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Relationship between the Photomechanical Response and the Thermomechanical Properties of Azobenzene Liquid Crystalline Polymer Networks

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ABSTRACT: We report on the influence of cross-link density of azobenzene-containing liquid crystal polymer networks (azo-LCNs) on the thermomechanical properties and the laser-directed bending of cantilevers consisting of these materials. Cross-link density of azo-LCN was increased by adjusting the length of photocuring from 1 to 120 min. The storage modulus (E'), loss modulus (E''), and glass transition temperature (T_g) of the azo-LCNs increase with cross-link density. Increasing the cross-link density of the polydomain azo-LCN reduces the magnitude of the bending angle of the cantilevers. The relationship between the thermomechanical and photomechanical properties of the polydomain azo-LCN reported here is further elucidated in the examination of laser-directed bending over a wide range of temperature. The temperature dependence of the equilibrium photodriven bending angle is shown to be strongly related to the temperature dependence of the storage modulus for a given azo-LCN sample. Normalizing the temperature dependence of the photomechanical response of the azo-LCN cantilevers by the T_g provides a master curve that can be used to tailor the photomechanical response.

Introduction

Transduction of light energy into mechanical work has been a topic of interest for nearly 50 years.[1,2] Light to work transduction leverages the temporal, spatial, and remote control of light, which can be advantageous over other forms of actuation. Most examinations to date have functionalized polymeric host materials with photoresponsive chromophores that are covalently bonded to the network. In some cases, photoresponsive groups have been doped into the polymer network as a guest molecule. A number of chromophores have been examined for both functionalized and guest−host approaches to synthesizing photoresponsive polymeric materials including spyropyranes,[3] azobenzenes,[4,5] and stilbenes.[6] Regardless of the approach or chromophore used, approximately 1% photogenerated expansive and contractive strains have been realized in conventional polymeric materials.

The limited photogenerated strain in photoresponsive polymeric systems was significantly advanced by Finkelmann et al., who bound azobenzene into a liquid crystal elastomer.[7] Using UV light to drive the trans to cis isomerization of azobenzene has been shown to induce an order to disorder transition, which in liquid crystal elastomers can yield as much as 400% strain. Since this original effort, a number of novel demonstrations have been presented including uniaxial contraction of a thin film,[8] light-directed bending of a film,[9,10] and reversible bending of a cantilever in a single direction.[11,12] The two primary chemistries examined to date are siloxane-based azo-LCN elastomers[7,13,14] and acrylate-based azo-LCN glasses.[10−12,15,16] In the *glassy* acrylate-based azo-LCNs examined here, the azobenzene mesogen concentration has been studied over a wide range of values including systems entirely composed of azobenzene mesogens[10,15,16] ("Ikeda type") and those with limited azobenzene concentration (less than 30 wt %)[11,12,17] ("Broer type").

As first demonstrated by Tabiryan and coauthors,[18] the utilization of longer wavelength light can yield distinctive photomechanical effects including the forward and reverse (bidirectional) bending of a cantilever controlled by polarization. As discussed in greater detail elsewhere,[1,19,20] this bidirectional bending observed for the polydomain azo-LCN (Ikeda-type) cantilevers has been hypothesized to be induced by a mechanism associated with trans−cis−trans reorientation of azobenzene, also known as the Weigert effect. Trans−cis−trans reorientation of azobenzene results from the statistical buildup of trans azobenzene rotated normal to the direction of the polarization of the light. Trans−cis−trans reorientation in polydomain azo-LCN can be used to induce surface contraction or expansion which in cantilever form results in forward or reverse (bidirectional) bending in Ikeda-type materials.[18] White *et al.* have used blue-green laser exposure to induce oscillations in monodomain azo-LCN cantilevers[19] (Ikeda type) as well as direct the bending angle of glassy monodomain azo-LCN systems[20] (Broer type).

