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Synthesis, NMR Relaxation, and Photoisomerization of Amphiphilic Polyelectrolytes Covalently Tethered with Azobenzene Moieties Having Bulky Hydrophobic Substituents

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ABSTRACT: Amphiphilic terpolymers [consisting of 50 mol % of sodium sulfonate groups, 49.5 mol % of lauryl (La) or cyclododecyl (Cd) groups, and 0.5 mol % of a moiety of azobenzene substituted with a La group (Abz-La) or with a Cd group (Abz-Cd)] were prepared. Reference copolymers [consisting of 99.5 mol % of sodium sulfonate groups and 0.5 mol % of the Abz-La or Abz-Cd residue] were also prepared. In the terpolymers, the Abz-La and Abz-Cd residues were incorporated in the self-organized hydrophobic phases in aqueous solution, while in the reference copolymers, they are exposed to the aqueous phase. The mobility of the hydrophobic groups and azobenzene moieties in the co- and terpolymers in D_2O was estimated by ^1H-NMR relaxation techniques. Spin–lattice and spin–spin relaxation times indicated that the motions of the azobenzene moieties in the terpolymers were highly restricted owing to the self-organization of the hydrophobic groups in aqueous solution. In particular, the hydrophobic self-organization of the Cd groups caused more pronounced restrictions on the motions of the azobenzene moieties than the La groups did. Effects of such motional restrictions on the trans-to-cis photoisomerization and cis-to-trans thermal back-isomerization of the azobenzene moieties were investigated, finding that the former was considerably impeded, while the latter was accelerated. As predicted by the NMR relaxation times, these effects on the isomerizations were more pronounced with the Cd groups than with the La groups; i.e., motional restrictions imposed on the trans isomer and residual strains in the photogenerated cis isomer are larger in the organized Cd phase than in the La phase. These findings indicate that the Cd groups are more densely packed than are the La groups in the self-organized hydrophobic phases presumably because the Cd residue has much less conformational freedoms than does the La residue.

Introduction

Photophysical behavior and photochemical reactivity of a chromophore covalently tethered to an amphiphilic polyelectrolyte can be greatly changed as a result of a macromolecular environmental effect.[1,2] An amphiphilic polyelectrolyte containing a sufficiently high mole fraction of bulky hydrophobic groups adopts a micellelike organized structure in dilute aqueous solution owing to self-aggregation of the hydrophobic residues.[3–7] The hydrophobic microdomain is "rigid and static" in nature in the sense that dynamical motions of the organized hydrophobic groups are considerably restricted.[1,2] This is in contrast to the dynamic nature of conventional surfactant micelles.[8]

When a small mole fraction of a hydrophobic chromophore group is covalently incorporated into such an amphiphilic polyelectrolyte, the chromophore can be encapsulated in the hydrophobic microdomain and forced to experience a rigid and hydrophobic environment.[9–11]

In our previous study, we incorporated azobenzene moieties in amphiphilic polysulfonates bearing bulky hydrophobic groups such as lauryl (La), cyclododecyl (Cd), and adamantyl (Ad) groups.[12] The trans-to-cis photoisomerization of the incorporated azobenzene moieties was significantly impeded, whereas the thermal cis-to-trans back-isomerization was accelerated. We discussed these findings in terms of conformational restrictions imposed on the azobenzene moieties compartmentalized in the hydrophobic microdomains. These restrictive effects on the isomerizations differed for different hydrophobic groups combined to the polysulfonates; i.e., the effect of the Cd groups was significantly larger than that of the La groups, despite the fact that the Cd and La groups are bulky hydrophobic groups having the same number of the carbon atoms. This suggests that the conformational freedoms of the Cd and La groups in the self-organized state are considerably different owing to the difference in packing densities.

In the present study, we attached the same hydrophobic groups to the azobenzene moieties as those in the amphiphilic polyelectrolytes to ensure that the motional freedoms of the azobenzene moieties are directly affected by the self-organization of the hydrophobic groups. We focus our attention on the difference in the packing densities and in the restriction effects between the Cd and La groups on the photoisomerization and the thermal back-isomerization of the azobenzene moieties.

Experimental Section

Materials. Sodium (Anilinomethylene)sulfonate. To a solution of 33.2 g (0.248 mol) of formaldehyde sodium bisulfite in 100 mL of water was added 21.8 g (0.234 mol) of aniline with stirring. The mixture was allowed to stand for 25 min at 70 °C. White needles which separated out upon cooling were collected, washed with cold water and ether, successively, and dried under vacuum: yield 31.7 g (65%).

4-[(4-Aminophenyl)azo]benzoic Acid. To a suspension of 19.3 g (0.141 mol) of 4-aminobenzoic acid in 82 mL of 5.5 M HCl, which was cooled in an ice bath, was added dropwise a 30-mL aqueous solution containing 11.0 g (0.159 mol) of sodium nitrite with stirring. This mixture was added to a 500-mL aqueous solution of 0.86 M sodium acetate containing 37.6 g (0.180 mol) of sodium (anilinomethylene)sulfonate over a period of 30 min under cooling in an ice bath with vigorous stirring. The reaction mixture was allowed to stand overnight at 4 °C. Orange crystals that separated out were collected, washed with water, and dissolved in 1 M NaOH. The alkaline solution was heated at 90 °C for 2 h. After cooling, crystals were filtered and recrystallized from 1 M NaOH. The orange crystals were then dissolved in water followed by the addition of 6 M HCl with stirring at room

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temperature to acidify the solution to pH 2. The orange solid that precipitated out was filtered off, washed with hot water, and dried under vacuum: yield 16.7 g (38.4%); mp >300 °C; ^{1}H NMR (DMSO-d_6) δ 6.3 (s, 2H), 6.7 (d, 2H), 7.7 (d, 2H), 7.7 (d, 2H), 8.1 (d, 2H), 13.0 (s, 1H). Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.40. Found: C, 64.71; H, 4.64, N. 17.42.

