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Azobenzene-Containing Thermoplastic Elastomers: Coupling Mechanical and Optical Effects

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ABSTRACT: Thermoplastic elastomers of a styrene−butadiene−styrene (SBS) triblock copolymer containing grafts of an azobenzene side-chain liquid crystalline polymer were prepared by polymerization of an azobenzene acrylate monomer in solutions with dissolved SBS. Stretching thin films at room temperature induces long-range orientation of the azobenzene mesogenic groups along the strain direction. Upon irradiation with polarized or unpolarized UV light at 360 nm, the orientation of azobenzene moieties in stretched films is erased as a result of the trans-to-cis photoisomerization, while on subsequent irradiation with polarized or unpolarized visible light at 440 nm, the initial stretching-induced orientation is recovered due to the cis-to-trans back-isomerization. Gratings can be inscribed on stretched films at different alignments with respect to the strain direction, whose fringe spacing can be modified through elastic extension or retraction of the films.

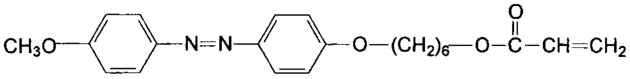
Introduction

Photoisomerization of azobenzene compounds has been extensively explored in the search for new functional materials, among which are azobenzene-containing polymers.[1−5] There are mainly two types of azobenzene polymers that have been the subject of intensive studies over the past decade because of their potential for photonic applications, namely amorphous polymers[4,5] and liquid crystalline polymers.[1−3] More recently, azobenzene polymer networks have also been used for photoalignment and stabilization of low-molar-mass liquid crystals.[6] In this paper, we report on the preparation of a system of azobenzene thermoplastic elastomers and investigations on the coupling effects between mechanically induced orientation of azobenzene moieties and their photoisomerization. The motivation for our studies on azobenzene-containing thermoplastic elastomers, whose thin films can easily be prepared and stretched, is to combine mechanical and optical effects, which we expect could result in interesting properties. For instance, elastic deformation of azobenzene polymers may lead to reversible changes in the properties generated by photoisomerization of azobenzene, which could be the basis for designing mechanically tunable optic and photonic devices. To the best of our knowledge, no such studies have been reported.

In a previous work carried out in this laboratory,[7] side-chain liquid crystalline polymers (SCLCPs) were grafted onto a styrene−butadiene−styrene triblock copolymer (SBS) through free radical polymerization of monomers of SCLCPs in solutions with dissolved SBS. The mechanisms for the grafting of SCLCPs were thought of as similar to the grafting of polystyrene (PS) on polybutadiene (PB).[8] These are either a radical transfer from a primary radical of the initiator or from a propagating radical to the methylene group of the PB block, which initiates the polymerization of the monomer, or a direct reaction between the double bonds of the PB block and chain propagating radicals. In the present study, the same technique was employed. A monomer of SCLCPs, whose mesogenic side group contains an azobenzene moiety, was polymerized in solutions with dissolved SBS, resulting in thermoplastic SBS that has grafts of the corresponding azobenzene SCLCP.

Experimental Section

The monomer used has the following chemical structure



and it was synthesized by following the method reported in the literature.[9] The SBS block copolymer, purchased from Aldrich, contains 30 wt % of PS. Unless otherwise stated, the following procedure was used to prepare SBS with azobenzene SCLCP grafted onto the central PB block. Weighted azobenzene monomer and SBS were dissolved in toluene at a monomer concentration of 5 wt %; the initiator used was benzoyl peroxide, and its concentration was kept at 5 mol % with respect to the monomer. The solution was then heated to 80 °C for thermal polymerization that last generally 10 h. All grafted SBS samples were purified through a 4-fold precipitation in methanol, ensuring the removal of unreacted monomer as well as the azobenzene polymer that was not chemically linked to SBS. An azobenzene homopolymer was also prepared, and its purification was made possible by repeated precipitation in cold ether. All purified samples were collected and dried in a vacuum.

Thin films were cast from chloroform solutions onto the surface of a glass plate, and the solvent was removed by drying the films at 60 °C in a vacuum. Unless otherwise mentioned, thicknesses of all stretched films were controlled to be about 10−12 μm. In other words, to obtain a film with a higher draw ratio λ, being defined as the film length after stretching over that before stretching, a thicker film was utilized to make sure that the film thickness fell into the range 10−12 μm after the stretching. Characterizations were carried out using differential scanning calorimetry (Perkin-Elmer DSC-7), polarizing microscopy (Leitz DMR-P), infrared spectroscopy (Bomem MB-200 FTIR), UV−vis spectroscopy (HP-8452A), and gel permeation chromatography (GPC, Waters), using polystyrene