As might be expected, the photogenerated work from azo-LCNs is governed by the underlying thermomechanical properties of the polymer network. To date, this association has been illustrated by the influence of cross-link density on the photomechanical response[15] including determination of the resulting photogenerated force as a function of azo-LCN cross-link density.[21] Broer and co-workers have shown that low azobenzene concentration (e.g., less than 5 wt %), glassy, high modulus azo-LCN (Broer type) are capable of accomplishing 175 kJ/m^3 of work in a splay alignment.[11,12]

In the work presented here, we examine the response of low azobenzene concentration (20 wt %), glassy azo-LCN (Broer type) cantilevers to exposure to 442 nm light as a function of

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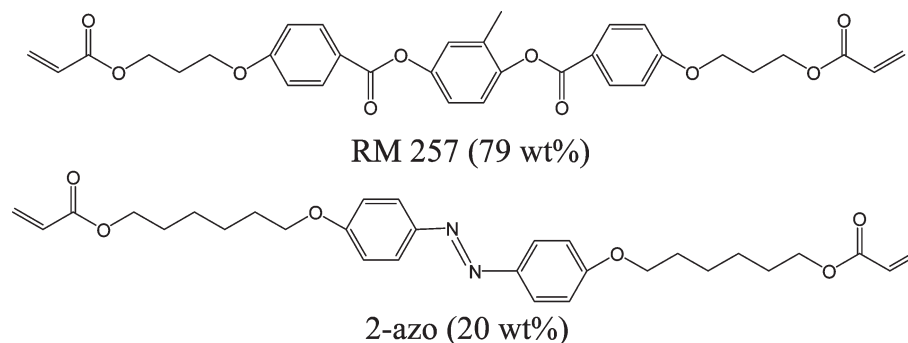
RM 257 (79 wt%)

2-azo (20 wt%)

Figure 1. Chemical structures of the diacrylate liquid crystal monomer RM257 and the diacrylate azobenzene liquid crystal monomer "2azo".

Table 1. Azo-LCN Sample Nomenclature and Summary of T_g, T_{high}, E'_{high}, and Cross-Link Density

sample code	$T_g{}^a$ (°C)	$T_{high}{}^b$ (K)	$E'_{high}{}^c$ (MPa)	ν_e (mol/dm³)
PD-20CL-1	44	367	23.08	2.09
PD-20CL-5	48	371	26.72	2.26
PD-20CL-15	61	384	31.5	3.29
PD-20CL-30	69	392	41.9	4.32
PD-20CL-60	80	403	73.9	7.25
PD-20CL-120	80	403	74.0	7.26

^{a} Obtained from peak of tan δ curve. ^{b} $T_{high} = T_g + 50$ °C. ^{c} Obtained value at T_{high}.

polarization. As with previous examination of an Ikeda-type azo-LCN cantilever, bending is observed in both the forward and reverse direction. To further elucidate the impact of material properties on the photogenerated response of these materials, photodirected bending was examined in samples of increasing cross-link density as well as a function of temperature. Complementary thermomechanical properties of the azo-LCN are reported and correlated to the photomechanical response of these materials.

Experimental Section

Synthesis of Azobenzene Liquid Crystalline Networks. Liquid crystal polymer networks containing azobenzene (azo-LCN) were synthesized by copolymerizing RM257 (Merck) and 4,4′-bis[6-(acryoloxy)hexyloxy]azobenzene (2azo) (BEAM Co.). The polymerization was initiated by 1 wt % of the inorganic photoinitiator Irgacure 784 (I-784) (Ciba).[7] The chemical structures of these molecules are shown in Figure 1. Mixtures of these solids were melted at 100 °C and drawn by capillary action into 15 μm thick Elvamide-coated (unrubbed) glass cells. To clear any filling artifacts, the cell was heated to 150 °C for 1 min. For photocuring, the sample was cooled to 125 °C and subjected to 60 mW/cm² of 532 nm laser light over a time period ranging from 1 to 120 min. The abbreviated nomenclature and the associated thermomechanical properties of the azo-LCN materials examined here are shown in Table 1. The large difference in curing time results in significant differences in the degree of conversion, which is evident in the calculated cross-link density of the samples. After photocuring, the films were removed from the glass substrates and washed in methanol to remove residual Elvamide alignment material.