4-(Nitrophenyl) 4-[[4-[(Trifluoroacetyl)amino]phenyl]azo]benzoate (I). To a 300-mL pyridine solution containing 9.65 g (40.9 mmol) of 4-[(4-aminophenyl)azo]benzoic acid and 5.69 g (40.9 mmol) of *p*-nitrophenol was added 5.57 g (40.0 mmol) of *p*-nitrophenyl trifluoroacetate. The mixture was stirred at room temperature for 40 min and then heated at 50 °C for 3.5 h. Pyridine was evaporated under reduced pressure. Remaining pyridine was completely removed by azeotropy with toluene. The crude product was recrystallized from benzene/acetone (7/1, v/v) twice to give red needles: yield 17.7 g (96.6%); mp 218–221 °C; ^{1}H NMR (DMSO-d_6) δ 7.6 (d, 2H), 8.0 (m, 6H), 8.4 (d, 4H), 11.6 (s, 1H). Anal. Calcd for $C_{21}H_{13}N_4O_5F_3$: C, 55.03; H, 2.84; N, 12.22. Found: C, 55.18; H, 2.85; N, 12.24.

***N*-Lauryl-4-[(4-aminophenyl)azo]benzamide (II).** To a 50-mL dimethyl sulfoxide (DMSO) solution containing 3.71 g (20.0 mmol) of laurylamine and 2.03 g (30.0 mmol) of imidazole was added a 100-mL DMSO solution containing 6.88 g (15.0 mmol) of I at room temperature. The mixture was stirred for 3 days. Orange solid was collected, washed with ether, dried under vacuum, and then suspended in 400 mL of methanol. To this suspension was added dropwise at room temperature 5 mL of methanolic sodium methylate (25 wt %). The suspension turned a red solution which was refluxed for 2 h. After evaporation of the solvent, the crude product was recrystallized from toluene to give orange needles: yield 0.989 g (39.6%); mp 147–149 °C; ^{1}H NMR (DMSO-d_6) δ 0.9 (t, 3H), 1.3–1.7 (m, 20H), 3.5 (q, 2H), 4.1 (s, 2H), 6.2 (t, 1H), 6.7 (d, 2H), 7.9 (m, 6H). Anal. Calcd for $C_{25}H_{36}N_4O$: C, 73.86; H, 8.43; N, 13.78. Found: C, 73.63; H, 8.37; N, 13.52.

***N*-Lauryl-4-[[4-(methacryloylamino)phenyl]azo]benzamide (Abz(La)MAm).** To a 150-mL tetrahydrofuran (THF) solution containing 2.50 g (6.15 mmol) of II and 18 mL (129 mmol) of triethylamine was added dropwise 12.0 mL (125 mmol) of methacryloyl chloride in 30 mL of THF under cooling in an ice bath over a period of 30 min with stirring. The mixture was stirred for 16 h at 0 °C. To this reaction mixture was added 100 mL of methanol, and the crude product was collected, washed with methanol, and recrystallized from THF/acetone (4/5, v/v) twice to give orange needles: yield 69.2%; mp 227–229 °C; ^{1}H NMR (DMSO-d_6) δ 0.9 (t, 3H), 1.3–1.6 (m, 20H), 2.0 (s, 3H), 3.3 (q, 2H), 5.6 (s, 1H), 5.9 (s, 1H), 7.9–8.1 (m, 8H), 8.6 (t, 1H), 10.1 (s, 1H). Anal. Calcd for $C_{29}H_{40}N_4O_2$: C, 73.07; H, 8.46; N, 11.75. Found: C, 73.14; H, 8.49; N, 11.62.

***N*-Cyclododecyl-4-[(4-aminophenyl)azo]benzamide (III).** To a 45-mL DMSO solution containing 3.66 g (20.0 mmol) of cyclododecylamine and 2.03 g (30.0 mmol) of imidazole was added a 90-mL DMSO solution containing 6.88 g (15.0 mmol) of I at room temperature. The mixture was stirred for 3 days. Orange solid was collected, washed with ether, dried under vacuum, and then suspended in 400 mL of methanol. To this suspension was added dropwise at room temperature 5 mL of methanolic sodium methylate (25 wt %). The suspension turned a red solution which was refluxed for 1.5 h. After evaporation of the solvent, the crude product was recrystallized from toluene/*n*-hexane (1/1, v/v) to give orange needles: yield 2.53 g (41.5%); mp 217–219 °C; ^{1}H NMR (DMSO-d_6) δ 1.2–1.7 (m, 22H), 4.2 (m, 1H), 6.2 (s, 2H), 6.7 (d, 2H), 7.7 (d, 2H), 7.8 (d, 2H), 8.9 (d, 2H), 8.2 (d, 1H). Anal. Calcd for $C_{25}H_{34}N_4O$: C, 73.86; H, 8.43; N, 13.78. Found: C, 73.63; H, 8.37; N, 13.52.

