Journal of Polymer Science Part A: Polymer Chemistry / Volume 52, Issue 6 / p. 876-882

Article | Full Access

Photomechanical effects in liquid crystal polymer networks prepared with *m*-fluoroazobenzene

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First published: 25 December 2013
https://doi.org/10.1002/pola.27072
Citations: 17

ABSTRACT

The photomechanical response and photochemistry of a conventional, unsubstituted azobenzene-functionalized liquid crystalline polymer network (azo-LCN) is contrasted to that of an analogous material prepared with *meta*-fluorinated azobenzene chromophores. The polydomain azo-LCN materials exhibit nearly identical thermomechanical and optical properties. Photomechanical characterization indicates that the fluorination of the azobenzene chromophore reduces the deflection of cantilevers composed of the materials by 50%, which spectroscopic analysis reveals is due to a reduction in the ability of this material to isomerize and potentially reorient. This work is further confirmation that the underlying photochemistry of azobenzene is a primary contributor to the generation of photomechanical work in these materials. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 876–882

INTRODUCTION

Photomechanical effects in soft materials have been a topic of recent interest to groups around the world.[1], [2] One of the primary motivations for these pursuits is the ability to remotely (noncontact) cue desired responses leveraging spatio-temporal control of light. A variety of materials have been developed and examined. Early work from Lovrien,[3] Agolini,[4] and Eisenbach[5] focused on the preparation and characterization of azobenzene-functionalized amorphous polymers. The renaissance in the study of photomechanical polymeric materials can be in part attributed to a report from Finkelmann *et al*. on the preparation of an elastomeric azobenzene-functionalized liquid crystal polymer network (azo-LCN) in which photogenerated strain of as much as 20% was reported (nearly two orders of magnitude larger than prior reports).[6] Subsequent experimental work by Ikeda,[7] Terentjev,[8, 9] Palffy-Muhoray,[10] Broer,[11-13] and others[14-26] have extended upon these reports. Recently, we and others have reported on analogous responses observable in amorphous, azobenzene-functionalized polyimides (azo-PI).[27-30] Other groups have investigated photoresponsive material systems employing a variety of novel photochemical reactions.[31-35]

In most reports to date, UV light has been employed to trigger trans–cis isomerization in azobenzene-functionalized polymeric materials. In elastomeric azo-LCN, such as the work of Finkelmann,[6] UV-induced trans–cis isomerization results both in a change in the molecular axis of azobenzene as well as a phototropic phase transition. In glassy azo-LCN, UV-induced trans–cis isomerization does not significantly affect the order parameter (<5%) of the material and the mechanical effects are primarily attributable to the change in the molecular axis of the azobenzene units in the polymer.[11, 12, 36] We have employed what has been referred to as trans–cis–trans reorientation (Weigert effect) as the photochemical mechanism.[15, 18, 21, 27, 29, 37, 38] This mechanism is observed when azobenzene materials are irradiated with light that is nearly equivalently absorbed by both the trans and cis azobenzene isomeric forms. For conventional, unsubstituted azobenzenes, the isobetic point of the trans and cis isomers is typically around 440 nm. Exposure of azobenzene materials to light near this wavelength (blue-green light of either 442 or 445 nm) can drive both trans–cis and cis–trans isomerization. Due to the rotational freedom of the azo bond as well as the dichroic absorbance of the chromophore, exposure to linearly polarized blue-green irradiation generates a statistical buildup of azobenzene-oriented orthogonal to the electric field vector of the polarized light source.

A few recent reports have detailed the impact of functionalization of the azobenzene chromophore with a variety of functional groups.[35, 39-43] Fluorination of the azobenzene chromophore has been shown to shift the absorbance of the thermodynamically stable trans conformation into the visible spectrum.[39, 41, 43, 44] Another recent report details similar results in azobenzenes prepared with ortho-substituted chloro- and bromo- groups.[42] Notably, recent synthesis and photochemical characterization of ortho-substituted azobenzene molecules has been shown to extend the half-life of the cis conformer to as much as 700 h.[41] However, in one recent report, the long half-lives of these ortho-functionalized azobenzene is not maintained when the molecules are covalently attached into peptides.[42] Fluorination can influence the surface properties and photoinduced surface effects have been reported in perfluorinated azobenzene polymers.[45] Very recently, photomechanical effects were reported in needle crystals isolated from the cis isomer of a per-fluorinated azobenzene.[35, 40]

The focus of this work is to examine the functionalization of the azobenzene unit on the photochemistry and resulting photomechanical response of azo-LCN materials prepared with pendant azobenzene mesogens. To facilitate this examination, we prepared an azobenzene liquid crystal monomer with *meta*-fluorine substitution (1azo-f, inset Fig. 1 and Scheme 1). An azo-LCN was then prepared by copolymerization of this material with the crosslinking liquid crystal diacrylate (1azo-f-LCN). The baseline material properties, photochemistry, and photomechanical response of 1azo-f-LCN are contrasted to an 1azo-LCN prepared with a conventional, unsubstituted azobenzene pendant mesogen.

