

Confinement Effects on Photoalignment, Photochemical Phase Transition, and Thermochromic Behavior of Liquid Crystalline Azobenzene-Containing Diblock Copolymers

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ABSTRACT: Two diblock copolymers composed of polystyrene and a liquid crystalline azobenzene-containing polymethacrylate were used as model systems to investigate the confinement effects on the photoalignment, photochemical phase transition, and thermochromic behavior of the azobenzene polymer. The study finds that when confined in the microphase-separated domains in the diblock copolymers, the azobenzene polymer behaves differently with respect to the homopolymer having no confinement. The confinement effects are manifested by (1) decreased photoinduced and thermally enhanced orientation of azobenzene mesogenic groups in different aggregation states, (2) slower transformation from a liquid crystalline phase to the isotropic state triggered by the trans–cis photoisomerization and slower recovery of the liquid crystalline phase after the thermally induced cis–trans back-isomerization, and (3) severely reduced and even suppressed changes in the aggregation states of azobenzene groups on heating, which is at the origin of the thermochromic property. The common cause of these confinement effects is the restriction imposed by the confining geometry on either an order–disorder or a disorder–order reorganization process involving the motion and rearrangement of azobenzene groups.

Introduction

Polymers containing an azobenzene moiety in the side chain have been the subject of extensive investigations over the past decade due to their potential utilities in optical and photonic applications.^{1–14} Generally, when the flexible spacer (alkyl chain) linking the azobenzene unit and the chain backbone is sufficiently long, the polymer may display the liquid crystallinity with the azobenzene groups forming the mesophases. Liquid crystalline (LC) azobenzene polymers have a number of distinct features as compared to their amorphous counterparts. The first is about the thermal stability of the alignment of azobenzene groups induced by irradiation with linearly polarized light. For amorphous polymers, if a photoinduced orientation is obtained at room temperature, it will be diminished by raising the temperature and disappear at $T > T_g$ due to the thermal relaxation.¹ For LC polymers, the opposite may happen since the initial photoinduced orientation may be enhanced at $T > T_g$ due to the tendency for self-organization of the azobenzene mesogenic groups in a LC phase.^{6,15,16} The second feature of LC azobenzene polymers is the photochemically induced LC–isotropic phase transition that occurs when the rodlike trans isomer is converted into the contracted cis isomer as the latter destabilizes the LC phase.^{17,18} This phenomenon has been used to record volume holographic gratings¹⁸ and to realize optical switching when combined with the thermally or visible-light-induced cis–trans back-isomerization.¹⁹ The third (not the last) interesting property of LC azobenzene polymers is the possible display of a thermochromic behavior which may be particularly prominent if an amorphous state is generated in spin-cast films or by fast quenching from the isotropic state.²⁰ In this case, as the temperature is

increased, disordered azobenzene chromophores will form ordered phases, leading to different aggregations (different associations of transition dipoles) that absorb different wavelengths.^{20,21}

Since the confinement may have profound effects on liquid crystal ordering and phase transition,^{22,23} it would be of interest to know how LC azobenzene polymers behave in a confined geometry with reference to the photoalignment, photochemical phase transition, and thermochromic property. Such a confining environment may be provided by self-organized microdomains in diblock copolymers. In a previous paper,²⁴ we have reported the synthesis and characterization of a series of diblock copolymers composed of polystyrene (PS) and a LC polymethacrylate bearing an azobenzene moiety in the side chain (PAzo). Besides, some preliminary measurements found that the birefringence induced by excitation with an Ar ion laser at 488 nm is smaller in block copolymers than in the azobenzene homopolymer, suggesting that the photoalignment of azobenzene groups is more difficult to develop in microdomains. Here, we report and discuss the results of a detailed study using the azobenzene-containing diblock copolymers to investigate the confinement effects on the various properties of LC azobenzene polymers as mentioned above.

Experimental Section

The synthesis of the azobenzene-containing diblock copolymers through the atom transfer radical polymerization technique was already reported.²⁴ Figure 1 recapitulates the essential information on the three polymers used in the present study. PAzo is the azobenzene homopolymer used as the reference having no confinement; SAzo1 and SAzo2 are two PS–PAzo diblock copolymers containing 74 and 57 wt % of the azobenzene polymer, respectively. Transmission electron microscope (TEM) observations found PS cylindrical microdomains in SAzo1 and alternating lamellar morphology in

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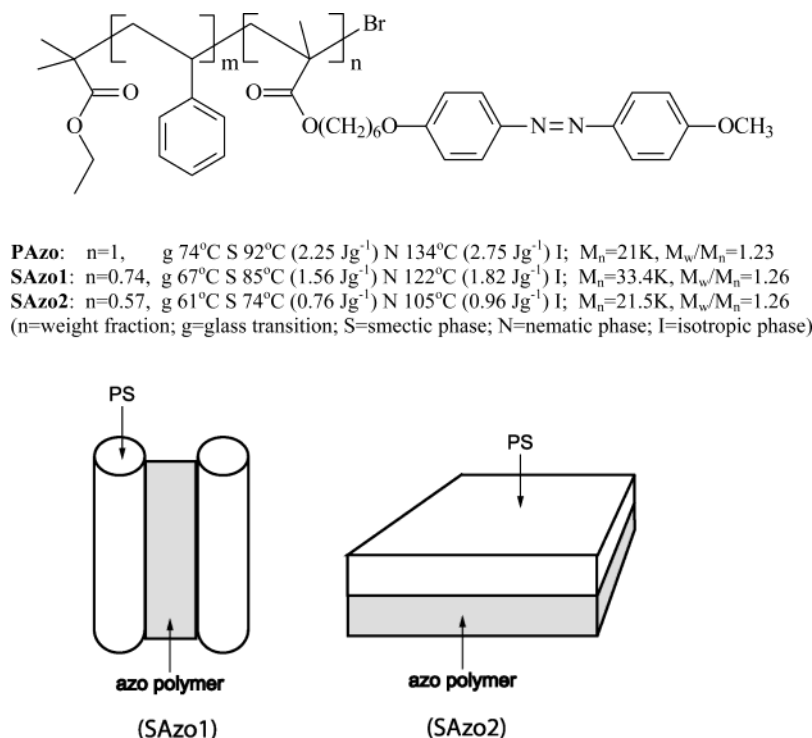


Figure 1. Chemical structures and characteristics of the polymers. The sketch illustrates the confinement of azobenzene polymer in the microphase-separated morphologies of the diblock copolymers.

SAzo2.²⁴ The azobenzene polymer in SAzo1 may be considered as being confined in the continuous space between the PS cylinders (the average inter-cylinder distance estimated from the TEM picture is about 5–6 nm), while in SAzo2 the azobenzene polymer is confined in its lamellas with thickness on the order of 6–7 nm (sketch in Figure 1). The molecular weight of the azobenzene polymer block of SAzo1 (~24K) is slightly higher than that of PAzo (21K) and higher than that of SAzo2 (~13K). All the three polymers are liquid crystalline displaying a smectic and a nematic phase. This LC azobenzene polymer is known to have a smectic-A phase.²⁵ Of them, PAzo has the highest T_g and mesophase transition temperatures. The reduced phase transition temperatures and enthalpies of the diblock copolymers would reflect the effects of microdomains on the thermal stability of and the degree of order in the LC phases. The lower molecular weight of the azobenzene polymer block of SAzo2 may also contribute to its decreased mesophase transition temperatures.

Polarized UV-vis spectroscopy is the main tool of study in this work. The UV-vis spectra were recorded with a HP 8452A spectrophotometer and a polarizer (Oriel), using thin films formed by spin-casting of THF solution on the surface of a quartz plate and dried under reduced pressure. In the case of polarized infrared measurements, the substrate used was CaF₂ window (10 mm diameter), and the spectra were recorded on a Bomem MB-102 FTIR spectrometer with a wire-grid polarizer and a DTGS detector. Irradiation of the films was performed using an UV and visible spot curing system (Novacure 2100) combined with UV and visible interference filters (10 nm bandwidth, Oriel). For the experiment of photoinduced orientation, unless otherwise stated, the intensity of the irradiation UV light at $\lambda = 360$ nm was about 15 mW/cm² and that of the visible light at $\lambda = 440$ nm was 4 mW/cm². For the experiment of photochemical phase transition, the intensity of UV light used was about 2 mW/cm.¹² The reason for using this low-intensity UV irradiation will be explained later. To monitor the change in optical transmittance related to the photochemical phase transition, a setup similar to that described elsewhere²⁶ was utilized. Basically, the film was placed inside a microscope hot stage (Instec), which was positioned between two crossed polarizers. A low-power (4 mW) He-Ne laser (633 nm) was used as the probe light with normal

incidence, and the optical transmission was measured with a high-speed photodetector (Displaytech) collected to a digital oscilloscope (Tektronix, TDS 420A). The UV irradiation beam was directed at an angle of about 30° to the normal of the film surface in order to avoid the direct entry of the excitation beam into the photodetector.

