Macromolecules

Room Temperature Rapid Photoresponsive Azobenzene Side Chain Liquid Crystal Polymer

Michael Petr and Paula T. Hammond*

Department of Chemical Engineering, Rm 66-352, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States

ABSTRACT: A new room temperature photoresponsive side chain liquid crystalline polymer has been synthesized and tested. It combines a side-on azobenzene LC with a low glass transition temperature polysiloxane backbone to obtain a nematic LCP at room temperature. The LCP also exhibits a crystalline phase that is kinetically trapped by the nematic phase at room temperature. Thermal transitions were observed at -7, 42, and 73 °C for the T_{gr} , $T_{m\nu}$ and T_{iso} , respectively, and polarizing optical microscopy with in situ UV irradiation was used to characterize the room temperature.



ture photoresponsive behavior of its metastable nematic phase. Upon irradiation, the nematic phase almost completely disappeared in about 35 s. The isotropization was linear with a rate of 1.9×10^{-11} mol/s at short times, but the final clearing process was exponential with a time constant of 4.6 s. These relatively short response times can be achieved at room temperature and are fast enough to be relevant for actuator and responsive elastomer applications.

INTRODUCTION

Liquid crystal polymers have been studied for several decades because they combine the properties of liquid crystals (LC's) with the advantages of polymer systems. When designing a side chain liquid crystalline polymer (SCLCP), there are three main structural components to consider: the LC side group, the polymeric backbone, and the linker group or functional group by which the two are attached to one another. The polymer can be from any number of backbone categories, including vinyl,¹⁻³ methacrylate,^{1,4-8} a strained cycloalkene product of ring-opening metathesis polymerization (ROMP),^{9–11} or even a dendrimer.¹² In particular, low glass transition temperature (T_g) polysiloxane backbones are important because they are flexible and do not constrain the ordering of the attached LC's; when functionalized with LC's, they are generally not glassy at room temperature, enabling the exhibition of LC phases at ambient conditions.^{13–34} The LC can also be selected to exhibit numerous phases, with the most common being smectic^{2,4–9,11,35–37} or nematic^{11,38–41} with a high^{4,5,9–11,42} or low^{3,38,43} isotropization temperature (T_{iso}). Finally, the LC can be attached "end-on"^{1,2,4,5,7–10,36,37} or "side-on"^{3,39–41,44,45} with respect to the unit director of the LC. More recently, photoresponsive SCLCP's, which contain azobenzene moieties, have gained interest for their ability to change properties by merely irradiating them with the correct wavelength of light in the appropriate temperature range.^{16,29,33,38–40,46–72} They are of particular interest for applications in which a quick response or actuation^{16,33,47,49,52,56–59,61,62,71,72} is necessary, such as artificial muscles,^{39,40} photomechanical cantilevers,^{51,62,66,69} photomechanical oscillators,⁷⁰ and even robotics.⁶⁸

Azobenzene SCLCP's are responsive to UV light by means of a trans-to-cis isomerization of the azobenzene moiety. The azobenzene starts in its thermodynamically stable trans conformation; then,

absorption of a UV photon promotes an electron from the HOMO π -orbital to the LUMO π^* -orbital, which switches the azobenzene to its cis conformation. In its trans conformation, azobenzene is straight and extended and able to pack effectively with its neighbors to form an LC phase; however, in its cis conformation, the azobenzene takes on a bent configuration and is no longer able to pack sufficiently to form an LC phase leading to the formation of an isotropic phase. This process is reversible and can be catalyzed by higher wavelengths of light as well as thermal energy because the trans conformation is thermodynamically favored.⁷³ Historically, this nematic formation has been the process used to study the phase change kinetics, and the nematic domains grow linearly with time when subject to a large enough temperature quench.⁷⁴⁻⁷⁷ On the other hand, there have been few kinetic studies on the nematic-toisotropic transition, though one simulation did predict a linear decrease in the order parameter with respect to time.⁷⁸

By the process described above, quick, reversible, and large responses have been achieved in photoresponsive SCLCP's. This observation is notable in that rapid responses in the bulk have, thus far, only been achieved at elevated temperatures. For example, the nematic side-on azobenzene polymethacrylate made by Li required 25 min of irradiation at 2.3 mW/cm² and room temperature for an 80.5 nm film³⁸ or a couple of minutes of irradiation at 100 mW/cm² and 70 °C for a 20 μ m film⁴⁰ for a complete response because the T_g of the polymer backbone was 60 °C. A photoresponsive smectic end-on azobenzene polysiloxane system was made by Verploegen; however, in that case, the transitions were only observed at or above 100 °C.

