

DESIGN AND STUDY OF NEW AZOBENZENE LIQUID CRYSTAL/POLYMER MATERIALS

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Abstract Discussion is presented on the use of the photoisomerization of azobenzene chromophore in the design and preparation of novel functional materials. The two systems reviewed are azobenzene polymer-stabilized liquid crystals and azobenzene elastomers. In the first case, a polymer network containing azobenzene moieties is used to optically induce and stabilize a long-range liquid crystal orientation without the need of treating the surfaces of the substrates. This optical and rubbing-free approach was applied to nematic and ferroelectric liquid crystals. In the second case, an azobenzene side-chain liquid crystalline polymer is grafted onto a styrene-butadiene-styrene triblock copolymer to yield a photoactive thermoplastic elastomer. Coupled mechanical and optical effects make possible the formation of diffraction gratings that may be useful for mechanically tunable optical devices.

Keyword Azobenzene polymers, Photoalignment of liquid crystals, Photoactive elastomers

INTRODUCTION

Photoactive polymers and liquid crystals using azobenzene chromophore have attracted much attention in recent years because of their potential for optical and photonic device applications^[1–7]. The reversible photoisomerization of azobenzene between the less stable *cis* and the more stable *trans* isomers is the property exploited in all work. What makes azobenzene particularly interesting as compared with other chromophores includes the high isomerization efficiency, the drastic change in shape of the molecule (switched between the stretched *trans* and the contracted *cis* conformations), and the photoinduced orientation. Two examples of important discoveries relating to azobenzene-containing polymers illustrate the excitement in this research area.

On the one hand, while studying amorphous azobenzene polymers, the groups of Natanshon and Tripathy independently reported in 1995 the formation of surface-relief gratings on thin polymer films exposed to an interference pattern generated by two laser beams^[8,9]. A photoinduced massive mass transport at the surface is believed to be at the origin of this phenomenon, although the exact mechanisms involved are still a subject of debate. This discovery provides the basis of an all-optic method for fabricating gratings, and its importance is reflected by the very impressive amount of research work that has been carried out since the original reports^[1c, 7b]. In the case of liquid crystalline polymers (LCPs), on the other hand, Ikeda and coworkers^[3] have found that when *trans*-azobenzene is part of the mesogenic group, its photoisomerization may result in an isothermal nematic-to-isotropic phase transition, being induced by the perturbation effect of the *cis* isomer. This fast photochemical phase transition has also been successfully used to record holographic gratings that show great promise for optical storage.

Currently, many research groups worldwide are exploring azobenzene and its derivatives for a wide variety of applications and functional materials such as azobenzene dendrimers^[10], photoregulation of proteins^[11],

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photocontrolled self-assembly^[12], azobenzene sol-gel materials^[13] and liquid crystal gels^[14]. The basic question that faces researchers interested in azobenzene polymers is the same, that is, how to make use of the photoisomerization of azobenzene for the design and preparation of new and useful advanced materials? My group has conducted research in this area over the last few years. This paper gives a brief review of two systems proposed and studied by us.

AZOBENZENE POLYMER NETWORKS IN LIQUID CRYSTALS

A major research topic in the area of low-molar-mass liquid crystals (LCs) is the use of polymers to either develop new or improve the properties of known LC devices. There are mainly two types of LC/polymer composites, namely polymer-dispersed liquid crystals (PDLCs) and polymer-stabilized liquid crystals (PSLCs)^[15, 16]. Unlike PDLCs that are generally composed of LC droplets dispersed in a polymer matrix, in PSLCs, a polymer network of low concentration (≤ 10 wt%) is dispersed in a LC host. In most cases, the polymer network is used to stabilize the long-range LC orientation induced by rubbed surfaces, or to stabilize a specific LC texture, *i.e.*, an orientational state of the LC molecules, or to improve the mechanical strength of the LC cells. To make a PSLC, a reactive monomer is dissolved in a LC host, and after the induction of the LC alignment or texture the polymerization is carried out either photochemically or thermally. The polymer network formed under these conditions can mimic the LC environment and become aligned or adopt a specific morphology, which in turn exerts the stabilization effect on the LC host. In 1999, we proposed the use of azobenzene-containing polymer networks in PSLCs^[17] and been working on this system since. The idea of using such a photoactive polymer is to explore possible new and active functions of the polymer network in addition to the known stabilization effect. More specifically, an interesting property of azobenzene is its photoalignment: when exposed to linearly polarized irradiation, as a result of photoisomerization azobenzene may be aligned in the direction perpendicular to the polarization of the irradiation light^[1]. We want to know if this property can be used to optically control the LC alignment. Before highlighting our work, it should be mentioned that we have designed and synthesized a number of network-forming azobenzene monomers. As shown by the examples in Fig. 1, these

