Photochromic Isomerization of Azobenzene Moieties Compartmentalized in Hydrophobic Microdomains in a Microphase Structure of Amphiphilic Polyelectrolytes

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ABSTRACT: Amphiphilic sodium polysulfonates containing 0.5 mol % of the azobenzene (Abz) moiety and 49.5 mol % of lauryl (La), cyclododecyl (Cd), or adamantyl (Ad) groups in the side chains were prepared. As a reference polymer, a sodium polysulfonate with 0.5 mol % of the Abz moiety without the hydrophobic group was also prepared. In the former, the Abz residues are "compartmentalized" in hydrophobic domains of the La, Cd, or Ad groups, while in the latter, the Abz residues are exposed to water in aqueous solution. Photoisomerization (trans to cis) of the Abz residues was significantly impeded as a result of the compartmentalization owing to motional restrictions imposed on the trans Abz isomers in the hydrophobic domains. The initial rates of the thermal cis-to-trans back-isomerization, on the contrary, were accelerated in the compartmentalized systems, presumably owing to conformational strains in photogenerated cis isomers in the hydrophobic domains. Such steric effects of the compartmentalization on both the photochemical and thermal isomerizations were dependent on the hydrophobic groups surrounding the Abz residues, the steric constraint decreasing in the order Cd > Ad > La.

Introduction

There has been increasing attention in recent years focused on the photophysics and photochemistry of chromophores covalently tethered to amphiphilic polyelectrolytes, because various photoprocesses can be greatly modified by a microenvironment provided by such polymers.[1] If the content of hydrophobic units in an amphiphilic polyelectrolyte is sufficiently low, the polymer assumes an expanded conformation characteristic of a polyelectrolyte in dilute aqueous solution, but if the content is high enough, the polymer adopts a micelle-like microphase structure where the hydrophobic units form an interior hydrophobic domain and charged segments form an outer layer.[2,3] The micelle-like microphase structure is rigid and "static" in nature as compared to the dynamic nature of conventional surfactant micelles.[4] In a way, the hydrophobic domain in the microphase structure can be viewed as a solid microparticle sustained in water by surrounding charged segments to give a clear aqueous solution. Such characteristics of the microphase structure largely depend not only on the number (mole fraction) of hydrophobic units in the amphiphilic polyelectrolyte[2a,b] but also on the size, shape, and conformational rigidity of the hydrophobic group.[2c]

When a small mole fraction of a hydrophobic photoactive-chromophore group is covalently incorporated in such amphiphilic polyelectrolytes, the chromophore is encapsulated in the hydrophobic microdomain and is forced to experience an unusual microenvironment;[5] i.e., (1) the chromophore is isolated from the aqueous phase and placed in a nonpolar environment (even less polar than benzene), (2) its molecular motions are highly restricted owing to the structural rigidity of the hydrophobic microdomain, and (3) an electrostatic potential is exerted to the chromophore by charged segments surrounding the hydrophobic microdomain.

Such unusual microenvironments for the compartmentalized chromophore, unlike the conventional molecular assembly systems, can drastically control the rate of photoinduced electron-transfer reactions as we have reported previously.[5]

In our continuing work on the photophysics and photochemistry of compartmentalized chromophore systems, we were motivated to study how photochromic isomerization reactions would be affected by the unusual microenvironments in amphiphilic polyelectrolytes. In the present study, we chose an azobenzene (Abz) moiety as a chromophore and prepared amphiphilic terpolymers containing 50 mol % of sodium sulfonate groups, 49.5 mol % of hydrophobic groups, and 0.5 mol % of Abz units (Chart I). The content of the Abz unit in the terpolymers was limited to 0.5 mol % to avoid complexities such as chromophore–chromophore interactions and to ensure that all Abz units were compartmentalized. For comparison, a sodium polysulfonate containing 0.5 mol % of Abz units without hydrophobic groups was also prepared as a reference polymer in which the Abz unit is exposed to water in aqueous solution.

