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Photochemical and Thermal Isomerizations of Azobenzene-Containing Amphiphilic Diblock Copolymers in Aqueous Micellar Aggregates and in Film

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ABSTRACT: Homopolymers of azobenzene methacrylates (azo) and their diblock copolymers with 2-(dimethylamino)ethyl metharylate (DMAEMA) were synthesized via atom transfer radical polymerization (ATRP). Polymers of cyano- and butoxy-substituted azobenzenes exhibited liquid crystalline textures. Water-soluble diblock copolymers could be obtained with a long DMAEMA block and a short azo block. These diblock copolymers self-assembled into polymeric micelles with core−shell structure in aqueous solutions. The rates of trans−cis photoisomerization were almost the same for the DMAEMA copolymers of 6-[4-phenylazo]phenoxy]hexyl methacrylate (PPHM), p($DMAEMA_{172}$-*b*-$PPHM_9$), and 6-[4-(4-cyanophenylazo)phenoxy]hexyl methacrylate (CPHM), p($DMAEMA_{172}$-*b*-$CPHM_7$), whereas slightly slower rates were observed for the copolymer of 6-[4-(4-butoxyphenylazo)phenoxy]hexyl methacrylate (BPHM), p($DMAEMA_{172}$-*b*-$BPHM_7$), most likely due to steric hindrance presented by the bulky butoxy group. The rates in aqueous micellar solutions were only marginally faster than those in films for all the three diblock copolymers. In contrast, marked rate differences for the thermal cis−trans isomerization of p($DMAEMA_{172}$-*b*-$CPHM_7$) were observed in film and in solution due to the donor−acceptor effect of CPHM. The observation of a sizable rate difference in different environment for p($DMAEMA_{172}$-*b*-$CPHM_7$) suggests that a rotational mechanism might be operative for these water-soluble amphiphilic diblock copolymers.

Introduction

Azobenzene-containing polymers are widely studied because of their potential applications in many fields which include optical data storage,[3,4] liquid crystal displays,[5] and holographic surface relief gratings.[6,7] The photoresponsive properties of the polymers are based on the trans-to-cis and the cis-to-trans photoisomerizations of azobenzene which lead to considerable changes in their molecular shape and dipole moments.[8,9] In addition, thermal cis-to-trans isomerization also occurs because the trans form has an energy lower by about 48 kJ mol^{-1}.[10] The mechanistic investigation of the thermal isomerization of azobenzene has been a subject of considerable interest because two different mechanisms: (i) inversion or (ii) rotation are possible.[10−16] The photoresponsiveness of azobenzene has also been exploited to induce changes of the aggregation properties. Reversible release control of organic solubilizates using photoresponsive micelles formed by azobenzene-linked cationic surfactants have been reported by Orihara et al.[17] Very recently, water-soluble azobenzene-centered dendrimers have been reported by Momotake et al.[18] The systems are considered to be potential drug delivery carriers which could be regulated by light. However, the aggregation behavior of the dendrimers has not been reported. One of the main advantageous properties of polymeric micelles or aggregates as drug/genes delivery carriers over their low molecular weight analogues is their much lower critical micelle concentration (cmc) or critical aggregation concentration (cac). Wang et al.[19] have recently reported the synthesis of azobenzene-containing amphiphilic diblock copolymers with poly(acrylic acid) (PAA) forming the hydrophilic block. However, the diblock copolymer is not soluble in water. Polymeric aggregates were formed in water/dioxane solvent mixture, and significant light-induced changes in aggregate morphology were observed. We have recently reported the synthesis of diblock copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with azobenzene methacrylates via ATRP.[20] Diblock copolymers with a long DMAEMA block relative to the azobenzene block are soluble in water and form core−shell micelles. These water-soluble azobenzene polymeric micelles, which were prepared for the first time, may exhibit unique photochemical and thermal isomerization properties. In this paper, the isomerization rates of these polymeric micelles in aqueous solutions and in films are described.

Experimental Section

Syntheses. The synthesis of azobenzene (azo) methacrylate monomers and p(DMAEMA-*b*-azo) diblock copolymers by ATRP have been reported in the previous paper.[20] The synthetic route of p(DMAEMA-*b*-azo) diblock copolymers via ATRP is outlined in Scheme 1. The ^{1}H NMR of poly($DMAEMA_{172}$-*b*-$BPHM_7$) is shown in Figure 1.

