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Reversible Phase Transformations in Concentrated Aqueous Block Copolymer Solutions of Poly(methyl acrylate)-*b*-poly(hydroxyethyl methacrylate-*co*-dimethylaminoethyl methacrylate)

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ABSTRACT: We have synthesized and characterized concentrated aqueous block copolymer solutions made with a series of poly(methyl acrylate)-*b*-poly(hydroxyethyl methacrylate-*co*-dimethylaminoethyl methacrylate), PMA/PHD, diblock copolymers with varying dimethylaminoethyl methacrylate (DMAEMA) content. The concentrated aqueous block copolymer solution consisting of PMA/PHD with high DMAEMA content (75 mol %) exhibits reversible morphological transitions from disordered, interacting spherical micelles to hexagonally packed cylinders to alternating lamellae over a narrow temperature range (30 °C) due to decreased hydrophilicity of DMAEMA units with increasing temperature. Between morphological transformations, the microstructures experience a decrease in characteristic spacing, reminiscent of a lower critical solution temperature-type response. By changing the DMAEMA content within the PHD block, we are able to tune the swelling characteristics of concentrated PMA/PHD solutions, as well as the range of morphologies accessible.

Introduction

The study of concentrated block copolymer solutions has enabled the investigation of a wide range of morphological transitions,[1−9] and the observation of several morphologies that are not common in diblock copolymer melts.[5] For example, Lodge et al. observed alternating lamellae, interconnected gyroids, hexagonally packed cylinders, and spheres organized in face-centered- and body-centered-cubic lattices in a symmetric polystyrene-*b*-polyisoprene, PS/PI, diblock copolymer by changing both temperature and the amount of diethyl phthalate (a selective solvent for polystyrene) that is present.[6] In addition to PS/PI in a variety of other organic solvents,[1,3,4,6,8,10] other common polymer−solvent combinations used in the investigation of concentrated block copolymer solutions include poly(ethylene oxide)-based amphiphilic block copolymers in water.[2,7,9,11] In all the above-mentioned systems, the block copolymer−solvent interactions are only weakly affected by external stimuli, e.g., temperature or pH. Drastic changes in polymer concentration are thus also necessary to access different morphologies. The incorporation of stimuli-responsive units within block copolymer architectures should provide an added dimension of tunability, allowing access to further morphological richness and kinetic complexity in the phase behavior of concentrated block copolymer solutions. For example, poly(dimethylaminoethyl methacrylate), poly(DMAEMA), is pH-responsive[12] and exhibits a lower critical solution temperature (LCST) in water.[13] Concentrated aqueous block copolymers solutions containing DMAEMA units should provide a greater temperature response thereby allowing the investigation of morphological transformations by tuning temperature alone.

Controlled free-radical polymerization techniques, such as atom transfer radical polymerization (ATRP),[14] have been shown to yield well-defined DMAEMA-containing homo- and block copolymers.[15−21] It has been suggested, however, that the use of LCST-exhibiting polymers to investigate the phase behavior of concentrated block copolymer solutions might limit accessible morphological transitions due to weak temperature response above and below the LCST.[8] As such, it is more suitable to copolymerize DMAEMA with a second monomer in order to better control the degree of temperature response. To this end, we have reported the statistical copolymerization of hydroxyethyl methacrylate (HEMA) and DMAEMA at their compositional azeotrope in *N*,*N*-dimethylformamide[15] or over a broad range of compositions in dimethyl sulfoxide (DMSO).[16] It is well established in the hydrogel community that the material properties of gels containing HEMA and DMAEMA can be significantly altered by changing the amount of DMAEMA present in the system.[22] Concentrated aqueous block copolymers solutions containing statistical copolymers of HEMA and DMAEMA at varying DMAEMA content should thus exhibit morphological richness that is accessible by tuning temperature and pH, and the tunability present in these systems offer intriguing prospects for gene[12] and drug delivery.[22]

In this work, we present concentrated aqueous block copolymer solutions of poly(methyl acrylate)-*b*-poly(HEMA-*co*-DMAEMA), PMA/PHD, that undergo thermally reversible morphological transformations over a large phase space but over a narrow temperature window. PMA was chosen as a second block because it does not sorb water significantly,[23] and has a glass transition temperature below room temperature (T_g = 12.5 °C). The low glass transition temperature of PMA enables the diblock copolymers to reorganize at and above ambient temperatures. As such, we can reversibly access multiple morphological transitions in a single concentrated aqueous block copolymer solution by changing temperature alone. Moreover, we demonstrate that the swelling characteristics and the adopted morphology of the concentrated aqueous PMA/PHD solution can be tuned by adjusting the DMAEMA composition within the PHD block at the onset of synthesis.