The photoisomerizations of Abz moieties dissolved in polymer matrices[6–8] or covalently incorporated into polymers[9–12] either as pendant groups or as a part of the main chain have been investigated. It has been reported that the rates of the photoisomerization of Abz moieites covalently incorporated into polymers are essentially the same as those of low molecular weight analogues in dilute solution.[9] However, the rate is affected by restricted molecular motions in the glassy state of polymers.[9,11a,c] In this context, it should be of interest to verify whether the compartmentalization of Abz moieties installs a steric restriction to block molecular motions required for the photoisomerization.

It is also important from a practical point of view to study the effects of steric restrictions on the mobility of Abz units, because the photochromic isomerizations of Abz moieties have been expected to be utilized as a photochemical switch in various molecular systems.[12] This

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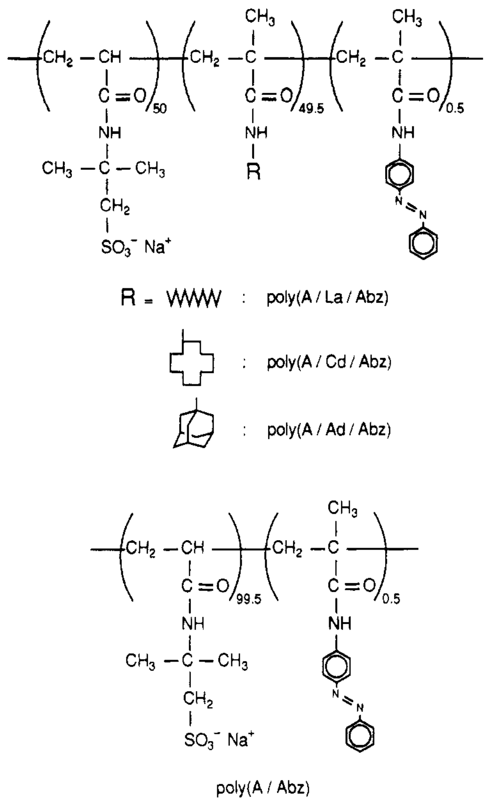
Chart I



idea of the switch is based on a change in molecular conformations due to the isomerization to generate a steric perturbation in a molecular system.

Experimental Section

Monomers. (4-Phenylazo)methacrylanilide was synthesized by reacting *p*-aminoazobenzene with methacryloyl chloride in benzene according to the literature.[9a] *N*-Laurylmethacrylamide,[2c] *N*-cyclododecylmethacrylamide, and *N*-(1-adamantyl)methacrylamide were prepared as reported previously.[5c] 2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) was used as received from Nitto Chemical Industry Co.

Terpolymers and Copolymer. The terpolymers and the reference copolymer were prepared by free-radical polymerization initiated by 2,2′-azobis(isobutyronitrile) (AIBN). The procedure for the terpolymerization is as follows. A glass ampule containing known amounts of (4-phenylazo)methacrylanilide, AMPS, one of the hydrophobic monomers, and AIBN in *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 polymers. The polymers were purified by three reprecipitations from methanol into ether and then dissolved in dilute aqueous NaOH. The solution was dialyzed against pure water for a few days and finally lyophilized. The compositions of the terpolymers were determined by N/C and S/C ratios and absorption spectra. The reference copolymer of AMPS and (4-phenylazo)methacrylanilide was prepared in a similar manner.

Photoisomerization. The polymers were dissolved in deionized water, and the pH of the aqueous solutions was adjusted to 11 at room temperature. Absorbances of the sample solutions were adjusted to 0.1 at 355 nm, and 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 a 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. Irradiations were 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.

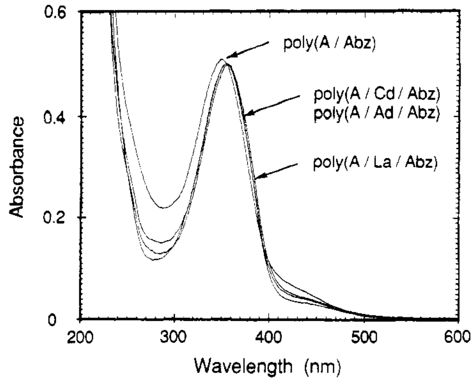


Figure 1. UV–vis absorption spectra of Abz residues in the co- and terpolymers in dilute aqueous solution.