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Table 1. Characteristics of the Samples

acronym of polymer	feed ratio (monomer/SBS)	azobenzene content (wt %)	M_w (g/mol)	M_w/M_n
SBS			184 200	1.1
AE1	1:1	10.1	234 900	1.5
AE2	2:1	8.2	235 000	1.4
AE3	3:1	21.9	208 100	1.6

standards and THF as eluent. For irradiation of the films, a 1000 W Hg (Xe) lamp (Oriel) was used with filters and, when necessary, a polarizer; the actual irradiation intensity was measured by a powermeter placed in front of the sample. Without polarizer the intensity was about 2 mW/cm^2 at 360 nm and 7 mW/cm^2 at 440 nm. With polarizer the intensity was cut by about half. The orientation of azobenzene mesogenic groups was measured by means of polarized infrared spectroscopy. Its characteristic band at 1254 cm^{-1}, assigned to the phenyl−oxygen stretching vibration,[10] is well-suited to the measurements since it is not overlapped with phenyl bands from the PS block of SBS. As the transition moment of this band is parallel to the long axis of the azobenzene group, the order parameter could be calculated from $S = (A_{\parallel}/A_{\perp} - 1)/(A_{\parallel}/A_{\perp} + 2)$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of the 1254 cm^{-1} band obtained with the electric vector of the infrared beam parallel and perpendicular, respectively, to the orientation direction, which was taken as the film strain direction.

Results and Discussion

Characterization of the Samples. Three samples of azobenzene-grafted SBS were prepared, and their characteristics are summarized in Table 1. The concentration of the azobenzene SCLCP grafts was determined from both ^{1}H NMR and UV measurements in THF solutions. For the UV measurements, it was assumed that the azobenzene monomer has the same extinction coefficient as the polymers. The two methods yielded very similar results, and the values given in Table 1 are the average values. The slightly greater content of azobenzene in AE1 than in AE2, despite a lower feed ratio of the azobenzene monomer to SBS for the former, is likely caused by a different polymerization condition used for AE1. For this sample, weighted SBS and monomer were dissolved in two separate THF solutions, the solution of SBS was first heated to the polymerization temperature, and the monomer solution containing the initiator was then added dropwise into the SBS solution.

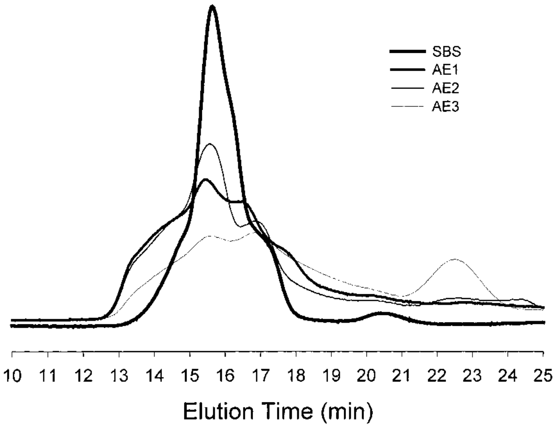
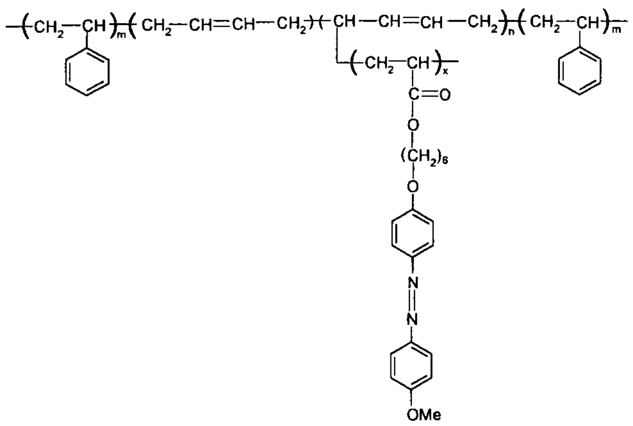


Figure 1. GPC curves of SBS and azobenzene-grafted SBS samples.

The grafting of the azobenzene SCLCP on the PB block of SBS was confirmed by GPC. The grafting of azobenzene branches should result in an increase in the average molecular weight of the SBS sample if there is no SBS chain breaking during the polymerization. Figure 1 shows the GPC curves for the three samples and pure SBS. It is seen that peaks of the azobenzene-grafted SBS samples are broader than that of the pure SBS, with a significant portion of the peaks shifted to lower elution times, corresponding to higher molecular weights. The observed increase in the weight-average molecular weight (Table 1) is accompanied by an increase in the molecular weight distribution, which is no surprise for free radical polymerization. In the case of AE3, which, among the samples, was obtained using the highest feed ratio of azobenzene monomer to SBS (3:1), a lower mass peak is present, which may be indicative of the presence of some homopolymer remained in this sample. Experiments reported in this paper were mainly obtained using the samples of AE1 and AE2. The following is a suggested chemical structure of the azobenzene-grafted SBS, assuming that a radical transfer to the methylene group of the PB block was the main mechanism for initiating the graft polymerization of the azobenzene monomer.