Results and Discussion

Photoinduced and Thermally Enhanced Orientation. The photoalignment of the azobenzene homopolymer, PAzo, on linearly polarized UV irradiation at 365 nm was investigated by Han and Ichimura.¹⁵ They found that an alignment of azobenzene mesogenic groups could be induced only with a small dose (<30 mJ/cm²). Beyond that point, the high concentration of cis isomer essentially randomizes the polymer due to the increased mobility. These authors also found that if the polymer with an initial alignment induced by the low-dose UV light was annealed at temperatures above T_g , the alignment could be drastically enhanced owing to the self-organization of the mesogens in the LC phase. In another study by Ikeda et al. using different polymers,²⁷ the general inability of inducing photoalignment with polarized UV irradiation in LC azobenzene polymers with no strong electron-donor and electron-acceptor groups was clearly identified as the result of the photochemical phase transition due to the trans-cis isomerization of the chromophore. They found, however, that this UV-light-induced photochemical phase transition might be served as a means to promote the formation of the isotropic state and that a subsequent linearly polarized visible light irradiation could result in oriented *trans*-azobenzene in the direction perpendicular to the polarization.²⁷ To study the confinement effects by comparing the photoalignment of PAzo and the diblock copolymers, we have chosen, on one hand, to use unpolarized UV light to reach the photostationary state with the highest content of cis isomer (the film is homogeneous showing no orientation) and then use

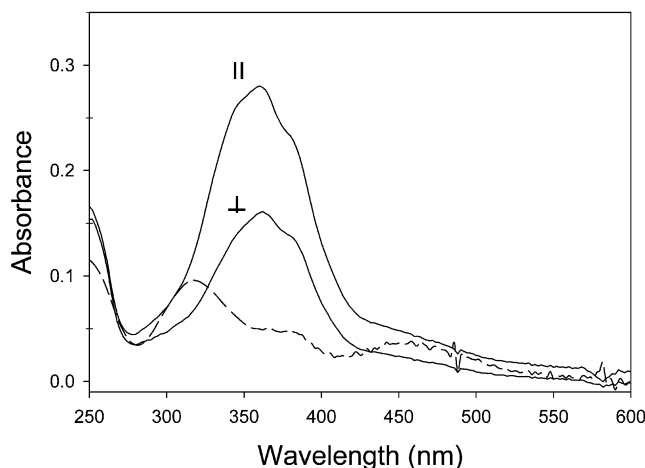


Figure 2. Polarized UV-vis spectra of a thin film of the diblock copolymer SAzo1 after unpolarized UV irradiation (dashed line) and subsequent linearly polarized visible irradiation (solid lines). In the latter case, the two spectra were recorded with the spectrophotometer's beam polarized parallel and perpendicular, respectively, to the reference direction that is taken as being perpendicular to the polarization of visible light irradiation.

linearly polarized visible light to induce the orientation of azobenzene groups. On the other hand, we have investigated the effect of thermal annealing on the photoinduced orientation. The main results are reported below.

Figure 2 gives an example of polarized UV-vis spectra with a thin film of SAzo1. After 5 min unpolarized UV light irradiation, the spectra show no polarization-dependent absorbance for both the $\pi-\pi^*$ transition of trans isomer around 360 nm and the $n-\pi^*$ transition of cis isomer near 450 nm (only the spectrum with one polarization is shown), which indicates the absence of any preferential orientation of azobenzene groups in the plane of the film. Also, the photostationary state is reached with about 78% cis isomer. When polarized visible irradiation is applied to this UV-pretreated film for 3 min, most of trans isomers ($\sim 80\%$) are recovered; the absorbance of the 360 nm peak becomes polarization-dependent, indicating a photoinduced orientation of azobenzene groups of trans conformation. Note that the visible light was applied immediately after the UV exposure (it took about 20 s to change the filters), while the thermally induced cis-trans back-isomerization was slow at room temperature (it took 30 min to get about 50% cis isomer relaxed to trans isomer). Taking the direction perpendicular to the polarization of the visible light irradiation as the reference direction, the absorbance of the 360 nm peak, A , is the highest with the spectrophotometer's beam polarized parallel to the reference direction ($A_{||}$) and the lowest with the perpendicular polarization (A_{\perp}), which is indicative of a preferential orientation of *trans*-azobenzene in the expected direction. The order parameter, S , can be determined from the dichroism through $S = (A_{||} - A_{\perp}) / (A_{||} + 2A_{\perp})$. Similar spectral features under these conditions were also observed for PAzo and SAzo2, which have both about 80% cis isomer at the photostationary state on UV irradiation and display orientation of *trans*-azobenzene groups on polarized visible irradiation.

Figure 3 compares the increase in order parameter of azobenzene groups in the three polymers over time of polarized visible irradiation (4 mW/cm^2). In all cases, the photoalignment develops quickly within the first

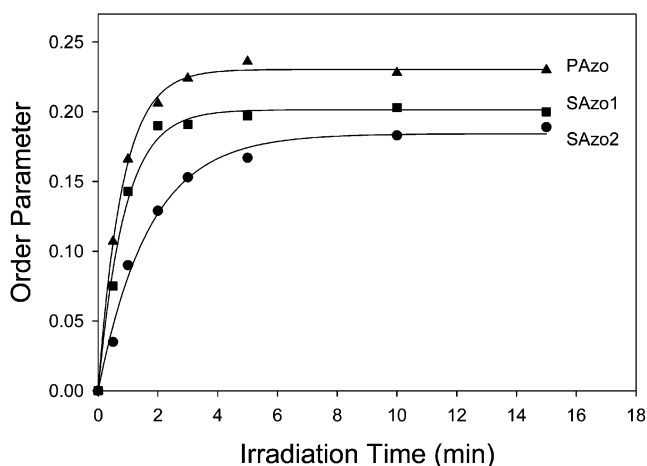


Figure 3. Order parameter of azobenzene groups vs irradiation time for the homopolymer and the two diblock copolymers. The curve fitting using a simple exponential rise is shown.

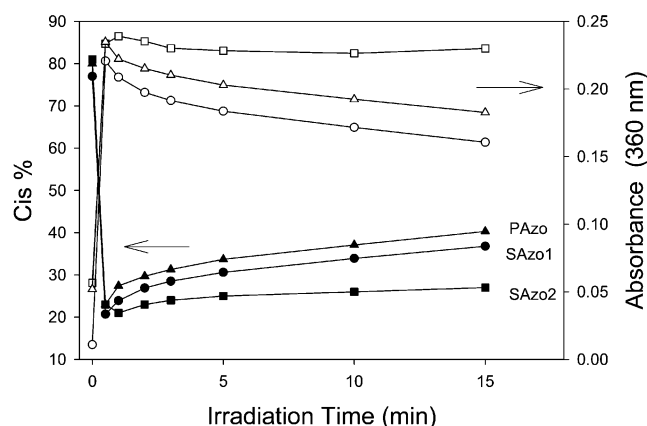


Figure 4. Changes in the apparent concentration of cis isomer (solid symbols) and the absorbance at 360 nm (open symbols) vs irradiation time for the same experiment as in Figure 3.