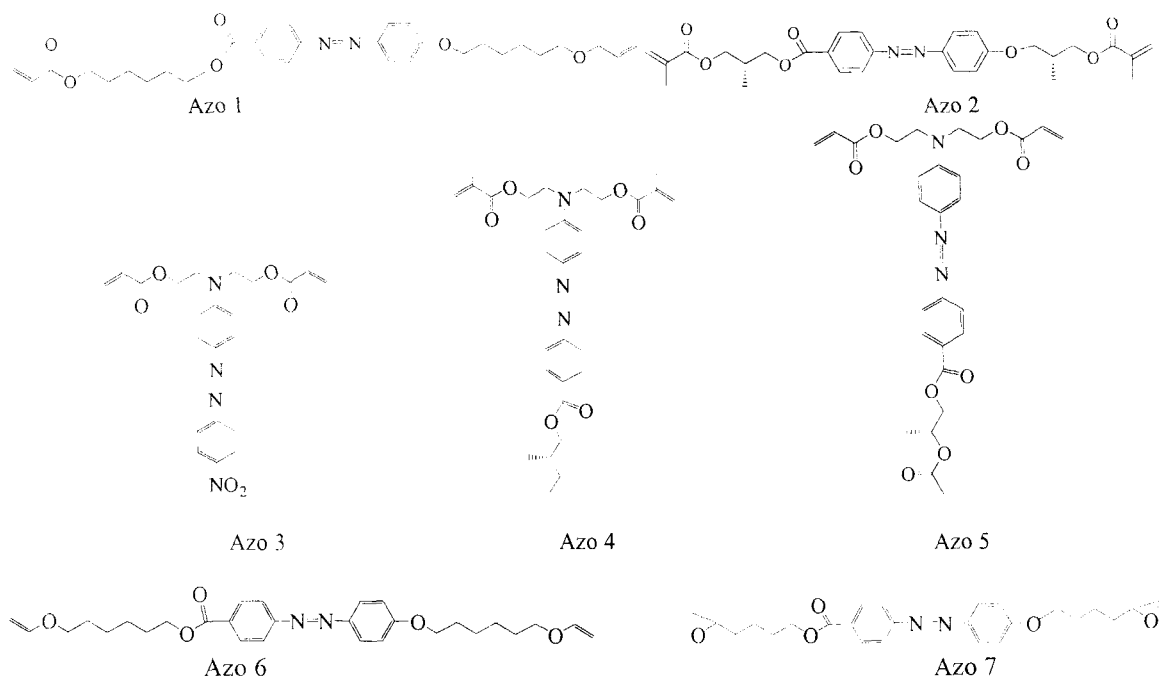


Fig. 1 Chemical structures of some network-forming azobenzene monomers

include diacrylate, dimethacrylate, divinyl ether and diepoxide monomers, being either achiral or chiral and having azobenzene moiety both in the main chain and as side group after polymerization.