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Table 1. Physical Characteristics of PMA/PHD Diblock Copolymers

identifier	$M_{n,PMA}$ (kg/mol)	$M_{n,PHD}$ (kg/mol)	M_w/M_n	x_{PHD}[a]	υ_{PHD}[b]	x_D[c]
PMA/PHD$_{75}$	13.2	10.6	1.10	0.315	0.440	0.753
PMA/PHD$_{63}$	10.0	9.67	1.07	0.361	0.491	0.633
PMA/PHD$_{50}$	12.0	14.7	1.11	0.423	0.556	0.500
PMA/PHD$_{28}$	8.04	12.7	1.15	0.497	0.610	0.279

[a] Mole fraction of PHD. [b] Volume fraction of PHD; calculated using molar compositions from ^{1}H NMR and polymer densities of $\rho_{PHD75} = 1.27$ g/cm^3, $\rho_{PHD63} = 1.25$ g/cm^3, $\rho_{PHD50} = 1.21$ g/cm^3, ρ_{PHD28}[15] $= 1.20$ g/cm^3, and $\rho_{PMA} = 1.24$ g/cm^3. All polymer densities were determined using a pycnometer according to ASTM D153−84[25] with cyclohexanes as nonsolvent. [c] Mole fraction of DMAEMA within PHD.

Experimental Section

Materials. HEMA (Acros, 98%) was vacuum distilled (40 mTorr, 65 °C) to remove ethylene glycol dimethacrylate[24] and stored at 0 °C prior to use. DMAEMA (Acros, 98%) and methyl acrylate (Acros, 99%) were passed through columns of activated basic alumina and stored at 0 °C prior to use. Ethyl α-bromoisobutyrate (EB*i*B, Aldrich, 98%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamene (PMDETA, Aldrich, 99%), Cu^{I}Br (Aldrich, 98%), Cu^{II}Br (Acros, anhydrous 99%), Cu^{I}Cl (Acros, 99%), Cu^{II}Cl$_2$ (Acros, 99%), and dimethyl sulfoxide (extra dry, Fisher Scientific) were used as-received.

Synthesis of Bromine-Terminated PMA Macroinitiator by ATRP. In a typical polymerization, methyl acrylate (50.0 g, 348 mmol), CuBr (255 mg, 1.74 mmol), CuBr$_2$ (19.4 mg, 0.087 mmol), and PMDETA (386 μL, 1.83 mmol) were added to a 100 mL flask equipped with a magnetic stir bar. The flask was sealed with a septum, wired shut, placed in an oil bath preheated to 75 °C, and purged with N$_2$ for 20 min. The reaction was then initiated by the addition of EB*i*B (235 μL, 1.30 mmol) and was carried out for 90 min. Positive N$_2$ pressure was maintained throughout the polymerization. Following polymerization, the reaction flask was removed from the oil bath and quenched in liquid nitrogen. The reaction contents were subsequently exposed to air, diluted with tetrahydrofuran, and mixed with silica gel to remove copper salts. Finally, the solution was concentrated and precipitated into hexanes. The polymer was dried in vacuo for 24 h at 50 °C. PMA macroinitiators of different molecular weights were synthesized in a similar fashion by varying reaction times.