The triblock SBS copolymer grafted with azobenzene SCLCP should have a complex morphology, with the azobenzene SCLCP forming a microphase that is embedded in the rubbery PB matrix. On the optical microscope, no birefringent spots can be observed under crossed polarizers, suggesting that azobenzene grafts be confined in small microdomains, which is consistent with the observation that films of all grafted samples appear transparent like pure SBS. By contrast, mixtures of SBS and the azobenzene homopolymer with similar compositions, which were prepared for comparisons, exhibit larger-scale phase separation and display birefringent areas on polarizing microscope; their films look translucent. From DSC measurements using a heating rate of 10 °C/min, the azobenzene homopolymer has a T_g around 40 °C, a smectic-to-nematic phase transition at 79 °C, and a nematic-to-isotropic transition at 114 °C. Those transition endotherms could not be clearly identified for the azobenzene elastomers, probably due to the small concentrations of azobenzene grafts and the small domains in which they are located, meaning important interfacial interaction with the PB matrix that can reduce order in the liquid crystalline phases. In the case of AE3, two phase-transition peaks can be noticed at about 80 and 120 °C. Despite the lack of direct detection of liquid crystalline phases in AE1 and AE2 by DSC and polarizing microscopy, as will be seen, orientation behaviors of these elastomers imply that azobenzene grafts form liquid crystalline microphases that are separated from the PB matrix.

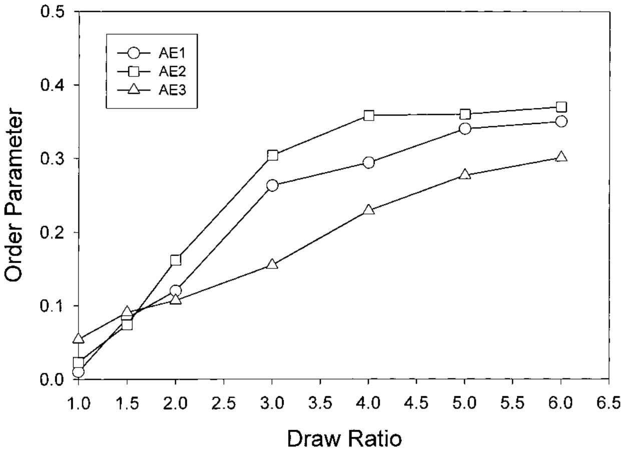


Figure 2. Order parameter of azobenzene moieties vs draw ratio for azobenzene-grafted SBS samples stretched at room temperature.

Stretching-Induced Orientation and Photoisomerization. Similar to pure SBS, azobenzene-grafted SBS is thermoplastic elastomer. Thin films of all samples show good mechanical strength and can be repeatedly stretched and retracted at room temperature. The stretching-induced orientation of azobenzene groups at room temperature was determined for the three samples; the results are shown in Figure 2 by plotting the order parameter S as a function of draw ratio. In all cases, the orientation of azobenzene moieties is parallel to the strain direction and increases with the film extension. Upon retracting the films, the orientation decreases in the same way (data not shown). While the orientation in AE3 seems to increase linearly with draw ratio, the orientation in both AE1 and AE2 develops rapidly and reaches a plateau value close to $S = 0.30$ after $\lambda = 3$. This behavior is reminiscent of SCLCPs subjected to a mechanical stretching[11] and implies that the azobenzene grafts are in a liquid crystalline phase at room temperature. Moreover, if the azobenzene grafts were not microphase-separated from the PB matrix, they should be very short and behave like side groups of the PB chains. In that case, the orientation of azobenzene groups should have a linear relationship with film extension like for rubbery PB chains.[12] Another supporting evidence is worth being mentioned. It is known that[12,13] when stretched SBS is annealed at temperatures below but close to T_g of the PS cylindrical microdomains, oriented PB chains can be relaxed as a result of the rearrangement of the PS cylinders, and the film loses the elasticity. A number of stretched films of azobenzene-grafted SBS were annealed at 55 °C until the films showed no elasticity and thus no PB chain orientation. If the azobenzene grafts were side groups as part of the PB block, orientation of azobenzene moieties should disappear. However, an important degree of azobenzene orientation was found to remain in the relaxed films ($S \sim 0.2$), suggesting that the azobenzene grafts are in their own microphases.

We first irradiated stretched films, i.e., films under strain, with linearly polarized UV light at 360 nm in order to observe possible effects of photoalignment of azobenzene groups on the mechanically induced orientation. If photoalignment occurs in stretched films and adds up to the stretching induced orientation, the orientation would be expected to increase under irradiation polarized perpendicularly to the strain direction but to decrease under irradiation polarized parallely. However, it was found that oriented azobenzene moieties were randomized by UV irradiation regardless of the polarization direction of the irradiation light, indicating the absence of an effective photoalignment of azobenzene moieties. Spectroscopic investigations on solid films and solutions suggest that this situation is caused by a slow thermal cis-to-trans back-isomerization of the azobenzene moieties. It is known that a fast thermal cis-to-trans back-isomerization is required for effective photoalignment.[1-5] For these azobenzene elastomers, after irradiation with UV light on the films, it took several hours for the cis-rich photoequilibrated state to return to the initial trans-rich state. Without effective photoalignment, irradiation at 360 nm, whether polarized or not, only accomplishes the photoisomerization of azobenzene moieties, and the conversion of rodlike *trans*-azobenzene to bent-shaped *cis*-azobenzene leads to randomization of the azobenzene groups in the stretched films and results in the loss of the mechanically induced orientation. If this is true, a second irradiation with visible light at 440 nm, polarized or unpolarized, should make a fast cis-to-trans back-isomerization and restore the orientation of the azobenzene groups in the stretched films. This mechanism indeed was confirmed by polarized infrared and UV spectroscopic measurements.

