Photo-responsive polysiloxane-based azobenzene liquid crystalline polymers prepared by thiol-ene click chemistry

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ABSTRACT

In this work, a novel polysiloxane-based azobenzene-containing liquid crystalline polymer (LCP) PMMS-A44V6 has been designed and synthesized via a facile thiol-ene click chemistry method by grafting a side-on azobenzene mesogenic group A44V6 onto poly-[3-mercaptopropylmethylsiloxane] (PMMS) backbone. \(^1\)H NMR, \(^{13}\)C NMR, GPC, TGA, DSC, POM and WAXS were used to investigate the mesogenic properties and photo-responsive behaviour of PMMS-A44V6. Taking advantage of the azobenzene’s trans–cis isomerization effect, PMMS-A44V6 can perform an isotropization process under UV irradiation in its nematic phase. Initially, the isotropization process starts in a linearly decreasing manner with a rate of ca \(-6.5 \times 10^5\) intensity/s, and eventually finishes in an exponential decrease regime to form cis-azobenzene moieties. The reversible UV-response behaviour of PMMS-A44V6 can be performed in a relatively low temperature range of 30 ~ 75°C, which might help this azobenzene-containing LCP material to find potential application in control devices.

1. Introduction

Azobenzene, as one of traditional photochromic moieties, can perform a photo-induced reversible isomerization under UV irradiation.\([1–3]\) The absorption of a UV photon promotes an electron from the highest occupied molecular orbital (π-orbital) to the lowest unoccupied molecular orbital (π*-orbital), which switches the azobenzene from its thermodynamically stable trans-conformation to cis-conformation. The length of the azobenzene molecule reduces from 10 to 5.6 Å, while its molecular dipole moment increases from 0.5 to 3.1 D. The cis-azobenzene can recover to its original state under irradiation of visible light or heating.\([4]\) This reversible photo-isomerization property of azobenzene endows azobenzene-incorporated materials with potential applications in control devices and soft actuator technologies.\([5–10]\)

In recent decades, azobenzene-containing liquid crystal (LC) system has attracted lots of researchers because the reversible photo-isomerization process of azobenzene moieties can deeply impact the order of mesophase.\([11–22]\) In trans-conformation, the azobenzene-containing molecules are prone to form an anisotropic phase; On the contrary, in cis-conformation, the azobenzene moieties bend and the ordered molecular arrangement is disrupted, leading to the formation of an isotropic phase.

In particular, polysiloxane-based liquid crystalline polymers (LCPs) \([23,24]\) containing azobenzene moieties have received extensive attention for their wealth of advantageous physical properties brought by both mesogen moieties and siloxanes. As is known to all, the
highly flexible polysiloxane backbone can significantly reduce glass transition temperatures \( (T_g) \), LC phase transition temperatures, surface tension, and surface energy, meanwhile increase hydrophobicity, thermal and mechanical stabilities, etc.\[13,14,25–27\] Besides, the changes of azobenzene’s geometrical shapes, molecule sizes and molecular polarities can drive the macroscopic deformation of LCP systems. In 2001, Finkelmann group introduced the azobenzene mesogen into polysiloxane-based LCPs to synthesize nematic liquid crystalline elastomers (LCEs).\[28\] In that report, the azobenzene process an isomerization to from a cis-conformation, which could disrupt the mono-domain alignment, leading to a 20% contraction along the molecular director. Afterwards, Terentjev,\[17\] Zentel,\[28–30\] Hammond\[31,32\] and our group\[33\] have reported several research works about deformation of polysiloxane-based azobenzene-containing LCPs and LCEs under merely irradiation of light with certain wavelength.