Synthesis of PMA/PHD Diblock Copolymers. PMA/PHD block copolymers were made by copolymerizing HEMA and DMAEMA at varying DMAEMA molar monomer feed compositions; polymerizations were initiated with PMA macroinitiators. A molar ratio of 300:1:1.3:0.1:1.2 total monomer:PMA:PMDETA: CuCl:CuCl$_2$ was used for all copolymerizations, which were performed in DMSO with a monomer concentration of 0.2 g/mL. We have previously demonstrated that copolymerizations of HEMA and DMAEMA in DMSO yield statistical PHD copolymers.[16] Specific experimental details have been described in earlier works.[15,16] Copper salts were removed with silica gel following the copolymerizations. For clarity, all PMA/PHD diblock copolymers will be referred to as PMA/PHD$_F$, where F is the composition (in mol %) of DMAEMA in the PHD block. The physical characteristics of the diblock copolymers investigated in this study are listed in Table 1. The absolute molecular weights of the diblock copolymers range from 19.7 kg/mol to 26.7 kg/mol.

Characterization. Gel permeation chromatography was performed using a GPC system equipped with a Waters 515 HPLC solvent pump, two PLgel mixed-C columns (5 μm bead size, MW range 200−2000000 g/mol, Polymer Laboratories Inc.) connected in series with an Optilab DSP interferometric refractometer and a multiangle laser light scattering (MALLS) detector ($\lambda = 690$ nm, DAWN-EOS, Wyatt Technology Corp.). The absolute molecular weights of PMA macroinitiators were obtained from GPC using THF as eluent at a flow rate of 1.0 mL/min at 40 °C given a measured d*n*/d*c* of 0.0548 (also in THF at 40 °C). GPC was performed using *N*,*N*-dimethylformamide with 0.05 M LiBr[25] (Aldrich) as eluent at 60 °C to obtain the polydispersity index of the block copolymers. ^{1}H NMR spectroscopy was performed in deuterated *N*,*N*-dimethylformamide on a Varian Unity+ 300 MHz NMR spectrometer. The absolute molecular weights of the diblock copolymers were determined from ^{1}H NMR, given the absolute molecular weight of the PMA macroinitiator, per previous reports.[15,26] Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer DSC 7 equipped with Intracooler II, at a heating rate of 10 °C/min. Temperature and enthalpy calibrations were performed with indium ($T_{m,peak} = 156.6$ °C) and zinc ($T_{m,peak} = 419.5$ °C) standards. The glass transition temperatures were extracted at the midpoint of a step change in heat capacity during the second heat following controlled cooling at a rate of −5 °C/min. Small-angle X-ray scattering (SAXS) was performed in a long-range sample chamber, and scattered photons were collected on a 2D multiwire gas-filled detector (Molecular Metrology, Inc.). X-rays were produced by a rotating copper anode X-ray generator (Bruker Nonius; $\lambda = 1.5406$ Å) operating at 3.0 kW. Zero angle was calibrated with a silver behenate (CH$_3$(CH$_2$)$_{20}$-COOAg) standard. SAXS profiles were acquired for either 1 h or 2 h. Temperature ramp experiments on the neat block copolymers were performed using a custom-designed hot stage (Molecular Metrology, Inc.) that was calibrated with high-density polyethylene ($T_{m,final} = 131$ °C) and syndiotactic polystyrene ($T_{m,final} = 271$ °C).[26] Aluminum foil was placed on either side of the sample window during these temperature experiments to ensure temperature uniformity across the sample cell. SAXS experiments on the swollen block copolymer samples were performed using a liquid cell (Molecular Metrology, Inc.), with poly(ethylene glycol) methyl ether methacrylate ($M_n = 1100$ g/mol, $T_{m,final} = 33$ °C) and poly(*trans*-isoprene) ($T_{m,final} = 61$ °C) as calibration standards.

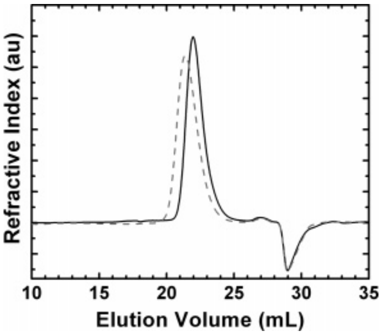

Figure 1. Gel permeation chromatography traces with *N*,*N*-dimethylformamide (0.05 M LiBr) as the eluent at 1 mL/min of PMA macroinitiator ($M_n = 13.2$ kg/mol, $M_w/M_n = 1.02$; values extracted from GPC with tetrahydrofuran as eluent; solid line) and PMA/PHD$_{75}$ ($M_n = 23.8$ kg/mol, $M_w/M_n = 1.10$; dashed line).