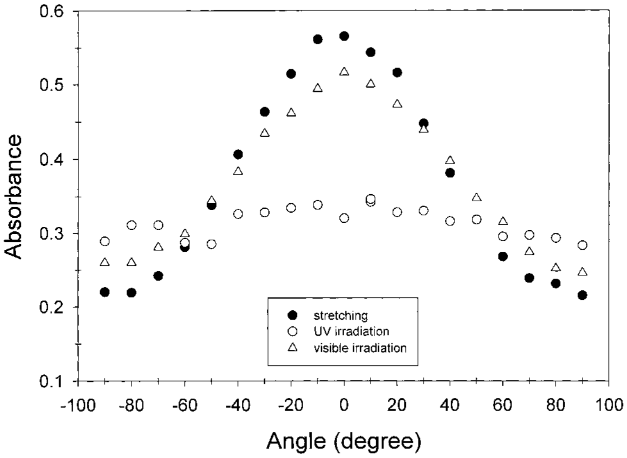


Figure 3. Absorbance of the 1254 cm^{-1} band vs angle between strain and the electric vector of infrared beam for a film of AE2 stretched at room temperature and then subjected to unpolarized UV and visible irradiations.

Figure 3 shows an example of the infrared measurements. The absorbance of the 1254 cm^{-1} band for a film of AE2 stretched to $\lambda = 6$ is measured as a function of the angle between the strain direction and the electric vector of the infrared beam. Prior to irradiation, the stretching-induced orientation of azobenzene groups along the strain direction is indicated by the highest absorbance at 0°. After a 10 min irradiation with unpolarized UV light, the orientation is randomized as revealed by an almost constant absorbance. However, a subsequent 2 min irradiation with unpolarized visible light results in a recovery of the orientation. Figure 4 shows the polarized UV spectra recorded for a stretched thin film of AE1 having a thickness of about 5 μm. (A thickness below 10 μm was necessary for obtaining UV spectra whose absorption was not too intense to be analyzed even qualitatively.) Before irradiation (Figure 4a), the dichroism of the broad absorption peak of the *trans*-azobenzene groups around 360 nm indicates orientation of their long axes along the strain direction, with a higher absorption for the spectrum taken with

