(sodium methacrylate) [PNaMAA; PMAA is used to denote its neutral poly(methacrylic acid) form] was purchased from Aldrich as a 30 wt % aqueous solution. According to the supplier, this polymer had an M_n of 5400 and an M_w of 9500. Silica (silica-60 gel) was purchased from E. Merck (Germany).

Diblock Copolymer Synthesis. The poly(ethylene oxide-*block*-2-(diethylamino)ethyl methacrylate) (PEO−PDEA) was synthesized via atom transfer radical polymerization (ATRP) in a 2:1 v/v IPA/water mixture at 20 °C using a poly(ethylene oxide) macroinitiator[16] and a Cu(I)Br catalyst, using 2,2′-bipyridine as a solubilizing ligand. After 1.5 h the DEA conversion was more than 95%.

Diblock Copolymer Characterization. Gel permeation chromatography analyses were carried out using a Polymer Labs ERC-7517A instrument equipped with refractive index detector. The aqueous eluent comprised 0.50 M acetic acid and 0.30 M Na_2SO_4 at pH 2; a series of near-monodisperse poly(2-vinylpyridine) standards (PSS, Germany) were used for calibration purposes. All ^1H NMR spectra (16 scans per spectrum) were recorded at 20 °C in D_2O using a 300 MHz Bruker Avance spectrometer. The solution pH was adjusted as required using either DCl or NaOD.

Aqueous Solution Characterization. Dynamic light scattering (DLS) measurements were made on 1.0% w/v aqueous solutions at 20 °C using a Brookhaven BI-9000AT instrument equipped with a 125 mW laser operating at $\lambda = 532$ nm. A scattering angle of 90° was used in all DLS studies of the micellar/colloidal aggregates. However, a scattering angle of 30° was used for the determination of the molecularly dissolved PEO−PDEA copolymer chains at pH 5.6 in order to avoid problems caused by short correlation times. Intensity correlation data were analyzed by the cumulants method to provide the average decay rate $\langle\Gamma\rangle$ ($\langle\Gamma\rangle = q^2D$, where D is the diffusion coefficient). The intensity-average hydrodynamic diameter was calculated from the measured diffusion coefficients using the Stokes−Einstein relation and assuming the viscosity of the dilute aqueous solution to be that of pure water. TEM studies (see Supporting Information) indicate relatively broad size distributions for these micellar/colloidal aggregates. Thus, the hydrodynamic diameter measured at a scattering angle of 90° is almost certainly an underestimate of the true hydrodynamic diameter due to polydispersity effects. A full angular dependence study is required for more rigorous DLS characterization, but this is beyond the scope of the present study.

Static light scattering (SLS) studies were carried out at 25 °C using a Brookhaven Instrument Corp. (BI9000) instrument equipped with a Lexal 2 W argon ion laser operating at 488 nm. The scattering angle, θ, was varied from 30° to 150° to produce Zimm plots.[17] The dn/dc values for aqueous solutions of the $PEO_{113}-PDEA_{50}$ diblock copolymer alone at pH 11 and its binary mixtures with PMAA at pH 7.3 and pH 2.2 were determined to be 0.250, 0.236, and 0.211, respectively, using an Optokem differential refractometer operating at $\lambda = 488$ nm. To ensure accurate dn/dc measurements, stock solutions of each type of micelle/colloidal aggregate were diluted with water at constant pH to maintain a constant ionic strength. The resulting multipoint calibration plots at pH 11, 7.3, and 2.2 are provided as Supporting Information. We estimate that the error in such dn/dc determinations is around ±2%, which normally leads to an approximate error in the micelle molecular weight of around 10%. Measurement of the angular dependence of the excess absolute time-averaged scattered light intensity, known as the Rayleigh ratio, of a series of dilute polymer solutions allows determination of the weight-average molar mass $(M_w)_{app}$ and the root-mean-square z-average radius of gyration $\langle R_g^2\rangle_z^{1/2}$ (usually written as $\langle R_g\rangle$). The SLS studies were carried out on binary mixtures of the $PEO_{113}-PDEA_{50}$ diblock copolymer and the PNaMAA homopolymer. A 1.0 wt % solution of the diblock copolymer was prepared by initial dissolution at pH 2, followed by addition of NaOH to obtain pH 11. A 1.0 wt % solution of PNaMAA at pH 11 was prepared and then added to the diblock copolymer solution to prepare a binary mixture (15 mL of the diblock copolymer and 5.7 mL of PNaMAA, corresponding to a DEA/MAA molar ratio of unity) at three different solution pH's. Four SLS experiments were carried out: (1) the $PEO_{113}-PDEA_{50}$ diblock copolymer alone at pH 11; (2) the diblock copolymer/homopolymer binary mixture at pH 11; (3) the same binary mixture at pH 7.3; (4) the same binary mixture at pH 2.2. Serial dilutions were carried out at constant solution pH. The polydispersity effects noted in the DLS studies will also affect the SLS studies described above. For this reason, and also given the strong fluctuations observed in the scattered light intensities, radii of gyration are considered unreliable, and we estimate that the M_w values are only accurate to within ±30%.