Results and Discussion

The synthesis of PMA macroinitiators and PMA/PHD diblock copolymers by ATRP resulted in well-controlled polymers with narrow molecular weight distributions. Figure 1 shows the GPC traces for a PMA macroinitiator ($M_n = 13.2$ kg/mol, $M_w/M_n = 1.02$; solid line) and PMA/PHD$_{75}$ ($M_n = 23.8$ kg/mol, $M_w/M_n = 1.10$; dashed line). Both GPC traces are narrow and monomodal, and the GPC trace of the diblock copolymer is shifted to a lower elution volume from that of the macroinitiator, indicating an increase in molecular weight. The composition of DMAEMA in the PHD block for this particular diblock copolymer, as determined by ^{1}H NMR, is 75.3 mol %. This composition is the same as the monomer feed composition, which is expected for copolymerizations of HEMA and DMAEMA in DMSO given that both the monomer reactivity ratios are near unity.[16]

To assess the solid-state morphology of PMA/PHD, the diblock copolymers were molded into 0.25 mm thick samples

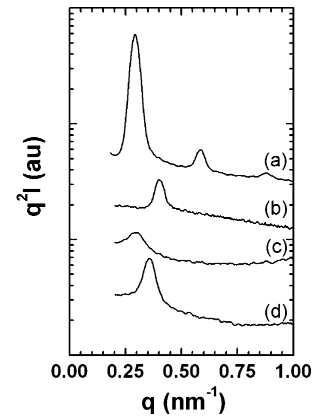

Figure 2. Small-angle X-ray scattering profiles of neat PMA/PHD diblock copolymers of (a) PMA/PHD$_{75}$, (b) PMA/PHD$_{63}$, (c) PMA/PHD$_{50}$, and (d) PMA/PHD$_{28}$.

in a melt press at 90 (PMA/PHD$_{75}$ and PMA/PHD$_{63}$) or 110 °C (PMA/PHD$_{50}$ and PMA/PHD$_{28}$). The samples were then annealed for 48 h at the specified molding temperatures in a vacuum oven. The molding and annealing temperatures were chosen to be above the glass transition temperatures of both blocks ($T_{g,\mathrm{PMA}} = 12.5$ °C; $T_{g,\mathrm{PHD}}$ ranges from 30.5 to 82.0 °C, depending on composition[16]). One-dimensional SAXS profiles of the molded PMA/PHD samples, collected at room temperature, are shown in Figure 2. The SAXS profile of PMA/PHD$_{75}$ (Figure 2a) exhibits a narrow and intense primary peak at $q^* = 0.290$ nm^{-1} and higher-order reflections at q/q^* ratios of 2 and 3, consistent with that of an alternating lamellar morphology. The SAXS profiles of PMA/PHD$_{63}$ (Figure 2b), PMA/PHD$_{50}$ (Figure 2c), and PMA/PHD$_{28}$ (Figure 2d) exhibit primary peaks at $q^* = 0.393$, 0.292, and 0.352 nm^{-1}, respectively. Given the volume fractions of PHD (in Table 1), the PMA/PHD diblock copolymers examined in this study should all adopt an alternating lamellar morphology.