Figure 1

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Absorption spectra for solutions containing azobenzene monomers 1azo (–) and 1azo-f (---) mixed with acetone (15 mg/L). (Inset) Chemical structures of RM257, 1azo, and 1azo-f.

Scheme 1

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Synthesis of *meta*-fluorinated azobenzene liquid crystal monomer (1azo-f).

EXPERIMENTAL

Synthesis of Fluorinated Azobenzene Liquid Crystal Monomer

A new, meta-fluorinated azobenzene liquid crystal monoacrylate monomer was prepared by the synthetic procedure shown in Scheme 1. Briefly, this compound was synthesized by diazotization reaction and azo-coupling of commercially available fluorinated anilines with 2,6-difluorophenol (TCI America), followed by alkylation reaction with 6-chloro-1-hexanol and acylation reaction with acryloyl chloride.[46]

Preparation of Azobenzene-Functionalized Liquid Crystal Polymer Networks

The azobenzene-functionalized liquid crystal networks (azo-LCN) were prepared as previously reported.[16] Briefly, the mixtures were drawn into self-prepared liquid crystal alignment cells of 15 µm thickness. The glass substrates in the cell were coated with Elvamide but were unrubbed so as to facilitate preparation of the polydomain orientation. Mixtures contained either 20 wt %

of 1azo or 1azo-f (Fig. 1, inset), 78.5 wt % RM257 (Fig. 1, inset), and 1.5 wt % Irgacure 784. The alignment cells were filled with mixtures heated to 125 °C (isotropic phase) to avoid flow-induced alignment. After filling, the samples were cooled to 75 °C (nematic phase) and photopolymerized with 50 mW/cm^2 of 532 nm irradiation for 60 min. Due to the lack of rubbing, the samples form the so-called polydomain orientation. Thus, the polydomain materials examined here are of "nematic genesis".[47] The samples were removed from the glass substrates and washed to remove the any residual Elvamide coating.

Characterization of Azobenzene-Functionalized Liquid Crystal Polymer Networks

After polymerization, the baseline optical and thermomechanical properties, photomechanical response, and photochemistry of the materials were characterized. Absorption spectra were collected on a Cary 5000 UV–vis spectrometer with a polarization accessory. The absorption spectra for the two azobenzene monomers were measured in an acetone solution (15 mg/L) (Fig. 1). As evident in Figure 1, fluorination of the azobenzene monomer in the meta position does not shift the position of the π–π* absorption. Polarized absorbance data were normalized (Fig. 6) based on the absorbance values before irradiation. The phase behavior of the monomer (1azo-f, 1azo) and the monomer mixtures were examined with polarized optical microscopy (POM) and a Mettler–Toledo heating accessory. As evident in Figure 2, the mixtures of 1azo-f/RM257 exhibit a nematic phase on cooling at approximately 95 °C, while the mixtures of 1azo/RM257 exhibit a nematic phase on cooling at approximately 105 °C. Both mixtures begin to crystallize around 70 °C.

Figure 2

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Phase characterization of mixtures of RM257 and 20 wt % 1azo (a) or 20 wt % 1azo-f (b). In (a), the polarized optical micrographs were taken on cooling at (i) 95 °C, (ii) 90 °C, (iii) 85 °C, (iv) 80 °C, (v) 70 °C, (vi) 60 °C, (vii) 50 °C, (viii) 30 °C. In (b), the polarized micrographs were taken on cooling at (i) 110 °C, (ii) 105 °C, (iii) 100 °C, (iv) 90 °C, (v) 80 °C, (vi) 60 °C, (vii) 50 °C, (viii) 30 °C.

The thermomechanical properties were examined by dynamic mechanical analysis. Storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were determined by dynamic mechanical analysis (DMA) (RSA III, TA Instruments) operating at a strain of 0.5% and frequency of 1 Hz with a heating rate of 2.5 °C/min over the temperature range 0–110 °C. Glass transition temperatures (T_g) are reported from the maximum of the tan δ curve.

The photomechanical response of the materials was visualized as cantilever bending with dimensions 5 mm (length) × 1 mm (width) × 15 μm (thickness). The samples were irradiated in air and water with 100 mW/cm^2 of 442-nm light. The bending was imaged with a camera. The bending angle of the cantilever was measured with a Labview image analysis program.