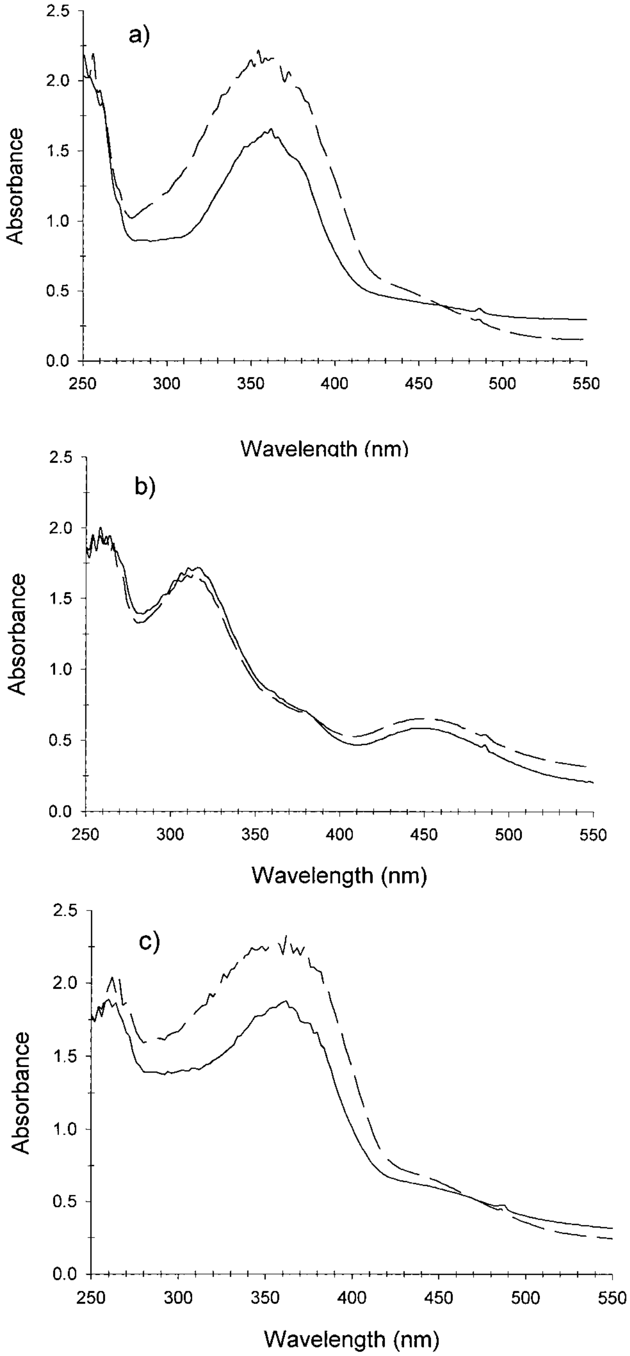


Figure 4. Polarized UV spectra for a film of AE1: (a) after stretching at room temperature; (b) after exposure to unpolarized UV irradiation; and (c) after irradiation with unpolarized visible light (solid and dashed lines for polarizations perpendicular and parallel, respectively, to the strain direction).

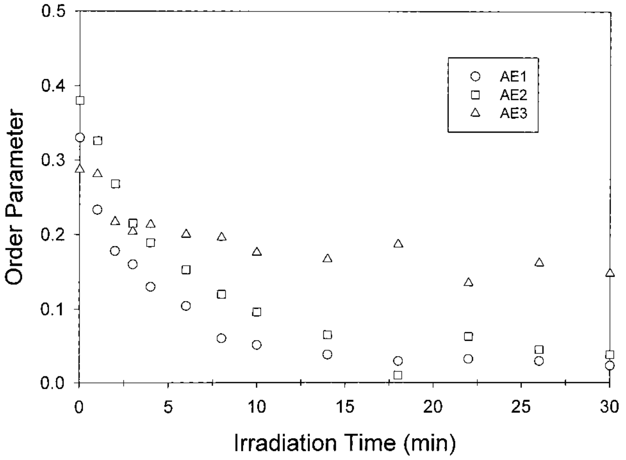


Figure 5. Order parameter of azobenzene moieties vs irradiation time with unpolarized UV light for stretched azobenzene-grafted SBS.

polarization of the beam parallel to the stretching direction. After irradiation with unpolarized UV light for 5 min (Figure 4b), on one hand, the dichroism is no longer present, indicating the loss of azobenzene orientation, and on the other hand, the dominant population of *cis*-azobenzene moieties in the stretched film is clearly seen by the new absorption peaks around 320 and 450 nm. Upon a second irradiation with unpolarized visible light for 2 min (Figure 4c), the reappeared peak at 360 nm as well as its dichroism indicates that the trans-rich state and the orientation along the strain direction are restored in the film. These UV measurements clearly confirm that photoisomerization of the azobenzene groups is at the origin of their orientation loss and recovery in the stretched films.

The rate of orientation decrease of the azobenzene groups in stretched films upon irradiation with unpolarized UV light was investigated for the three samples. Figure 5 shows the plots of order parameter as a function of irradiation time for films stretched to $\lambda = 6$. For both AE1 and AE2, the orientation drops sharply within the first 10 min of irradiation, leaving only a small residual orientation. By contrast, the orientation in AE3 decreases only partly, and a significant amount remains even after 30 min of irradiation. Films used for these experiments were relatively thick ($\sim$15 μm under strain). As AE3 contains much more azobenzene moieties than AE1 and AE2, the limited loss of orientation may be caused by a saturation of the irradiation because of the high absorption of the azobenzene groups.

The rate for the orientation recovery of the azobenzene groups on irradiation with unpolarized visible light was found to be faster. However, the recovered orientation is always slightly below the initial orientation induced by stretching (Figure 3). Interestingly, when polarized visible light was used for the orientation recovery, a contribution from photoalignment of azobenzene was observed. The results obtained for AE2 are presented in Figure 6 for the sake of argument. Two films were stretched to draw ratios of 2 and 6 for orientation of the azobenzene mesogens and then subjected to a 10 min irradiation with UV light for randomization. Afterward, both films were exposed to polarized visible light with the polarization direction parallel and perpendicular to the strain direction, and the orientation recovery as a function of irradiation time was measured. If the conversion from *cis*-azobenzene to *trans*-azobenzene were the only reason for the orientation recovery, one would expect the same achievable orientation for the two polarization directions. It is clear from Figure 6 that this is not the case. For the two films, having different draw ratios and different initial orientations, the recovered orientation, completed after about 2 min of irradiation, is significantly higher when the polarization of the visible light is perpendicular to the strain of the film; the achieved orientation is actually similar to the initial stretching induced orientation ($S \sim 0.35$ for the film at $\lambda = 6$ and $S \sim 0.15$ for the film at $\lambda = 2$). In both cases, the recovered orientation under unpolarized light is intermediate between