With the exception of the SAXS profile of PMA/PHD$_{75}$ (Figure 2a), however, the SAXS profiles of the other diblock copolymers (Figure 2b−d) do not exhibit any higher-order reflections. We attribute the absence of higher-order reflections in the SAXS profiles of PMA/PHD$_{63}$, PMA/PHD$_{50}$, and PMA/PHD$_{28}$ to two factors: that these block copolymers are not particularly strongly segregated and that the electron density contrast between PMA and PHD is low. Visual inspection of PMA/PHD$_{75}$ and PMA/PHD$_{63}$ indicate that these diblock copolymers flow under their own weight above 110 °C. This observation is accompanied by a significant broadening of the primary peak in the SAXS profiles acquired between 100 and 110 °C. We also observe a broadening of the primary peak in the temperature ramp SAXS profiles of PMA/PHD$_{28}$ at 140 °C. Both experimental observations suggest order−disorder transition temperatures below 150 °C for the PMA/PHD diblock copolymers in this study. Quantitative determination of the order−disorder transition temperatures of these diblock copolymers, however, is difficult due to a competing transesterification reaction[27] that induces cross-linking of the PHD above 100 °C. Furthermore, the electron density contrast between PMA/PHD changes significantly with DMAEMA content. The change in electron density contrast with DMAEMA content can be seen in the primary peak intensities of the individual SAXS profiles of the diblock copolymers. While PMA/PHD$_{75}$ exhibits a narrow and intense primary peak above background, the primary peak intensities of PMA/PHD$_{63}$, PMA/PHD$_{50}$, and PMA/PHD$_{28}$ are all significantly reduced, with the primary peak in the SAXS profile of PMA/PHD$_{50}$ being the weakest. Electron density calculations for the PMA and PHD blocks based on polymer densities and chemical compositions of the PHD block (see Table 1) are consistent with our observations. Specifically, PHD$_{75}$ is more electron-rich than PMA; the ratio of the electron densities of PHD$_{75}$ and PMA in PMA/PHD$_{75}$ is 1.044. The ratio of electron densities of PHD and PMA in PMA/PHD$_{63}$, PMA/PHD$_{50}$, and PMA/PHD$_{28}$ are 1.022, 1.005, and 0.9769, respectively. For reference, the same calculations carried out for PS/PI yields an electron density contrast of 1.121.[28] We thus believe that it is the combination of low segregation strength and weak electron density contrast in PMA/PHD that has made morphological assessment of neat PMA/PHD$_{63}$, PMA/PHD$_{50}$, and PMA/PHD$_{28}$ diblock copolymers by SAXS difficult.

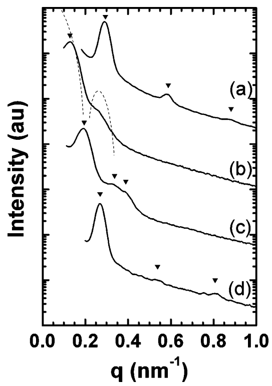

Figure 3. Small-angle X-ray scattering profiles of PMA/PHD$_{75}$ under different conditions: (a) neat (▼ placed at q/q^* ratios of 1, 2, and 3), (b) concentrated aqueous solution at $T = 22$ °C (form factor for 22 nm spheres shown as dashed curve), (c) concentrated aqueous solution at $T = 37$ °C (▼ placed at q/q^* ratios of 1, $\sqrt{3}$, and $\sqrt{4}$), and (d) concentrated aqueous solution at $T = 52$ °C (▼ placed at q/q^* ratios of 1, 2, and 3).

Reversible Phase Transformations of a Concentrated PMA/PHD$_{75}$ Aqueous Solution. Previously annealed, SAXS-verified ordered PMA/PHD$_{75}$ samples (0.08−0.25 g) were placed in approximately 50 mL of deionized water and were allowed to equilibrate for 24 to 48 h. PMA/PHD$_{75}$ swells significantly but does not dissolve in water. At room temperature, the swollen sample consists of approximately 70% water by total mass. The water uptake at specific temperatures appears to be independent of the amount of water the specimen is immersed in. It has been previously demonstrated that the swellability of polystyrene-*b*-poly(acrylic acid), PS/PAA, diblock copolymers at temperatures above the glass transition temperature of the PS block is determined by the hydrophobicity of PS and the degree of ionization of PAA.[29,30] In our system, PMA is the hydrophobic component that prevents the diblock copolymer from dissolution in water. Additionally, since poly(HEMA) only swells and is not completely soluble in water, its incorporation within the PHD block further suppresses solubility. When immersed in water for extended periods of time, PMA/PHD$_{75}$ remains optically clear and homogeneous. We can, however, ionize the DMAEMA units within the PHD block when we immerse PMA/PHD$_{75}$ in an aqueous buffer below the pKa of DMAEMA at 7.5.[12] Swelling the diblock copolymer under these circumstances results in partial dissolution and macroscopic disintegration of the sample.