Results and Discussion

Azo-Functionalized Amphiphilic Polyelectrolytes. The amphiphilic co- and terpolymers prepared in the present study have a completely random sequence distribution of the monomer units. In addition, their compositions were equal to the monomer feed compositions, allowing us to prepare co- and terpolymers of well-defined composition. In fact, we ascertained in a separate experiment that the monomer combinations of AMPS and each of the methacrylamides including (4-phenylazo)methacrylanilide used in this study provided "ideal copolymerization" systems; i.e., the copolymer composition was found to be proportional to the monomer composition in the feed, showing a diagonal relationship in the copolymerization composition curve.

The hydrophobic groups employed in this work have similar numbers of carbon atoms but have different conformational freedoms. Hence, the steric nature or structural rigidity of the self-aggregate of the hydrophobic groups is expected to be also different.[2c] A 49.5 mol % content of the hydrophobic units in the terpolymers is high enough to form a microphase structure in aqueous solution.[2c] Since Abz moieties are hydrophobic in nature, they are expected to be incorporated into the hydrophobic domain of the terpolymers in aqueous solution.

Figure 1 shows UV–vis absorption spectra of Abz residues in the trans form in the co- and terpolymers in aqueous solution. The Abz chromophores in the terpolymers showed a significant red shift in the π,π^* absorption maximum; i.e., Abz residues in the reference copolymer showed λ_{max} = 350 nm, while the peaks were red-shifted by 4, 5, and 8 nm for the terpolymers with Ad, Cd, and La groups, respectively. This red shift is apparently due to a lower polarity of microenvironments surrounding the Abz chromophores, indicative of the effective compartmentalization of the Abz residues. A similar red shift in the π,π^* absorption owing to a less polar microenvironment has been observed by Bortolus and Monti[13] for an azobenzene–α-cyclodextrin inclusion complex; i.e., λ_{max} = 320 nm of azobenzene in aqueous solution shifted to 325 nm in the presence of α-cyclodextrin.

Photoisomerization. To examine the effect of hindered motions of the compartmentalized Abz moieties on their isomerization, we studied the rates and kinetics of photochemical trans-to-cis and thermal cis-to-trans back-isomerizations of Abz moieties in the terpolymers in aqueous solution. The compartmentalized Abz groups are expected to be sterically hindered perhaps to a different extent with different hydrophobic groups.

In Figure 2 are shown changes in the absorption spectra

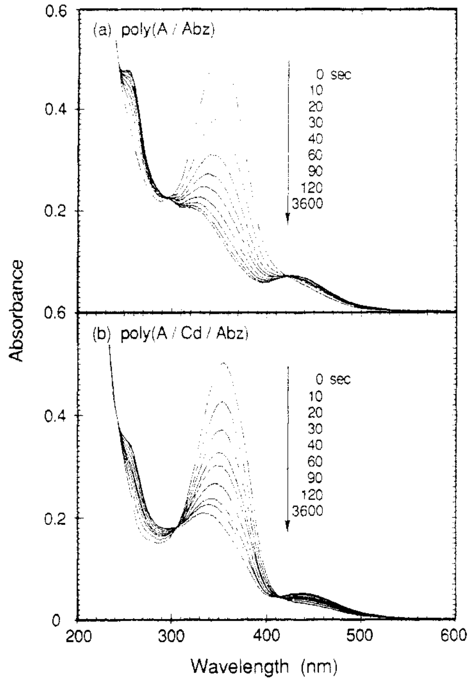


Figure 2. Changes in absorption spectra of Abz residues in (a) poly(A/Abz) and (b) poly(A/Cd/Abz) in aqueous solution caused by irradiation of 355-nm light at 298 K. The irradiation times are indicated in the figure.

for the Abz units in poly(A/Abz) and poly(A/Cd/Abz) by irradiation of 355-nm light. Absorbances of the π,π^* band at about 350 nm progressively decreased with irradiation time and reached an equilibrium state in about 5 min under the irradiation conditions employed in this experiment. The occurrence of the isosbestic points, which are maintained for a prolonged irradiation after reaching a photostationary state, indicates that the isomerization is the only photochemical change and no side reactions such as photodegradations are involved.