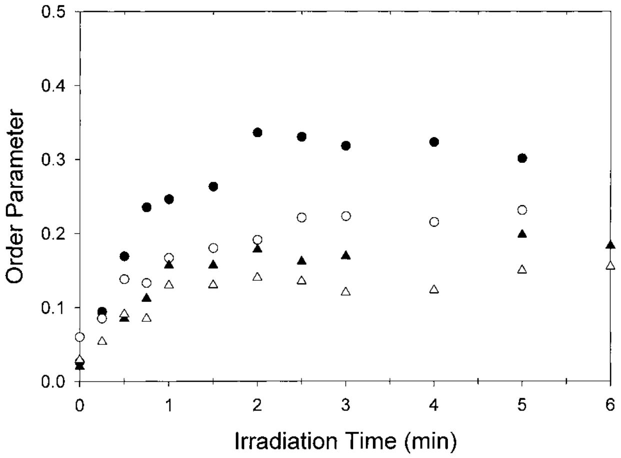


Figure 6. Order parameter of azobenzene moieties vs irradiation time with polarized visible light for two films of AE2, which were stretched to $\lambda = 2$ (triangle) and $\lambda = 6$ (circle) and randomized by UV irradiation, the polarization of visible light being perpendicular (solid symbols) and parallel (open symbols) to the film strain direction.

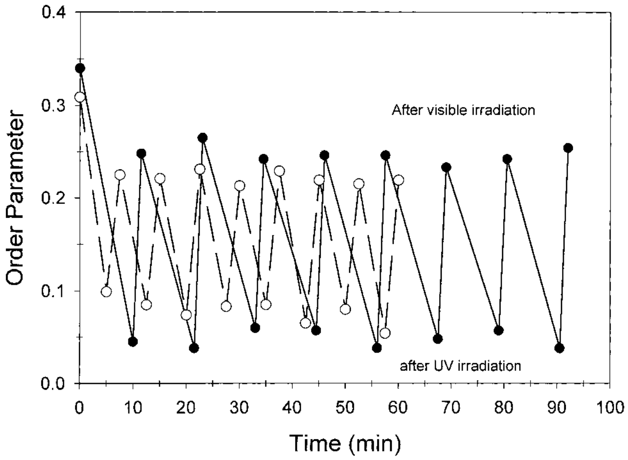


Figure 7. Changes in orientation of azobenzene moieties for two films of AE1, stretched to $\lambda = 6$, subjected to repeated cycles of unpolarized UV irradiation for orientation loss and unpolarized visible irradiation for orientation recovery.

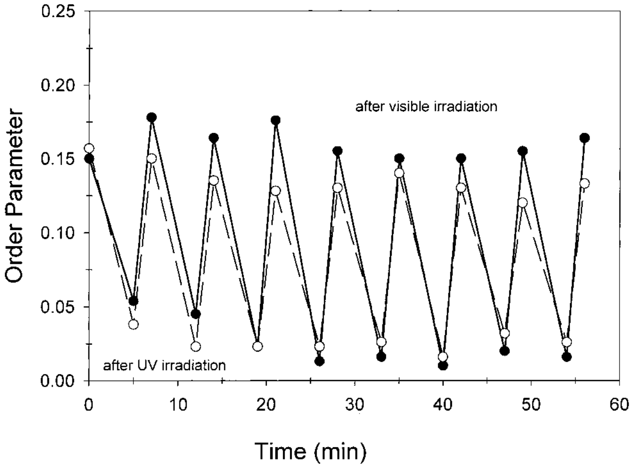


Figure 8. Changes in orientation of azobenzene moieties for two films of AE1, stretched to $\lambda = 2$, subjected to repeated cycles of unpolarized UV irradiation for orientation loss and polarized visible irradiation for orientation recovery (solid and dashed lines for polarization of visible light perpendicular and parallel, respectively, to the film strain direction).

those under polarized light with the two polarization directions (data not shown). These results suggest that photoalignment of azobenzene groups in the cis-rich state takes place under polarized irradiation with visible light. When the polarization direction is normal to the strain of the film, this photoalignment adds up to the orientation recovery, resulting from the cis-to-trans isomerization; when it is parallel to the strain, the photoalignment opposes to the orientation recovery in the strain direction. Photoalignment of azobenzene moieties under irradiation with visible light, preceded by UV irradiation to attain a cis-rich state, was reported for azobenzene side-chain liquid crystalline polymers.[2b]

Using azobenzene-grafted SBS elastomer, a mechanical stretching readily aligns azobenzene mesogens, while randomization and recovery of this orientation are accomplished through photoisomerization of the azobenzene moieties upon irradiations with UV and visible lights. Such a coupling between the mechanical and optical effects can be used to create an optical switching. The principal is demonstrated in Figure 7, where the order parameters measured after unpolarized UV and visible irradiations is plotted as a function of irradiation time for two different films of AE1 stretched to $\lambda = 6$, yielding a similar initial orientation ($S \sim 0.33$). Eight cycles of irradiation were conducted, and the orientation loss and recovery were recorded. Experiments on the two films differed in the time for the orientation erasure, being 5 and 10 min, but had the same time for the orientation recovery, being 3 min. Faster switching can be obtained by using shorter irradiation times, but the orientation loss is partial upon UV irradiation; i.e., the difference in orientation between the two states is smaller. Another example is shown in Figure 8 using polarized visible light for the orientation recovery. Two films were stretched to $\lambda = 2$ and subjected to repeated cycles composed of a 5 min irradiation with unpolarized UV light and a 3 min irradiation with polarized visible light, the polarization being parallel and perpendicular, respectively, to the strain direction of the two films. The results show that switching can be made on films with low draw ratio and, thus, smaller initial orientation and that photoalignment of azobenzene can contribute to the orientation recovery on irradiation with visible light polarized perpendicularly to the strain. It should be emphasized that thick films were used in these experiments to demonstrate the principle, which explains the long irradiation times needed for the orientation loss and recovery. In principle, fast optical switching could be realized through the use of thin films, because fast photoisomerization processes trigger changes in the orientation of azobenzene.