RESULTS AND DISCUSSION

The thermomechanical properties of an azo-LCN material can profoundly influence the photomechanical output.[16] Thus, to qualify the relevance of the direct comparison of the photomechanical response of the conventional 1azo-LCN to the 1azo-f-LCN, the thermomechanical properties were measured by DMA. Figure 3 plots the storage modulus and loss tangent (tan δ) as a function of temperature. The storage modulus and glass transition temperatures (T_g) for the 1azo-LCN material are 0.72 GPa at 25 and 65 °C and 0.74 GPa at 25 and 71 °C for 1azo-f-LCN. The photomechanical response for these azo-LCNs is measured at room temperature. Given the nearly identical thermomechanical properties, any differences in the mechanical response of these materials can be attributed to the influence of *meta*-fluorination on the photochemistry.

Figure 3

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Thermomechanical analysis [E', (–); Tan δ, (---)] of (a) 1azo-LCN and (b) 1azo-f-LCN. (Inset) Polarized optical micrographs of polydomain orientation of the materials.

The photomechanical response of the two materials was visualized as bending in cantilevers with dimensions 5 mm (length) × 1 mm (width) × 15 μm (thickness). The response was examined in both air and water. Figure 4 presents images of the cantilevers before irradiation (vertical) as well as after 1 h of irradiation with 445-nm light linearly polarized parallel to the long axis of the cantilever (bent). The temporal response of the bending for the two materials is summarized in Figure 5. Two major conclusions can be drawn from the data presented in Figures 4 and 5. First, the media of the experiment reduces the observed bending angle at 1 h in both the 1azo-LCN and 1azo-f-LCN materials. This is attributed to the differences in viscous forces that slow the rate of transduction of light to mechanical deformation (bending). Second, the bending angle of 1azo-f-LCN is 50% less than 1azo-LCN in both media (air or water).

Figure 4

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Photomechanical response of 1azo-LCN (a, b) and 1azo-f-LCN (c, d) in air and water upon irradiation with 100 mW/cm^2 442-nm light for 1 h.

Figure 5

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Summary of the photomechanical response of 1azo-LCN (•, air; ▲, water) and 1azo-f-LCN (○, air; △, water) during irradiation with 100 mW/cm^2 445-nm light for 1 h.

Figure 6

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Photochemistry of (i) 1azo and (ii) 1azo-f in monomeric and polymeric form. (a) Normalized absorption of monomers during irradiation with 50 mW/cm^2 of 365 nm light. (b) Thermal isomerization of the monomers in dark conditions. Temporal response of (i) 1azo-LCN and (ii) 1azo-f-LCN after (c) UV (50 mW/cm^2) and (d) 445 nm (60 mw/cm^2) irradiation.

The correlation of the photomechanical response evident in Figure 5 to the impact of *meta*-fluorination on the photochemistry of the materials is summarized in Figure 6. The photoisomerization of the monomeric form of 1azo and 1azo-f when irradiated with 50 mW/cm^2 of UV light for 5 min is summarized in Figure 6(a), which plots the normalized value from the maximum of the π–π* absorbance (360 nm for 1azo, 353 nm for 1azo-f) as a function of time. UV irradiation efficiently isomerizes the monomers from a normalized absorbance of 1.0 to less than 0.2, or an approximate photostationary state cis isomer concentration of 80%. The thermal cis–trans isomerization of the monomers is summarized in Figure 6(b). Once again, the normalized value from the maximum of the π–π* absorbance (360 nm for 1azo, 353 nm for 1azo-f) is examined as a function of time. From Figure 6(b), it is clear that *meta*-fluorination dramatically slows down the rate of thermal cis–trans isomerization—similar to recent literature reports[35], [40], [41] for ortho-substituted molecules. The photochemistry also was examined in polymeric form. The normalized value from the maximum of the π–π* absorbance (360 nm for 1azo, 353 nm for 1azo-f) is plotted as a function of time after irradiation of the materials with UV light [Fig. 6(c)] and 445 nm light [Fig. 6(d)]. A number of conclusions can be drawn from the data reported in Figure 6(c,d). First, the degree of the isomerization/reorientation in 1azo-f-LCN with UV light irradiation is dramatically decreased in polymeric form. The photostationary state cis isomer concentration is only approximately 25% in azo-f-LCN, compared to 80% in monomeric form. Second, the slow thermal cis–trans isomerization observed in the 1azo-f monomer [Fig. 6(b)] is not apparent in polymeric form (1azo-f-LCN) when irradiated with either UV [Fig. 6(c)] or 445 nm [Fig. 6(d)] irradiation. This result seems to parallel a prior examination of crosslinked ortho-functionalized azobenzenes in polypeptides.[42] Finally, the rate of thermal isomerization of both the classical azobenzene and *meta*-fluorinated azobenzene in the polydomain LCN polymers prepared and examined here is approximately equal.