Received:	June 14, 2011
Revised:	October 6, 2011
Published:	October 25, 2011

This is because, although the $T_{\rm g}$ of the polymer was very low, the $T_{\rm iso}$ of the smectic phase was 126 °C.⁶⁸ Below 100 °C, the smectic phase was too viscous for a fast response. In fact, these two examples illustrate the importance of the $T_{\rm g}$ of the polymer backbone and the $T_{\rm iso}$ of the LC because they define the temperature range in which the bulk photoresponsive SCLCP can be used. The $T_{\rm g}$ defines the absolute lower limit, and the $T_{\rm iso}$ defines the upper limit as well as a potential lower limit whereby, if it is too far below the $T_{\rm iso}$, the LC becomes too viscous for a quick response. Consequently, a photoresponsive SCLCP with a low $T_{\rm g}$ and a low $T_{\rm iso}$ is necessary for a quick response at room temperature; this work is an example of such a material.

EXPERIMENTAL SECTION

Materials. 1,3,5-Trivinyl-1,3,5-trimethylcyclotrisiloxane (V3) and 1,4-bis(hydroxydimethylsilyl)benzene were purchased from Gelest, Inc., and all other reagents were purchased from Sigma-Aldrich. No purification was performed on any of the reagents or solvents, except for the tetrahydrofuran (THF) polymerization solvent, which was taken from an Innovative Technologies, Inc., solvent purification system and dried with sodium.

Instrumentation. Anionic polymerization in an Innovative Technologies, Inc., glovebox was used to make poly(vinylmethylsiloxane) (PVMS), and gel permeation chromatography (GPC) with a Waters 717plus autosampler running THF as the mobile phase was used to determine the molecular weight (MW) and the polydispersity index (PDI) of the PVMS. ¹H NMR on a Bruker AVANCE-400 was used to determine molecular structure and degree of conversion for the LC synthesis and attachment. Differential scanning calorimetry (DSC) on a Thermal Analysis (TA) Instruments DSC Q1000 was used to measure the various transition temperatures of the material. Polarizing optical microscopy (POM) with a Zeiss Axioskop 2 MAT and an AxioCam MRc camera recorded with CamStudio screen-capture software was used to characterize the LC phase, and during this characterization, UV light centered at 360 nm from a Dymax Blue Wave 200 with a Thorlabs, Inc. FGUV W53199 UV filter was shined on the material. Finally, anisotropic spectroscopic ellipsometry on a J.A. Woollam Co., Inc., XLS-100 was used to measure refractive indices and birefringence.

Synthesis of 4-Butoxy-2′,**4**′**-dihydroxyazobenzene (1).** This synthesis has been reported previously.³⁸ 7.821 g of crude 1 was obtained for a conversion of 90%.

Synthesis of 4-Butoxy-2'-hydroxy-4'-(4-butoxybenzyloxy) azobenzene (2). This synthesis has been reported previously.³⁸ 6.320 g of red 2 was obtained for a conversion of 57%.

Synthesis of 4-Butoxy-2'-allyloxy-4'-(4-butoxybenzyloxy) azobenzene (3). This synthesis is similar to that reported previously³⁸ but with allyl alcohol in place of 4-hydroxybutyl methacrylate. To 100 mL of dichloromethane was added 6.320 g of 2, and the solution was cooled in an ice bath. Next, 1.001 g of allyl alcohol and 5.402 g of triphenylphosphine were added, and then 3.541 g of 40 wt % DEAD in toluene was added dropwise. The solution was stirred overnight in the ice bath, and then the dichloromethane was removed. The orange 3 was separated with 1:9 v/v ethyl acetate:hexane on a silica gel column and recrystallization in ethanol from 60 °C to room temperature to obtain 5.060 g of 3 for a conversion of 74%. ¹H NMR: δ 6.8–8.2 (m, 11H, Ar), 6.10 (m, $-0-CH_2-CH=CH_2$), 5.47 (t, $-0-CH_2-CH=CH_2$ (Z), 5.34 (q, $-0-CH_2-CH=CH_2$ (E)), 4.74 (d, $0-CH_2-CH=CH_2$), 4.65 (br s, $0-CH_2-CH=CH_2$).