***N*-Cyclododecyl-4-[[4-(methacryloylamino)phenyl]azo]benzamide (Abz(Cd)MAm).** To a 170-mL THF solution containing 2.50 g (6.15 mmol) of III and 17.1 mL (123 mmol) of triethylamine was added dropwise 12.0 mL (125 mmol) of methacryloyl chloride in 30 mL of THF under cooling in an ice bath over a period of 30 min with stirring. The mixture was stirred for 9 h at 0 °C. To the reaction mixture was added 100 mL of methanol, and the crude product was collected, washed with methanol, and recrystallized from THF/acetone (1/1, v/v) twice to give orange needles: yield 30.6%; mp 304–310 °C; ^{1}H NMR (DMSO-d_6) δ 1.3–1.7 (m, 22H), 2.0 (s, 3H), 4.2 (m, 1H), 5.6 (s, 1H), 5.9 (s, 1H), 7.9–8.1 (m, 8H), 10.1 (d, 1H). Anal. Calcd for $C_{29}H_{38}N_4O_2$: C, 73.37; H, 8.07; N, 11.80. Found: C, 73.25; H, 8.07; N, 11.74.

Other Monomers. *N*-Laurylmethacrylamide (LaMAm)[5] and *N*-cyclododecylmethacrylamide (CdMAm)[11] were prepared as reported previously. 2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) was used as received from Nitto Chemical Industry Co.

Polymers. The terpolymers and the reference copolymers were prepared by free-radical polymerization initiated by 2,2′-azobis(isobutyronitrile) (AIBN). A procedure for the terpolymerization is as follows. A glass ampule containing known amounts of Abz(La)MAm (or Abz(Cd)MAm), AMPS, LaMAm (or CdMAm), and AIBN in a *N*,*N*-dimethylformamide (DMF) solution was outgassed by five freeze–pump–thaw cycles on a vacuum line. The sealed ampule was maintained at 60 °C in a water bath. The mixture was poured into a large excess of ether to precipitate the resulting polymer. The polymer was purified by three reprecipitations from methanol into ether and then dissolved in dilute aqueous NaOH. The solution was dialyzed against pure water for 1 week and finally lyophilized. The compositions of the terpolymers were determined by N/C and S/C ratios and absorption spectra. The reference copolymers of AMPS–La(Abz)MAm and AMPS–Cd(Abz)MAm were prepared in a similar manner.

Measurements. ^{1}H-NMR. Proton NMR spectra were obtained with a JEOL EX-270 spectrometer using a deuterium lock at a constant temperature of 40 °C during the whole run. NMR tubes containing 1 wt % D_2O solutions of the co- and terpolymers were outgassed on a vacuum line and flame-sealed prior to the measurements. The resonance due to impurity water in the D_2O solutions was decoupled. Proton spin–lattice relaxation times (T_1) were determined by using a simple inversion–recovery technique with a $180°–\tau–90°$ pulse sequence.[13–15] Proton spin–spin relaxation times (T_2) were determined by using the Carr–Purcell–Meiboom–Gill (CPMG) method.[16]

Photoisomerization. The polymers were dissolved in deionized water, and the pHs of the aqueous solutions were adjusted to 11 at room temperature. The absorbances of the sample solutions were adjusted to 0.5 at 365 nm. The solutions were kept in the dark for a few days at room temperature to ensure that all Abz residues were in the trans form.

For trans-to-cis photoisomerization experiments, a quartz cell with 1-cm light pass containing a sample solution was irradiated with 355-nm light at 25 °C. The cell was set in a temperature-controlled water-circulating holder connected with a magnetic stirrer for mixing of the sample solution during irradiation. The irradiation was carried out with a 500-W xenon arc lamp combined with a Jasco CT-10 monochromator. Absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer at 25 °C.

The cis-to-trans thermal isomerization of the polymer solution, equilibrated by irradiation with 355-nm light, was followed by absorption spectroscopy at 298 K.

Results and Discussion

Syntheses. *N*-Cyclododecyl-4-[[4-(methacryloylamino)phenyl]azo]benzamide (Abz(Cd)MAm) was synthesized according to the sequence of reactions shown in Scheme I. 4-[(4-Aminophenyl)azo]benzoic acid was prepared by a coupling reaction between sodium (anilinomethylene)sulfonate and 4-diazobenzoic acid which was generated from 4-aminobenzoic acid by treating with sodium nitrite in acidic aqueous solution. *p*-Nitrophenyl active ester of 4-[(4-aminophenyl)azo]benzoic acid was prepared by the reaction with an equimolar amount of *p*-nitrophenyl trifluoroacetate in the presence of *p*-nitrophenol in pyridine. The yield of this reaction was almost quantitative.