Aqueous electrophoresis data were obtained using a Malvern Instruments Zetamaster S instrument. The zeta potential, ξ, was calculated from the electrophoretic mobility (u) using the Smoluchowsky relationship $\xi = \eta u/\epsilon$, where it is assumed that $\kappa a \gg 1$ (where η is the solution viscosity, ϵ is the dielectric constant of the medium, and κ and a are the Debye−Hückel parameter and particle radius, respectively). The solution pH was adjusted using NaOH and HCl.

Results and Discussion

In 1999, we reported the pH-induced micellization of a PEO−PDEA diblock copolymer that had been synthesized by oxyanionic polymerization.[18] In the present work a similar PEO−PDEA diblock copolymer was prepared using ATRP chemistry. The diblock composition was determined to be $PEO_{113}-PDEA_{50}$ (i.e., $M_n = 14\,300$) by ^1H NMR spectroscopy in d_4-methanol using PEO as an “end group”. Gel permeation chromatography studies indicated a polydispersity of 1.25 for the final $PEO_{113}-PDEA_{50}$ diblock copolymer. A phase diagram showing the three types of micelles formed by the binary mixture of the PEO−PDEA diblock copolymer and the PNaMAA homopolymer on varying the solution pH was constructed from DLS studies (see Figure 1). Control experiments were also conducted on the $PEO_{113}-PDEA_{50}$ diblock copolymer in the absence of any PNaMAA homopolymer.

Formation of Micelles with Hydrophobic Cores (pH > 8). The $PEO_{113}-PDEA_{50}$ diblock copolymer

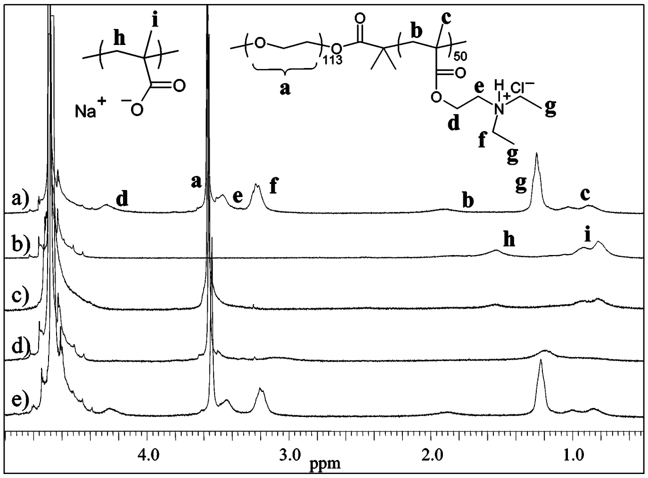

Figure 2. ^{1}H NMR spectra recorded at 20 °C for (a) $PEO_{113}-PDEA_{50}$ diblock copolymer at pH 2.2, (b) PNaMAA homopolymer at pH 11.8, (c) the PDEA-core micelles formed by the PEO−PDEA diblock copolymer in the presence of the PNaMAA homopolymer (1:1 DEA/NaMAA molar ratio) at pH 11.8, (d) the polyion complex with charge-compensated PDEA/PNaMAA micelle cores and PEO coronas formed by a binary mixture of the PEO−PDEA diblock copolymer and PNaMAA homopolymer at pH 8.3, and (e) the same 1:1 binary mixture at pH 1.6, where attenuation of the PEO signal at δ 3.6 indicates the formation of colloidal aggregates due to hydrogen bonding between the PEO and the PMAA chains, with the protonated, cationic PDEA chains remaining solvated.

