

New photoactive polymer and liquid-crystal materials*

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Abstract: The reversible *trans*–*cis* photoisomerization of azobenzene and azopyridine chromophore was used to design and exploit novel photoactive materials based on polymers and liquid crystals. This paper reviews our recent studies on several systems. These include azobenzene-containing thermoplastic elastomers that can be used to prepare mechanically tunable diffraction gratings, side-chain azopyridine polymers for combined self-assembly and photoactivity, azobenzene polymer-stabilized ferroelectric liquid crystals whose bulk alignment can be achieved by light with no need for surface orientation layers, and, finally, self-assembled photoactive liquid-crystal gels that can display light-induced reorganization leading to the formation of electrically switchable diffraction gratings.

INTRODUCTION

Studies on azobenzene-containing polymers and liquid crystals represent a very active research field [1–7]. The reason is twofold. From a fundamental research point of view, there are many opportunities for using the reversible *trans*–*cis* photoisomerization of the chromophore to design new advanced materials, to discover new phenomena, and to understand the underlying mechanisms. In terms of applications, these materials have potential utilities for optical storage and other device applications [1–7]. A fascinating example is the recent discovery by Ikeda's group that thin films of crosslinked azobenzene liquid-crystalline polymers (LCPs) may display fast, light-directed bending and unfolding [8], which may be used as a light-controlled actuator for microdevice applications. Another example is the surface relief grating (SRG), reported independently by two groups in 1995 [9,10]. Typically, SRG is formed when a thin film of azobenzene polymer (amorphous or liquid-crystalline) is exposed to an interference pattern produced by two coherent laser beams, as a result of mass transport on the surface. Over the past years, the discovery of SRG has sparked off intense research effort into synthesizing new polymers and understanding the mechanisms for SRG formation [11]. Currently, the photoactivity of azobenzene is being exploited in diverse structures such as dendrimers [12], proteins [13], micelles [14], and sol-gel materials [15], to name a few.

Our effort in this field has been directed to the design and study of various new azobenzene-containing materials that range from polymers (thermoplastic elastomers, diblock copolymers, π -conjugated polymers, and side-chain azopyridine polymers) to polymer/liquid-crystal composites to liquid crystals. In this paper, we review the recent progress made on some of the systems.

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AZOBENZENE THERMOPLASTIC ELASTOMERS

Azobenzene was first incorporated in some nematic elastomers to trigger the nematic-isotropic phase transition by light, resulting in contraction of the polymer [16,17]. These are covalently crosslinked elastomers, and the interest of study is the development of optical actuators. We have prepared the first azobenzene thermoplastic elastomer by grafting a side-chain LCP with an azobenzene moiety onto a styrene-butadiene-styrene (SBS) triblock copolymer [18–21], whose basic structure is shown in Fig. 1. The idea is to couple the action of photoisomerization of azobenzene with the anisotropy induced by a large and reversible deformation of the polymer. Such a coupling effect is illustrated by the following experiment. Stretching a solution-cast film at room temperature easily leads to a long-range orientation of *trans*-azobenzene mesogens along the strain direction, and this is the mechanical effect. When the stretched film is exposed to UV light (360 nm, either polarized or unpolarized), the *trans*–*cis* photoisomerization takes place and results in disordered *cis*-isomer, while on subsequent irradiation with visible light (440 nm, either polarized or unpolarized), the *cis*–*trans* back-isomerization brings the *trans*-isomer back and recovers the orientation induced by stretching. More interestingly, we found that such photoactive elastomers were worth being exploited as elastic holographic materials for two reasons. On