2–3 min of irradiation and reaches a plateau value, S_{max} , at longer times. The data could fairly be fitted with an exponential rise through $S = [1 - \exp(-t/\tau)]S_{\text{max}}$, where τ is the characteristic time for the rate of orientation induction. The curve fitting shown in Figure 3 yielded $\tau = 0.81 \text{ min}$, $S_{\text{max}} = 0.23$ for PAzo; $\tau = 0.88 \text{ min}$, $S_{\text{max}} = 0.20$ for SAzo1; and $\tau = 1.71 \text{ min}$, $S_{\text{max}} = 0.18$ for SAzo2. The results indicate that inside the microdomains the photoinduced orientation of azobenzene groups develops more slowly and the achievable orientation degree is smaller. Note that for this experiment the thickness of the spin-cast films was carefully controlled to give a similar absorbance of about 0.3 at 360 nm for all the polymers, thus taking into account the differences in the content of the azobenzene polymer. Unlike the photoinduced birefringence, which may be contributed by all natures of anisotropy in the polymers, the order parameter determined from the dichroism of the 360 nm peak characterizes the orientation of *trans*-azobenzene. Therefore, these results confirm that a decreased orientation of azobenzene groups in the diblock copolymers is indeed at the origin of the smaller photoinduced birefringence.²⁴ During the experiment in Figure 3, the nonpolarized UV-vis spectrum at each visible light irradiation time was also recorded in order to follow the cis-trans back-isomerization. Plotted in Figure 4 are the changes in the apparent percentage of cis isomers, which is calculated from $\text{cis}\% = 100(A_0 -$

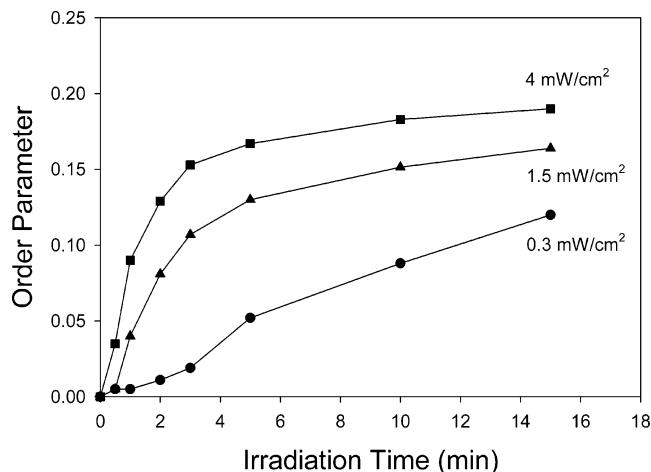


Figure 5. Order parameter of azobenzene groups vs irradiation time at different intensities of visible light irradiation for the diblock copolymer SAzo2.

A_t/A_0 , where A_0 and A_t are the absorbance of trans isomers at 360 nm before and after a time t of visible light irradiation, respectively. The data at $t = 0$ min refer to the film after the UV pretreatment. It is seen that most of the cis–trans back-isomerization process is completed after 30 s irradiation with visible light, which implies that the continuous increase in orientation of *trans*-azobenzene after the first 30 s (Figure 3) is not due to an increased concentration of trans isomer. Interestingly, the concentration of cis isomer apparently goes up again at longer irradiation times, which obviously is unrealistic. The reason for this can be found by plotting the absorbance at 360 nm as a function of irradiation time, also shown in Figure 4. The apparent increase in cis% is due to a decrease in the absorbance, A_t , over irradiation time. This suggests that an increased portion of *trans*-azobenzene groups may be photoaligned perpendicularly to the plane of the film (parallel to the light propagation direction), which have no contribution to the absorbance. The phenomenon seems to be more important in the homopolymer than in the two diblock copolymers, particularly for SAzo2 whose absorbance decreases only slightly.

The increase in order parameter of azobenzene groups (Figure 3) is reminiscent of the photoinduced birefringence.²⁴ As discussed previously, there seems to have two mechanisms for the development of orientation with the UV pretreatment followed by visible irradiation. In essence, when the linearly polarized visible irradiation is applied, most cis isomers are converted to trans isomers, and during this process a fraction of the recovered trans isomers already have their transition moments aligned perpendicularly to the polarization of irradiation. This accounts for the rapid increase in orientation at short irradiation times. After that, the orientation develops mainly following the angular selection mechanism involving trans–cis–trans cycles.¹ As expected, the intensity of the polarized visible irradiation affects the photoalignment of azobenzene. An example of the results is given in Figure 5 for SAzo2. The orientation can be induced even at a low intensity of 0.3 mW/cm², but it is much smaller and increases continuously up to 15 min irradiation. Here, the low intensity has effects on the two possible mechanisms. First, at the beginning it takes longer time to convert most cis isomers (~80%) to trans isomers (about 6 min with 0.3 mW/cm² as compared to less than 30 s with 4

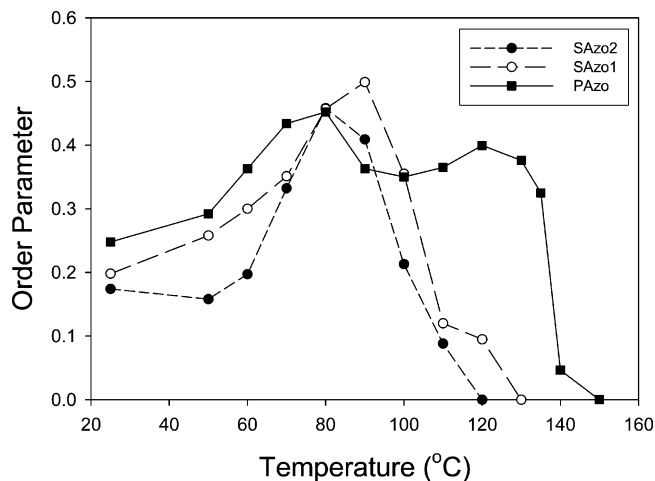


Figure 6. Order parameter of azobenzene groups vs annealing temperature for the homopolymer and the two diblock copolymers. Data at 25 °C are the photoinduced orientations before thermal treatment.

mW/cm²) and results in less oriented trans isomers. At longer times, it activates fewer *trans*-azobenzene groups to undergo the trans–cis–trans isomerization cycles for further photoalignment.²⁸

The photoalignment of azobenzene induced by polarized visible light following the unpolarized UV light preirradiation could be enhanced by thermal treatment. We used samples that were photoaligned as described in Figure 3 for this experiment. For each polymer, after the photoalignment the film was placed inside an oven with a predetermined temperature for 10 min and then cooled to room temperature for the polarized UV–vis measurement. The changes in order parameter as a function of annealing temperature are plotted in Figure 6 for the three polymers, the data at room temperature (25 °C) being the photoinduced orientation. It is seen that the degree of orientation of azobenzene groups can be increased significantly by annealing at $T > T_g$ for all polymers. The order parameters of the two diblock copolymers may reach as high as the homopolymer in the vicinity of 80–90 °C, despite their initial lower photoinduced orientation. This result suggests the occurrence of thermally enhanced self-organization and ordering of azobenzene mesogens in their LC phases even under the confinement of microdomains. The diblock copolymers, however, exhibit significant differences as compared to the homopolymer. After reaching the highest level ($S \sim 0.45$), their orientation drops sharply at higher annealing temperatures. This is in contrast with the homopolymer that shows only a moderate decrease in orientation at $T > 80$ °C, and its thermally enhanced orientation remains almost constant over an extended range of temperature before the drop when annealed in the isotropic phase. For the homopolymer, it appears quite clear that when annealed in the smectic phase, the self-organization of azobenzene groups leads to the highest degree of orientation, at around 80 °C, and this orientation is reduced in the nematic phase while remaining higher than the initial photoorientation. For the two diblock copolymers, the highest orientation apparently is reached in the nematic phase based on the phase transition temperatures determined by DSC (Figure 1), at about 90 °C for SAzo1 and 80 °C for SAzo2. In both cases, the further increase in annealing temperature results in fast decrease in orientation, which is particularly notable for SAzo1,

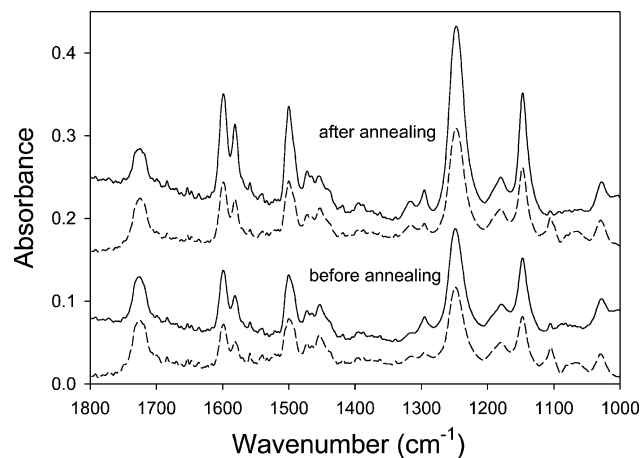


Figure 7. Polarized infrared spectra for a film of photoaligned diblock copolymer SAzo1 before and after annealing at 90 °C for 10 min. The spectra were recorded with the infrared beam polarized parallel (solid lines) and perpendicular (dashed lines), respectively, to the reference direction.

whose clearing temperature T_{hi} is about 12 °C below that of PAzo. These results imply that the self-organization of azobenzene groups in the smectic phase may be difficult to develop inside the microdomains, and an increased fluidity in the nematic phase may favor the orientation development. But in the same time, the confinement has as effect the destabilization of the nematic phase, i.e., decrease in thermal stability, so that the orientation of azobenzene could not be sustained at higher temperatures.