Characterization. The ^{1}H NMR spectra of the block copolymers were recorded using a Bruker DRX400 instrument. An Agilent 1100 series GPC system equipped with a LC pump, PLgel 5μm MIXED-C column, and RI detector was used to determine polymer molecular weights and molecular weight distributions. The column was calibrated with narrow molecular weight polystyrene standards. HPLC grade THF contain-

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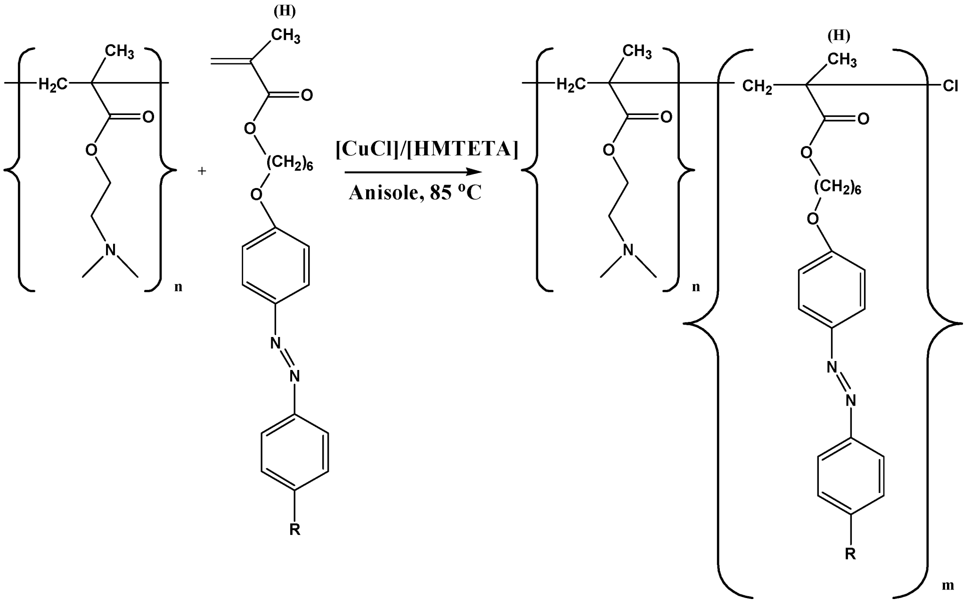
Scheme 1. Synthesis Route of p(DMAEMA-*b*-azo methacrylates)



ing 1% triethylamine stabilized with BHT was used as the mobile phase. The flow rate was maintained at 1.0 mL/min.

The transition temperatures were recorded using a Perkin-Elmer PYRIS diamond DSC differential scanning calorimeter (heating and cooling rates: 20 °C/min). UV−vis spectra were recorded with a Cary 50 Bio UV−vis spectrophotometer equipped with a digital temperature controller. UV irradiation was performed at 366 nm with the light intensity 670 μW/cm^2. Polymer films were spin-coated using Specialty Spin-coater, model P6700 series, from THF solution (4 wt %) at 500 rpm onto a quartz surface.

Laser Light Scattering (LLS). A Brookhaven BI-200SM goniometer system equipped with a 522-channel BI9000AT digital multiple τ correlator was used to perform dynamic light scattering experiments. The inverse Laplace transform of REPES in the Gendist software package was used to analyze the time correlation functions with probability of reject setting at 0.5. Deionized water was used from the Millipore Alpha-Q purification system equipped with a 0.22 μm filter. Polymer solutions were filtered through a 0.2 μm filter for light scattering experiments. A PolyScience water bath was used for temperature control. The power-adjustable argon ion laser with a wavelength of 488 nm was used as the light source.

Results and Discussion

Synthesis of Amphiphilic Diblock Copolymers. The synthesis of the azo methacrylate homopolymers and azo diblock copolymers with DMAEMA by ATRP has been reported in a previous paper.[20] Because of the high hydrophobicity of the azobenzene moiety, only diblock copolymers with long hydrophilic DMAEMA block and short azo block (~10 monomer units) were