Most of the previously reported polysiloxane-based photo-responsive LCPs containing azobenzene moieties were prepared by hydrosilylation of polymethylhydrosiloxane (PMHS) with mesogenic alkenes using Pt complex catalysts. However, classical hydrosilylation reactions are plagued by several critical problems, including uncontrollable catalyst grafting ratio, expensive Pt complex catalyst, complicated polymerization kinetics, forming the mixture of Markovnikov and anti-Markovnikov addition products, etc.\[34\] In order to overcome the disadvantages, inspired by Hawker’s work,\[35–37\] our group have reported a sequential

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**Figure 1.** The synthetic routes of mesogenic monomer A44V6 and the corresponding liquid crystalline polymer PMMS-A44V6.
thiol-ene click chemistry protocol to prepare polysiloxane-based LCPs, LCEs and gold nano-particles/LCE composites by using poly-[3-mercaptopropylmethylsiloxane] (PMMS), which possesses one thiol group in every monomer unit, to take place of tradition PMHS as the starting polysiloxane backbone for mesogen grafting.[38,39] As a cleaner and greener approach, thiol-ene click protocol requires only cheap radical initiators as catalysts, which can be easily removed during polymer precipitation step. Based on this sequential thiol-ene click strategy, we further prepared thermo-sensitive electrospun fibres,[40] magnetic stir bar-encapsulated polysiloxane-based organocatalyst gels, and developed a Stir Bar-Encapsulated Catalysis (SBEC) technique with potential applications in heterogeneous catalysis systems.[41]

Herein, we report a polysiloxane-based azobenzene-containing LCP PMMS-A44V6. As shown in Figure 1, the vinyl-terminated side-on azobenzene-containing mesogen A44V6, whose acrylate-analogue was first invented by Keller,[6,7,42] was successfully synthesized and grafted onto PMMS backbone as not only optical chromophore but also mesogenic unit via a facile thiol-ene click chemistry method under benign conditions. The characterizations of such an azobenzene-containing LCP material PMMS-A44V6 were performed by 1H NMR, 13C NMR, GPC, TGA, DSC, POM and WAXS. The UV-responsive behaviour and kinetic studies of isotropization process of PMMS-A44V6 are also investigated in this work.

2. Experimental details

2.1. Materials and instrumentation

Poly[3-mercaptopropylmethylsiloxane] (PMMS, SMS-992, M.W. 4000–7000, 95 cst) was purchased from Gelest Inc. Dicyclohexylcarbodiimide (DCC), azodibutyronitrile (AIBN), diisopropyl azodicarboxylate (DIAD) and 4-dimethylaminopyridine (DMAP) were purchased from Aladdin Inc. THF was purified by a routine procedure and distilled from sodium benzenophenone ketyl under nitrogen. All other chemicals were of commercially analytical grade and used without further purification. The isolation of polymers was performed by using a Sigma 2K 15 centrifuge. Macherey-Nagel MN Kieselgel 60 (0.063–1.2 mm) was used on flash chromatography.

The 1H NMR spectra of all monomers and polymers were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300) to determine molecular structure and degree of conversion of LC grafting. A Shimadzu LC20AD high-performance liquid chromatography (HPLC), equipped with an RID-20A refractive index detector and a Shodex KF-803 300–8 mm column packed with 6 μm particles, was used to perform gel permeation chromatography (GPC) in THF (1 mL/min) at 40°C to determine the molecular weight (MW) and the polydispersity index (PDI) of polymers. The column packing allowed the separation of polymers over a molecular weight range of 200–70,000. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7. A TA Instruments Q100 instrument (New Castle, DE) was used to record differential scanning calorimetry (DSC) spectra under nitrogen purge at a heating rate of 10°C/min from −20 to +120°C, and to measure the various transition temperatures of the materials. An Olympus BX53P microscope, equipped with a Mettler PF82HT hot stage and a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver.2.2 software, was used to obtain the polarized optical microscopy (POM) images of the liquid crystalline textures of the monomer and polymer. A high-flux small angle X-ray scattering instrument (SAXSess, Anton Paar), equipped with Kratky block-collimation system and a Anton Paar TCS300 temperature control unit, was used to perform the X-ray scattering experiments. At each single steady temperature, both small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were recorded on an imaging-plate (IP) which extended to high-angle range at 40 kV and 40 mA for 20 min. A TU-1810 ultraviolet-visible spectrophotometer (UV/VIS spectrometer, Beijing Purkinje General Corp., China) was used to obtain the UV-Vis absorption spectra. The UV-responsive behaviour experiment was performed by using an LP-20A UV lamp (5 mW/cm², λ = 365 nm; LUYOR Corporation) to irradiate the sample.