The photoinduced and thermally enhanced orientation of azobenzene groups was also confirmed by polarized infrared spectroscopic measurement. In this case, films were prepared on CaF₂ windows and subjected to the same irradiation and thermal annealing conditions. Figure 7 shows an example of the polarized infrared spectra with a film of SAzo1. Before annealing at 90 °C for 10 min, the photoinduced orientation can be noted from the dichroism of several bands of the azobenzene mesogenic group such as 1147, 1249, 1500, and 1599 cm⁻¹.¹⁵ After the annealing, the dichroism of all these bands increases significantly. It is noted that the order parameter based on the infrared dichroism apparently is smaller than that from the polarized UV-vis measurement. This was caused by the use of much thicker films in this experiment in order to have measurable infrared absorbance. The purpose of the polarized infrared measurement was to qualitatively confirm the observation from the UV-vis spectroscopy.

One common feature for the three polymers is the formation of aggregates of azobenzene chromophores in the solid state. This is visible from the differences between the UV-vis spectra of a spin-cast film of SAzo1 and its dilute solution in THF (Figure 8). In the solution, the aggregation of chromophores is minimized, and the absorption maximum at 360 nm comes from nonassociated (free) azobenzene groups. In the solid state, azobenzene groups at close proximity may associate from each other to form aggregates with coplanar transition dipoles.^{21,29} The H-aggregate and J-aggregate, which are sketched in the figure, are known to cause a blue shift and a red shift, respectively, of the absorption of nonassociated chromophores.^{21,29} This happens in films of the three polymers as exemplified by the spectrum of SAzo1 in Figure 8. In an attempt to gain more information on the photoinduced and thermally

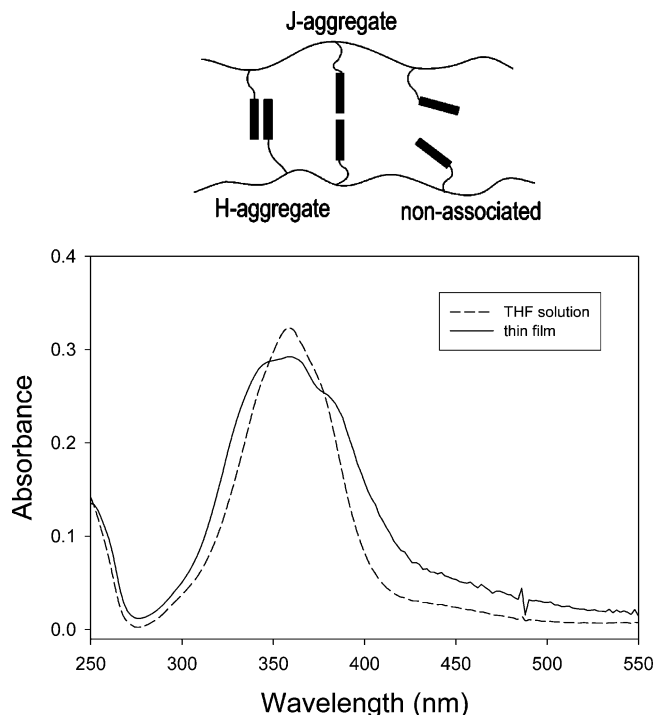


Figure 8. UV-vis spectra of the diblock copolymer SAzo1 in THF solution and thin film showing an increased aggregation of azobenzene chromophores in the solid state. The sketch illustrates the H-aggregation and J-aggregation of the chromophores, which are responsible for the blue and red shift, respectively, of the absorption of nonassociated chromophores centered at 360 nm.

enhanced orientation of azobenzene groups in the confining microdomains, we have used the curve-fitting method (Grams/32 from Galactic Corp.) to separate the absorptions from azobenzene groups in the three different aggregation states. An example of the curve fitting applied to polarized UV-vis spectra is shown in Figure 9. Good and reproducible fitting results were obtained by introducing three peaks with fixed absorption maxima at 334 nm for H-aggregated, 360 nm for nonassociated, and 384 nm for J-aggregated chromophores. Note that the absorption maxima used for the H- and J-aggregated chromophores are consistent with the literature.²¹ Figure 9 shows that the deconvolution of polarized spectra makes it possible to estimate not only the populations of azobenzene groups in the different aggregation states (peak areas) but also the order parameters of nonassociated, H-aggregated, and J-aggregated chromophores in a thin film simultaneously.

The order parameter data reported in Figure 6 were calculated from the dichroism of the peak maximum at 360 nm which, prior to the peak deconvolution, is the result of the superimposition of the absorption peaks of the three aggregation states. We have applied the curve-fitting analysis to all the data in Figure 6 and obtained the order parameters of azobenzene groups in the different aggregation states for the three polymers. From the results presented in Figure 10, some interesting observations can be made. First, before the thermal annealing, i.e., at 25 °C, the photoinduced orientation of the H-aggregate in the three samples is much higher than the orientations of the J-aggregate and the free (nonassociated) azobenzene. In the homopolymer, the J-aggregate is more orientated than the free azobenzene. By contrast, in the diblock copolymers SAzo1, the

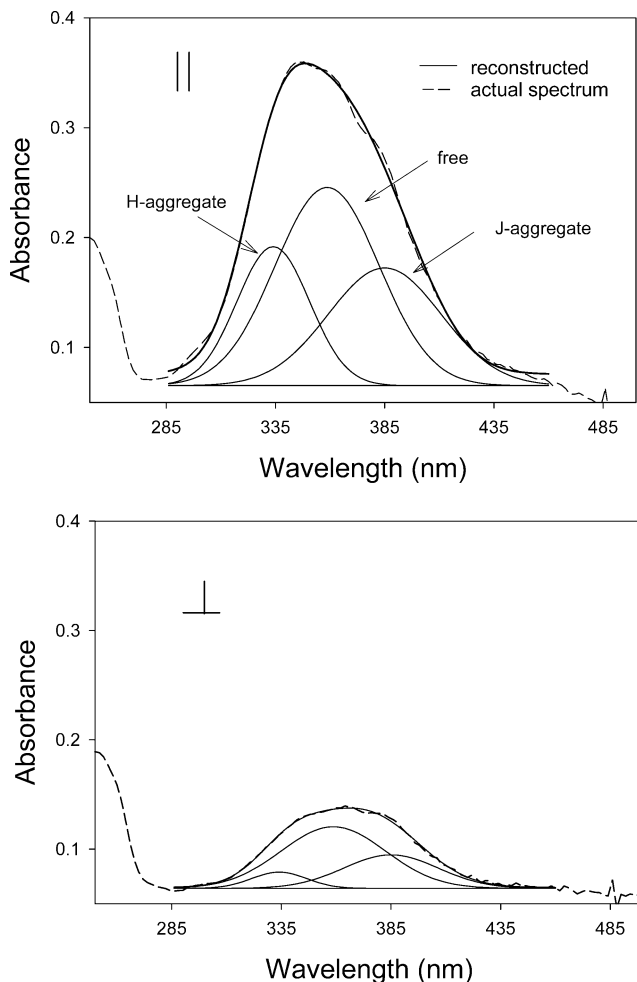


Figure 9. An example of the curve-fitting procedure applied to polarized UV-vis spectra showing the dichroism of the absorption peaks of azobenzene chromophores in the different aggregation states.

orientations of the J-aggregate and the free azobenzene are about the same, while in SAzo2, the orientation of free chromophores is actually higher than that of the J-aggregate. Second, upon thermal annealing at $T > T_g$, the enhanced self-organization of the chromophores results in an increased orientation degree for the three aggregation states. The orientation of the H-aggregate can become nearly perfect in the homopolymer, with $S \sim 0.9$. In the diblock copolymers, the highest orientation of the H-aggregate reaches $S \sim 0.6$ – 0.7 . On the other hand, the differences between the orientations of the three aggregation states remain essentially the same at various temperatures, and the similar thermal instability can be noticed for all the aggregation states.