Figure 3 contains the SAXS profiles of the concentrated block copolymer solution at three representative temperatures (22, 37, 52 °C). The SAXS profiles acquired at a specific temperature are identical whether we approach this temperature by heating or cooling. The SAXS profile of neat PMA/PHD$_{75}$ (Figure 3a) is also included for comparison. The SAXS profile collected on the concentrated PMA/PHD$_{75}$ solution at 22 °C (Figure 3b) exhibits a primary peak at $q^* = 0.128$ nm^{-1}, which is significantly lower than the primary peak position in the SAXS profile acquired on the neat polymer ($q^* = 0.290$ nm^{-1}). Figure 3b also exhibits a broad bump between $q = 0.24-0.33$ nm^{-1}. This bump is consistent with a form factor maximum for spheres with an average radius of 22 nm (dashed curve).[31] Given that water is only absorbed in the PHD phase and not in PMA, PMA must constitute spheres in a PHD matrix. The absence of higher-order structure factor peaks and the broad primary peak (fwhm $= 0.074$ nm^{-1}; compared to the neat block copolymer) in the SAXS profile at 22 °C indicates that the specimen is disordered. Characteristically similar SAXS profiles have previously been described as a disordered, interacting micellar morphology.[8]

The SAXS profile collected at 37 °C (Figure 3c) exhibits a primary peak at $q^* = 0.190$ nm^{-1} (fwhm $= 0.066$ nm^{-1}) with higher-order reflections at q/q^* ratios of $\sqrt{3}$ and $\sqrt{4}$, suggestive of a hexagonally packed cylindrical morphology. Since PMA does not sorb water,[23] PMA must form the discrete cylinders in the water-swollen PHD matrix. The morphological transformation from disordered micelles to ordered PMA cylinders on increasing temperature thus implies a smaller water uptake at 37 °C compared to that at 22 °C. We attribute this deswelling in the PHD matrix to a decrease in hydrophilicity of the DMAEMA units with increasing temperature.[32] In aqueous poly(DMAEMA) homopolymer solutions, this decrease in hydrophilicity gives rise to the presence of an LCST at 46 °C,[13] below which the solution is homogeneous and above which the polymer becomes completely insoluble and precipitates out of solution.[32] In PMA/PHD, the PMA block and the HEMA units in the PHD block serve to limit the solubility of the diblock copolymer in water. We are thus able to reversibly access different morphologies associated with states of intermediate water uptake in PMA/PHD system. We have attempted to track the kinetics of transformation from disordered micelles (D) to hexagonally packed cylinders (H) in PMA/PHD$_{75}$ and found the transition to be fast. D to H transformations are generally completed in less than 1 h (the time required to obtain a single SAXS profile).

The SAXS profile of the same concentrated aqueous PMA/PHD$_{75}$ solution collected at 52 °C (Figure 3c) exhibits a primary peak at $q^* = 0.269$ nm^{-1} (fwhm $= 0.047$ nm^{-1}) and higher-order reflections at q/q^* ratios of 2 and 3. The primary peak position at 52 °C now approaches that of the neat diblock copolymer. The spacing of the higher-order reflections indicates that the PMA/PHD$_{75}$ solution adopts a lamellar morphology at 52 °C and suggests that the sample has undergone a second morphological transition from H to alternating lamellae (L) on heating. Previous reports on phase transformations in concentrated block copolymer solutions have relied on tuning both the polymer concentration and temperature[1-9] so multiple samples at varying concentrations were required to access changes in morphologies. In our case, we have been able to traverse a large phase space with a single specimen of PMA/PHD$_{75}$ in water by changing temperature alone. We attribute the expanded range of morphological transitions in the concentrated PMA/PHD$_{75}$ solution to the presence of functional DMAEMA units within the PHD block. Specifically, the change in hydrophilicity of the DMAEMA units as a function of temperature augments the swelling characteristics; we are thus able to access multiple morphologies over a narrow temperature window (ΔT = 30 °C).