Characterization Methods. The polydomain structure of the azo-LCNs was confirmed by polarized optical microscopy (POM, Nikon) with a heating accessory (Mettler). Thermomechanical properties of the azo-LCN films were determined in cantilevers with gauge length of 6 mm × 1 mm x 15 μm (length width and thickness, respectively). 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

0−200 °C. Glass transition temperatures (T_g) are reported from the maximum of the tan δ curve.

Photodirected Bending of Azo-LCN Cantilevers. Polarization controlled, bidirectional bending was directed with the linearly polarized 442 nm line of a 130 mW helium−cadmium (HeCd, Kimmon) laser. Note that 442 nm light is absorbed by both the trans and cis isomers of azobenzene. The HeCd laser beam was expanded and collimated with a spherical lens to a diameter of 15 mm, uniformly exposing the entirety of the cantilever with an intensity 80 mW/cm². The polarization direction of the laser was controlled with a Fresnel rhomb (Newport). The optical setup has been illustrated and described in detail elsewhere.[20] The photomechanical bending of azo-LCN cantilevers was monitored with a charge coupled device (CCD). The bending angle was analyzed with a program that determined the tip displacement angle between the mounting point of the cantilever and the outside edge of the tip of cantilever. The effect of temperature on photomechanical response of these materials was investigated by mounting the cantilevers in a Peltier heating device. At each temperature, the bent cantilever was allowed to equilibrate at the set temperature before measurement. The instantaneous bending angle was taken as the maximum bending angle observed before subsequent material relaxation.

Results and Discussion

Photogenerated mechanical responses have been a topic of considerable interest in the past decade. Primarily, UV light has been used to isomerize trans azobenzene into cis-azobenzene, which in liquid crystalline polymer networks (azo-LCN) induces an isothermal order−disorder transition. Recently, we have reported on distinctive photomechanical behaviors that are observed when blue-green (440−514 nm) laser light is used to photogenerate a mechanical response in azo-LCN.[18] Light in this wavelength regime has been extensively utilized in the formation of surface relief gratings by polarization holography of azobenzene thin films, through a phenomena referred to as trans−cis−trans reorientation or Weigert effect.[22] In a previous examination of polydomain azo-LCN system composed entirely of azobenzene mesogens (Ikeda-type) this mechanism was invoked to explain the polarization directed forward and reverse bending of a cantilever exposed to 457−514 nm (blue-green) laser light. Recently, the polarization controlled bending, including bidirectional bending, of monodomain azo-LCN cantilevers with much lower concentration of azobenzene (Broer-type) was examined under blue-green laser light exposure.[20]