A number of other experiments confirmed that a trans-rich state in a stretched film is all what is needed for orientation of the long axes of azobenzene moieties along the strain direction. For example, if a film is exposed to UV irradiation prior to stretching to reach the cis-rich state, no orientation can be seen from infrared dichroism in the stretched film. However, orientation appears after the cis-to-trans back-isomerization induced either photochemically by irradiation with visible light for 2–3 min or thermally by leaving the film under strain at room temperature for about 10 h. It is reasonable to assume that in stretched films the microdomains of the azobenzene grafts are elongated along the strain direction and that energetically it is favorable for rodlike azobenzene moieties in the trans state to align their long axes in the strain direction. However, it should be mentioned that there is another way to look at the phenomenon, which is based on the photochemical phase transition.[2] In a stretched film, orientation should be erased if irradiation with UV light results in transformation from a liquid crystalline phase into the isotropic phase for the azobenzene mesogens as a result of the trans-to-cis photoisomerization. The liquid crystalline phase of the azobenzene grafts reappears after the cis-to-trans back-isomerization and therefore realigned in the stretched film. At this point, we do not know whether this is the main mechanism. The azobenzene-grafted SBS would be in the smectic phase at room temperature, while the photochemical phase transition is usually observed for the nematic-to-isotropic transition.[2]

Formation of Gratings. The orientation loss and recovery of the azobenzene moieties in stretched films upon irradiation with polarized or unpolarized UV and visible lights can be used to inscribe gratings whose fringe spacing can then be modified through elastic extension or contraction of the films. Gratings can be written in two ways. The first method consists of irradiating a stretched film behind a photomask with UV light; the exposed areas lose the orientation due to photoisomerization, while the unexposed areas retain the orientation. In the second method, a flood UV irradiation is first applied to the stretched film to randomize the oriented azobenzene groups, then the photomask is on, and a visible light irradiation is applied to the film. In this way, the exposed areas have the orientation recovered, while the unexposed areas do not. However, gratings obtained by the second method were not as clear and stable as those obtained by the first method. Using both methods, the obtained gratings should be birefringent gratings that are induced by different orientations of the azobenzene moieties.

Figure 9 shows an example of the gratings obtained using unpolarized UV irradiation on a stretched film of AE2 ($\lambda = 6$) covered by a photomask of 20 μm fringe spacing. The optical micrographs were taken under crossed polarizers at a small angle to the strain direction. Gratings were inscribed parallely (photo a) and perpendicularly (photo b) to the film strain direction (indicated in the figure). When the film was allowed to retract to $\lambda = 1.5$ (photo c), the fringe spacing for the grating perpendicular to the strain becomes much smaller (on the right of the picture), being reduced by a factor of 4 as determined by the longitudinal retraction. By contrast, the grating parallel to the strain direction increases its fringe spacing by a factor of about 2 (on the left of the picture), which corresponds to the lateral dilatation of the film. These changes were reversible upon repeated film extension or retraction. When a flood UV or visible irradiation was applied to the grating on the stretched film, a cis-rich or trans-rich state is regained throughout the film; grating obtained by UV irradiation became much less visible on the microscope, but was not removed completely, while grating obtained by visible irradiation following a UV treatment could be erased completely.

Polarized infrared measurements on stretched AE2 films before and after inscription of the gratings confirm that the formation of gratings is mainly related to the photoisomerization-induced changes in orientation of azobenzene. A film had an initial stretching-induced orientation of $S = 0.36$; after inscription of the grating using UV irradiation, the orientation dropped to $S = 0.16$, which is consistent with the randomization of the azobenzene moieties in about half of the film, whereas another film having the same stretching induced orientation was used for grating writing using the second method. The randomization of oriented azobenzene moieties by flood UV irradiation resulted in $S = 0.03$; after inscription of the grating with visible light, the orientation was recovered to $S = 0.22$. In both cases, the orientation loss or recovery was slightly higher than what would be expected if photoisomerization occurred in half of the film. This is probably caused by a somewhat loose contact between the film and the photomask, leading to light diffraction from the mask into some areas of the film behind the dark fringe. If the photochemical phase transition is at the origin of the orientation loss and recovery, the perturbation resulting from the phase transition in exposed areas (bright fringes) could be propagated into unexposed areas (dark fringes),[2c] which accounts for the results.