Isotropic Azobenzene Polymer Networks in Liquid Crystals

In our first study^[17] the monomer Azo1 was dissolved in a nematic LC, E7, and free-radical polymerization was carried out in the absence of irradiation. The polymer network formed under these conditions was isotropic and contained in a polydomain nematic matrix. We found that subsequent irradiation with linearly polarized light could induce orientation of the LC molecules in the direction perpendicular to the polarization. Clearly, this orientation induction is due to the photoalignment of azobenzene groups on the polymer network. Figure 2 shows the increase in orientation of the LC molecules with irradiation time for samples having different polymer network concentrations (the order parameter was measured from polarized infrared dichroism). The orientation induction effect is stronger for higher concentrations of azobenzene groups on the network. Due to the polymer network, the photoinduced LC orientation remains after the irradiation is turned off. This behavior is different from that of azo dye-doped LCs, for which the LC orientation is lost once the irradiation is turned off because of the relaxation. The induced orientation, however, cannot be recovered after the sample is heated to form the isotropic phase. Furthermore, we studied this system using a laser as irradiation light^[18]. Even with the irradiation wavelength $\lambda = 514.5$ nm, which is far from the absorption maximum of Azo1 at $\lambda = 358$ nm, strong residual birefringence can be obtained, arising from the photoinduced orientation of the LC host. This feature was used to record electrically tunable diffraction gratings on such materials^[19]. These studies demonstrate that LCs containing an isotropic azobenzene polymer network are interesting photoactive materials. The photoalignment of azobenzene groups on the network can lead to orientation of the LC molecules in the same direction, and the network provides a certain stability for this orientation until the clearing temperature. In principle, this makes it possible to optically and selectively reconfigure the LC orientation.

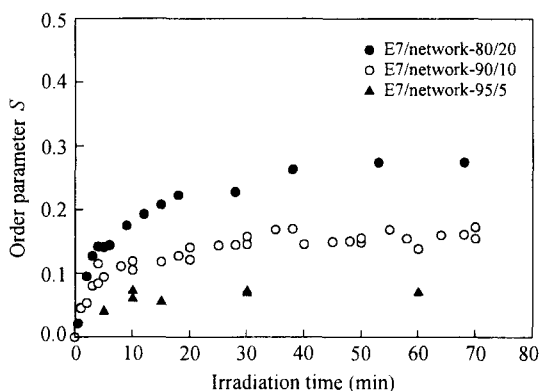


Fig. 2 Order parameter of E7 versus irradiation time for samples having different concentrations of azobenzene polymer network

Anisotropic Liquid Crystal Gels Prepared from Optical Alignment

An interesting development in using azobenzene polymer networks in LCs was achieved when we exposed the LC/azobenzene monomer mixture to linearly polarized light in the course of polymerization^[20, 21]. As is schematically illustrated in Fig. 3, under this condition the photoalignment of azobenzene monomer and/or groups on the growing polymer chains may result in an anisotropic azobenzene network, which, on cooling the mixture from the isotropic phase under irradiation, can serve as a framework to induce long-range orientation of the LC molecules in the nematic phase, and this orientation induction takes place in the absence of rubbed surfaces. If, however, the irradiation is turned off in the isotropic phase, the anisotropic polymer network would relax and subsequent cooling into the nematic phase ends up with an isotropic network dispersed in a polydomain LC, which is similar to the system discussed in the previous section. The oriented samples appear as birefringent films like the anisotropic LC gels prepared by polymerizing the monomer (non-azobenzene) after obtaining the

LC orientation through rubbed surfaces^[22]. Using the monomers of Azo1 and Azo3 dissolved in the nematic LC hosts of E7 and BL006, we showed that this rubbing-free technique could work by carrying out thermally induced free radical polymerization either in the nematic phase^[20] or in the isotropic phase^[21]. We also investigated the use of photopolymerization by means of two lasers, a visible laser at $\lambda = 532$ nm for orientation induction and a UV laser at $\lambda = 350$ nm for photopolymerization^[23]. Unlike the photoinduced LC orientation from isotropic azobenzene networks, the orientation induced by anisotropic polymer networks shows the memory effect. An example is given in Fig. 4, where the order parameter of E7 is plotted as a function of temperature. For two heating-cooling cycles, the orientation disappears after the nematic-isotropic phase transition on heating but is completely recovered on subsequent cooling into the nematic phase. Figure 5 shows scanning electron microscope (SEM) pictures of the polymer network in both irradiated and nonirradiated areas after removal of the LC in hexane. The fibrous azobenzene network is indeed aligned in the irradiated (oriented) area but disordered in the nonirradiated (randomly oriented) region.