dissolved molecularly at low pH due to protonation of the tertiary amine groups on the PDEA chains (confirmed by ^{1}H NMR and DLS studies). Above pH 7.5, the PDEA block becomes hydrophobic and PDEA-core micelles were obtained with PEO coronas, as described by Vamvakaki et al.[18] Inspection of the ^{1}H NMR spectrum recorded at pH 11.8 (not shown) confirmed that the PDEA signals were no longer visible. If the PNaMAA homopolymer is added to this alkaline solution, it simply remains molecularly dissolved as an anionic polyelectrolyte (methacrylate backbone signals due to PNaMAA appear in the ^{1}H NMR spectrum recorded for the binary mixture) and does not interact with the diblock copolymer micelles at this pH (see Figure 2). Regardless of whether the PNaMAA is present or not, DLS studies indicate the formation of micelles with an intensity-average micelle diameter of 25 nm and a polydispersity of 0.08.

Formation of Micelles with Mixed Polyion Cores (pH 6−8.5). On lowering the solution pH of the above binary solution to approximately pH 8.5, the PDEA block becomes partially protonated and hence cationic, while the PNaMAA chains lose some of their anionic character. Under these conditions, efficient charge compensation occurs, and micelles are formed that comprise PNaMAA and PDEA mixed ionic cores with the PEO chains forming the micelle coronas (see Figure 2). These “polyion complex” micelles have an intensity-average mean diameter of around 32−35 nm and a narrow size distribution (polydispersity = 0.03). On further lowering the solution pH to below pH 6, charge imbalance occurs. Given the dramatic decrease in the scattered light intensity, it appears that the polyion complex micelles begin to dissociate. However, the observed particle diameter of 10 nm at pH 5.6 suggests that there is still some weak interaction between the highly protonated PEO−PDEA diblock and the near-neutral, weakly hydrophilic PMAA chains rather than true molecular dissolution. In contrast, control experiments conducted in the absence of any PNaMAA confirmed that the PEO−PDEA diblock copolymer micelles formed in alkaline media simply dissociate below around pH 7.3 to give unimers, with no supramolecular assemblies being observed. The hydrodynamic diameter estimated for a 10.0 g/L unimer solution at pH 5.6 was 3 nm. Finally, it is noteworthy that, if the solution pH is raised from pH 7.6 to pH 11, the anionic PNaMAA chains are released from the polyion complex micelles, which become simple PEO−PDEA micelles with hydrophobic cores (see Supporting Information for NMR evidence).

Table 1. Summary of the Dynamic and Static Light Scattering Characterization of $PEO_{113}-PDEA_{50}$ Micelles at pH 11 and Binary Mixtures of $PEO_{113}-PDEA_{50}$ Diblock Copolymer/PNaMAA Homopolymer Solutions at pH 7.3 and 2.2, Respectively

light scattering parameters	$PEO_{113}-PDEA_{50}$ alone at pH 11	binary mixture at pH 7.3	binary mixture at pH 2.2
hydrodynamic diam/nm	25	33	120
polydispersity[a]	0.16	0.03	0.08
M_w (g mol^{-1})	6.25×10^5	2.08×10^6	3.09×10^7
N_{agg}	35	152[b]	2430[b]

[a] The polydispersity, μ_2/Γ^2, is defined as the ratio of the second moment of the cumulant fit (μ_2) to the first moment (Γ) squared. [b] These aggregation numbers were calculated assuming 1:1 stoichiometry between the $PEO_{113}-PDEA_{50}$ diblock copolymer and the PNaMAA (or PEO).