Synthesis of 4-Butoxy-2'-(3-(1,1,3,3-tetramethyldisiloxanyl) propoxy)-4'-(4-butoxybenzyloxy)azobenzene (4). This synthesis is similar to that reported previously.³² 13.468 g of 1,1,3,3-tetramethyldisiloxane and 25 mL of toluene were mixed at room temperature. A second solution with 5.060 g of 3, 25 mL of toluene, and 10 drops of



Figure 1. Synthesis of new photoresponsive SCLCP.

Pt(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene (Pt \sim 2%) was mixed. This solution was added dropwise to the first solution to obtain a red solution and then stirred overnight at 60 °C under N₂. The orange 4 was separated with 1:9 v/v ethyl acetate:hexane on a silica gel column to obtain 1.922 g for a conversion of 30%. ¹H NMR: δ 6.8–8.2 (m, 11H, Ar), 4.73–4.62 (m, –Si(CH₃)₂–O–SiH(CH₃)₂), 0.0–0.3 (m, –Si(CH₃)₂–O–SiH(CH₃)₂).

Synthesis of Poly(vinylmethylsiloxane) (PVMS) (5). This synthesis has been reported previously.³² Roughly 1 g was made, and a sample was run on the GPC, which measured the number-average MW as 18 000 g/mol and the PDI as 1.18 against polystyrene standards.

LC Attachment. This attachment procedure has been reported previously.³² The resulting **6**, made from 1.922 g of 4 and.134 g of **5**, was a dark brown oil. ¹H NMR confirmed removal of the excess 4 by disappearance of the Si–H peak as well as the complete disappearance of the vinyl peak of **5** for an attachment of 100%. ¹H NMR: δ 8.12 (d, $-O_2C-ArH_2H_2-O-bu$), 7.90 (d, $-N_2-ArHH_2-O_2C$), 7.82 (d, $bu-O-ArH_2H_2-N_2(Z \text{ to spacer})$), 7.06–6.64 (m, $bu-O-ArH_2H_2-N_2-bu-O-ArH_2H_2-N_2(E \text{ to spacer}) -N_2-ArHH_2-O_2C--O_2C-ArH_2H_2-O-bu$), 4.04 (td, $-O-CH_2CH_2CH_2CH_3$), 4.15–3.67 (br t, $-O-CH_2CH_2CH_2CH_2-Si-$), 1.96–1.56 (br m, $-O-CH_2CH_2CH_2CH_3-Si-$), 1.80 (p, $-O-CH_2CH_2CH_2CH_3$), 1.50 (sex, $-O-CH_2CH_2CH_2CH_3$), 1.23, (t, $-O-CH_2CH_2CH_2-Si-$), 0.98 (t, $-O-CH_2CH_2CH_2CH_3$), 0.94–0.32 (br m, $-O-Si-(CH_3)_2-CH_2CH_2-Si(CH_3)-O-$), 0.17–0.07 (br m, $-Si(CH_3)$).

RESULTS AND DISCUSSION

Synthetic Scheme. The procedure used to synthesize the new SCLCP, shown in Figure 1, uses the mesogen synthesis described



Figure 2. Differential scanning calorimetry (DSC) at 10 $^{\circ}$ C/min with two cycles on SCLCP 1 week after annealing.

by Li³⁸ and the PVMS backbone and side chain attachment approach of hydrosilylation described previously by Verploegen.³² The PVMS backbone is a siloxane with a glass transition temperature approaching -100 °C in its nonfunctionalized form. It was chosen to enable a low glass transition even after the attachment of polymer side chains. The LC has its point of attachment at the center of the mesogen core so that its LC unit director falls parallel, rather than perpendicular, to the polymer main chain, yielding a socalled "side-on" SCLCP. This side-on arrangement creates polymer systems whose chain conformations are highly responsive to the arrangement of the LC mesogens^{3,39–41,44,45} and was specifically chosen for this work to induce a stronger rheological response to mesogen isotropization as compared to the end-on side chain LC functionalization studied in the earlier polysiloxane-based system.⁶⁸