A closer look at the results can be made from the data collected in Table 1, where the order parameters of the three aggregation states, as well as their populations in percentage determined from the relative peak areas, are compared for two representative temperatures: 25 and 80 °C. To calculate the populations, unpolarized UV-vis spectra were utilized. As mentioned earlier, the orientation at 25 °C is the photoinduced alignment prior to the thermal treatment, while the orientation at 80 °C is the thermally enhanced alignment. Analyzing the data at 25 °C, it appears clear that the confining geometries in the diblock copolymers reduce the achievable photoinduced orientation of azobenzene groups regardless of the aggregation state and affect the

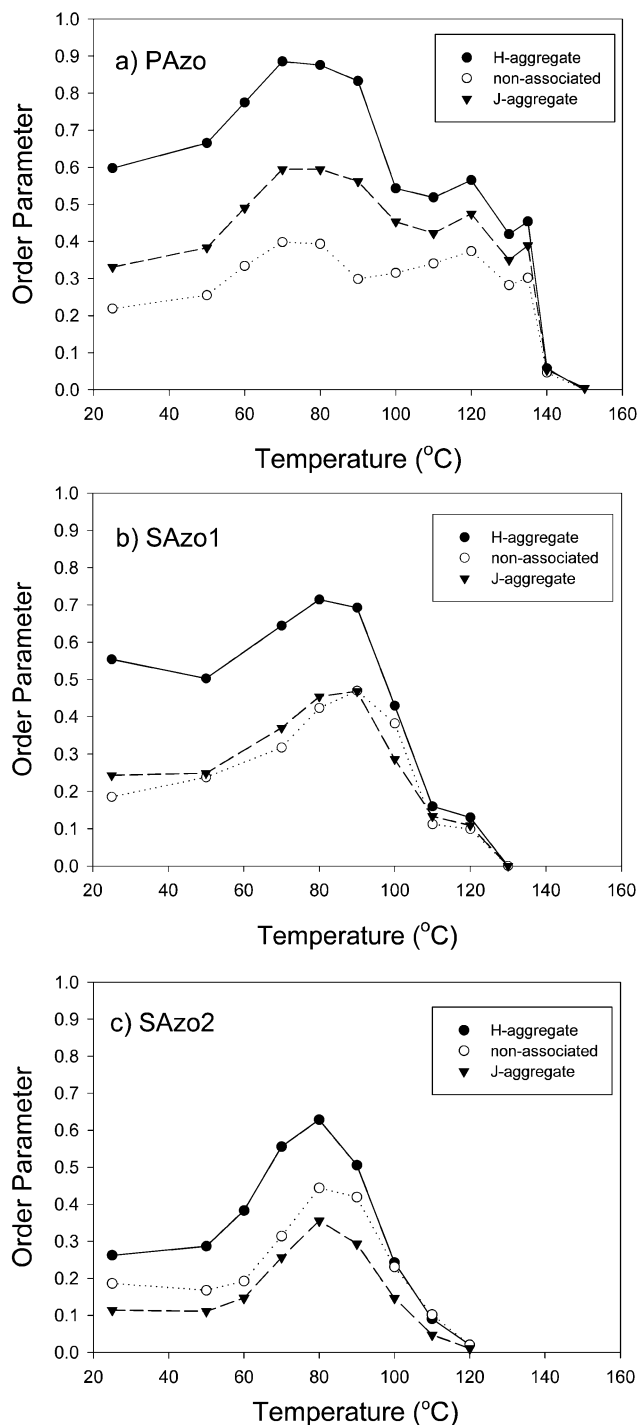


Figure 10. Order parameters of azobenzene groups in different aggregation states vs annealing temperature for (a) the homopolymer PAzo, (b) the diblock copolymer SAzo1, and (c) the diblock copolymer SAzo2.

relative populations of the aggregates as well. Indeed, the order parameters of the three aggregation states are smaller in the diblock copolymers than in the homopolymer. The decrease for the H- and J-aggregates in SAzo2 is particularly important. The two diblock copolymer have also more nonassociated azobenzene chromophores in the films. After the annealing at 80 °C, the enhanced self-organization of azobenzene groups in the LC phase leads to two noticeable changes. First, the orientation degrees (order parameters) of all aggregation states are increased in the three polymers. The increases in SAzo2 are particularly striking. Although the orientation

Table 1. Order Parameters and Populations in Percentage (in Parentheses) of Azobenzene Groups in the Different Aggregation States at 25 °C (Photoinduced Orientation without Annealing) and after Annealing at 80 °C for the Homopolymer and the Two Diblock Copolymers

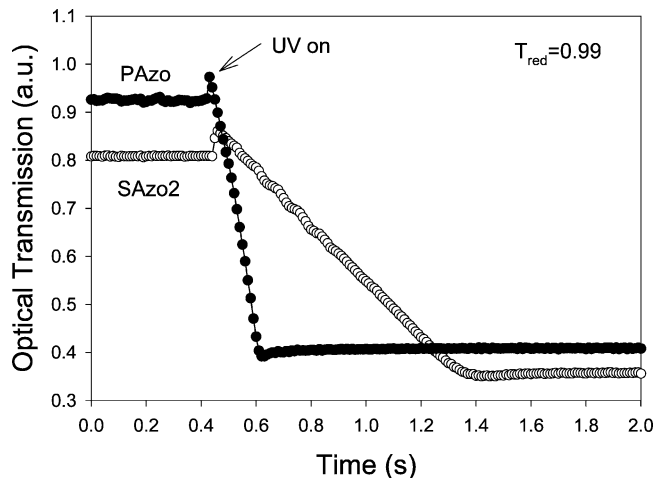
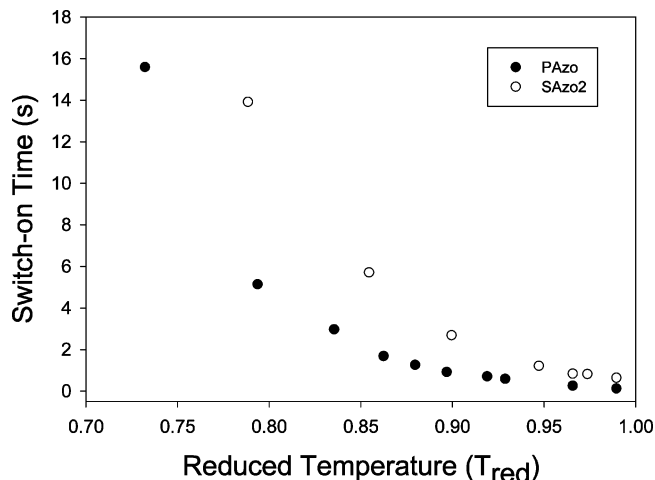
	PAzo		SAzo1		SAzo2	
	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
H-aggregate	0.60 (16%)	0.88 (22%)	0.55 (14%)	0.71 (23%)	0.26 (19%)	0.63 (18%)
J-aggregate	0.33 (15%)	0.59 (16%)	0.24 (9%)	0.45 (11%)	0.11 (6%)	0.36 (10%)
nonassociated	0.22 (69%)	0.39 (62%)	0.19 (77%)	0.42 (66%)	0.19 (75%)	0.44 (72%)

degrees of the H- and J-aggregates in the two diblock copolymers are still smaller than the homopolymer, the situation for nonassociated azobenzene groups seems to be reversed after the annealing. Second, the thermal treatment decreases the population of nonassociated azobenzene groups in favor of the H- and/or J-aggregates. But overall, this effect is much less important than the changes in orientation degree, particularly for SAzo2.

In summary, this part of work finds that under the confinement imposed by microphase-separated domains the achievable photoinduced orientation of azobenzene groups, in either H-aggregate or J-aggregate or non-associated state, is lowered. The subsequent thermal annealing in the LC phase results in higher orientation degrees for all aggregation states. Inside microdomains, the orientation degrees of the H- and J-aggregates remain smaller than the homopolymer having no microdomain confinement, while the orientation degree of nonassociated azobenzene groups may exceed that of the homopolymer.

Photochemical Phase Transition. The above study on the photoalignment found that the diblock copolymer SAzo2 behaves more differently from the homopolymer than SAzo1. The lamellar microdomain geometry in SAzo2 may be the cause of the more severe confinement effects. Therefore, SAzo2 was used with the homopolymer PAzo for a comparative study aiming to reveal the possible confinement effects on the photochemical phase transition initiated by the *trans*-*cis* isomerization of azobenzene mesogenic group. For this study, spin-cast films of the two polymers were first annealed at $T < T_{ni}$ for a sufficiently long time to allow the LC phase to develop. In the LC state, when the birefringent film is placed between crossed polarizers, the transmission of the probe He-Ne laser can be detected. When the film is exposed to unpolarized UV light, the *trans*-*cis* isomerization takes place, and the perturbation destabilizes the LC phase, which leads to the isotropic state and, consequently, a drop in the optical transmission of the probe light. In this study, the use of the low UV light intensity of about 2 mW/cm² was meant to keep a significant concentration of *trans*-azobenzene chromophores (about 50%) in the photostationary state on UV irradiation. Under this condition, even the *trans*-*cis* photoisomerization is very fast, it would take some time for the *cis* isomers to disorder the *trans*-azobenzene groups to finish the LC-isotropic phase transition. The rate of the phase transformation may be related to the decay of the optical transmission of the probe light on UV irradiation.