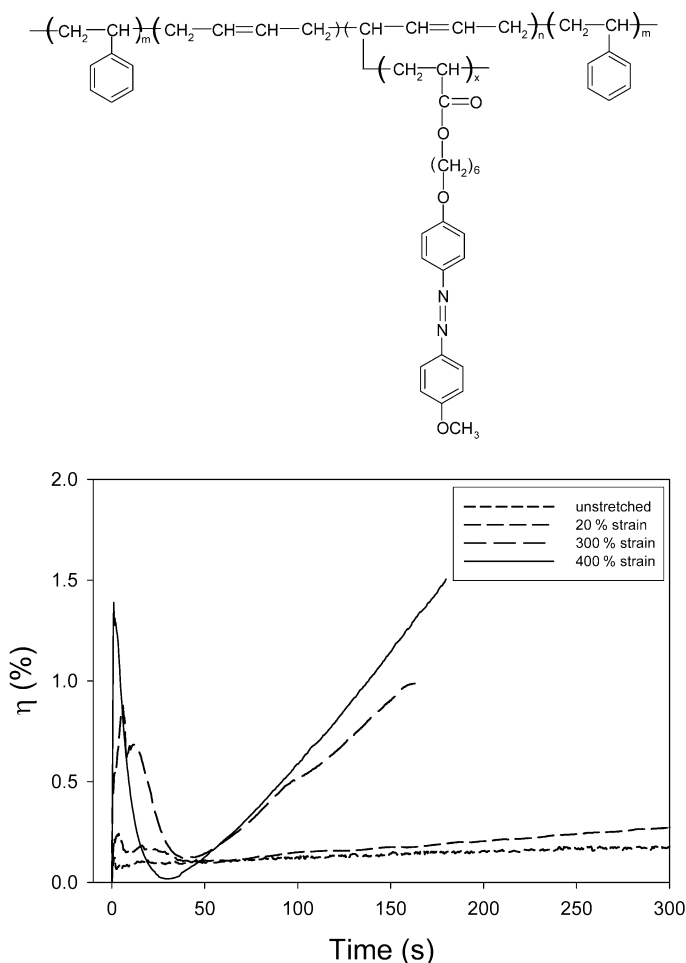


Fig. 1 Chemical structure of the azobenzene thermoplastic elastomer and the first-order (+1) diffraction efficiency vs. exposure time for films stretched to various strains. The period of grating is $2 \mu\text{m}$, and the power per recording beam is 160 mW/cm^2 .

one hand, the easy deformation can be used to enhance the diffraction efficiency, as can be seen in the experiment of recording holographic gratings on films stretched to various strains (Fig. 1) [21]. Note that these grating formation dynamics measurements also revealed two volume gratings of different natures: the one formed quickly upon excitation is from the photoisomerization of oriented *trans*-azobenzene mesogens, and the one developed at longer exposure times may originate from structural changes of the SBS matrix as being activated by the photochemical phase transition in the polymer. On the other hand, the large and reversible elastic deformation gives the tunability to the grating in such a way that the period of grating, diffraction angle, and efficiency can be changed reversibly by simple mechanical deformation [21]. Figure 2 shows optical micrographs of a grating in a relaxed film (1 μm period) and in the film under a strain of 150 % (2.5 μm period). More studies are underway in search for new interplay between optical and mechanical effects and new azobenzene elastomers that may be useful for mechanically tunable optical devices.

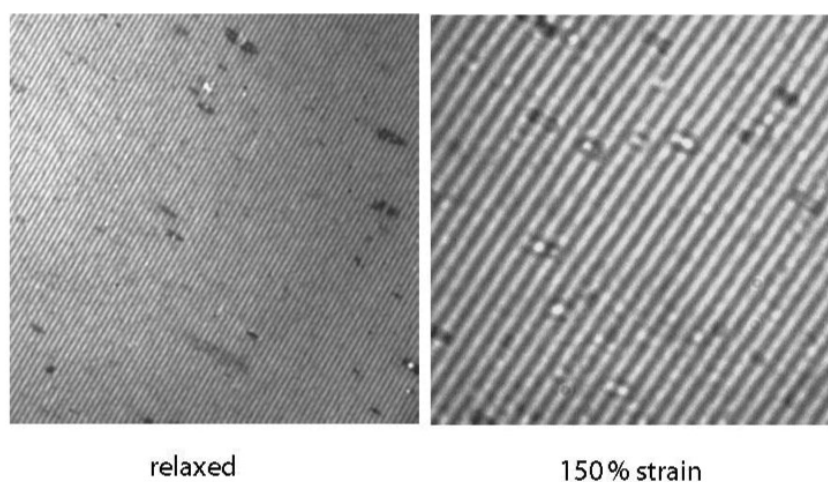


Fig. 2 Polarizing optical micrographs showing the grating remained in a film seven months after the recording under 400 % strain. The period in the relaxed state is 1 μm , and it increases to 2.5 μm under a strain of 150 %.