SCLCP Properties and Characterization. The freshly synthesized, solvent-cast, or annealed SCLCP is a dark brown gel-like viscous liquid. After being stretched, spread, or strained in any way or after sitting for a few days to a week at room temperature, the SCLCP turns into a light brown crystalline solid. This behavior can be explained by the DSC in Figure 2, which shows two scan cycles for a sample of SCLCP a week after annealing at 100 °C. Both cycles show an LC isotropization (T_{iso}) peak at about 73 °C, but the first cycle shows an extra crystalline melting peak (T_m) at 42 °C. The T_m does not show up on the second cycle because, after the crystalline phase has melted from the first heating cycle, it takes at least several days to reform again. The glass transition temperature (T_g) of the LC-functionalized polysiloxane backbone is approximately -7 °C; although higher than that of most polysiloxanes,⁷⁹ this value is quite low compared to that of most photoresponsive SCLCP's and is also well below room temperature. $^{4,5,9-11,42}$

As for the LC phase itself, the POM image in Figure 3 is pink and green, which is due to the birefringence of an LC phase. The ordinary and extraordinary refractive indices and the birefringence of a spin-cast sample were measured as 1.59, 1.66, and 0.07, respectively, using anisotropic ellipsometry. Figure 3 also shows a Schlieren texture with 2- and 3-point disclinations, which is positive evidence for a nematic LC phase. Furthermore, this nematic phase persists down to the $T_{\rm g}$ because the crystalline phase forms so slowly, thus making it a long-lived metastable phase.

Photoresponsive Characterization. The SCLCP is photoresponsive because the azobenzene moiety can absorb a photon to promote an electron from the HOMO π -orbital to the LUMO π^* orbital, resulting in a conformational change of the azobenzene



Figure 3. Polarizing optical microscopy (POM) image of SCLCP at a magnification of $\times 50$ showing a Schlieren texture with 2- and 3-point disclinations.



Figure 4. UV-vis absorbance spectrum.



Figure 5. Trans-to-cis conformation change resulting in the nematic-toisotropic phase change.

from the trans isomer, which is thermodynamically stable, to the cis isomer.⁷³ Figure 4 shows a UV–vis absorption spectrum for the SCLCP, which has an absorbance peak in the near-UV and visible region from about 306–417 nm corresponding to this π to π^* transition.

The SCLCP forms a nematic phase because the straight azobenzene and benzoate moieties in the trans conformation tend to line up to reduce free volume, as in the first schematic in Figure 5. Upon irradiation with UV light in this π to π^* region, the azobenzenes' change from trans to cis disrupts the nematic



Figure 6. Polarizing optical microscopy (POM) at a magnification of \times 50 of SCLCP with UV irradiation. The first picture was taken before the UV light was turned on, and it shows a nematic Schlieren texture with 2-, 3-, and 4-point disclinations. The next pictures are from 5 to 30 s and show the nematic phase disappearing, and the last picture is at 35 s and shows the nematic phase almost completely gone.

phase of the SCLCP because, when they change to cis, they become bent and, therefore, cannot line up with each other, as in the second schematic in Figure 5.

This nematic disruption was monitored using POM with in situ UV irradiation at 60 mW/cm^2 . The first image in Figure 6 was taken with no UV light. At 0 s, the UV light was turned on, and the Schlieren texture was monitored with screen-capture software that recorded an image every couple of seconds. The last seven images in Figure 6 were taken every 5 s and show the disappearance of the birefringent Schlieren texture in the exposed area over a total of about 35 s. For these images, as well as the intermediate ones, the red, green, and blue 24-bit color intensities were evaluated for each pixel and summed over the entire picture for an overall color intensity. This color intensity is plotted as a function of time in Figure 7. The decrease in birefringence first exhibits a linear regime, producing data similar to that of previous photoresponsive nematic systems, $^{67,80-94}$ with a rate of 1.0×10^7 intensity/s and finishes with an exponential regime with a time constant of 4.6 s. The rate in the linear regime can be converted to a traditional rate of



Figure 7. Integrated color intensity from polarizing optical microscopy (POM) images. The first portion has rate a of 1.0×10^7 intensity/s and a linear r^2 of 0.9995, and the second portion has an exponential time constant of 4.6 s and an r^2 of 0.998.