2.2. Synthesis of monomer A44V6

All the 1H NMR spectra are listed in the Supporting Information. As shown in Figure 1, the synthetic routes of monomer A44V6 was inspired by Keller’s methacrylate analogue.[43] 4-Butoxyaniline (2.00 g, 12.2 mmol) and concentrated HCl (2.1 mL, 24.4 mmol) were added into 30 mL of a mixture of PEG200/1,4-dioxane/water (60/30/10, 30 mL) in an ice-bath. A 2 mL solution of NaN3 (0.90 g, 13.4 mmol) dissolved in water (10 mL) was added dropwise into the above mixture and stirred at 0 ~ 5°C for 2 h to form the diazonium salt (2). Resorcinol (4.00 g, 36.4 mmol) and NaOH (0.54 g, 13.4 mmol) were dissolved in 30 mL of the mixed
solvent (PEG200/1,4-dioxane/water (60/30/10)). The mixture was added into the diazonium salt solution and stirred for 15 min. A 100 mL of water was poured into the mixture and appropriately concentrated HCl (1.5 mL) was added to adjust the pH of the mixture to 4 ~ 5. After filtration, the collected red powder was washed with water and dried in vacuum. The final purification was carried out by column chromatography using cyclohexane/ethyl acetate (90/10) to give the product 3 (3.10 g, Yield: 77.7%) as a red solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.77 (m, 3 H), 6.99 (d, $J = 6.8$ Hz, 2H), 6.54 (m, 2H), 4.03 (t, $J = 6.8$ Hz, 2H), 1.81 (m, 2H), 1.51 (m, 2H), 1.01 (t, 3H, $J = 6.5$ Hz).

Compound 3 (2.4 g, 8.6 mmol), DCC (2.2 g, 10.4 mmol) and 4-butoxybenzoic acid (1.7 g, 8.6 mmol) were added into CH$_2$Cl$_2$ (50 mL) and stirred at room temperature under nitrogen overnight. After filtration, the solution was washed with 60 mL of water, 60 mL of 5% aqueous acetic acid and 60 mL of water in turns. The organic solution was dried over anhydrous Na$_2$SO$_4$. After evaporation off the solvent, the residue was recrystallized twice from toluene/ethanol (80/20) to give the product 5 (3.9 g, Yield: 74%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.16 (d, $J = 8.9$ Hz, 2H), 7.93 (d, $J = 8.9$ Hz, 2H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.02~6.89 (m, 6H), 4.07 (t, $J = 6.5$ Hz, 4H), 1.86 (m, 4H), 1.59 (m, 4H), 1.00 (t, $J = 7.4$ Hz, 6H).

5-hexen-1-ol (0.8 g, 5.4 mmol), phenol (2.2 g, 20.4 mmol), 4-dimethylaminopyridine (0.2 g, 1.0 mmol) and 4-butoxybenzoic acid (1.7 g, 8.6 mmol) were added into CH$_2$Cl$_2$ (50 mL) and stirred at room temperature under nitrogen overnight. After filtration, the solution was washed with 60 mL of water, 60 mL of 5% aqueous acetic acid and 60 mL of water in turns. The organic solution was dried over anhydrous Na$_2$SO$_4$. After evaporation off the solvent, the residue was recrystallized twice from toluene/ethanol (80/20) to give the product 5 (3.9 g, Yield: 74%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.16 (d, $J = 8.9$ Hz, 2H), 7.93 (d, $J = 8.9$ Hz, 2H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.02~6.89 (m, 6H), 4.07 (t, $J = 6.5$ Hz, 4H), 1.86 (m, 4H), 1.59 (m, 4H), 1.00 (t, $J = 7.4$ Hz, 6H).