SIDE-CHAIN AZOPYRIDINE POLYMERS

The continuing effort of synthesizing azobenzene polymers of various structures aims to find materials with improved properties such as large photoinduced anisotropy or birefringence. Generally, altering the polymer structure may be achieved by changing either the chain backbone or the spacer length or the electron-donor and electron-acceptor substituents on the azobenzene unit [3]. Another way would be to replace the azobenzene moiety by an azopyridine that can also undergo the *trans*-*cis* photoisomerization. There is a report showing the use of an epoxy-based polymer bearing an azopyridine group to inscribe SRGs [22]. In a recent study, we have prepared the first polymethacrylate containing an azopyridine moiety in the side chain, PAzPy [23] (Fig. 3), with the idea of combining the photoactivity of the azo chromophore with the ability for self-assembly provided by the pyridyl group, which can readily complex with hydrogen-bond donors [24] or metals [25]. One interest would be the possibility of preparing a number of new photoactive polymers through self-assembly with a single azopyridine polymer. To demonstrate this approach, a series of aliphatic and aromatic carboxylic acids (Fig. 3) was used to complex with the azopyridine polymethacrylate. All acids, except one (10OBA), are commercially available, and the complexation was achieved by mixing the polymer and the acid in tetrahydrofuran (1:1 molar ratio of acid and pyridyl groups) followed by evaporation of the solvent. In all cases, the amorphous azopyridine polymer was transformed into an LCP due to grafting of the acid

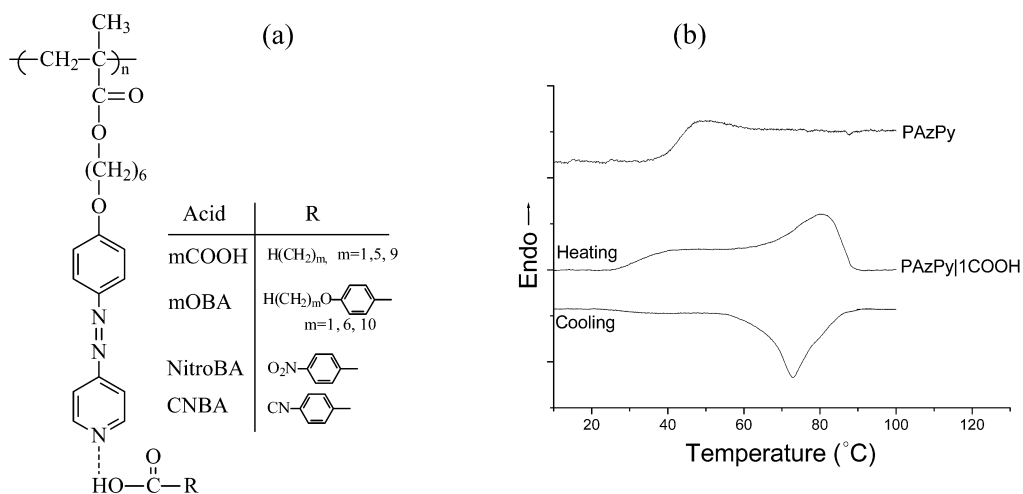


Fig. 3 (a) Chemical structures of the amorphous azopyridine polymer, PAzPy, and the acids used for complexation. (b) DSC curves (10 °C/min, 2nd scan) for PAzPy and its complex with acetic acid.

on the azopyridine unit via the H bond [23]. Figure 3 shows an example of the complex with acetic acid, where the DSC curves show that PAzPy has only a T_g at about 40 °C, while the complex displays a mesophase melting endotherm on heating and a mesophase formation exotherm on cooling. Polarizing optical microscope and X-ray diffraction measurements confirmed the formation of a monolayer smectic-A phase.