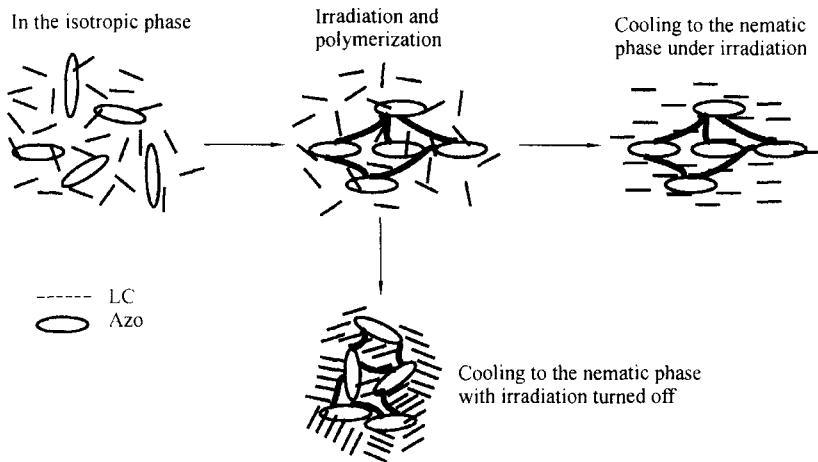


Fig. 3 Schematic illustration for the formation of an anisotropic azobenzene polymer network and its effects on the induction of liquid crystal orientation in the nematic phase

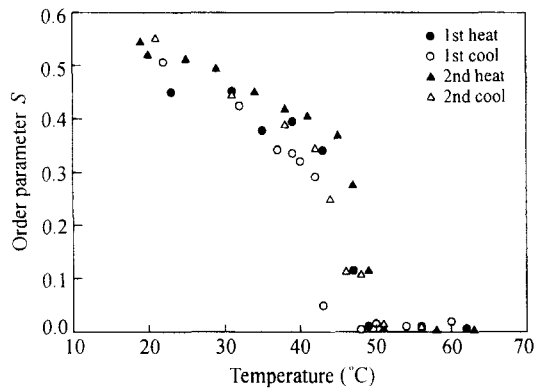


Fig. 4 Order parameter of E7 versus temperature for a sample subjected to two heating (closed symbols) and cooling (open symbols) cycles with the irradiation turned off

Azobenzene Polymer-Stabilized Ferroelectric Liquid Crystals

More recently, we have been applying this optical and rubbing-free approach to ferroelectric liquid crystals (FLCs)^[24, 25]. FLCs command great technological interest because of their advantages over other types of LCs

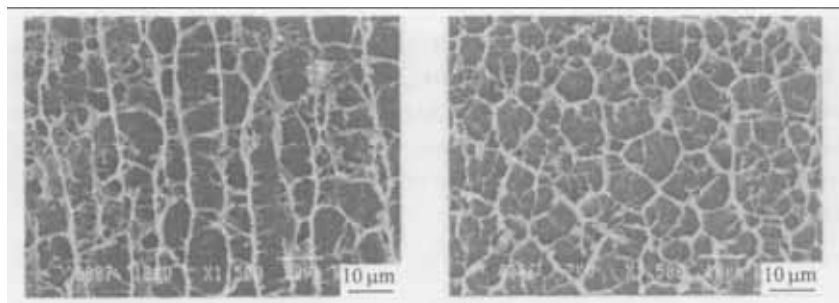


Fig. 5 SEM pictures showing aligned and disordered polymer networks in irradiated and nonirradiated areas, respectively
The scale bars are 10 μm .