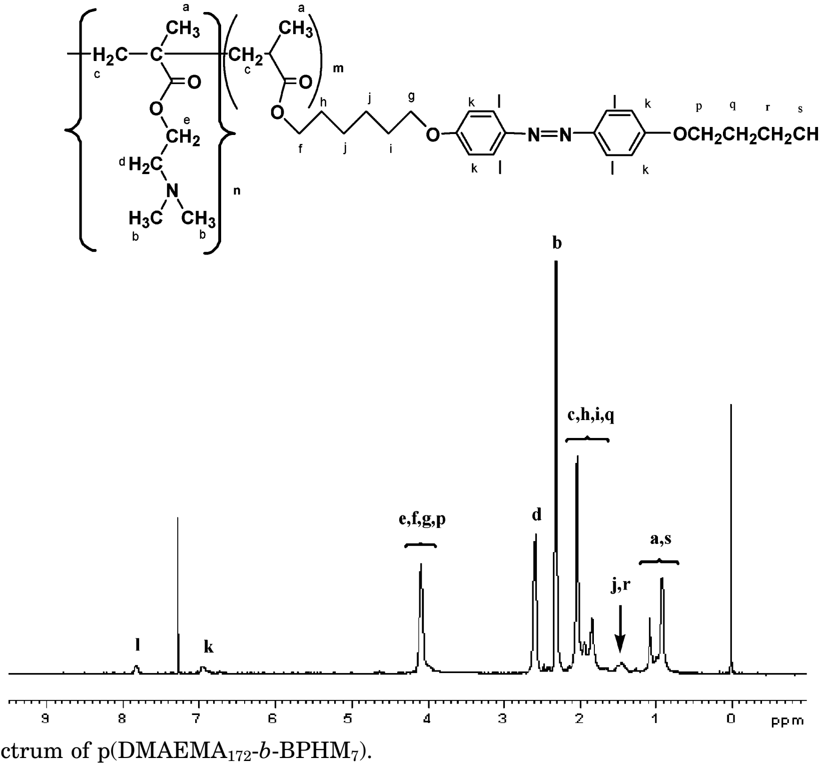


Figure 1. ^{1}H NMR spectrum of p(DMAEMA$_{172}$-*b*-BPHM$_7$).

Table 1. Synthesis Conditions and Characteristics of p(BPHM$_{25}$) Homopolymer and p(DMAEMA-*b*-azo methacrylate) Diblock Copolymers

sample	[M$_0$]/[I$_0$]	time (h)	M_n (GPC)	M_n (NMR)^a	PDI
p(BPHM$_{25}$)	50	24	11 100		1.16
p(DMAEMA$_{46}$-*b*-BPHM$_{11}$)	25	7	12 000	12 000	1.15
p(DMAEMA$_{172}$-*b*-BPHM$_7$)	20	5	30 000	29 600	1.13
p(DMAEMA$_{172}$-*b*-PPHM$_9$)	30	24	30 300	29 900	1.14
p(DMAEMA$_{172}$-*b*-CPHM$_7$)	30	5	29 900	29 100	1.20

^{a} Based on M_n (GPC) of p(DMAEMA)$_{172}$.

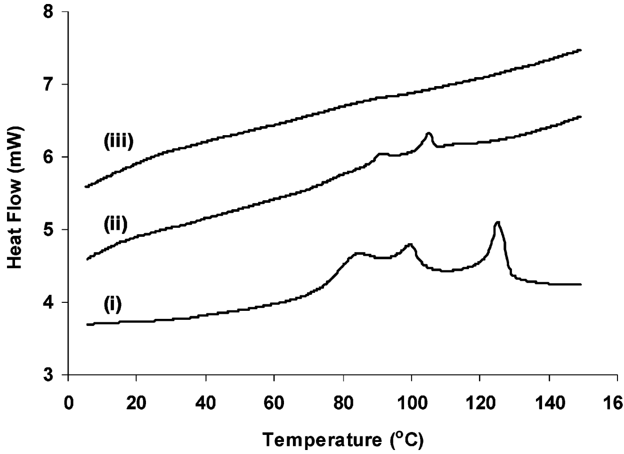


Figure 2. DSC heating curves of (i) p(BPHM$_{25}$), (ii) p(DMAEMA$_{46}$-*b*-BPHM$_{11}$), and (iii) p(DMAEMA$_{172}$-*b*-BPHM$_7$).

soluble in pure water. The synthesis conditions and the characteristics of the polymers are presented in Table 1.

In copolymerization, almost complete incorporation of the azo methacrylate monomers could be obtained with low molecular weight macroinitiator p(DMAEMA)-Cl, whereas macroinitiators of long chain length, i.e., p(DMAEMA)$_{172}$-Cl, did not give full conversion. Because of the long chain length, it is likely that the active chain ends may have been embedded due to chain folding, greatly retarding the propagation rate. Steric hindrance caused by the highly bulky azo methacrylate monomers may also be a factor for the incomplete chain extension.

Thermal Behavior. Butoxy- and cyano-substituted azo methacrylate homopolymers and copolymers display liquid crystalline phase transitions. The DSC heating curves of butoxy-substituted azo homopolymer p(BPHM)$_{25}$ and its diblock copolymer p(DMAEMA$_{46}$-*b*-BPHM$_{11}$) and p(DMAEMA$_{172}$-*b*-BPHM$_7$) are shown in Figure 2. The liquid crystalline phase transitions are clearly observed, i.e., curve (i) for p(BPHM$_{25}$) and (ii) for p(DMAEMA$_{46}$-*b*-BPHM$_{11}$). However, no LC phase transitions were observed for p(DMAEMA$_{172}$-*b*-BPHM$_7$) (curve (iii)) due to the relatively low content of BPHM$_7$ in the copolymer. For homopolymer p(BPHM$_{25}$), the glass transition was observed to occur at T_g = 79 °C, the liquid crystalline transition at 99 °C, and the isotropic transition at 125 °C. The diblock copolymer p(DMAEMA$_{46}$-*b*-BPHM$_{11}$) shows similar DSC thermogram, but with lower corresponding transitions at 76, 92, and 105 °C, respectively, due to the presence of long DMAEMA block. Liquid crystalline textures were observed for p(BPHM$_{25}$) homopolymer (Figure 3a) and p(DMAEMA$_{46}$-*b*-BPHM$_{11}$) diblock copolymer (Figure 3b) under annealing conditions at 113 °C for 5 h and 100 °C for 24 h for 24 h, respectively. No liquid crystalline phase was observed for p(DMAEMA$_{172}$-*b*-BPHM$_7$) due to low azobenzene content, consistent with the DSC thermogram showing no LC transitions for this sample.