An advantage of this reaction was that the amino group was almost quantitatively trifluoroacetylated. This amino-blocked active ester of the azo compound was reacted with cyclododecylamine in the presence of imidazole. The trifluoroacetylamino group was readily hydrolyzed by

Scheme I. Synthesis of Abz(Cd)MAm

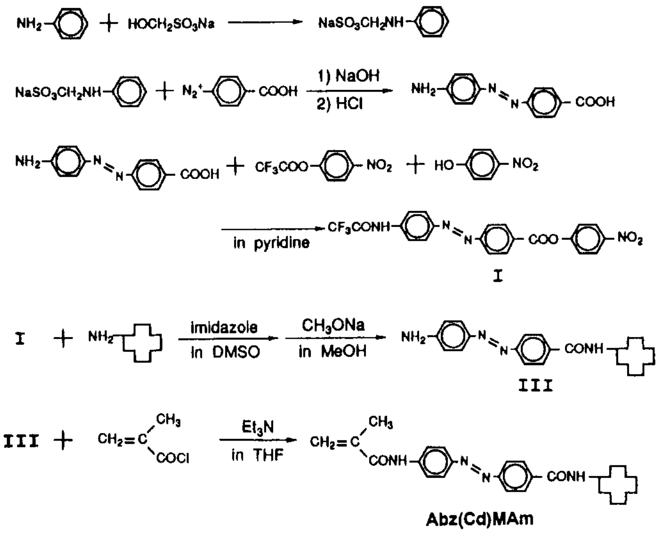
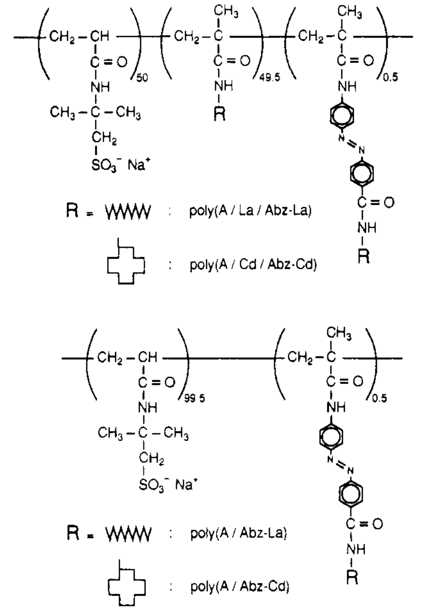


Chart I. Structural Formulas of the Co- and Terpolymers



treatment with a catalytic amount of sodium methylate in methanol to give free amine III.

The Schotten–Baumann type reaction of III with methacryloyl chloride in the presence of triethylamine in THF gave the monomer Abz(Cd)MAm.

N-Lauryl-4-[[4-(methacryloylamino)phenyl]azo]benzamide (Abz(La)MAm) was synthesized in an analogous manner using laurylamine in place of cyclododecylamine.

Small mole fractions of the azo monomers Abz(Cd)MAm and Abz(La)MAm were copolymerized with AMPS to obtain the reference polymers poly(A/Abz-Cd) and poly(A/Abz-La) (Chart I), respectively. These azo monomers were also terpolymerized with AMPS and *N*-cyclododecylmethacrylamide (CdMAm) and *N*-laurylmethacrylamide (LaMAm) to give the terpolymers poly(A/Cd/Abz-Cd) and poly(A/La/Abz-La) (Scheme II), respectively. The results of the co- and terpolymerizations are summarized in Tables I and II. The contents of the Abz(La)MAm and Abz(Cd)MAm units in the co- and terpolymers were limited to low levels (0.56–0.74 mol %) to avoid photophysical complexities due to chromophore–chromophore interactions. In our previous studies,[11] we ascertained that the monomer combinations of both AMPS–LaMAm and AMPS–CdMAm gave rise to "ideal copolymerization" systems giving copolymer compositions equal to monomer feed compositions. Therefore, the monomer units are randomly distributed along the chains in the present terpolymers.

Table I. Radical Co- and Terpolymerizations of AMPS, LaMAm, and Abz(La)MAm[a]

	monomer (mmol)					
polymer code	AM-PS	LaM-Am	Abz(La)-MAm	time (h)	conv (%)	Abz-La[b] (mol %)
poly-(A/Abz-La)	19.9		0.100	8	23.5	0.57
poly-(A/La/Abz-La)	10.0	9.89	0.101	17.5	13.6	0.56

[a] Initiator, AIBN 0.5 mol % based on total monomers; solvent, DMF; temperature, 60.0 °C. [b] Content of the Abz(La)MAm units in the co- and terpolymers.

Table II. Radical Co- and Terpolymerizations of AMPS, CdMAm, and Abz(Cd)MAm[a]

	monomer (mmol)					
polymer code	AM-PS	LaM-Am	Abz(Cd)-MAm	time-(h)	conv-(%)	Abz-Cd[b] (mol %)
poly-(A/Abz-Cd)	19.9		0.100	7.5	26.6	0.57
poly-(A/La/Abz-Cd)	10.0	9.91	0.100	17.5	31.6	0.74

[a] Initiator, AIBN 0.5 mol % based on total monomers; solvent, DMF; temperature, 60.0 °C. [b] Content of the Abz(Cd)MAm units in the co- and terpolymers.