The work presented here focuses on exploring the relationship between the thermomechanical properties of glassy, polydomain azo-LCN composed of 20% azobenzene cross-linker (Broer-type) and the resulting photomechanical response. The cross-link density of the azo-LCN films was varied by adjusting the length of photocuring, which in turn affects the degree of conversion. Parts a, c, and e of Figure 2 present the storage modulus, loss
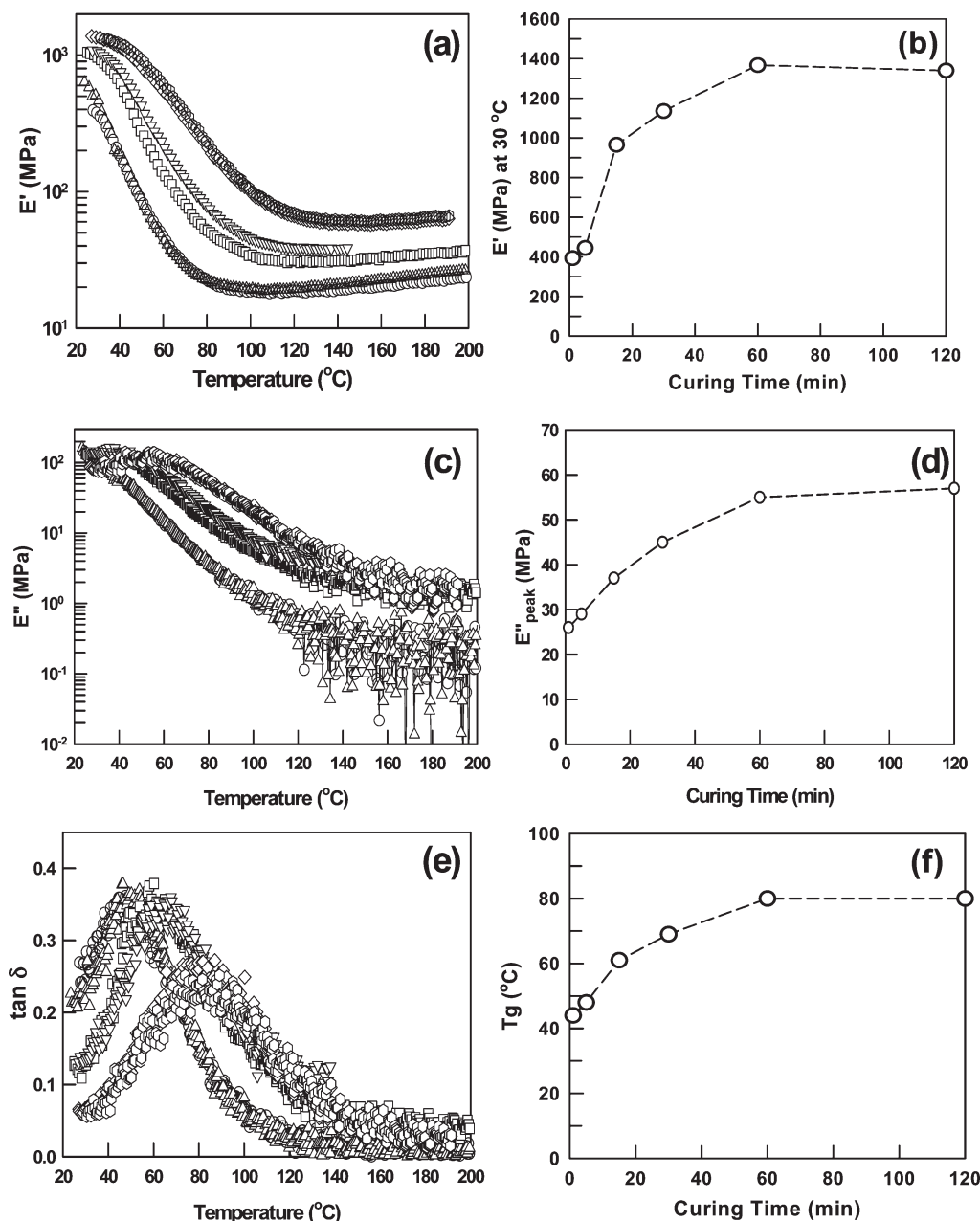
Figure 2. Dynamic mechanical analysis (DMA) of PD-20CL-*xx* samples cured at 125 °C for 1 min (○), 5 min (△), 15 min (□), 30 min (▽), 60 min (◇), and 120 min (◯). The raw data for (a) storage modulus (*E'*), (c) loss modulus (*E''*), and (e) loss tangent (tan δ) are summarized in parts b, d, and f, respectively.