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[7c,8]

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

where [c] 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}. The $\epsilon_{cis}/\epsilon_{trans}$ ratio for the Abz moieties in the present study was determined to be 0.055 by using the method proposed by Fisher.[14] This value is in agreement with reported values of 0.050 and 0.052 for azobenzene itself.[8,15] The cis fraction in the photostationary state ($[c]_s/[t]_0$) can be related to the rate coefficients by

$$[c]_s/[t]_0 = k_1/(k_1 + k_2 + k_3) \quad (2)$$

where k_1 and k_2 are the apparent rate coefficients for trans-to-cis and cis-to-trans photoisomerizations, respectively, and k_3 is the rate constant for cis-to-trans thermal isomerization. Therefore, the change in the trans fraction ([t]) with time t can be given by the first-order rate equations[7b] for photoisomerization

$$(1 - [t]_s/[t]_0) \ln \{([t]_0 - [t]_s)/([t] - [t]_s)\} = k_1 t \quad (3)$$

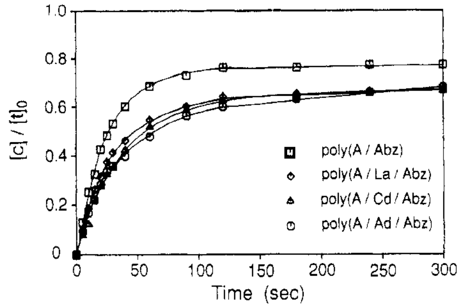


Figure 3. Changes in the cis fractions as a function of irradiation time for trans-to-cis photoisomerization in aqueous solution at 298 K.

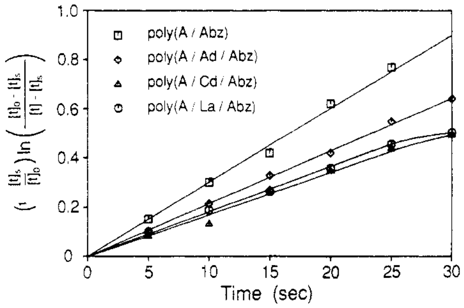


Figure 4. First-order plots for trans-to-cis photoisomerization in aqueous solution at 298 K.

and for thermal back-isomerization

$$\ln \{([t]_s - [t]_0)/([t]_s - [t])\} = k_3 t \quad (4)$$

Increases in the cis fraction with irradiation time are plotted in Figure 3. As can be seen from Figure 3, the photoisomerizations of the Abz residues in the terpolymers are impeded as compared to those in the reference copolymer. The photostationary cis fractions for the compartmentalized Abz residues are significantly lower than that for the Abz moieties in the reference copolymer, the former ranging from 0.673 to 0.697 with the latter being 0.780. The first-order plots for the photoisomerization are presented in Figure 4. The photoisomerizations of poly(A/Abz) and poly(A/La/Abz) followed first-order kinetics until the reactions reached the stationary states. On the other hand, poly(A/Cd/Abz) and poly(A/Ad/Abz) followed first-order kinetics only in the initial stage of the photoisomerization, and the plots deviated downward from the linear relation as the isomerization proceeded. It is evident from the comparison of the first-order plots shown in Figure 4 that the photoisomerization rate is affected by the compartmentalization of Abz moieties; i.e., the rate was significantly slower in the compartmentalized Abz residues than that of free Abz residues in poly(A/Abz). Among the hydrophobic groups which compartmentalize Abz residues, the Cd and Ad groups impede the photoisomerization to a greater extent than the La group does.