Diisopropyl azodicarboxylate (DIAD) (1.2 g, 10.4 mmol) and triphenylphosphine (TPP) (1.7 g, 6.4 mmol) were added dropwise into the above ice-cooled solution. The mixture was stirred at room temperature under nitrogen overnight. After evaporation of the solvent, the mixture was purifed by column chromatography on silica gel using cyclohexane/ethyl acetate (90/10) as eluent. The product was recrystallized from absolute ethanol to give the desired monomer A44V6 (yellow crystal, 1.8 g, 69%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.15 (d, $J = 8.9$ Hz, 2H), 7.90 (d, $J = 8.9$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 1H), 6.99 (dd, $J = 8.9$, $J = 2.1$ Hz, 5H), 6.87 (dd, $J = 8.8$, 2.2 Hz, 1H), 5.84 (m, 1H), 5.14~4.84 (m, 2H), 4.18 (t, $J = 6.4$ Hz, 2H), 4.06 (t, $J = 6.5$ Hz, 4H), 2.17 (m, 2H), 2.01~1.88 (m, 2H), 1.88~1.73 (m, 4H), 1.73~1.60 (m, 4H), 1.53 (m, 4H), 1.00 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 163.7, 138.6, 132.3, 124.8, 117.6, 114.7, 114.4, 114.1,108.3, 69.8, 68.1, 33.4, 31.2, 28.6, 25.4, 19.2, 13.8. Phase sequence and transition temperatures: Cr $\rightarrow$ 45.1°C $\rightarrow$ N $\rightarrow$ 107.3°C $\rightarrow$ Iso (on heating, determined by POM), Iso $\rightarrow$ 104.1°C $\rightarrow$ N $\rightarrow$ 36.1°C $\rightarrow$ Cr (on cooling).

### 2.3. Synthesis of polymer PMMS-A44V6

A44V6 (577 mg, 1.0 mmol), PMMS (144 mg, 1.08 mmol –SH), AIBN (17 mg, 0.12 mmol) were added into toluene (4 mL) stirred at 65°C for 24 h under nitrogen. After cooling back to room temperature, the mixture was poured into methanol (50 mL) to precipitate the polymer. The resulting yellow solid was further purified by several cycles of dissolving in THF, reprecipitating from methanol, and drying in vacuum to give the desired polymer (620 mg, 90%) as a yellow powder. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.17 (s, 2H), 7.95 (s, 2H), 7.80 (s, 1H), 7.01 (s, 5H), 6.90 (s, 1H), 4.19 (s, 2H), 4.08 (s, 4H), 2.71 (s, 4H), 2.54 (s, 2H), 1.94~1.30 (m, 20H), 1.03 (s, 6H), 0.66 (s, 2H), 0.12 (s, 4H).

### 3. Results and discussion

#### 3.1. Synthesis and mesomorphic properties

As shown in Figure 1, we designed and synthesized a side-on vinyl-terminated azobenzene-containing monomer A44V6. 4-butoxyaniline (I) was changed into a diazonium salt as intermediate 2 in an ice-bath, and further formed compound 3 by reacting with resorcinol. After a DCC coupling reaction between compound 3 and 4-butoxybenzoic acid (4), the key intermediate phenol 5 was synthesized, and then modified with 5-hexen-1-ol by a Mitsunubo etherification reaction to prepare the side-on vinyl-terminated azobenzene monomer A44V6. The corresponding polymer, PMMS-A44V6, was prepared by a radical-initiated thiol-ene addition reaction of PMMS and vinyl-terminated mesogen A44V6 in toluene.

The $^1$H NMR spectra of monomer A44V6 and the corresponding polymer PMMS-A44V6 are shown in Figure 2. After thiol-ene reaction, the terminal olefin protons of A44V6 originally located at 5.0~5.7 ppm disappeared, while the resonance signals of the aromatic protons still remained at 7.0~8.0 ppm on the $^1$H NMR spectrum, which implied that the monomer A44V6 has been grafted onto PMMS backbone successfully and all the unreacted monomers have been removed. On the basis of the integral ratio of the methylene protons (H$_4$ $\sim$ 0.6 ppm, Si–CH$_2$–) of PMMS and the aromatic proton (H$_6$ $\sim$ 7.9 ppm) of A44V6, the actual graft density can be roughly calculated to give a result of around 100%. Based on the
data, it is convinced that the thiol-ene click chemistry is a simple and efficient method to graft mesogens onto polysiloxane backbone and the graft density can be calculated and furtherly controlled by mixing the functional polysiloxane with monomers at desired molar ratios.