Figure 4 compares the photoinduced birefringence for the azopyridine polymer and its complex with one of the aromatic carboxylic acids (6OBA). Basically, the amorphous azopyridine polymer behaves like amorphous azobenzene polymers [3]: a birefringence is quickly induced on illumination with a linearly polarized laser, a significant relaxation occurs when the laser is turned off, and the remaining anisotropy can be erased by a circularly polarized laser beam. By contrast, the self-assembled LCP behaves very differently. During the same cycle of irradiation, the photoinduced birefringence increases

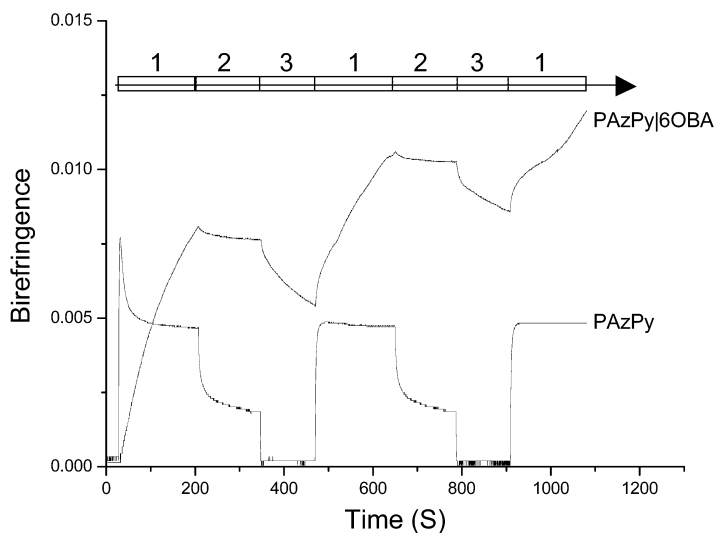


Fig. 4 Photoinduced birefringence for PAzPy and its complex with a carboxylic acid: (1) linearly polarized laser (350 nm, 25 mW/cm²) is on; (2) laser turned off; and (3) circularly polarized laser is on.

ment of smectic domains at room temperature (S_C^* phase) achieved with up to 5 wt% of azobenzene polymer. No alignment can be obtained with 10 % polymer because the network is too dense to allow the alignment to develop. Interestingly, the azobenzene polymer network also exerts a commanding effect on the alignment of FLC as being able to reorient the FLC by changing the polarization direction of subsequent irradiation. Figure 6 shows the polymer network revealed by scanning electron microscope (SEM) after extraction of the FLC host in hexane [33]. The network is formed by small colloidal particles (~ 250 nm in diameter) with a large surface/volume ratio. The sketch beside illustrates the suggested mechanism for the photoinduced reorientation of FLC. The orientation of a large number of azobenzene moieties on the surface of polymer may be switched by light, which brings the FLC molecules to align in the same direction. Unlike the so-called “commanding surface” [1], the photoalignment of FLC by an azobenzene polymer network comes from a volume effect, since the network is dispersed in and microphase-separated from the FLC host. Our systematic study has confirmed that the use of an azobenzene polymer network for optical alignment and stabilization of FLC (or liquid crystals, in general) represents a generic approach. We are currently investigating the effects of the substrate surface on the photoalignment and the use of photopolymerization in order to establish conditions suitable for possible practical applications. The concentration of azobenzene polymer network required for the photoalignment may be as low as 0.5 % using a liquid-crystalline azobenzene monomer [36].