Formation of Micelles with Hydrogen-Bonded Cores (pH < 3). Below pH 3, the degree of ionization of the PMAA chains is essentially zero, and hydrogen bonding of these neutral chains with the PEO blocks can occur. Intuitively, micelles comprising hydrogen-bonded PMAA/PEO cores and cationic PDEA coronas were expected. However, DLS measurements indicated the formation of colloidal aggregates of around 120 nm diameter with low polydispersities (0.01−0.08).

The estimated contour length of a single PEO−PDEA diblock copolymer chain is around 60 nm, but this theoretical upper limit is calculated for the fully stretched chains, which is physically unrealistic. Thus, the DLS diameter is clearly too large for simple core−shell micelles. Vesicle formation is an alternative explanation, but the calculated density of these aggregates (0.057 g cm^{-3}) is probably too low to support this hypothesis. The polyelectrolytic nature of the PDEA chains at low pH is expected to produce bigger aggregates than the micelles obtained at neutral or high pH. Moreover, ^{1}H NMR studies indicate that the PEO chains are merely attenuated rather than completely suppressed (see Figure 2).[19] This suggests a relatively high degree of hydration for these aggregates. However, the combination of these two factors is not sufficient to account for the observed hydrodynamic diameter. Another possible explanation is that micellar aggregates or compound micelles are formed, as described by Zhang and Eisenberg.[20] In summary, we believe that the hydrogen-bonded structures formed at low pH are more complicated than simple core−shell micelles, and further work is in progress to investigate this aspect.

Static Light Scattering Studies. Allowing for the effect of dilution, the addition of PNaMAA to the DEA-core diblock copolymer micelles at pH 11 had no significant effect on the scattering intensity at all angles, since the anionic homopolyelectrolyte scatters

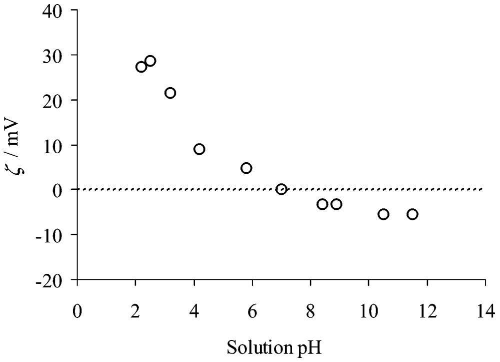

Figure 3. Zeta potential vs pH curve for a 0.10% w/v solution of a 1:1 binary mixture of the $PEO_{113}-PDEA_{50}$ diblock copolymer with the PNaMAA homopolymer.

light very weakly compared to the much larger diblock copolymer micelles. Static light scattering (SLS) studies yielded weight-average micelle masses of approximately 6.25×10^5, 2.08×10^6, and 3.09×10^7 g mol^{-1} for the $PEO_{113}-PDEA_{50}$ micelles at pH 11, polyion complex micelles at pH 7.3, and hydrogen-bonded aggregates at pH 2.2, respectively (see Table 1 and also the three Zimm plots in Figures 1−3 of the Supporting Information). On the basis of the respective weight-average molecular weights of the diblock copolymer and the homopolymer, the micelle aggregation numbers (N_{agg}) can be calculated. For the simple diblock copolymer micelles formed at pH 11, there are 35 copolymer chains per micelle. The diblock copolymer/homopolymer binary mixture was optimized to promote formation of a polyion complex at pH 7.3 with a 1:1 DEA/NaMAA molar ratio; this assumed charge-compensated composition leads to a calculated micelle aggregation number of 152. In the absence of any other data it is also assumed, though with less justification, that the same 1:1 stoichiometric complex is formed via hydrogen bonding between the PEO and PMAA chains at pH 2.2, which leads to an aggregation number of 2430. This latter value is relatively high; if correct, it may indicate the presence of compound micelles.[20]