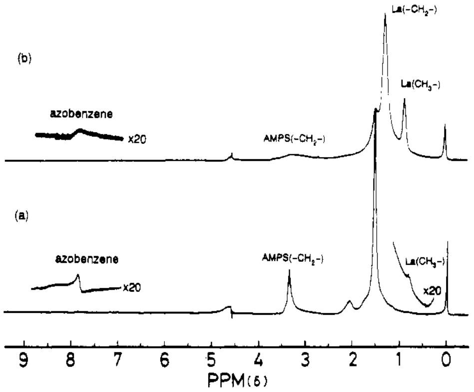


Figure 1. ^{1}H-NMR spectra of poly(A/Abz-La) (a) and poly(A/La/Abz-La) (b) in D_2O at 40 °C.

The contents of the La and Cd residues in the terpolymers (ca. 50 mol %) were high enough for the self-organization to occur to form the microphase structure in aqueous solution.[5,11] The La and Cd substituent groups of the *N*-lauryl-4-(phenylazo)benzamide (Abz-La) and *N*-cyclododecyl-4-(phenylazo)benzamide (Abz-Cd) residues are expected to be incorporated into the aggregates of the La and Cd groups, respectively, in the terpolymers in aqueous solution.

NMR Relaxation. ^{1}H-NMR spectroscopy provides a useful tool for studies of structural and dynamic characteristics of macromolecules and molecular assemblies.[13-15,17,18] The self-organization of hydrophobic groups in amphiphilic polyelectrolytes in aqueous solution leads to considerable line broadening of the NMR resonance peaks.[3,5,19]

Figures 1 and 2 show the ^{1}H-NMR spectra of the co- and terpolymers measured in D_2O at 40 °C. The NMR spectra of the reference copolymers were very similar to that of the homopolymer of AMPS except for small resonance peaks and shoulders due to the Abz-La and

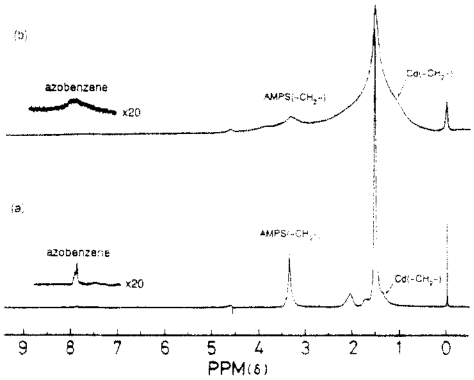


Figure 2. ^{1}H-NMR spectra of poly(A/Abz-Cd) (a) and poly(A/Cd/Abz-Cd) (b) in D_2O at 40 °C.

Abz-Cd residues existing in small mole fractions in the copolymers. In the NMR spectrum of the La copolymer, small resonance peaks at 0.8, 1.3, and 7.9 ppm are attributed to the La methyl, La methylene, and azobenzene protons, respectively (Figure 1a). In the NMR spectrum of the Cd copolymer, a small peak at 7.9 ppm due to the azobenzene protons and a small shoulder at 1.3 ppm due to the Cd methylene protons are noticeable (Figure 2a). The resonance peaks at 1.5 ppm observed for both the reference copolymers were assigned to the overlaps of the AMPS methyl and main-chain methylene protons, while those at 2.1 and 3.4 ppm were assigned to the main-chain methine and AMPS methylene protons, respectively. These assignments were ascertained by comparing the NMR spectra of the reference copolymers with that of the AMPS homopolymer.

The NMR peaks for the terpolymers were much broader than those for the reference copolymers, as can be clearly seen, for example, from the comparison of the peaks at 3.4 ppm in Figures 1 and 2. The peaks at 0.9 and 1.4 ppm for the La terpolymer are attributable to the methyl and methylene protons in the La residues, respectively. In the Cd terpolymer, on the other hand, the methylene protons in the Cd residues gave no large peaks but a broad shoulder at ca. 1.2 ppm, despite the fact that the number of the Cd methylene protons is larger than the total of the AMPS methyl and main-chain methylene protons giving a peak at 1.5 ppm. This is because the resonance line of the Cd methylene in the terpolymer is extremely broad due to restricted motions.

The NMR relaxation techniques give information about local segment motions in polymers.[13-15] In Table III are listed the measured spin-lattice relaxation times (T_1) and spin-spin relaxation times (T_2) for the protons of the azobenzene moieties, AMPS methylene, La and Cd methylene, and La methyl groups in the co- and terpolymers in D_2O at 40 °C. The relaxation times of the protons in the La and Cd groups in the reference copolymers were only approximately estimated because the resonance peaks were too small.

It is clear in Table III that the T_2 values for the terpolymers were considerably smaller than the corresponding T_2 values for the reference copolymers. In particular, the T_2 values for the azobenzene protons in the terpolymers were much smaller than those for the azobenzene protons in the reference copolymers. This is indicative of highly restricted mobility of the azobenzene moieties owing to the self-organization of the hydrophobic groups in aqueous solution. It should be noted that the T_2 value for the azobenzene moiety in the Cd terpolymer is significantly smaller than that for the azobenzene moiety in the La terpolymer. The T_2 value for the Cd methylene protons in the Cd terpolymer estimated at the 1.2 ppm shoulder was also significantly smaller than those for the La methyl and La methylene protons in the La terpolymer. These findings indicate that motions of the Cd groups in the hydrophobically organized phase are more restricted than those of the La groups. Hence, the motions of the azobenzene moieties are more restricted in the organized Cd phase than in the La phase.