modulus, and loss tangent data for the PD-20CL-*xx* samples as curing time is increased (where *xx* represents curing time in minutes). The plot of storage modulus (*E'*, Figure 2a) and of loss modulus (E'', Figure 2c) show that as expected *E'* and *E''* begin to decrease through T_g before a plateau is reached in the rubbery region to a level dependent on the cross-link density.[11,12] The plot of loss tangent (Figure 2e) indicates that these samples have a relatively broad T_g, which is typical of this type of chemistry.[11,12] As summarized in parts b, d, and f of Figure 2, the storage modulus (at 30 °C), loss modulus (at 30 °C), and T_g of the PD-20CL-*xx* samples increase as the length of photocuring is increased from 1 to 60 min. The samples are fully cured by 60 min of 532 nm exposure at 60 mW/cm², as the thermomechanical properties do not change between 60 and 120 min of photocuring. Adjusting the curing time from 1 to 60 min can tune the storage modulus at 30 °C from 400 MPa to 1.35 GPa with a respective increase in T_g from 44 to 80 °C.

Using the thermomechanical data reported in Figure 2, the cross-link density of these azo-LCNs was calculated by eq :[13,14]

$$v_e = E'_{high}/(3RT_{high})$$

where v_e is the cross-linking density and E'_{high} is *E'* at T_{high}. T_{high} is the temperature 50 °C higher than T_g (e.g., in the rubbery plateau region). The values for the cross-link density of the PD-20CL-*xx* samples are summarized in Table 1. As expected, cross-link density increases with curing time from 2.1 to 7.3 mol/dm³. The relatively large cross-link density of the azo-LCNs is dictated by the use of two diacrylate cross-linkers with relatively low molecular weights (2azo-522 g/mol, RM257-588 g/mol). The use of cross-linking monomers and the relatively small molecular length of the monomers results in a tightly packed mesh of cross-links in these azo-LCNs.

The strong correlation between the cross-link density and thermomechanical properties of the PD-20CL-*xx* samples is
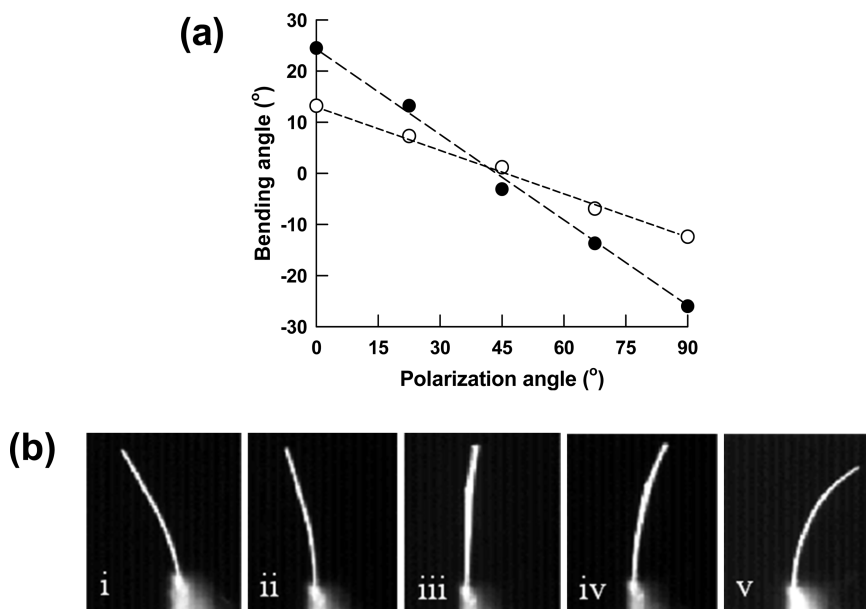
(a)

(b)

Figure 3. (a) Photodirected bending of an azo-LCN cantilever composed of PD-20CL-5 (●) and PD-20CL-60 (○) to exposure of 80 mW/cm² of a 442 nm laser as a function of polarization angle. The polarization was rotated from 0° (e.g., polarization parallel to the long axis of the cantilever) to 90° (e.g., polarization normal to the long axis of the cantilever). (b) CCD images of the PD-20CL-5 cantilever to laser exposure (442 nm laser light filtered). The laser is exposing the cantilevers (originally vertical) from the left side of the image. Key: (i) 0°, (ii) 20°, (iii) 45°, (iv) 70°, and (v) 90°.