It is known that Abz groups undergo photoisomerization in dilute solutions at a similar rate regardless of whether they are covalently incorporated in a polymer backbone[9b] or in a side chain[9a] or they are low molecular weight analogues. Furthermore, photoisomerization of a polymer-bound Abz group occurs at an equivalent rate in the rubbery state as in dilute solution, while in the glassy state the rate is significantly slowed.[11a–c] Chen and Morawetz[9b] studied the photoisomerization of Abz groups incorporated in the main chain of polyamides and showed that quantum efficiencies for photoisomerization in dilute solutions were the same for Abz residues in the polymer

Table I
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)	30 ± 1	8.9	0.780
poly(A/La/Abz)	21 ± 1	16	0.673
poly(A/Cd/Abz)	15 ± 2	22[a]	0.674
poly(A/Ad/Abz)	17 ± 1	17[a]	0.697

[a] Determined from the slopes in the time region of 0–30 min in Figure 6.

backbone and low molecular weight analogues. They also showed that in glassy films the quantum yield for the photoisomerization was much lower than that of the low molecular weight analogues. Paik and Morawetz[9a] studied photoisomerization of Abz residues incorporated in the side chains of poly(methyl methacrylate), poly(ethyl methacrylate), and polystyrene. Their results showed that the photostationary composition was similar in bulk and in dilute solution when the bulk specimens were irradiated above the glass transition temperature (T_g), but the rate of the photoisomerization was substantially slower below T_g. Similar observations have been reported by Sung et al.[11a–c] for Abz residues incorporated in the backbone of polyurethane. Sung et al.[11d] incorporated Abz groups in the main chain or side chain, or at the chain ends of polystyrene, and studied the photoisomerization by repeating irradiation of laser pulses. In dilute solution, they observed a small difference in photoisomerization rate for Abz groups linked at different sites of the polymer chain; the rate was a little faster for Abz groups at the chain end than those in the main chain or in the side chain. In the glassy state, however, they observed a much greater difference, especially between the Abz residues in the main chain and those at the chain end.

Important observations in the present study, in comparison with these earlier reports, is that even in dilute solution the rate of the photoisomerization of Abz residues is significantly slowed when they are compartmentalized in the hydrophobic domain of the amphiphilic polyelectrolytes and that the rate is affected by the steric nature of the hydrophobic groups of the domain. The rate coefficients k_1 and the photostationary composition determined from the data shown in Figure 4 are listed in Table I. The observed differences in the isomerization behavior among the hydrophobic groups in this study are attributable to the differences in restrictions on the mobility of the compartmentalized Abz groups.

Bortolus and Monti[13] recently reported that the quantum yields of the trans-to-cis photoisomerization of azobenzene inclusion complexes with α-cyclodextrin in aqueous solution are significantly lower than that of free azobenzene in a water/methanol (80/20, v/v) medium. They attributed the observed decrease in the photoisomerization quantum yield to constrained molecular motion of azobenzene in the inclusion complex. However, they also pointed out that the apolar microenvironment of the cyclodextrin cavity could, at least in part, be responsible for the lower quantum yield. Since the microenvironments of our compartmentalized Abz systems are hydrophobic in nature, we may have to take into account the similar apolar effect on the photoisomerization. Nevertheless, we would presume the microenvironmental polarity effect to be a rather minor one, if any, because, among our compartmentalized systems, the photoisomerization rate was found to be fastest for the Abz moieties in the La domain. The microenvironment of the La domain is actually less polar than those of the Cd and Ad domains as discussed in a previous study on the basis of the fluorescence information from a compartmentalized pyrene probe.[5c]

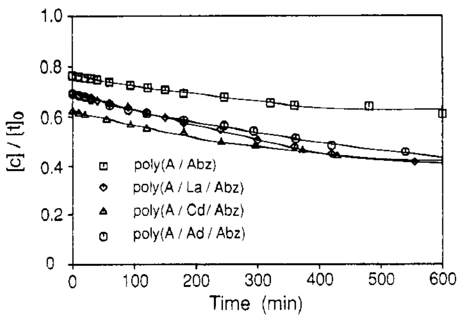


Figure 5. Changes in the cis fractions as a function of time for cis-to-trans thermal back-isomerization in aqueous solution at 298 K.