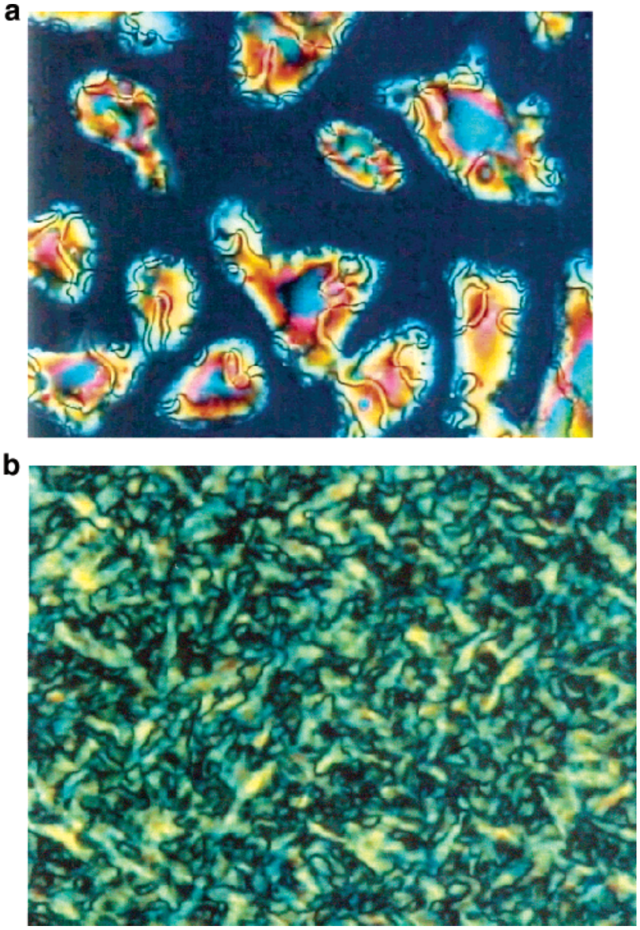


Figure 3. Polarizing optical micrographs (dimension 11 cm × 8.5 cm) for (a) p(BPHM$_{25}$) (113 °C, 200×) and (b) p(DMAEMA$_{46}$-*b*-BPHM$_{11}$) (100 °C, 500×).

Aggregation Behavior in Aqueous Solutions. The formation of micelles was established by laser light scattering (LLS) studies. All the three azo methacrylate amphiphilic block copolymers formed core−shell micelles, with R_h values of 31 nm for p(DMAEMA$_{172}$-*b*-BPHM$_7$), 26 nm for p(DMAEMA$_{172}$-*b*-CPHM$_7$), and 32 nm for p(DMAEMA$_{172}$-*b*-PPHM$_9$).[20] Figure 4a shows the decay time distribution functions of p(DMAEMA$_{172}$-*b*-CPHM$_7$) aqueous solution at different scattering angles. Only one decay mode is evident in the relaxation time distribution function, and the distribution function shifts to lower relaxation time with increasing scattering angles. Figure 4b shows that the decay rate Γ is q^2 dependent, suggesting the decay mode is caused by the translational diffusion of the particles in solutions. This implies only one type of particle was present in the solution. p(DMAEMA$_{172}$-*b*-BPHM$_7$) and p(DMAEMA$_{172}$-*b*-PPHM$_9$) show the same characteristic features. The R_h values were found to be concentration independent, as shown in Figure 5, suggesting the aggregates were of same core−shell structures.

Photoisomerization and Thermal Isomerization. The trans−cis photoisomerization and cis−trans thermal isomerization of p(DMAEMA$_{172}$-*b*-PPHM$_9$), p(DMAEMA$_{172}$-*b*-BPHM$_7$), and p(DMAEMA$_{172}$-*b*-CPHM$_7$) in films and in aqueous solutions were studied. The polymer samples were irradiated with 366 nm UV light