Table III. Spin-Lattice Relaxation Times (T_1) and Spin-Spin Relaxation Times (T_2) for the Protons of Hydrophobic Groups, AMPS Residues, and Azobenzene Moieties in the Co- and Terpolymers in D_2O at 40 °C

chemical shift (ppm)	assignment	T_1 (ms)	T_2 (ms)
	Poly(A/Abz-La)		
0.8	La methyl	ca. 500	ca. 60
1.3	La methylene	ca. 500	ca. 60
3.4	AMPS methylene	351	44
7.9	azobenzene	1500	114
	Poly(A/La/Abz-La)		
0.9	La methyl	651	34
1.4	La methylene	511	15
3.4	AMPS methylene	370	9
7.9	azobenzene	500	11
	Poly(A/Abz-Cd)		
1.3	Cd methylene	ca. 500	ca. 40
3.4	AMPS methylene	376	46
7.9	azobenzene	1500	133
	Poly(A/Cd/Abz-Cd)		
1.2	Cd methylene	190	7
3.4	AMPS methylene	380	11
7.9	azobenzene	580	5

The T_1 values for the azobenzene resonances in the terpolymers were much smaller than those for the reference copolymers, which is consistent with the tendency observed for T_2. The T_1 value for the Cd methylene in the Cd terpolymer was much smaller than that for the La methylene in the La terpolymer, which is also consistent with the tendency observed for T_2. The spin-lattice relaxation occurs most efficiently through molecular motion whose frequency is comparable to the NMR frequency.[20] Therefore, T_1 decreases concurrently with T_2 as molecular motion decreases. Reaching a minimum value, T_1 then increases with a further decrease in the molecular motion, while T_2 remains as a minimum value. The smaller T_1 value for the Cd methylene than that for the La methylene in the terpolymers also indicates that the Cd groups are more densely packed in the self-organized hydrophobic phases than are the La groups.

Photoisomerization. Figure 3 compares the UV-vis absorption spectra of the Abz-La and Abz-Cd residues in the co- and terpolymers in aqueous solution before and after irradiation with 355-nm light. The Abz-La and Abz-Cd residues in the terpolymers showed significant red shifts in the π,π^* absorption maxima of their trans isomers. The Abz-La and Abz-Cd residues in the reference copolymers showed λ_{max} of 358 and 358 nm, respectively, while these peaks were red-shifted by 7 and 10 nm for the Abz-La and Abz-Cd residues in the terpolymers, respectively. These considerable red shifts are presumably due to lower polarities of microenvironments surrounding the azobenzene chromophores[12,21] and indicative of their incorporation in the self-organized hydrophobic phase.

By irradiation with 355-nm light the absorbances of the π,π^* bands monotonically decreased owing to the photoisomerization from the trans to cis isomer. It can be seen from Figure 3 that the absorbances after irradiation with 355-nm light for 300 s significantly differ between the co- and terpolymers.

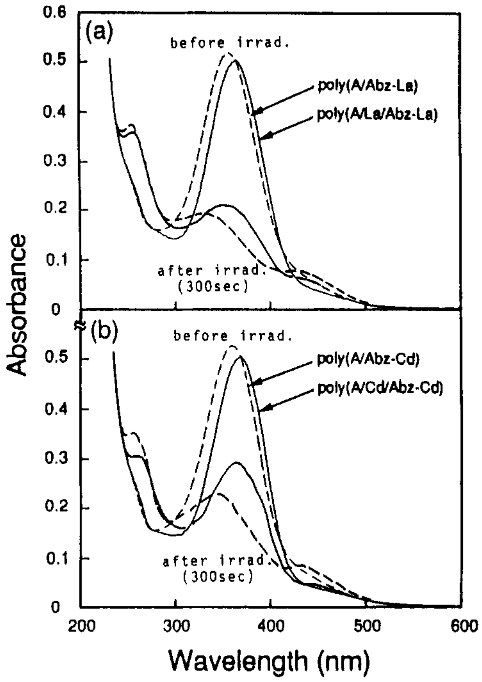


Figure 3. Absorption spectra of the azobenzene moieties in the co- and terpolymers in dilute aqueous solution before and after irradiation of 355-nm light at 298 K.

The fraction of the cis isomer at irradiation time t can be calculated from the absorbance (A) at λ_{max} for the π,π^* absorption of the trans isomer at time t by[22,23]

$$[c]_t/[t]_0 = (1-A/A_0)/(1-\epsilon_{cis}/\epsilon_{trans}) \qquad (1)$$

where $[c]_t$ is the concentration of the cis isomer at time t, $[t]_0$ is the initial concentration of the trans isomer, A_0 is the initial absorbance for the trans only isomer present, and $\epsilon_{cis}/\epsilon_{trans}$ is the ratio of the molar absorption coefficients of the cis and trans isomers at λ_{max}. An $\epsilon_{cis}/\epsilon_{trans}$ ratio of 0.055 for the azobenzene moieties, which was determined by the method proposed by Fisher,[24] was used for the calculation of $[c]_t/[t]_0$.

The fractions of the cis isomers are plotted against irradiation time in Figure 4. It is clearly seen that the photoisomerizations of the azobenzene moieties in the terpolymers are impeded as compared to those in the reference copolymer. An important observation was that there was a difference in the extent of the impeding effect between the Cd and La groups in the terpolymers. The photoisomerization of the Abz-Cd residues occurred much more slowly than did the Abz-La residues in the terpolymers.