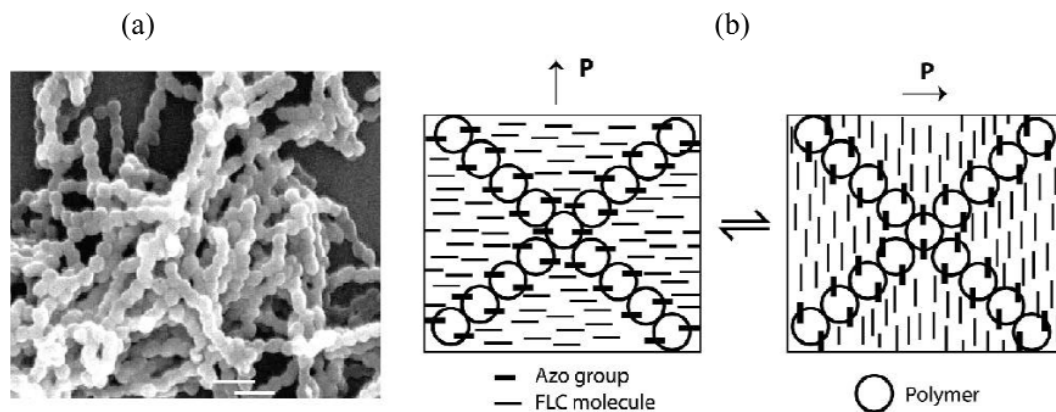


Fig. 6 (a) Scanning electron microscope image of the azobenzene polymer network formed from 3 % monomer (the scale bar is 1 μm). (b) Schematic illustration of the photoinduced reorientation of FLC with a network of colloidal particles of azobenzene polymer.

PHOTOACTIVE SELF-ASSEMBLED LIQUID-CRYSTAL GELS

Kato and coworkers were the first to investigate self-assembled liquid-crystal gels (SALCGs), which refer to an LC contained by a physical network of fibrous aggregates formed from a gelling compound called gelator [37–39]. Similar to organic gels [40], specific intermolecular interactions, such as hydrogen bonding, between gelator molecules are responsible for the gelation process. SALCGs are potentially useful materials for fast response to an electric field [38] or easy processing of LC cells [41]. We have initiated investigations on SALCGs based on an azobenzene-containing gelator, with the purpose of adding the photoactivity or optical control to this type of LC materials [42–45]. Even though various interesting phenomena were found in our studies with azobenzene gelators, including self-assembled anisotropic nematic LC gels [42] and pitch compensation before gelation leading to easy bulk alignment for an FLC gel [44], no particular phenomena related to the photoisomerization of azobenzene was observed until recently.

In our latest study [46], an azobenzene gelator (0.5–1 wt%) was dissolved in a cholesteric LC host, and thin fibrous aggregates (~100 nm in diameter) were formed by fast cooling from the isotropic phase to room temperature (SEM picture in Fig. 7). As shown by the polarizing optical micrographs in Fig. 7, when the gel inside a 10- μm electro-optic cell is placed behind a photomask and exposed to UV light (360 nm), a light-induced reorganization process occurs, resulting in the removal of the nanofibers of the gelator from the irradiated area into the nonirradiated area and, consequently, the formation of a diffraction grating. This process was discussed in terms of dissolution of gelator molecules from the aggregate surface in the irradiated area, which is followed by diffusion into and condensation in the neighboring nonirradiated area [46]. Since the cholesteric LC in regions with and without the aggregates responds to a voltage in a very different way [45], the diffraction efficiency of such a grating can be tuned or switched by an electric field. An example of the electrical switching is shown in Fig. 8. When the voltage is on, LC molecules in regions with no aggregates are oriented along the field direction (homeotropic alignment), which creates a larger refractive index modulation depth for the grating and leads to the increase in diffraction efficiency, while when the voltage is off, LC molecules relax to the initial state and the diffraction efficiency drops. Note that almost in the same time Kato's group also reported the use of an azobenzene-containing gelator to induce reversible structural changes in SALCGs [47]. This recent progress points out the potential of exploiting photoactive LC gels for new materials and new applications.