Figure 11 shows an example of the recorded changes in optical transmission on UV irradiation for PAzo and SAzo2 at the same reduced temperature $T_{red} = TT_{ni} = 0.99$. It is visible that the drop of the optical transmission takes longer time to complete for the diblock copolymer. Note that the instantaneous, slight increase in optical transmission when the UV irradiation is

**Figure 11.** Photochemical liquid crystalline-isotropic phase transition on UV irradiation for the homopolymer PAzo and diblock copolymer SAzo2 as revealed by changes in optical transmission of the probe light.**Figure 12.** Switch-on times for the photochemical liquid crystalline-isotropic phase transition vs reduced temperature for the homopolymer PAzo and the diblock copolymer SAzo2.

applied is due to the entry to the photodetector of a small portion of the UV light. The characteristic time required for the transmission to decrease from 90% to 10% of the initial level could be measured and considered as the optical switch-on time. We performed the measurements at various temperatures for PAzo and SAzo2, and the obtained switch-on times are plotted as a function of the reduced temperature in Figure 12. It is seen that the photochemical phase transition of azobenzene mesogens is slowed down under the confinement of the lamellar microdomain geometry and that the confinement effect becomes more and more prominent at lower T_{red} . It is interesting to note that the photochemical phase transition occurs even in the glassy state but takes much longer times to develop (the T_g of

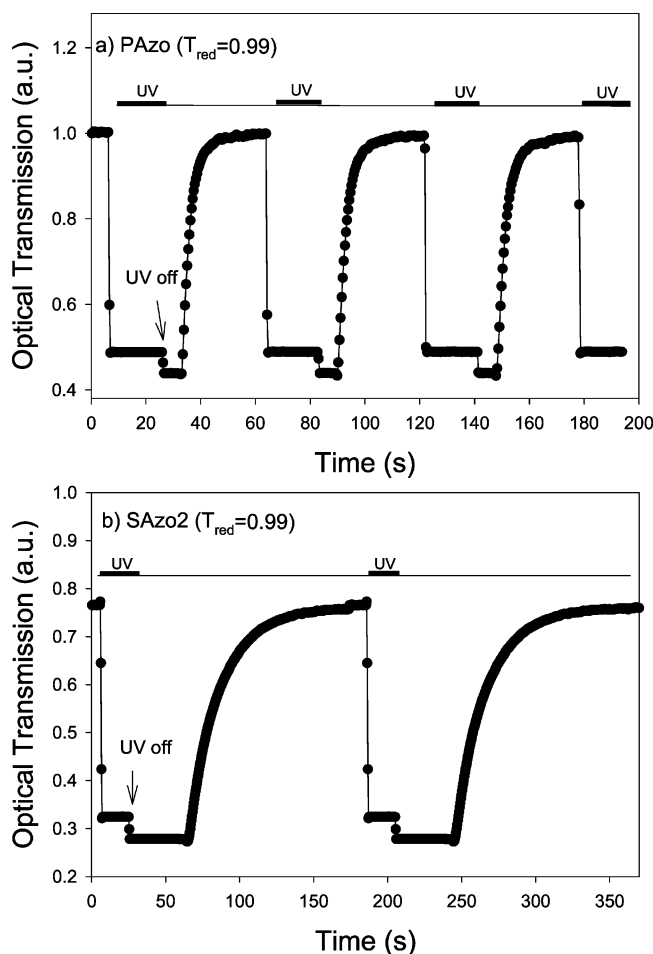


Figure 13. Cycles of the photochemical liquid crystalline-isotropic phase transition and the thermally induced recovery of the liquid crystalline phase for (a) the homopolymer PAzo and (b) the diblock copolymer SAzo2.

PAzo corresponds to $T_{red} = 0.85$ and that of SAzo2 ($T_{red} = 0.88$).

Under UV irradiation, the *trans*-*cis* isomerization transforms azobenzene mesogens from a LC phase into the isotropic phase. After the UV irradiation is turned off, the thermally induced *cis*-*trans* back-isomerization would take place, and the LC phase of *trans*-azobenzene mesogens should be recovered over time. This was also observable from changes in optical transmission of the probe light. Figure 13 shows an example of the results recorded over a much longer period of time, the measurement being carried out at $T_{red} = 0.99$. For both polymers, the removal of the UV irradiation from the film results instantaneously in a slight decrease in the optical transmission for the reason mentioned above. Here, the small portion of the UV excitation light entering the photodetector is eliminated once the UV light is turned off. It is seen that the recovery of the optical transmission, which corresponds to the reorganization of the LC phase, starts after an apparent induction period. It was found that the length of the induction period is determined by the absolute temperature. The induction period is the same for both PAzo and SAzo2 at the same temperature, indicating that the confinement has no effect on the rate of the thermally induced *cis*-*trans* back-isomerization. The induction period becomes longer as the temperature is lowered, as can be seen from Figure 13, where the measurement for SAzo2 was performed at a lower temperature (101

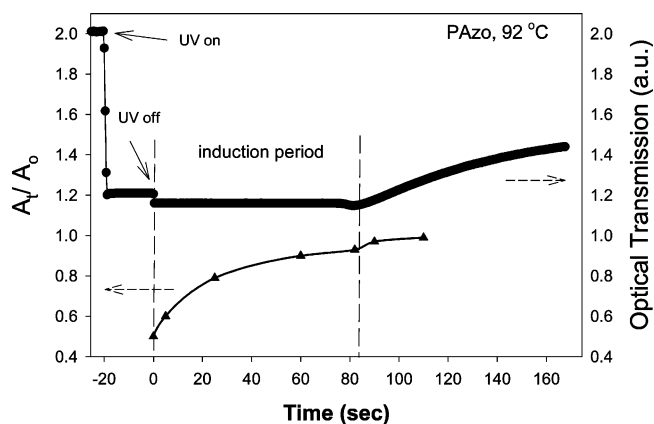


Figure 14. Progress of the thermally induced *cis*-*trans* back-isomerization after the UV irradiation is turned off. The increase in the concentration of *trans* isomers is monitored by the ratio of the absorbance at 360 nm at a given time (A_t) over that before UV irradiation (A_0). The induction period prior to the liquid crystalline phase recovery is indicated.

°C) than for PAzo (129 °C) to have the same reduced temperature for comparison. The explanation can be found from the experiment described in Figure 14, where the UV light was applied to and then removed from a film of PAzo at $T = 92$ °C, and changes in optical transmission were recorded showing a long induction period. Another film was used in the same conditions to see how the absorbance of *trans*-azobenzene evolved during the induction period. To do this, the hot stage holding the film at 92 °C was mounted in the compartment of the UV-vis spectrophotometer prior to the UV irradiation. Immediately following the removal of the UV irradiation, the spectra were taken at various times. The change in absorbance of *trans*-azobenzene is also plotted in Figure 14. Two observations are pertinent. First, right after the UV irradiation, there is about 50% of *trans* isomers remained in the film due to the use of a low-intensity UV light, as mentioned earlier. This ensures that the photochemical LC-isotropic phase transition observed corresponds to the reorganization of *trans*-azobenzene groups from an ordered state to a disordered state due to the perturbation of *cis* isomers. Second, after the irradiation is turned off, most of the *cis*-*trans* back-isomerization takes place during the induction period. Similar behavior was also found for SAzo2. This result indicates that the induction period corresponds essentially to the completion of the thermal relaxation of the *cis*-azobenzene groups. This is why its length is determined by the temperature; faster relaxation at higher temperatures reduces the induction time.