expected to also influence the resulting photodirected bending of cantilevers composed of these materials. To illustrate the influence of cross-link density on the photomechanical response of these systems, Figure 3a plots the bending angle of a cantilever composed of PD-20CL-5 and PD-20CL-60 to exposure to 80 mW/cm² of 442 nm laser light with the direction of the linear polarization rotated from 0° (e.g., parallel to the long axis of the cantilever, referred to here as $E//x$) to 90° (e.g., normal to the long axis of the cantilever, referred to here as $E\perp x$). In the images shown in Figure 3b, the direction of the laser exposure is from left to right. The response of these polydomain azo-LCN cantilevers containing 20 wt % cross-linking azobenzene mesogens is similar to that previously reported[18] for higher azobenzene concentration systems (Ikeda-type). Comparatively, the magnitude of bending is reduced by the increase in cross-link density from 2.1 to 7.3 mol/dm³. Bending occurs at the intermediate polarization angle of 20° toward the light source and conversely, away from the source at 70°. Interestingly, bending in both PD-20CL-5 and PD-20CL-60 show a linear dependence of bending angle on polarization, with negligible bending observed in the case when the polarization is oriented 45° to the long axis of the cantilever. Comparatively, the magnitude of bending for the PD-20CL-*xx* samples is larger with reduced cross-link density (e.g., for lower curing times). Close examination of the inset images of Figure 3b reveals that some twisting can be observed to exposure of the intermediate polarization angles from 15 to 75°, with the greatest twisting occurring at 45°.

The results presented in Figure 3 confirm that bidirectional bending is observed in these glassy, Broer-type azo-LCNs when exposed to 442 nm light and that magnitude of bending of these systems is related to the mechanical properties of the azo-LCN. To further understand the relationship between the photomechanical response of the polydomain azo-LCN cantilevers and the thermomechanical properties, the temporal response of photodirected bending of a cantilever composed of PD-20CL-5 is examined in the glassy state (at 20 °C, Figure 4a) and in the rubbery state (at 90 °C, Figure 4b). In the glassy state, bending of PD-20CL-5 is slow and takes approximately 90 min of continuous exposure to near maximal bending. When the PD-20CL-5 cantilever is elevated above T_g and becomes rubbery, photodirected bending is

rapid and maximum bending angle can be observed in less than 5 s. However, after reaching this maximum angle, the bending angle of this cantilever reduces.