Aqueous Electrophoresis Data. Aqueous electrophoresis studies (see Figure 3) indicated weakly negative zeta potentials (−3 to −7 mV) for the PDEA-core micelles above pH 8.5. On lowering the pH, the PDEA block becomes protonated and the anionic PNaMAA chains are incorporated into the micelle cores due to electrostatic attraction, leading to charge compensation. An isoelectric point is observed at pH 7.0, which is approximately the midpoint between the pK_a of the PMAA and the conjugate acid form of the PDEA. On decreasing the pH further, the zeta potential remains almost zero. Below pH 3.5, when the PEO block forms a hydrogen-bonded complex with the neutral PMAA chains, the PDEA chains become highly cationic and the zeta potential increases dramatically to +29 mV, as expected.

Effect of Additives on Micelle Formation. It is well-known that polyion complex micelles cannot be formed at high salt concentrations, since electrostatic interactions are substantially attenuated under these conditions.[7b] To test the hypothesis that the micelles formed at pH 6−8.5 comprised polyion complex cores, additional DLS studies were carried out in the presence of added electrolyte (0.50 M NaCl). The presence of salt did not affect the formation of either hydrophobic DEA-core micelles in alkaline media or hydrogen-bonded aggregates below pH 3. However, no polyion complex micelles were observed at intermediate pH, as expected.

In summary, the reversible formation of three types of micelles/aggregates in aqueous solution is reported for the first time. This unprecedented self-assembly behavior is readily achieved by adjusting the solution pH of a simple binary mixture of a judiciously selected neutral−cationic diblock copolymer and an anionic polyelectrolyte at ambient temperature. The driving force for aggregation is different in each case: conventional micelles are formed by hydrophobic interactions at high pH, polyion complexation occurs at intermediate pH, and hydrogen-bonded complexes are produced at low pH.

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Supporting Information Available: The d*n*/d*c* calibration plots for (a) the PEO−PDEA diblock copolymer alone at pH 11, (b) the binary mixture of this diblock copolymer and the PNaMAA homopolymer at pH 7.3, and (c) the binary mixture of this diblock copolymer and the PMAA homopolymer at pH 2.2; three Zimm plots for the $PEO_{113}-PDEA_{50}$ diblock copolymer at pH 11 in the absence of PNaMAA, for the 1:1 binary mixture of $PEO_{113}-PDEA_{50}$ and PNaMAA at pH 7.3, and for the 1:1 binary mixture of $PEO_{113}-PDEA_{50}$ and PMAA at pH 2.2; representative transmission electron micrograph of the PEO−PDEA micelles formed at pH 11 in the absence of any PNaMAA homopolymer; NMR studies of the effect of pH cycling between the polyion complex micelles formed at pH 7.6 and the hydrophobic PDEA-core micelles formed at pH 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) During the preparation of this manuscript, we became aware of a recent paper by Gohy and co-workers (see ref 7b), who examined the self-assembly behavior of a binary pair of asymmetric diblock copolymers based on a near-monodisperse poly(2-vinylpyridine)−poly(ethylene oxide) (P2VP−PEO) and a highly polydisperse poly(methacrylic acid)−poly(ethylene oxide) (PMAA−PEO). At high pH the P2VP−PEO diblock formed P2VP-core micelles, with the PMAA−PEO remaining molecularly dissolved, at intermediate pH a mixed polyion complex micelle comprising charge-compensated P2VP and PMAA residues was formed, and at low pH the PMAA−PEO blocks formed micelles due to intrachain hydrogen bonding between the short PMAA and the long PEO blocks. Thus, there are certainly some similarities between this work and the present study.

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(19) Assuming that the PDEA chains are fully solvated, an apparent EO/DEA block ratio of 1.45 can be calculated. Since the actual EO/DEA block ratio is 2.26 (determined from the diblock copolymer's ^{1}H NMR spectrum recorded in d_4-methanol), this indicates that the PEO chains are less solvated/mobile at low pH, which is consistent with the formation of hydrogen bonding between the PEO and PMAA chains. Hydrogen bond complexation between PEO and PMAA was also postulated by Scranton and co-workers (see ref 9).

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