In the end of the induction period, most *trans*-azobenzene mesogens are recovered and begin to reorganize to form the LC phase. Therefore, the data for the increase in optical transmission reveal the kinetics of the isotropic-LC phase transformation. Back to Figure 13, it is clear that at the same $T_{red} = 0.99$ the formation of the LC phase is much slower in the diblock copolymer than in the homopolymer, which should be accounted for by the confinement of azobenzene groups inside the microdomains. Similarly, a thermal switch-off time, which is the time required for the optical transmission to recover from 10% to 90% of the initial level, could be measured. Figure 15 compares the switch-off times obtained for PAzo and SAzo2 at various reduced temperatures. They are much longer for the

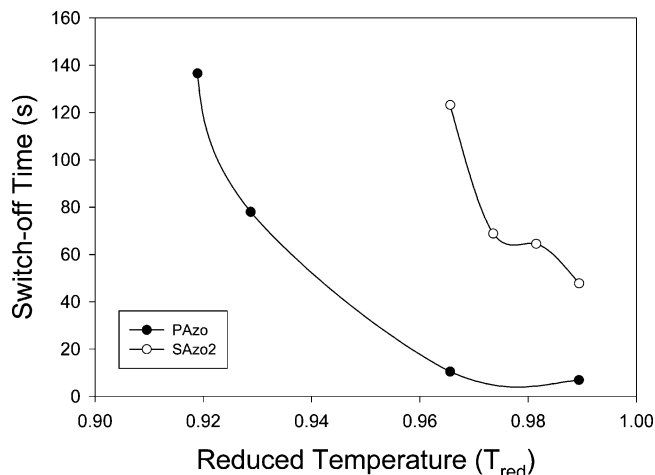


Figure 15. Switch-off times for thermally induced liquid crystalline phase recovery vs reduced temperature for the homopolymer PAzo and the diblock copolymer SAzo2.

diblock copolymer than for the homopolymer, which suggests the difficulty for azobenzene mesogens to reorganize in a confined geometry.

To summarize this part of work, the study finds that the confining lamellar microdomain in the diblock copolymer SAzo2 slows down the rate of the photochemical LC–isotropic phase transition process on UV irradiation. This finding is particularly significant because despite the less ordered LC phase in the diblock copolymer prior to the UV irradiation, it takes a longer time to complete the transformation into the disordered isotropic phase under the confinement. Moreover, the rate of the thermally induced LC phase recovery after the UV irradiation is turned off is also slower inside the microdomains. These confinement effects become increasingly important when comparing the diblock copolymer and the homopolymer at lower reduced temperatures. The choice of the reduced temperature as the reference temperature is appropriate because of the different phase transition temperatures for the two polymers investigated. Note that similar results of comparison were obtained by using $(T - T_g)/(T_{ni} - T_g)$ as the reference, which takes into account the difference in the extent of the temperature range between T_g and T_{ni} .

Thermochromic Behavior. The thermochromic behavior originates from changes in the absorption wavelengths of the chromophore, which may be quite prominent for some azobenzene LC polymers due to strong temperature-dependent aggregation states of the azobenzene chromophore.²⁰ To compare the thermochromic behaviors of the homopolymer and the two diblock copolymers, their thin films were prepared by spin-casting and dried at ambient temperature for several days. In other words, the films were not subjected to any thermal treatment or exposed to UV and visible light irradiations before the use. To observe the spectral changes, UV–vis spectra were recorded at various temperatures on heating (at a rate of 2 °C/min and the film was held at each temperature for 1 min before taking the spectrum). Using the same curve-fitting procedure as described above, the populations of azobenzene groups in the different aggregation states could be determined from their peak areas. The results for the three polymers are presented in Figure 16 plotting the normalized peak areas as a function of temperature.

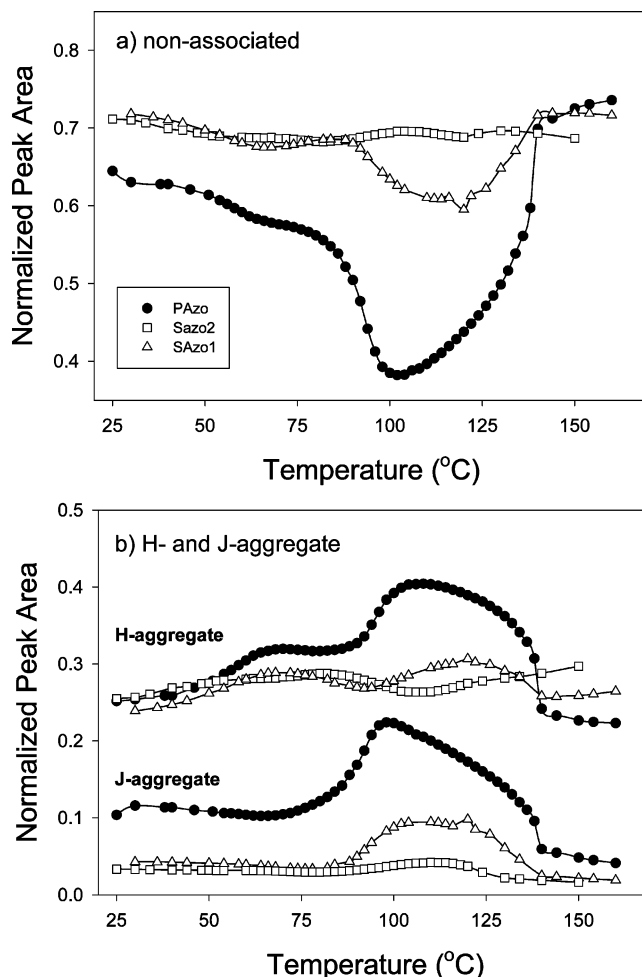


Figure 16. Changes in population of azobenzene chromophores in different aggregation states as a function of temperature for the homopolymer and the two diblock copolymers: (a) nonassociated and (b) H- and J-aggregated azobenzene.

Very different behaviors can be noticed. For the homopolymer, on heating the population of nonassociated azobenzene groups starts to decrease slowly until T_g and then drops quickly at $T > 80$ °C. Below 80 °C, the small decrease in the free azobenzene population is accompanied by an increase in the H-aggregation and apparently a very slight decrease in the J-aggregation. Above 80 °C, the sharp decrease in the free azobenzene population results in a significant rise in both the H- and J-aggregation. However, the two aggregation states do not reach their maximum population at the same temperature. The largest changes are observed at about 102 °C, at which the free azobenzene population drops from the initial 65% to 38%, while the population of the H-aggregates increases from 25% to 40% and that of the J-aggregates raises from 10% to 22%.

In the initial spin-cast films, the two diblock copolymers have more free azobenzene groups (~71%) than the homopolymer (~65%); i.e., they are more amorphous-like. They have about the same percentage of H-aggregates as the homopolymer (~25%) but a lower J-aggregate population (~4%). On heating, SAzo1 shows a significant decrease in the free azobenzene population at $T > 90$ °C, which is echoed by an increase in the populations of the H- and J-aggregates. However, these changes are much smaller than PAzo. Indeed, the largest changes occur at about 119 °C for this diblock

copolymer. At this temperature, its free azobenzene population decreases from 71% to 60%, while the population of H-aggregates increase from 25% to 31% and that of J-aggregates from 4% to 9%. It can be noted that, like PAzo, the increase of the J-aggregate population seems to happen at lower temperatures as compared to the H-aggregation. In the case of SAzo2, any large thermally induced changes in the aggregation states of the chromophores seem to be suppressed. On heating, there is only a slight fluctuation in the populations of the free azobenzene and the H-aggregates. The percentage of the J-aggregation is essentially unchanged within experimental errors.

The changes in the aggregation states of azobenzene chromophores could also be observed over time. For this experiment, spin-cast films were heated quickly to a predetermined temperature, and the UV-vis spectra were recorded over time. The results obtained at two temperatures for each polymer, which were chosen to have the same $T_{red} = 0.93$ and $T_{red} = 0.88$ for comparison, are reported in Figure 17. These isothermal measurements confirm the features in Figure 16. The homopolymer displays the largest changes in the aggregation of azobenzene chromophores. The changes are much less important in the diblock copolymer SAzo1 and almost negligible in SAzo2. In the last case, it is interesting to note that the slight fluctuation in the populations of the aggregation states as a function of temperature (Figure 16) is also manifested by the instability of the changes at short times (Figure 17). Especially at 81 °C, the free azobenzene population does decrease within the first minute but then returns to the initial level. This results in the up-and-down of the H-aggregate population.

The prominent thermochromic behavior of PAzo is due to the strong thermally induced enhancement of the self-organization of azobenzene mesogens in the LC phase. The ability of self-organization is severely reduced when azobenzene mesogens are confined in the microdomains in the diblock copolymers. The results show that, despite the liquid crystallinity of the azobenzene polymer block, the self-organization of azobenzene mesogens is difficult to develop in SAzo1, where the azobenzene polymer is located in a continuous space between the PS cylindrical microdomains, and it is almost suppressed in SAzo2 whose azobenzene mesogens are confined in the lamellas of the azobenzene polymer block.