From the perspective of light-to-work transduction, Figure 6 confirms that in the polydomain LCN materials the *meta*-fluorination reduces the ability of azobenzene to isomerize. This is directly evident in Figure 6(c) where UV light (which induces trans–cis isomerization) results in a photostationary cis isomer concentration of approximately 80% in 1azo-LCN and only approximately 25% in 1azo-f-LCN. We have typically invoked the reorientation of azobenzene as the underlying photochemical mechanism in photomechanical effects induced with 445 nm light. To further elucidate the photochemistry occurring within the polydomain azo-LCN materials, polarized UV–vis spectra were collected from both 1azo-LCN and 1azo-f-LCN after irradiation with 445 nm light. Figure 7 summarizes the experiments in plots of the value of the absorption peak from the π−π* absorbance collected from the films as a function of the angle of the polarization of the probe light in the spectrometer. As evident in Figure 7, before irradiation with 445 nm light, the absorption of the films exhibits no dependence on polarization. This is expected for polydomain materials, in which the azobenzene constituents are randomly organized. Upon irradiation with linearly polarized 445 nm light, the 1azo-LCN sample exhibits a sinusoidal dependence on polarization [Fig. 7(a)]. The dichroic ratio measured in this material is 1.24. Comparatively, the magnitude of the photoinduced orientation in the 1azo-f-LCN sample is considerably smaller, evident in a dichroic ratio of only 1.04 [Fig. 7(b)]. From Figure 7, it is clear that *meta*-fluorination of the azobenzene chromophore dramatically affects the alignment of the pendant azobenzene moieties. We hypothesize that the reduced photoinduced dichroism in the 1azo-f-LCN material may be related to hydrogen bonding among the fluorinated-azobenzene mesogens in the polymer network. As reported by Choudhurry, hydrogen bonding (C—H—F) can increase the potential energy difference between trans and cis conformers and accordingly could reduce the population of cis isomers to a given dose of UV or 445 nm light.[39] The impact of the photochemistry of fluorinated azobenzene has not been previously examined in LCN materials. Conceivably, the organization of the polymer network could further inhibit the isomerization and reorientation of the pendant azobenzene units.

Figure 7

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Summary of the peak absorbance of the π–π* absorption of the azobenzene chromophore at 365 nm for (a) 1azo-LCN (•, before exposure; ○, after exposure) and (b) 1azo-f-LCN (•, before exposure; ○, after exposure). Samples were continuously irradiated with 100 mW/cm^2 442-nm light for 1 h.

The results presented here illustrate the considerable impact of *meta*-fluorination of the azobenzene mesogen on the photochemistry and the resulting photomechanical output. Indirectly, these data confirm the critical nature of trans–cis isomerization of azobenzene to the observation light-to-work transduction in these materials. Evident in Figure 1 for the monomeric precursors and Figure 6 for the polymeric forms, the two materials exhibit nearly identical absorption properties. Countless papers have been presented focused on explaining the mysterious behavior of azobenzene photochemistry in glassy materials.48-51 Based on the nearly identical absorption coefficients of the two materials examined here, nearly identical photomechanical effects would be expected if the underlying mechanism was photothermal heating. However, evident in Figure 6, the reduced photomechanical response of 1azo-f-LCN is attributable the reduced photoisomerization of the *meta*-fluorinated azobenzene. Ultimately, the reduction in photoisomerization and reorientation account for the reduction in light to work transduction, illustrated here as bending of a cantilever (Figs. 4 and 5).

CONCLUSIONS

A fluorinated azobenzene liquid crystalline monomer is synthesized and used to prepare a novel, azobenzene-functionalized liquid crystal polymer network (1azo-f-LCN). The fluorinated 1azo-f-LCN is shown to have comparatively reduced photomechanical response in both air and water in relation to a conventional, unsubstituted 1azo-LCN. With UV–vis spectroscopy, we confirm that the reduction in photomechanical response is due to a reduction in the translation of the incident photon flux into photoisomerization and/or reorientation of the fluorinated azobenzene pendant mesogens. These results further confirm the critical nature of the photoisomerization efficiency and the local network environment in facilitating efficient transduction of light to mechanical work.

ACKNOWLEDGMENTS

K. M. Lee, B. M. Lynch, and T. J. White acknowledge the Air Force Office of Scientific Research and the Air Force Research Laboratory for financial support. P. Luchette acknowledges support from the National Science Foundation (Grant #0606357).

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