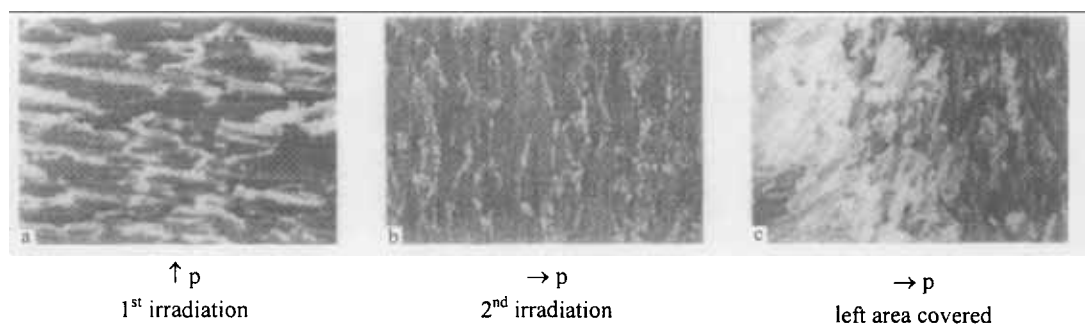


Fig. 6 Photomicrographs for an optically aligned FLC containing 5% of azobenzene polymer network
a) After polymerization under the 1st irradiation; b) After heating to and cooling from the isotropic phase under the 2nd irradiation with the polarization rotated by 90°; c) With part of the sample covered during the 2nd irradiation
The areas in the photos: 1000 $\mu\text{m} \times 750 \mu\text{m}$

such as much faster switching speed in an electric field. The bulk alignment of FLCs has always been a key issue in the development of FLC technologies. In essence, a bulk alignment in the chiral smectic-C phase (S_C^*) is necessary to have a macroscopic spontaneous polarization that can be switched following the polarity of an AC field applied across the cell, and this results in an in-plane switching of the FLC molecules, which is responsible for the electrooptic effects of FLCs. Until now, the utilization of surface orientation layers is the only option for alignment, which leads to the surface-stabilized FLCs^[26]. Therefore, the purpose of our studies is to investigate the possibility of using photoinduced anisotropic azobenzene networks to induce and stabilize FLCs in the absence of rubbed surfaces. In this project we have been studying various azobenzene monomers (Fig. 1) and using different polymerization methods. We found that if the monomer is fairly soluble in the FLC host, polymerization under linearly polarized irradiation can generally lead to stable bulk alignment of FLCs on substrates whose surfaces are not rubbed. An example is given in Fig. 6, which shows the photomicrographs taken under crossed polarizers for an FLC aligned by 5% of azobenzene network from Azo 6 (the FLC used was Felix-015 from Clariant, and cationic polymerization was performed for the divinyl ether monomer). Figure 6(a) shows the induced bulk alignment in the S_C^* phase, which is perpendicular to the polarization direction of the irradiation light (indicated in the figure). More interestingly, when the sample was reheated to and cooled from the isotropic phase under irradiation whose polarization was rotated by 90°, the bulk alignment of FLC followed the change by a rotation of 90° as well, Fig. 6(b). If, during the second irradiation, about a half of the sample was covered by an aluminum sheet, a clear boundary was formed between the exposed and unexposed areas. As seen from Fig. 6(c), a 90°-reorientation of the FLC domains was achieved in the irradiated area, while the alignment direction changed gradually across the boundary, with most domains in the nonirradiated area aligned at about

60° to the alignment in the irradiated area. These results show unambiguously that the azobenzene polymer network dictates the reorientation of the FLC molecules, because it is easy to picture that the reoriented part of the network would drag the rest of the network to follow, which creates a curvature that explains the gradual change in alignment of the FLC domains at the interface. The results demonstrate the possibility of reconfiguring the FLC alignment by light. In contrast to surface orientation layers, the aligning effect of azobenzene polymer networks is a bulk effect.