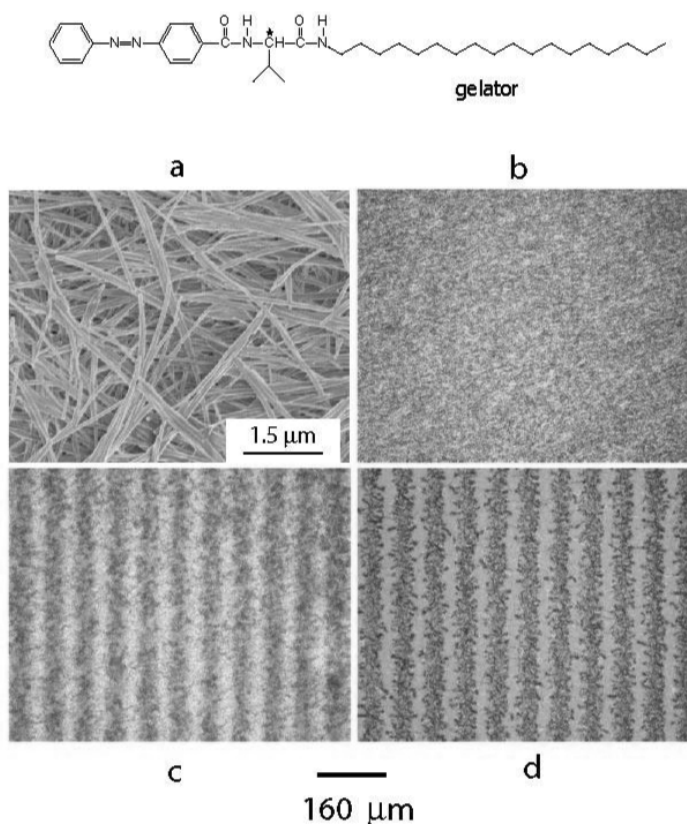


Fig. 7 (a) Scanning electron microscope image of the fibrous aggregates formed in the liquid crystal gel with 1 % gelator; (b) photomicrograph of the gel before irradiation through a photomask; (c) after 5 min irradiation; and (d) after 10 min irradiation. The chemical structure of the gelator is shown on top.

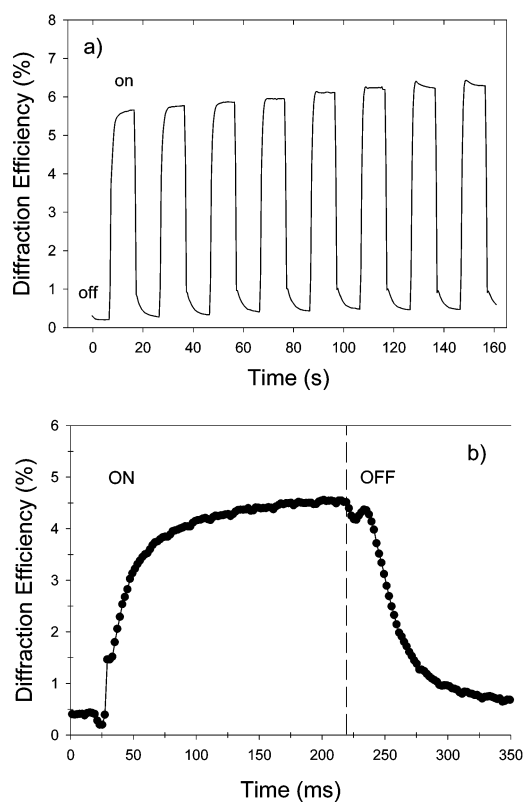


Fig. 8 Switching of diffraction efficiency for a grating formed in the liquid-crystal gel with 1 % gelator: (a) between 0 V (off-state) and 20 V (on-state) of a square-wave electric field; and (b) dynamic response to a pulse of 200 ms duration.

CONCLUDING REMARKS

The search for novel and useful photoactive polymers, liquid crystals, and their composite materials is an exciting research area. There are many opportunities for ingenious use of the photoisomerization of azobenzene and related structures in the design and study of advanced materials. Of the many possibilities, coupling the optical effects with other external stimuli such as mechanical, electrical, and surface effects may lead to interesting properties, while the addition of photoactivity or optical control to existing materials may result in new and useful functions.

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