The cis fraction at time t ($[c]_t$) can be expressed by a first-order rate equation[25]

$$([c]_s/[t]_0)\ln\{[c]_s/([c]_s-[c]_t)\} = k_1 t \qquad (2)$$

where $[c]_s$ is the concentration of the cis isomer in the photostationary state and k_1 is the rate constant of the trans-to-cis photoisomerization.

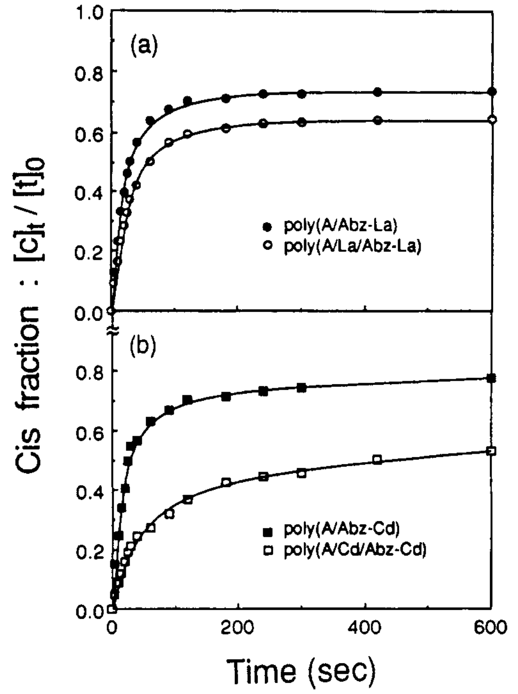


Figure 4. Changes in the cis fractions as a function of irradiation time for trans-to-cis photoisomerization in aqueous solution at 298 K.

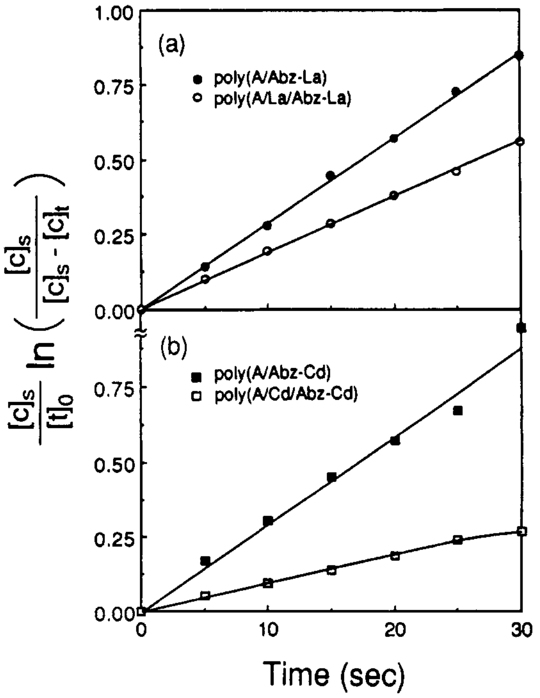


Figure 5. First-order plots for trans-to-cis photoisomerization in aqueous solution at 298 K.

Table IV. Rate Coefficients for Trans-to-Cis Photoisomerization (k_1) and Thermal Back-Isomerization (k_3) and Photostationary Cis Fractions at 298 K

polymer code	$k_1/10^{-3}$ s^{-1}	$k_3/10^{-6}$ s^{-1}	$[c]_s/[t]_0$
poly(A/Abz-La)	28 ± 1	13	0.739
poly(A/La/Abz-La)	17 ± 1	16	0.635
poly(A/Abz-Cd)	25 ± 2	7.2	0.767
poly(A/Cd/Abz-Cd)	10 ± 2	27	0.596

The first-order plots for the photoisomerization taken for an initial 30 s are compared in Figure 5. The photoisomerizations of the azobenzene moieties in the reference copolymers followed the first-order kinetics until the reactions reached the stationary states. On the other hand, those in the terpolymers followed the first-order kinetics only in the initial stage of the photoisomerization and the plots deviated downward from the linear relationship as the photoisomerization proceeded. It is evident from the comparison of the first-order plots shown in Figure 5 that the Cd groups impeded the photoisomerization to a greater extent than the La groups.

The rate coefficients k_1 and the photostationary compositions are listed in Table IV. In the reference copolymer case, there was not much difference in the photoisomer-

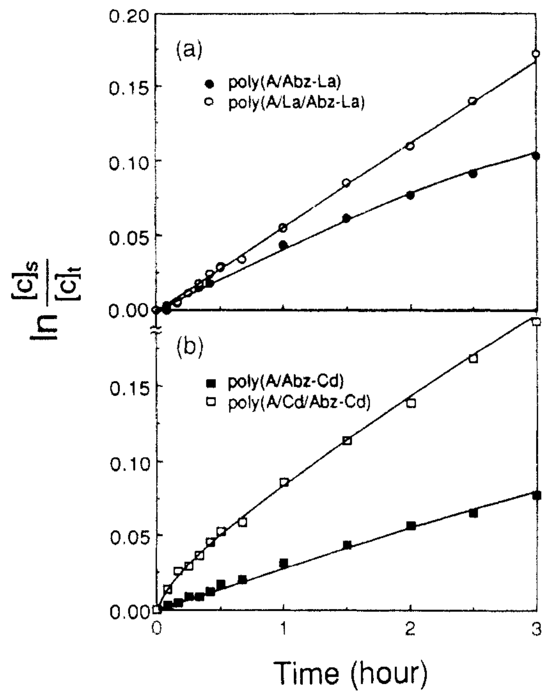


Figure 6. First-order plots for cis-to-trans thermal back-isomerization in aqueous solution at 298 K.