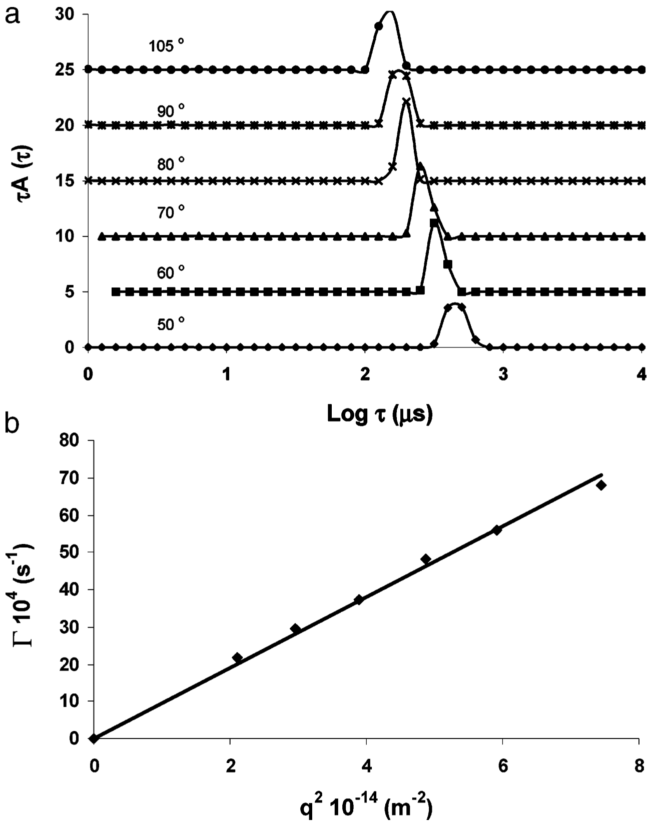


Figure 4. (a) Decay time distribution functions of 0.15 wt % aqueous solutions of p(DMAEMA$_{172}$-*b*-CPHM$_9$) for different angles at 25 °C. (b) Plot of Γ against q^2.

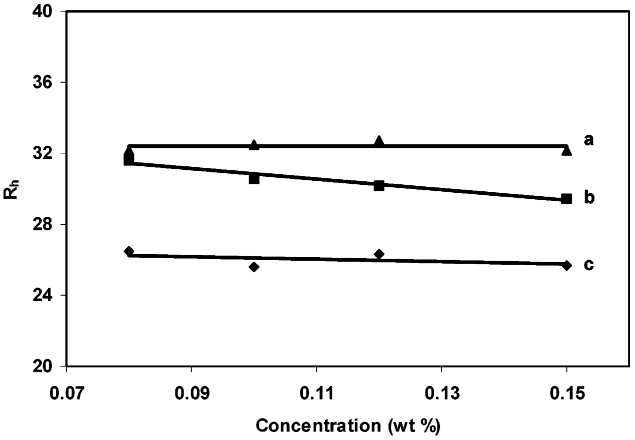


Figure 5. Plots of R_h vs concentration of (a) p(DMAEMA$_{172}$-*b*-PPHM$_9$), (b) p(DMAEMA$_{172}$-*b*-BPHM$_7$), and (c) p(DMAEMA$_{172}$-*b*-CPHM$_7$).

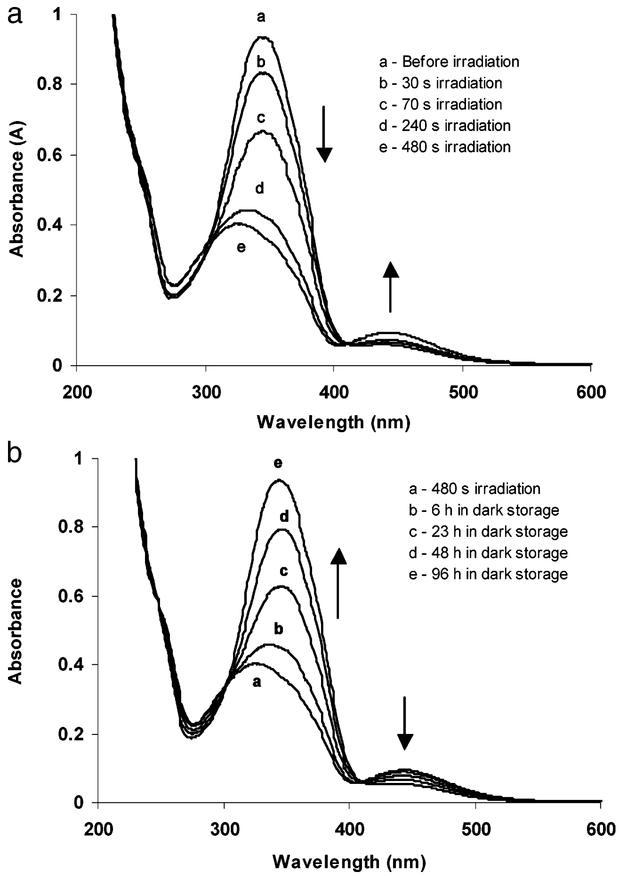


Figure 6. UV−vis spectra of p(DMAEMA$_{172}$-*b*-PPHM$_7$) film (a) before and after UV irradiation at 366 nm reaching the photostationary state and (b) after in the dark keeping at 23 °C.