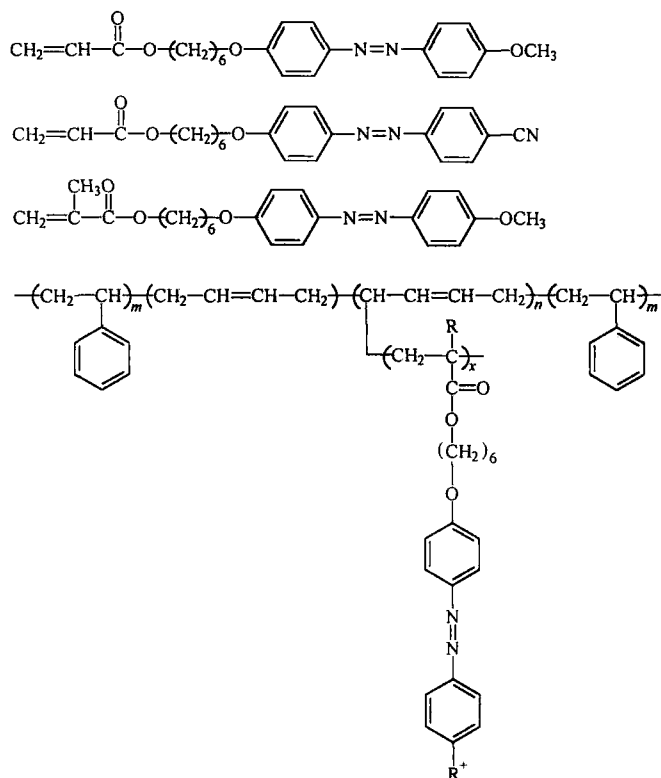


Fig. 7 Chemical structures of the azobenzene monomers and the azobenzene polymer-grafted SBS elastomers

AZOBENZENE ELASTOMERS

The second example of our work is a new type of azobenzene polymer first demonstrated by our group, namely azobenzene elastomer^[27–29]. The idea of incorporating azobenzene chromophore into an elastomer is to explore new functions of the materials by coupling the mechanical effects on molecular orientation and anisotropy, which arise from the characteristic large and reversible deformation of elastomers, with the optical effects related to the photoisomerization of azobenzene. The first azobenzene elastomers we made were prepared by grafting a side-chain liquid crystalline polymer (SCLCP), whose mesogenic group bears an azobenzene moiety, onto a styrene-butadiene-styrene (SBS) triblock copolymer, which is a thermoplastic elastomer. Shown in Fig. 7 are the chemical structures of some used azobenzene monomers and their corresponding azobenzene elastomers. The grafting occurred during the radical polymerization of the monomer in a solution with dissolved SBS, and the content of the azobenzene SCLCP was around 10 wt%. An illustrative example of the coupling effects is given in Fig. 8, with polarized UV-vis spectra of an azobenzene elastomer (made from the acrylate monomer with the $-\text{OCH}_3$ end group). After stretching at room temperature, the dichroism of the broad absorption peak of *trans*-azobenzene around 360 nm indicates the mechanically induced orientation of azobenzene mesogens along the strain direction (Fig. 8a). On UV irradiation under strain, the *trans*-*cis* photoisomerization results in disordered *cis*-azobenzene in the film (Fig. 8b), as is revealed by the absence of dichroism and the appearance of the

absorption peak of *cis*-azobenzene at 450 nm, accompanying the disappearance of the 360 nm peak. On subsequent irradiation with visible light (Fig. 8c), *cis-trans* back-isomerization occurs and oriented *trans*-azobenzene groups reappear in the film. This process is totally reversible. In other words, because of the coupling effects, an optical switching between orientation-on and orientation-off states can be realized on stretched films.