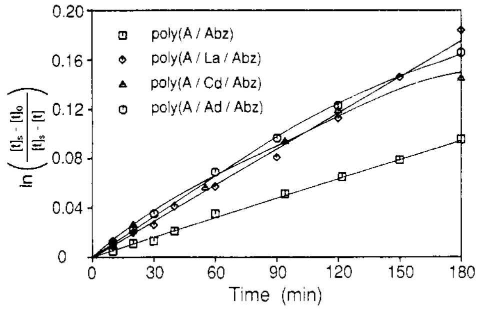


Figure 6. First-order plots for cis-to-trans thermal back-isomerization in aqueous solution at 298 K.

Thermal Back-Isomerization. In Figure 5 are shown thermal cis-to-trans isomerizations following photochemical trans-to-cis isomerizations of Abz residues in the co- and terpolymers in dilute aqueous solution at 298 K. The thermal recovery data are plotted according to eq 4 in Figure 6. The microenvironment surrounding the Abz residues affected the cis-to-trans isomerization rates, but in a different way from the trans-to-cis photoisomerization. It is evident from the first-order plots shown in Figure 6 that the terpolymer systems thermally recover faster than the reference copolymer system. The thermal cis-to-trans isomerizations for poly(A/Abz) and poly(A/La/Abz) occurred by single-rate processes at least up until 180 min, as can be seen from the linear relationship shown in Figure 6. On the other hand, the thermal isomerizations of the Abz residues compartmentalized in the Cd or Ad domain occurred by rather complex, multirate processes; i.e., faster initial rates gradually slowed down with time. In Table I are listed the values of k_3. For poly(A/Cd/Abz) and poly(A/Ad/Abz) the k_3 values were estimated from the initial slopes in a 0–30-min time window 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. This interpretation is based on the findings and the interpretation of the similar behavior of polymer-bound Abz groups in a glassy state reported by Paik and Morawetz.[9a] A similar observation has also been reported by Mita et al.[7b] for the thermal cis-to-trans isomerization of azobenzene molecularly dispersed in a polymer film. They have demonstrated the existence of residual strain in the photogenerated cis isomer in a polymer film on the basis of the fact that a cis-rich film prepared under UV irradiation shows no such anomalous fast processes but follows first-order kinetics in the thermal cis-to-trans isomerization reaction.

It should be noted that there are differences in the thermal isomerization behavior among the terpolymers.

With poly(A/Cd/Abz), the initial rate is the fastest and the deviation from the first-order plot is the most pronounced of all the terpolymers, implying that molecular motions of the Abz residues are most restricted in the Cd domain. This is consistent with the finding that the value of k_1 for poly(A/Cd/Abz) was the smallest of all as can be seen in Table I. The La groups, on the other hand, compartmentalize the Abz residues less rigidly than do the Cd and Ad groups. The difference in the extent of the restriction on the motions of the Abz moieties may be a reflection of the difference in the packing density of the hydrophobic groups in the domain.

Finally, it should be noted that conclusions in the present study regarding the difference in the effect of the compartmentalization for the different hydrophobic groups are consistent with the conclusions drawn from photoinduced electron-transfer reactions as reported in our previous paper,[5c] decreasing in the order Cd > Ad > La. Furthermore, we have recently estimated the packing density of various hydrophobic groups in the domains by an ESR technique using a compartmentalized nitroxyl radical as a spin probe.[16] The results revealed that the packing density was in the order of Cd > Ad > La domains, as will be discussed in detail in a subsequent paper.[16]

Conclusions

The compartmentalization of Abz residues impeded their trans-to-cis photoisomerization and accelerated cis-to-trans thermal isomerization in dilute aqueous solution. These findings were explained in terms of a motional restriction imposed on the trans isomer and a residual strain in the photogenerated cis isomer, respectively. These steric effects on the photochemical and thermal isomerizations were found to decrease in the order Cd > Ad > La.

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Registry No. (A)(La)(Abz) (copolymer), 142038-17-3; (A)(Cd)(Abz) (copolymer), 142004-99-7; (A)(Ad)(Abz) (copolymer), 142005-00-3; (A)(Abz) (copolymer), 142005-01-4.