until it reached the photostationary state. The samples were then kept in the dark where the reverse cis-to-trans isomerization occurred due to thermal energy as the trans form is thermodynamically more stable. In aqueous solutions, the copolymers formed core−shell micelles. The spectra changes with different irradiation time and the reverse cis−trans thermal isomerization at different time intervals are shown in Figure 6 for p(DMAEMA$_{172}$-*b*-PPHM$_9$) in films. Similar behavior was observed in aqueous solutions. The UV−vis spectra of p(DMAEMA$_{172}$-*b*-BPHM$_7$) and p(DMAEMA$_{172}$-*b*-CPHM$_7$) show similar features. The rate of isomerization was analyzed from the absorbance at 345 nm, corresponding to the $\pi-\pi^*$ transition. The first-order rate constants were determined by fitting the experimental data to eq 1.[21]

$$\ln \frac{A_\infty - A_t}{A_\infty - A_0} = -kt \qquad (1)$$

where A_t, A_0, and A_∞ are the absorbance at 345 nm at time t, time zero, and infinite time, respectively. The first-order kinetic plots for the trans−cis photoisomerizations and cis−trans thermal isomerizations for p(DMAEMA$_{172}$-*b*-PPHM$_9$), p(DMAEMA$_{172}$-*b*-BPHM$_7$), and p(DMAEMA$_{172}$-*b*-CPHM$_7$) in films are shown in Figures 7 and 8, respectively. Similar linear plots were obtained for the three copolymers in aqueous solutions. The corresponding first-order rate constants k_{t-c} (for trans to cis) and k_{c-t} (for cis to trans) obtained are shown in Tables 2 and 3, respectively.

The photoisomerization rates were found to be about the same for p(DMAEMA$_{172}$-*b*-PPHM$_9$) and p(DMAEMA$_{172}$-*b*-CPHM$_7$) films, whereas that of p(DMAEMA$_{172}$-*b*-BPHM$_7$) was clearly slower, by about 35%. Interestingly, the rates of photoisomerization were fractionally slower for all the corresponding copolymers in solutions, again with p(DMAEMA$_{172}$-*b*-BPHM$_7$) being the slowest. In aqueous solution, the diblock copolymers self-assembled into core−shell micelles with the azo block forming the hydrophobic core and DMAEMA block the hydrophilic shell. Apparently, the structural differences of the polymeric micelles and the films did not result in any significant differences in the rate of photoisomerization. Similar results were reported by

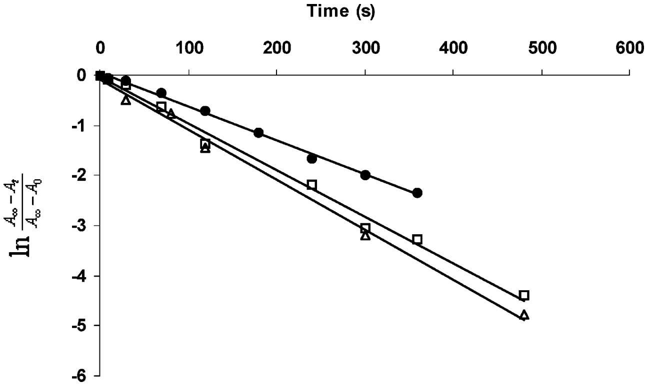


Figure 7. First-order plots for trans−cis isomerization of p(DMAEMA-*b*-azo) (□) p(DMAEMA$_{172}$-*b*-PPHM$_9$), (●) p(DMAEMA$_{172}$-*b*-BPHM$_7$), and (△) p(DMAEMA$_{172}$-*b*-CPHM$_7$) in film.

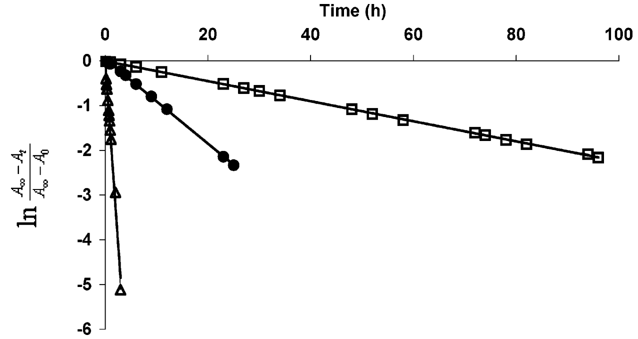


Figure 8. First-order plots for cis−trans thermal isomerization of p(DMAEMA-*b*-azo): (□) p(DMAEMA$_{172}$-*b*-PPHM$_9$), (●) p(DMAEMA$_{172}$-*b*-BPHM$_7$), and (△) p(DMAEMA$_{172}$-*b*-CPHM$_7$) in film.

Paik et al.[10] where polymers containing azobenzene residue in the side chains were found to photoisomerize in dilute solutions at approximately the same rate as in bulk above their glass-transition temperatures (T_g).