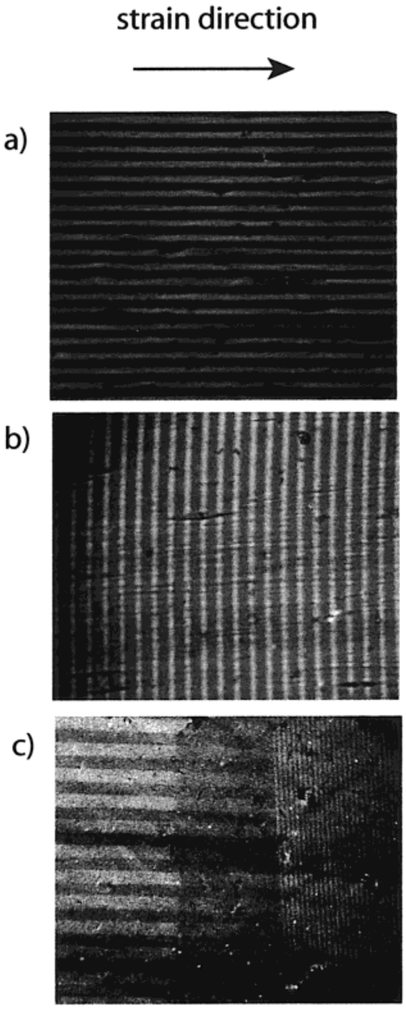


Figure 9. Gratings inscribed on a film of AE2 stretched to $\lambda = 6$ using unpolarized UV irradiation and a photomask of 20 μm fringe spacing: (a) grating parallel to the strain direction; (b) grating perpendicular to the strain direction; and (c) the two gratings on the film relaxed to $\lambda = 1.5$, showing a decrease in fringe spacing for the perpendicular grating and an increase in fringe spacing for the parallel grating.

Although changes in orientation of the azobenzene moieties are responsible for gratings on stretched azobenzene elastomer films, other observations and evidences suggest the occurrence of some permanent structural or morphological changes related to photoisomerization of azobenzene in the films under strain.

The most striking observation is that gratings are much more stable on films retracted right after the inscription of grating. For instance, as UV irradiation is applied to a stretched film with photomask, the irradiated areas lose the orientation because of the cis-rich sate of azobenzene, while the nonirradiated areas retain the orientation with azobenzene in the trans-rich state. When the film is relaxed after irradiation, the nonirradiated areas also lose the orientation of azobenzene moieties in the trans-rich state. (Infrared measurements confirmed the absence of any long-range orientation in relaxed films.) At that point, the grating on the relaxed film, looking very prominent under crossed polarizers, should be a refractive index grating related to the cis-rich and trans-rich states in irradiated and nonirradiated areas. If this conformational difference is the only reason for the grating, it should disappear after a couple of days as the thermal cis-to-trans back-isomerization converts azobenzene moieties in irradiated areas into the trans-rich state. However, a series of gratings on relaxed films, which were inscribed perpendicular to the strain of the film using photomasks with fringe spacing ranging from 5 to 50 μm, remained stable after 6 months. These gratings were found to diffract light, with the diffraction angle increasing or decreasing upon film retraction or extension. These gratings cannot be erased by flood UV or visible irradiation but can be removed by heating the films to above 120 °C, which is about the nematic-to-isotropic transition temperature of the azobenzene homopolymer. This is another indication that azobenzene grafts in the elastomer samples form liquid crystalline microphases. Investigations are underway in our laboratory to study mechanical tunable light diffraction of these azobenzene elastomers and to elucidate the evolution of gratings formed under various stretching and irradiation conditions. Results will be reported later.

Conclusion

An azobenzene side-chain liquid crystalline polymer is grafted on a SBS triblock copolymer through radical polymerization of the azobenzene monomer dissolved in SBS solutions. The resulting material is an azobenzene-containing thermoplastic elastomer, and stretching of its film induces long-range orientation of the azobenzene mesogenic groups in the strain direction. When the stretched film is exposed to polarized or unpolarized UV irradiation, orientation of the azobenzene moieties is lost as a result of the trans-to-cis photoisomerization. Subsequent irradiation with polarized or unpolarized visible light allows for a quick recovery of the orientation in the stretched film because of the cis-to-trans back-isomerization. This coupling between the mechanically induced orientation and the effects of photoisomerization can be used to generate optical switching between the orientation-on and orientation−off states. Using photomasks, stable gratings can be inscribed through either UV irradiation on stretched films or visible irradiation on UV-pretreated stretched films. Gratings are formed mainly by periodic differences in the orientation of the azobenzene moieties, but there may also be some mechanically and photochemically induced structural or morphological changes that remain to be understood. Gratings inscribed on this type of azobenzene-grafted SBS diffract light and can have their fringe spacing modified upon elastic extension or retraction of the films. This study demonstrates the potential of using azobenzene-containing elastomers in the search for mechanically tunable optical or photonic devices.

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