As with the transition from D to H, the H to L transition is also completed in less than 1 h. Subsequent cooling of the PMA/PHD$_{75}$ solution to 37 or 22 °C results in a morphological transition back to H or D, respectively. The transition back to H or D, however, is significantly slower compared to the morphological transformations we observe on heating, occurring over >10 h. Drastically different rates of phase transformation on heating and cooling have previously been reported for PS/PI and PS/polydimethylsiloxane block copolymers in selective solvents.[1,33]

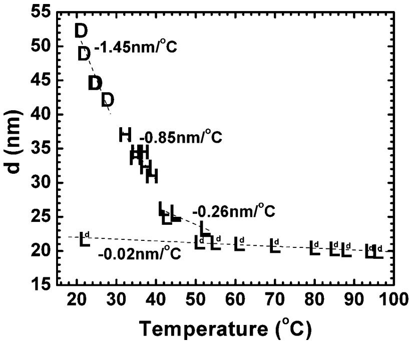

Figure 4. Characteristic spacing of the concentrated aqueous solution of PMA/PHD$_{75}$ at different temperatures. D indicates a disordered, micellar morphology, while H and L represent hexagonally packed cylindrical and lamellar morphologies, respectively. L^d represents data points that were collected on neat PMA/PHD$_{75}$ as a function of temperature.

In Figure 4, we have plotted the characteristic spacing (d, where $d = 2\pi/q$) of the concentrated aqueous PMA/PHD$_{75}$ solution as a function of temperature. Each data point represents an individual SAXS profile. The data points are labeled D, H, or L depending on which morphology the sample exhibits at the specified temperatures. Figure 4 shows the succession from D to H to L with increasing temperature; these phases are accessible reversibly as the individual SAXS profiles were collected at random on both heating and cooling. At low temperatures (T < 32 °C), the concentrated aqueous PMA/PHD$_{75}$ solution forms disordered micelles with an average correlation distance between micelles >40 nm. This correlation distance decreases with increasing temperature at a rate of −1.45 nm/°C. At intermediate temperatures (32 °C < T < 42 °C), the concentrated aqueous block copolymer solution adopts a hexagonally packed cylindrical morphology. The characteristic hexagonal spacing decreases with increasing temperature, at a rate of −0.85 nm/°C. At high temperatures (T > 42 °C), the PMA/PHD$_{75}$ solution adopts an alternating lamellar morphology; its characteristic lamellar spacing also decreases with increasing temperature, at a rate of −0.26 nm/°C. While concentrated solutions of PS/PI in selective solvents and poly(ethylene oxide)-*b*-poly(propylene oxide), PEO/PPO, in water swell with increasing temperarture,[11] concentrated solutions of poly(ethylene oxide)-*b*-poly(butylene oxide), PEO/PBO, have been reported to deswell with increasing temperature due to the hydrophobicity of the BO segments.[7] In addition to the hydrophobicity of the MA segments, we attribute deswelling in the concentrated PMA/PHD$_{75}$ solution to a decrease in hydrophilicity of the DMAEMA units with increasing temperature.[13] As a reference, we have also plotted the characteristic lamellar spacing of the neat PMA/PHD$_{75}$ (L^d) as a function of temperature in Figure 4. In PMA/PHD$_{75}$, the characteristic spacing also decreases with increasing temperature, due to a decreasing χ with temperature. The decrease in d in the neat block copolymer, however, is significantly smaller (−0.02 nm/°C) compared to those observed for the different morphologies in the concentrated block copolymer solution.

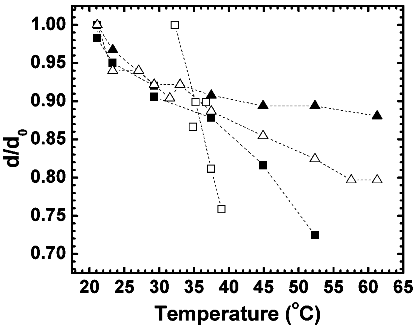

Figure 5. Normalized characteristic spacings of cylinder-forming concentrated aqueous solutions of PMA/PHD of varying DMAEMA content (□ = PHD$_{75}$, ■ = PHD$_{63}$, △ = PHD$_{50}$, and ▲ = PHD$_{28}$) at different temperatures. The reference characteristic spacing, d_0, is taken at the temperature at which the hexagonally packed cylindrical morphology is first observed in these concentrated block copolymer solutions during temperature ramp experiments. Dashed lines are added for clarity.