The photoinduced trans-to-cis isomerization of relatively simple azobenzene surfactants has been discussed by Shang et al.[22] According to the following mechanism

$$\mathrm{A} \underset{k_r}{\overset{\epsilon_A I}{\rightleftharpoons}} \mathrm{A}^* \xrightarrow{k_d} \mathrm{B}$$

where A is the trans isomer and A* is the excited state after photon absorption, B is the cis isomer, I is the beam intensity, k_r and k_d are the rate constants of A* reversing to A and conversing to B, respectively; the experimental first-order rate constant k_{t-c} can then be given by the following expression:

$$k_{t-c} = \epsilon_A I_0 \phi, \quad \text{where } \phi = \frac{k_d}{k_d + k_r}$$

Under the experimental conditions, I_0 is constant, and assuming that ϵ_A values do not vary significantly for similar azobenzene moieties, the value of k_{t-c} will depend on the relative values of k_d and k_r, which in turn are affected by the nature and property of the azobenzene and the environment surrounding the molecule. For the relatively simple azobenzene surfactant molecules, $\phi \sim 1$,[22] indicating $k_d \gg k_r$. However, ϕ may be less than unity for other azobenzene derivatives such as the azo copolymers in this study. Hence, p(DMAEMA$_{172}$-*b*-BPHM$_7$) was found to have a slower trans-to-cis isomerization rate than those of p(DMAEMA$_{172}$-*b*-PPHM$_9$) and p(DMAEMA$_{172}$-*b*-CPHM$_7$) due to the bulky butoxy group in BPHM. The similar values of k_{t-c} in film and in aqueous solution suggest that the relative values of k_d and k_r are not significantly affected in these two different environments.

Table 2. First-Order Rate Constants, k_{t-c}, for the Trans-to-Cis Photoisomerization of p(DMAEMA$_{172}$-*b*-PPHM$_9$), p(DMAEMA$_{172}$-*b*-BPHM$_7$), and p(DMAEMA$_{172}$-*b*-CPHM$_7$) in Film and Aqueous Solution at 23 °C

diblock copolymers	$10^3 k_{t-c}$ (s^{-1})
spin-coated films	
p(DMAEMA$_{172}$-*b*-PPHM$_9$)	9.4 ± 0.3
p(DMAEMA$_{172}$-*b*-BPHM$_7$)	6.5 ± 0.2
p(DMAEMA$_{172}$-*b*-CPHM$_7$)	10.2 ± 0.3
aqueous solutions	
p(DMAEMA$_{172}$-*b*-PPHM$_9$)	11.1 ± 0.3
p(DMAEMA$_{172}$-*b*-BPHM$_7$)	8.7 ± 0.2
p(DMAEMA$_{172}$-*b*-CPHM$_7$)	12. 8 ± 0.2

Table 3. First-Order Rate Constants k_{c-t} for the Cis-to-Trans Thermal Isomerization of p(DMAEMA$_{172}$-*b*-PPHM$_9$), p(DMAEMA$_{172}$-*b*-BPHM$_7$), and p(DMAEMA$_{172}$-*b*-CPHM$_7$) in Film and Aqueous Solution at 23 °C

diblock copolymers	$10^6 k_{c-t}$ (s^{-1})
spin-coated films	
p(DMAEMA$_{172}$-*b*-PPHM$_9$)	6.25 ± 0.04
p(DMAEMA$_{172}$-*b*-BPHM$_7$)	25.6 ± 0.3
p(DMAEMA$_{172}$-*b*-CPHM$_7$)	450 ± 2
aqueous solutions	
p(DMAEMA$_{172}$-*b*-PPHM$_9$)	6.61 ± 0.09
p(DMAEMA$_{172}$-*b*-BPHM$_7$)	25.6 ± 0.1
p(DMAEMA$_{172}$-*b*-CPHM$_7$)	83 ± 2

In contrast, the much slower rates of thermal recovery cis−trans isomerization were vastly different for the three copolymers. In films, slowest rate was observed for p(DMAEMA$_{172}$-*b*-PPHM$_9$). The fastest rate was recorded for p(DMAEMA$_{172}$-*b*-CPHM$_7$), which was about 72 times faster than that of p(DMAEMA$_{172}$-*b*-PPHM$_9$). This is attributed to the donor−acceptor effect. It has been observed that the thermal cis−trans isomerization of the donor−acceptor azobenzene proceeds more efficiently than that of the non-donor−acceptor azobenzene.[11,12,14−16] p(DMAEMA$_{172}$-*b*-CPHM$_7$) has an azobenzene moiety with an electron-donating group (−O−) and an electron-accepting group (−CN) at the 4,4′-positions. Molecules containing electron-donating and electron-accepting ("push−pull") groups effectively increase the energy of the N=N π-bonding orbital and lower the energy of the π^*-antibonding orbital, thus lowering the overall energy of the π−π^* transition.[23] Indeed, the trans absorption maximum of p(DMAEMA$_{172}$-*b*-CPHM$_7$) film (λ_{max} 358 nm) has red-shifted as compared to those of p(DMAEMA$_{172}$-*b*-PPHM$_9$) (λ_{max} 344 nm) and p(DMAEMA$_{172}$-*b*-BPHM$_7$) (λ_{max} 330 nm). Hence, the thermal cis−trans isomerization rate of p(DMAEMA$_{172}$-*b*-CPHM$_7$) is much faster than those of p(DMAEMA$_{172}$-*b*-PPHM$_9$) and p(DMAEMA$_{172}$-*b*-BPHM$_7$).