The data presented in Figure 4 is analogous to a creep experiment, in which a constant stress is applied (the 100 mW/cm² of 442 nm light) and the strain (magnitude of bending) is monitored over time. The polymer network in the glassy state has limited chain mobility. The response of glassy PD-20CL-5 is similar to a Kelvin–Voigt material, in which to constant stress, strain is continuously generated with the rate of creep slowing over time. Comparatively, the deformation of the rubbery PD-20CL-5 occurs quickly but is followed by reduced bending angle to continuous exposure. The reduction in bending angle to continuous exposure for PD-20CL-5 in the rubbery state is indicative of the network accommodating a portion of the photogenerated strain (assuming constant photogenerated stress). To further understand this behavior, the photomechanical response of PD-20CL-5 is examined as a function of temperature. Figure 5 plots the bending angle for PD-20CL-5 cantilevers to exposure to $E//x$ and $E\perp x$ (442 nm, 80 mW/cm²) examined over the temperature range 15–95 °C. Two representations of the bending response are plotted in Figure 5, referred to as the equilibrium bending angle and the instantaneous bending angle. The equilibrium bending angle represents the bending angle of the PD-20CL-5 cantilever at a given temperature after as much as 90 min of light exposure. As evident in Figure 5, the equilibrium bending angle of the PD-20CL-5 cantilever shows a strong dependence on temperature as the magnitude of the bending angle decreases by 20° over the 15–95 °C temperature range examined here. At temperatures above the T_g of PD-20CL-5, the relaxation behavior demonstrated in Figure 4b is observed. As the temperature is increased, the magnitude in the difference between the instantaneous and equilibrium response of the material increases from just a few degrees to as much as 20°. Although not shown in Figure 5, the rate at which the system reaches the equilibrium bending angle is also strongly related to temperature. At temperatures much higher than T_g, the bending angle decreases from instantaneous to equilibrium in a few seconds; while at temperatures near T_g the response occurs over many minutes.
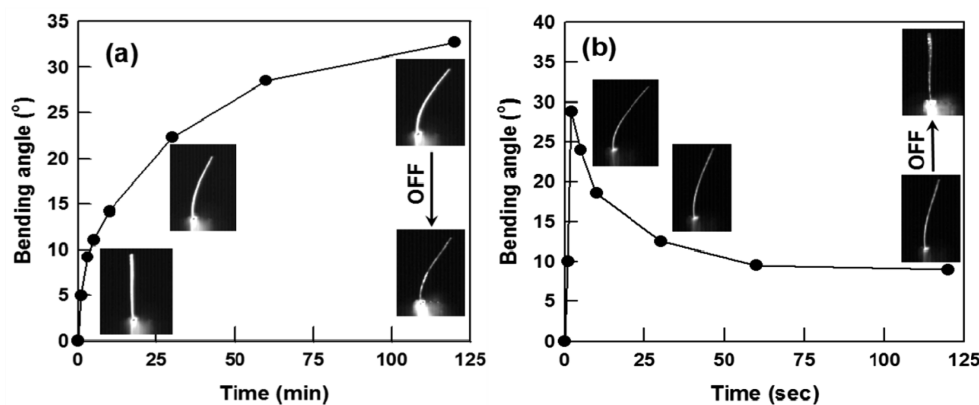
Figure 4. Temporal response of a PD-20CL-5 cantilever to exposure to 80 mW/cm^2 from a 442 nm laser at (a) 20 and (b) 90 °C. Inset images illustrate bending response during laser exposure, as well as after the state of the cantilever after the light is removed.
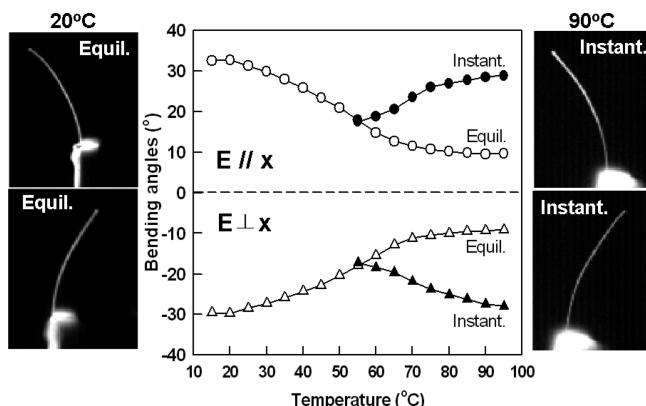

Figure 5. Instantaneous and equilibrium bending angle of a PD-20CL-5 cantilever to exposure to 80 mW/cm^2 from a 442 nm laser polarized $E//x$ and $E{\perp}x$ as a function of temperature.
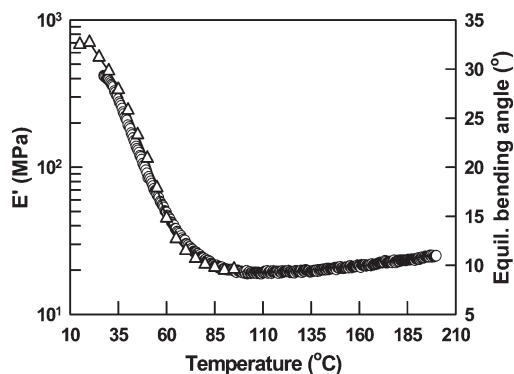

Figure 6. Plot of storage modulus (E') ($\bigcirc$) and bending angle ($\triangle$) for PD-20CL-5 cantilever bending as a function of temperature.