ization rates and also in the photostationary cis fractions between the Abz-La and Abz-Cd groups. In the terpolymer case, by contrast, the Abz-Cd group showed a considerably slower photoisomerization rate and a lower photostationary cis fraction than the Abz-La group. The difference in the photoisomerization rate between the Abz-La and Abz-Cd groups in the terpolymers is ascribed to the difference in the restriction on the molecular motions of the azobenzene moieties, as clearly seen from the comparison of the NMR relaxation times for the La and Cd terpolymers.

Thermal Back-Isomerization. Thermal back-isomerization can be expressed by a first-order rate equation[25]

$$\ln([c]_s/[c]_t) = k_3 t \qquad (3)$$

where k_3 is the rate constant of the thermal cis-to-trans isomerization. In Figure 6 are shown the first-order plots for thermal cis-to-trans isomerizations following photochemical trans-to-cis isomerizations of the Abz-La and Abz-Cd residues in the co- and terpolymers in dilute aqueous solution at 298 K. The self-organization of the hydrophobic residues affected the thermal back-isomerization rates in an opposite way to the trans-to-cis photoisomerization. It is evident from Figure 6 that the cis isomers in the terpolymers thermally isomerized back to the trans isomers faster than those in the reference copolymers. The thermal cis-to-trans isomerizations did not exactly follow first-order kinetics, but there was a tendency that the faster initial rates gradually slowed down with time.

In Table IV are listed the values of k_3 which were estimated from the initial slopes of the first-order plots shown in Figure 6. These rather anomalous fast recovery rates in the initial stage of the thermal cis-to-trans isomerization can be attributed to cis isomers trapped in a strained conformation, as discussed in the previous paper.[12]

It should be noted that there is a difference in the thermal isomerization behavior between the La and Cd terpolymers. With the Cd terpolymer, the initial rate is much faster and the deviation from the first-order plot is more pronounced than with the La terpolymer. These findings imply that, as indicated by the NMR relaxation times, molecular motions of the azobenzene moieties are more restricted by the organized Cd phase than by the La phase. This is consistent with the finding that the value of k_1 for the Cd terpolymer was smaller than that of the La terpolymer as can be seen from Table IV.

The difference in the extent of the restriction on the motions of the azobenzene moieties in the La and Cd terpolymers arises from the difference in the packing densities of the La and Cd groups in the self-organized hydrophobic phases. Since the self-organizations of the La and Cd groups in the terpolymers in aqueous solution are completely due to hydrophobic interactions, the bulky alkyl groups tend to associate one another so as to minimize the surface area exposed to the aqueous phase, thereby releasing a maximum number of structured water molecules into free water to gain a maximum positive entropy.[26,27]

If hydrophobic molecules can sterically fit with each other to attain a large contact area between them, a hydrophobic self-organized phase formed by their extensive hydrophobic associations may have a high packing density. Therefore, a conformation or a molecular shape of a hydrophobic group may be a factor to affect the packing density of the hydrophobic groups. Molecules with the same conformation may be packed most densely. Cyclododecane has much less conformational freedoms than dodecane because of its cyclic structure, which means that the numbers of the stable conformations of the former are more limited than those of the latter. The latter can adopt a variety of conformations. Therefore, it may be reasonable that the Cd groups are more densely packed than the La groups in the hydrophobic self-organized phases.

Conclusions

Amphiphilic polysulfonates bearing ca. 50 mol % of lauryl (La) or cyclododecyl (Cd) groups and a small mole fraction of an azobenzene moiety substituted with a La or Cd group were synthesized by free-radical terpolymerization of the corresponding monomers.

The mobility of the polymer chain segments, hydrophobic substituents, and azobenzene moieties was estimated by ^{1}H-NMR relaxation techniques. Spin–lattice and spin–spin relaxation times indicated that the motions of the azobenzene moieties were highly restricted when the self-organization of the hydrophobic groups occurred in aqueous solution. In particular, the hydrophobic self-organization of the Cd groups showed more pronounced restrictions on the motions of the azobenzene moieties than the La groups.

Effects of the self-organization of the hydrophobic groups on the trans-to-cis photoisomerization and cis-to-trans thermal back-isomerization of the azobenzene moieties were investigated. As predicted by the NMR relaxation studies, the photoisomerization was considerably impeded, whereas the thermal back-isomerization was accelerated, when the self-organization of the hydrophobic groups occurred in aqueous solution. These effects on the isomerizations were more pronounced with the Cd groups than with the La groups; i.e., motional restrictions imposed on the trans isomer and residual strains in the photogenerated cis isomer were greater in the organized Cd phase than in the La phase.

These findings indicate that the Cd groups are more densely packed than are the La groups in the self-organized hydrophobic phases, presumably because the Cd residue has much less conformational freedoms than does the La residue.

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