Concluding Remarks

The confinement of azobenzene mesogenic groups in microphase-separated domains has profound effects on the behaviors of azobenzene LC polymers. First, the photoinduced orientation of azobenzene groups is more difficult to develop inside the microdomains. Even though a subsequent thermal annealing at $T > T_g$ can significantly enhance the alignment, the achievable orientations of the H- and J-aggregates are smaller than that of the homopolymer having no confinement. Second, when the photochemical phase transition initiated by the *trans*-*cis* isomerization is compared at the same reduced temperature, it takes longer time for the LC phase inside the microdomains to transform into the isotropic state. And after the thermal relaxation of *cis* isomers, the reorganization of *trans*-azobenzene leading to the LC phase recovery is also much slower under the confinement. Third, unlike the homopolymer that dis-

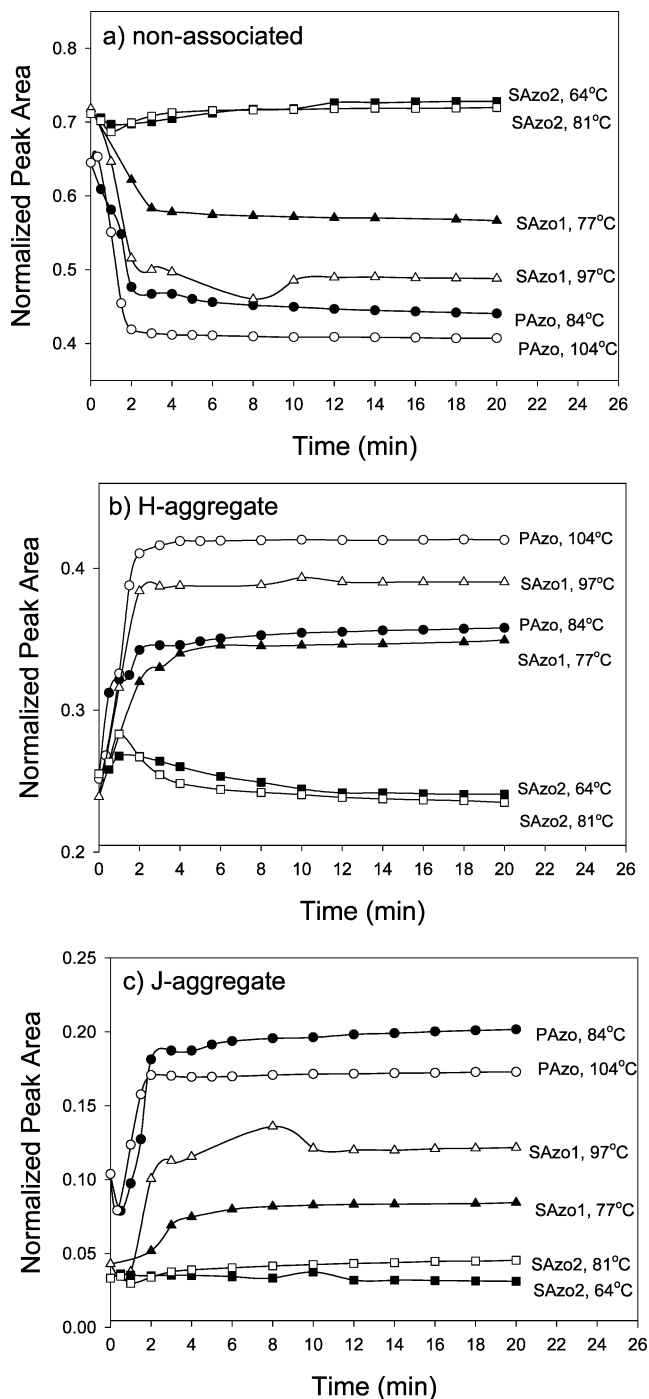


Figure 17. Changes in population of azobenzene chromophores in different aggregation states as a function of annealing time for the homopolymer and the two diblock copolymers, each annealed at two temperatures corresponding to reduced temperatures of 0.93 and 0.88: (a) nonassociated, (b) H-aggregated, and (c) J-aggregated azobenzene.

plays a prominent thermochromic behavior arising from an increase in the H- and J-aggregation of azobenzene groups on heating, the formation of the aggregates is severely hindered or even suppressed inside the microdomains. These various manifestations of the confinement effects point to a common cause. That is, in the confined geometries, changes in organization involving the motion and rearrangement of azobenzene groups are more difficult to proceed. Such changes may be an order-disorder transformation process such as the photochemical LC-isotropic phase transition or disor-

der–order evolution such as the thermally induced LC phase recovery as well as the orientation induced by linearly polarized visible light following unpolarized UV preirradiation.

What characterizes the motion and reorganization of liquid crystal molecules is the cooperative effect. In the diblock copolymers, the cooperative effect for the motion of azobenzene mesogens inside the microdomains may be weakened due to the nanometer scale confining spaces in the direction perpendicular to the PS cylinders or in the thickness direction of the lamellas (Figure 1). Moreover, the interfacial interaction between PS and azobenzene groups may play a key role in amplifying the restriction on the motion of azobenzene mesogens. As a matter of fact, the anchoring of liquid crystal molecules at the interface with polymers is a general phenomenon, whose strength varies depending on the system.²² The boundary anchoring in LC diblock copolymers may affect the mesophases and structures in different ways.²³ For the two diblock copolymers used in this study, based on the reduced mesophase transition temperatures and enthalpies (Figure 1), the confinement reduces the LC ordering of azobenzene mesogens and weakens the thermal stability of the LC phases. This, however, is not inconsistent with the observed confinement effects that render the various reorganization processes of azobenzene mesogens inside the LC phases more difficult. These processes are mainly photochemically induced transformations such as the photoalignment and photochemical phase transition but are also the LC phase recovery following the photochemical phase transition and the thermally induced changes in the aggregation states of azobenzene mesogens (thermochromic behavior).

At this point we do not know whether the interfacial interaction between PS and the azobenzene polymer gives parallel anchoring (azobenzene aligned parallelly to the interface) or perpendicular anchoring (perpendicular alignment) or anchoring at a certain angle. But in any case, the reduced mesophase transition enthalpies and temperatures suggest an anchoring effect that hampers the ordering of azobenzene groups. This may explain the difficulties in reorganizing azobenzene groups into a more ordered state, which is the case of photoinduced and thermally enhanced orientation as well as the LC phase recovery after the photochemical phase transition. However, such a randomizing effect cannot explain the difficulty in transforming the LC phase into the isotropic state. Other mechanisms may exist. The sketch in Figure 18 is an illustrative example. Under the effect of a parallel anchoring, the perpendicular orientation of azobenzene groups would be difficult to develop because the azobenzene mesogens parallelly anchored at the interface may oppose the process. With reference to the photochemical LC–isotropic phase transition, it can also be pictured that the anchoring (ordering) at the interface may slow down the propagation of the perturbation of cis isomers that is responsible for the destabilization of the ordered LC phase.

Block copolymers are increasingly used to make nanostructured materials. New materials are conceivable by exploiting the photoactivity of azobenzene-containing block copolymers. For instance, if the methacrylate-based LC azobenzene polymer block forms cylindrical microdomains and partially removed through, for example, hydrolysis reaction, light-responsible

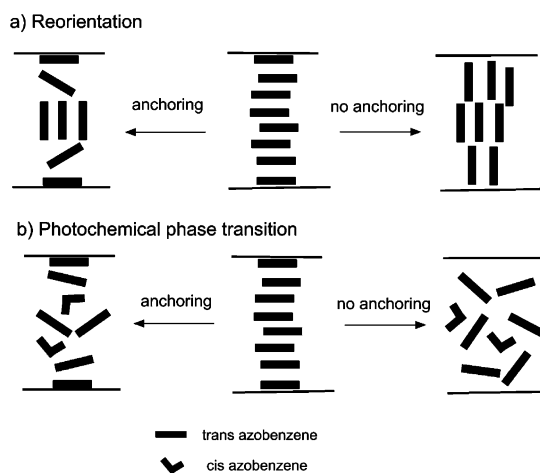


Figure 18. Schematic illustration of parallel anchoring of azobenzene groups at the interface between two polymers. The anchoring may restrict reorientation of azobenzene groups in the direction perpendicular to the interface (a) and hamper the development of the photochemical liquid crystalline–isotropic phase transition (b).

nanochannels may be obtained, whose transport properties could be reversibly tailored by irradiation. In studies of such applications, the confinement effects on the various properties of LC azobenzene polymers in the block copolymers, as revealed by this work, should be taken into account.

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