The results presented in Figure 3−5 indicate that the photomechanical bending of the PD-20CL azo-LCN cantilevers are closely related to cross-link density and temperature, both of which are well-known to govern the thermomechanical properties of a polymer network. Close examination of the temperature dependence of the log plot of storage modulus (E') in Figure 2a and the plot of bending angle in Figure 5 are remarkably similar in shape. For direct comparison, these curves are overlaid in Figure 6 and overlap nearly exactly over the temperature range 15−95 °C for the PD-20CL-5 material. The relationship between storage modulus and equilibrium bending angle presented in Figure 6 for PD-20CL-5 holds true for the entirety of the samples over the range of cross-link densities examined here. The close relationship between
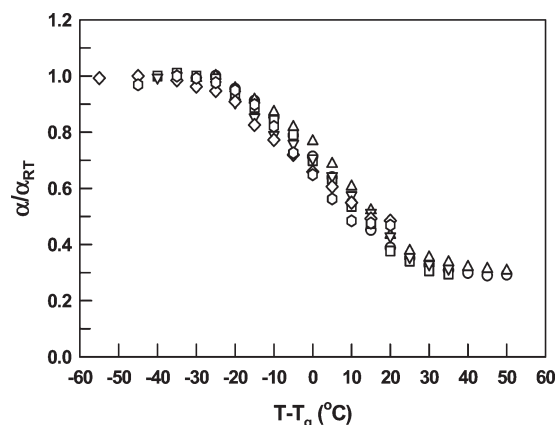

Figure 7. Photomechanical master curve for PD-20CL-*xx* azo-LCN samples with cross-link density of 2.26, 3.29, and 7.25 mol/dm^3. The normalized bending angle (α/α_{max}) is plotted against normalized temperature ($T - T_g$).

log E' and bending angle can be used to predict the magnitude and temperature dependence of the bending of a given material that has been examined with DMA. The physical meaning of this relationship is the subject of future examination.

The relationship between the thermomechanical and photomechanical properties are generalized in Figure 7 in the presentation of a WLF master curve. Motivated by the relationship between the storage modulus and the bending angle, Figure 7 plots a master curve of bending angle as a function of normalized temperature (e.g., $T - T_g$). As referenced in Figure 7, α and α_{RT} are, respectively, the bending angle at a given temperature and bending angle at room temperature. The absolute value of the bidirectional bending angle ($E{\parallel}x$ and $E{\perp}x$) of three azo-LCNs with cross-linking densities of 2.26, 3.29, and 7.25 mol/dm^3 are plotted. Evident in Figure 7 are three regions correlating to the glassy, leathery, and rubbery regions. The glassy region is 25−30 °C below T_g and typified by large bending angles. The leathery region spanning $T_g \pm 25$−30 °C sharply reduces the bending response as the material transitions from glassy to rubbery. In the rubbery region that begins 25−30 °C above T_g, the normalized equilibrium bending angle (α/α_{max}) is relatively constant at a reduced value of 0.3. The generation of the master curve representing the photomechanical bending of the azo-LCN as a function of T_g illustrates the interrelation of the photoresponse of the system and the underlying thermomechanical properties of the material.

Conclusions

The relationship between the photomechanical response of polydomain azo-LCN cantilevers to their underlying thermomechanical properties was examined. Notably, polarization dictated

bidirectional bending was observed in these glassy, high modulus azo-LCN cantilevers. The magnitude of the photomechanical deformation of these materials is strongly related to the thermomechanical properties of the polymer network, evident in the comparison of cantilevers of different cross-link density. The examination of photomechanical bending of these polydomain azo-LCN as a function of temperature indicate dramatic differences in the photomechanical response that occur in the glassy and rubbery states. Ultimately, the thermomechanical properties and photoresponse of the azo-LCN materials over a wide range of cross-link density is used to generate a WLF master curve that correlates these material properties.

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