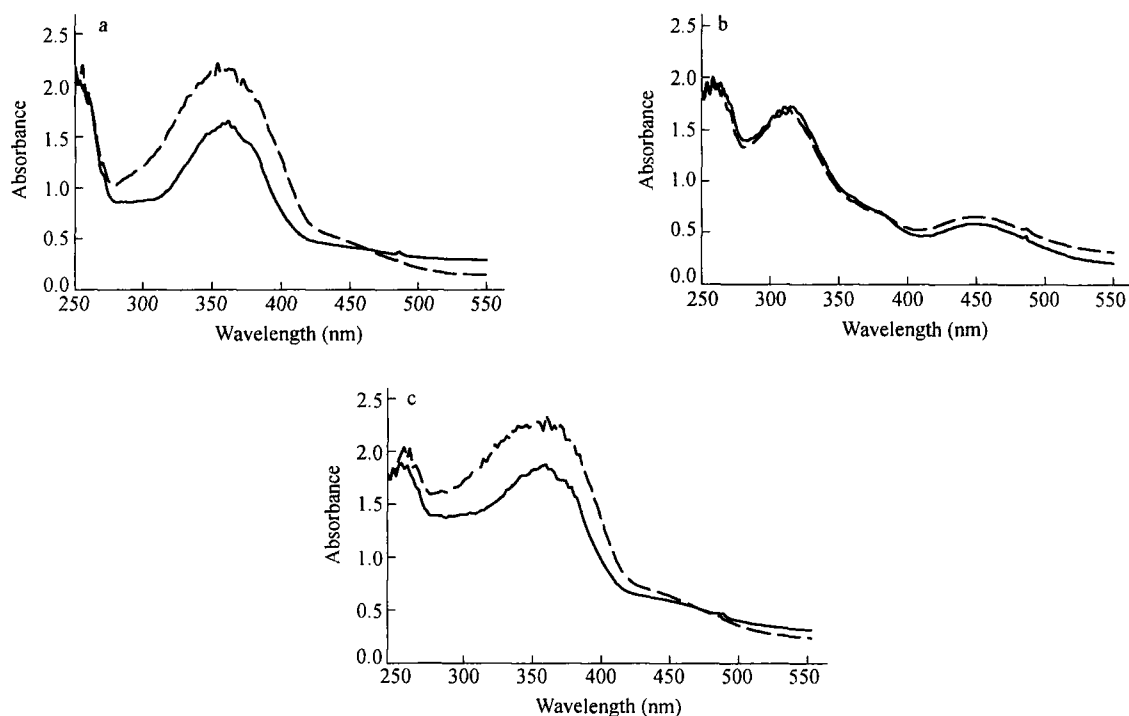


Fig. 8 Polarized UV-vis spectra for a film

a) After stretching at room temperature; b) After exposure to UV irradiation; c) After irradiation with visible light
solid and dashed lines for polarizations parallel and perpendicular, respectively, to the strain direction

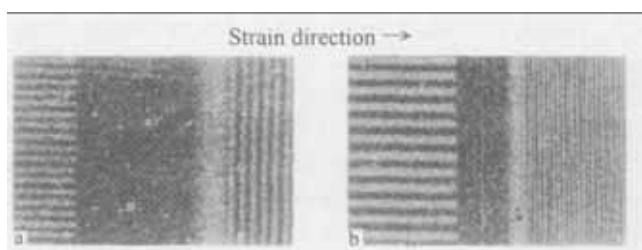


Fig. 9 Polarized photomicrographs for a) two gratings (10 μm period) inscribed on an azobenzene elastomer film stretched to 300% extension, with their fringes parallel and perpendicular, respectively, to the strain direction; and b) the two gratings on the same film retracted to the half-length

An attractive property of azobenzene elastomers is that diffraction gratings can be obtained on stretched films, using either photomasks or holographic recording. The gratings display elasticity for the diffraction properties, since their period, diffraction angle and diffraction efficiency can be changed reversibly through elastic deformation of the film^[28, 29]. Figure 9 shows the photomicrographs of two gratings (10 μm period) written on a stretched film, the fringes being parallel and perpendicular to the strain direction respectively. As the film is relaxed to its half-length, the period of the perpendicular grating decreases while that of the parallel grating increases; the changes are simply proportional to the decrease in length and increase in width of the film. Our

recent holographic studies^[30] have revealed that there are two grating formation processes taking place when a stretched film is exposed to the interference pattern. Once the writing beams are on, the isomerization of oriented *trans*-azobenzene resulting in disordered *cis*-azobenzene leads to the modulation of refractive index and accounts for the first grating. At longer exposure time, a structural rearrangement of SBS, which is activated by the photoisomerization of azobenzene, occurs and results in a more stable grating with high diffraction efficiency. Our ongoing studies in this project include exploration of using the azobenzene elastomers for mechanically tunable optic devices and the syntheses of other types of photoactive elastomers.

CONCLUDING REMARKS

Azobenzene-containing polymers and liquid crystals represent an exciting research field. There are still many opportunities for making original contributions to the design and preparation of new functional materials. The key issue that needs reflection is how to ingeniously use the photoisomerization and photoalignment of azobenzene to add desirable new functions or more values to existing materials. In addition to the two systems reviewed in this paper, we are also conducting research projects on azobenzene-containing block copolymers, π -conjugated polymers and self-assembled LC gels^[31].

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