Concentrated Aqueous Solutions of PMA/PHD$_{63}$, PMA/PHD$_{50}$, and PMA/PHD$_{28}$. It has been reported that the temperature-sensitive nature of poly(DMAEMA) can be tailored by copolymerizing DMAEMA with other hydrophilic monomers.[13] To demonstrate the tunability of the PMA/PHD system, we carried out temperature-response experiments on concentrated aqueous block copolymer solutions of PMA/PHD$_{63}$, PMA/PHD$_{50}$, and PMA/PHD$_{28}$. Unlike the concentrated solution of PMA/PHD$_{75}$ which exhibits a disordered micellar phase, these concentrated aqueous block copolymer solutions readily adopt a hexagonally packed cylindrical morphology at room temperature. The characteristic spacings of each of the concentrated aqueous PMA/PHD solution decrease with increasing temperature indicating deswelling of the H phase. Only the concentrated solution of PMA/PHD$_{63}$ undergoes a phase transformation from H to L (at 54 °C) in the temperature range we explored. The other two concentrated block copolymer solutions retain the H morphology over the entire temperature window. The range of morphologies accessible by concentrated solutions of PMA/PHD thus appears to decrease with decreasing DMAEMA content. This observation is consistent with the notion that the swelling and deswelling characteristics of PMA/PHD are governed by the hydrophilicity of DMAEMA, which in turn is temperature dependent.

We have chosen to focus on the thermal response of concentrated aqueous PMA/PHD solutions in the H phase. For ease of comparison, we compared the characteristic spacing of the hexagonal lattice at given temperatures, d, with the characteristic spacing of the concentrated block copolymer solution when it first exhibited the H phase during our temperature ramp experiments (d_0; so d_0 is the characteristic spacing of the concentrated solutions at room temperature for solutions involving PMA/PHD$_{63}$, PMA/PHD$_{50}$, and PMA/PHD$_{28}$ while d_0 is the characteristics spacing of the concentrated solution at 32 °C for the PMA/PHD$_{75}$ solution). The normalized characteristic spacings, d/d_0, for all four concentrated block copolymer solutions in the H phase are plotted in Figure 5 (□ = PMA/PHD$_{75}$, ■ = PMA/PHD$_{63}$, △ = PMA/PHD$_{50}$, ▲ = PMA/PHD$_{28}$). We have connected successive data points with dashed lines for clarity. The temperature dependence of deswelling within the H phase appears to be strongest in the concentrated solution of PMA/PHD$_{75}$, and it weakens with decreasing DMAEMA content. Decreasing the DMAEMA content in the block copolymers thus not only impacts the range of morphologies accessible by concentrated aqueous solutions of PMA/PHD, it also dramatically influences the temperature response of the deswelling characteristics.

Conclusions

We have successfully synthesized a series of PMA/PHD amphiphilic diblock copolymers with varying DMAEMA content. We observe reversible morphological transitions from disordered, interacting spherical micelles to hexagonally packed cylinders to alternating lamellae in a concentrated aqueous solution of PMA/PHD$_{75}$ by varying temperature alone. The swelling characteristics and the wide range of morphologies accessible in these concentrated aqueous block copolymer solutions are attributed to a decrease in hydrophilicity of the DMAEMA units within the PHD block with temperature. We are further able to tune the temperature response of these concentrated aqueous PMA/PHD copolymer solutions by adjusting the DMAEMA content at the onset of synthesis. In this manner, we are able to design block copolymers that exhibit zero, one, or multiple morphological transformations in the concentrated solution regime over a narrow temperature range, and we are similarly able to tune the swelling response of these concentrated block copolymer solutions exhibiting a particular morphology.

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