In solutions, the same trend was again observed. The rates in solutions were almost identical to those in films for p(DMAEMA$_{172}$-*b*-PPHM$_9$) and p(DMAEMA$_{172}$-*b*-BPHM$_7$). However, the rate enhancement due to the donor−acceptor effect of p(DMAEMA$_{172}$-*b*-CPHM$_7$) had diminished considerably in solution, which was only about 12.5 times faster than that of p(DMAEMA$_{172}$-*b*-PPHM$_9$). Interestingly, the rate was about 5.4 times slower ($k_{c-t} = 83 \times 10^{-6}$ s^{-1}) than that in film ($k_{c-t} = 450 \times 10^{-6}$ s^{-1}). It is known that the thermal cis−trans

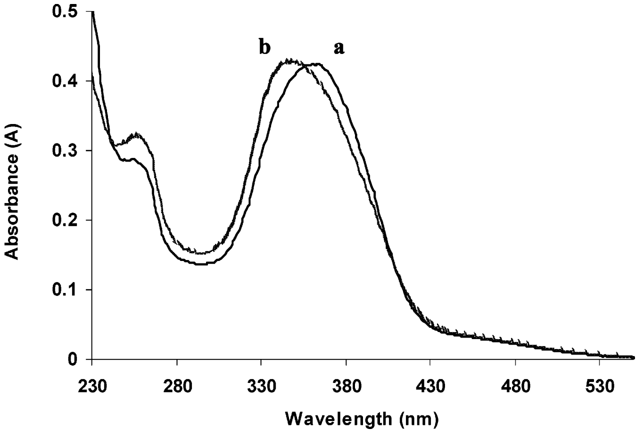


Figure 9. UV−vis spectra of p(DMAEMA$_{172}$-*b*-CPHM$_7$) (a) in film and (b) in aqueous solution (0.15 wt %).

isomerization of azobenzene can proceed via two different mechanisms: (i) rotational mechanism involving rotation about the N=N bond and (ii) inversion mechanism involving flip-flop inversion of one of the nitrogen atoms.[10−16] The essential difference between the two mechanisms is that the rotational mechanism proceeds through a dipolar transition state accompanying a large volume change, and it exhibits a relatively large solvent effect.[11,12,15,16]

It is unlikely that solvation effect by water is operative here as the formation of micelles will shield the core azobenzene from the solvent water. In fact, the core azobenzene was in a more hydrophobic environment than in film. In general, the $\pi-\pi^*$ absorption band of aromatic compounds red shifts in polar solvents due to stabilization of the $\pi-\pi^*$ excited state by polar solvent.[18] The absorbance at the ~346 nm region corresponding to the $\pi-\pi^*$ transition was blue-shifted in aqueous solution as compared to the solid film (Figure 9). The thermal cis−trans isomerization of azobenzenes are slower in less polar environment if they proceed via the rotational mechanism.[11,12,15,16] The observed thermal isomerization rates of p(DMAEMA$_{172}$-*b*-CPHM$_7$), being environment-sensitive, suggests that a rotational mechanism might be operative for this water-soluble amphiphic diblock copolymer. However, further studies are required for the confirmation of actual mechanism.

Conclusions

Diblock copolymers of DMAEMA and azobenzene methacrylate monomers synthesized via ATRP self-assembled into polymeric micelles with core−shell structures in water. This paper reports for the first time the kinetic studies of the photochemical trans−cis isomerization and the reverse thermal cis−trans isomerization of azobenzenes in well-defined polymeric micelle structures. The rates of trans−cis isomerization of azobenzenes in films and in the hydrophobic core of polymeric micelles in aqueous solutions were almost the same for p(DMAEMA$_{172}$-*b*-PPHM$_9$) and p(DMAEMA$_{172}$-*b*-CPHM$_7$), whereas slightly slower rates were observed for p(DMAEMA$_{172}$-*b*-BPHM$_7$) due most probably to the presence of a bulky butoxy group. Marked differences in the rate of thermal cis−trans isomerization were observed for p(DMAEMA$_{172}$-*b*-CPHM$_7$). This is attributed to the donor−acceptor effect of the substituted azobenzene.

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