 1.9×10^{-11} mol/s by applying eq 1, which uses the initial volume of the film divided by the initial color intensity as a scale factor:

$$r = r_1 \frac{A_i h_i}{I_i} \frac{\rho}{M} \tag{1}$$

where *r* is the rate in mol/s, $r_{\rm I}$ is the rate in intensity/s, $A_{\rm i}$ is the initial area of the film calculated as 2.4×10^{-4} cm² from the manufacturer's technical data, $h_{\rm i}$ is the initial height of the film estimated at 13 μ m using a Michel–Levy plot, $I_{\rm i}$ is the initial intensity of the film found to be 2.1×10^8 , ρ is the density of the film estimated to be 0.95 g/cm³, and *M* is the molar mass of the SCLCP repeat unit calculated to be 753.16 g/mol. The film height was estimated with a Michel–Levy plot because, even though the film height was uniform in the small viewing window of the microscope, it was nonuniform across the entire sample, so direct measurement in the specific area of the POM images would have been difficult. Basically, a Michel–Levy plot is a graphical link between film thickness, birefringence, and viewed POM color. Given two of these, the third can be estimated.

It was a somewhat counterintuitive result to have two regimes for the SCLCP's isotropization. Because the azobenzene's isomerization is unimolecular, it is expected to follow first-order kinetics with rates on the order of minutes to hours,⁹⁵ and indeed, this was, most likely, the case given the previous photochemical characterization of the LC.³⁸ However, the SCLCP's isotropization is not necessarily linearly correlated with the azobenzene's isomerization. The bent cis LC moieties act as bulky impurities in the nematic phase to lower its T_{iso}^{50} and to effectively destroy it at a given temperature below the original T_{iso} . Once the UV light was introduced, the nematic phase was destabilized, and the linear regime followed by the exponential regime is consistent with the kinetics of a nematic phase with a distribution of domain sizes that is supersaturated with *cis*-azobenzene impurities.^{77,78} Figure 6 actually shows isotropization starting from the domain boundaries and moving inward, leading to linear kinetics, followed

by convergence of the growing isotropic domains—i.e., disappearance of the nematic domains—leading to exponential kinetics. Because there is a distribution of nematic domain sizes in the beginning, the individual domains disappear at different times, smaller ones followed by larger ones. Coincidentally, the camera is centered on a cluster of smaller domains, which disappear faster and produce the artifact of isotropization seeming to start in the center of the screen. The fourth image in Figure 6 then shows some of the smaller nematic domains in the center as they disappear, signifying the transition to the exponential regime whereby the growing isotopic domains begin to coalesce and stop growing. A decreasing number of growing isotropic domains means a decreasing isotropization rate, which corresponds to the exponential kinetics.

CONCLUSIONS

The new material presented here fills the need of a room temperature bulk photoresponsive SCLCP. It combines the side on azobenzene LC from ${\rm Li}^{38}$ with the polysiloxane backbone and the attachment procedure from Verploegen³² to obtain a nematic SCLCP with a low $T_{\rm iso}$ and a low $T_{\rm g}$. It does have a crystalline phase, but the nematic phase is metastable at room temperature because the crystalline phase takes several days to form. Consequently, the photoresponsive behavior was demonstrated at room temperature using POM with in situ UV irradiation. Upon irradiation, the nematic phase quickly began to undergo isotropization, and this process started with a linear regime, with isotropic domains emanating from the nematic domain boundaries, and finished with an exponential regime, corresponding to convergence and coalescence of the growing isotropic domains. In the future, reversibility in the isotropization of this material will be shown as well as the functional temperature range in which photoresponsive behavior is observed, from well below room temperature to well above room temperature as defined by its T_{g} and T_{iso} . This is an important range because most of its potential applications as an actuator material are in the common ambient living range around room temperature.

ACKNOWLEDGMENT

The authors of this paper thank the United States Army's Institute for Soldier Nanotechnologies (ISN) for equipment, facilities, and financial support of this research.

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