Gel permeation chromatography (GPC) was further used to confirm the grafting result of this polysiloxane-based azobenzene-containing LCP PMMS-A44V6. Although the $M_n$ value of PMMS was 4000–7000 g/mol listed on the merchant label, it could be found that PMMS is a mixture of short oligomers with the major $M_n$ peak value around 713 g/mol according to polystyrene standard as shown in Table 1. Similarly, on the basis of GPC experiment, the polymer PMMS-A44V6 is also a mixture of short oligomers with the major $M_n$ peak value around 3851 g/mol and a polydispersity index value around 1.28.

The thermal properties of azobenzene-containing polymer PMMS-A44V6 were investigated by TGA and DSC. Basically, for PMMS-A44V6, two main endothermic peaks can be observed during the temperature-rise period in the range of 250–500°C as shown in Figure 3(a). The temperature at 13% weight loss ($T_{d}$) of the polymer PMMS-A44V6 under N$_2$ was about 264°C which belonged to the first endothermic peak. The whole sample further decomposed at 390°C corresponding to the second endothermic peak. It indicated that the polymer PMMS-A44V6 had a good thermal stability. As shown in Figure 3(b), the DSC curve of monomer A44V6 showed an enantiotropic nematic (N) phase in the temperature range of 45.1–107.3°C. In contrast to

Table 1. Molecular weights of PMMS and PMMS-A44V6 measured by GPC based on calibration using polystyrene standards.

| Polymer     | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ |
|-------------|---------------|---------------|-----------|
| PMMS        | 713           | 613           | 1.16      |
| PMMS-A44V6  | 3851          | 4166          | 1.28      |

$M_n$ is number-average molecular weight; $M_w$ is weight-average molecular weight.

Figure 2. $^1$H NMR spectra of (a) monomer A44V6 and (b) the corresponding polymer PMMS-A44V6.

Figure 3. (colour online) (a) Thermogravimetric analysis of polymer PMMS-A44V6, DSC curves of (b) monomer A44V6 and (c) polymer PMMS-A44V6.
the monomer A44V6, the DSC curve of azobenzene-containing LCP PMMS-A44V6 (Figure 3(c)) presented a low glass transition temperature \((T_g)\) around 30°C and a quite low clearing point temperature \((T_{iso})\) about 75°C which belonged to LC-to-isotropic transition. It implied that the photo-responsive phenomenon of PMMS-A44V6 could be performed at around room temperature.

The mesomorphic behaviour of polymer PMMS-A44V6 was investigated by polarized optical microscopy (POM). In complete agreement with DSC results, the monomer A44V6 and corresponding polymer PMMS-A44V6 both have one single enantiotropic LC phase under POM observations during the heating and cooling cycles. As shown in Figure 4, the POM image of the monomer A44V6 (Figure 4(a)) presented a Schlieren texture with 2-point or 3-point disclinations, which was a solid proof of a nematic phase. Differently, the POM image of polymer PMMS-A44V6 (Figure 4(b)) showed ambiguous birefringent textures which were typical for polymers due to their high viscosities.

One-dimensional temperature-varied wide-angle X-ray scattering (WAXS) experiments were further performed to elucidate the mesomorphic properties of PMMS-A44V6. As shown in Figure 5, the WAXS patterns of polymer PMMS-A44V6 sample presented one diffuse peak in wide-angle region and no obvious sharp peak in low-angle region during the heating and

Figure 4. (colour online) POM images of (a) monomer A44V6, (b) polymer PMMS-A44V6 recorded at room temperature.

Figure 5. (colour online) One-dimensional WAXS patterns of PMMS-A44V6.

Figure 6. (colour online) The UV-Vis spectra of A44V6 and PMMS-A44V6 dispersed in THF with a concentration of ca. 1.0 \times 10^{-4}\text{ mol/L}. 
cooling cycle, which demonstrates a highly disordered position of mesogens. Taking into account the DSC, POM and WAXS results, the polymer PMMS-A44V6 possesses an enantiotropic nematic (N) phase in the temperature range of 37.2–72.5°C.

3.2. Photo-responsive characterization

As shown in Figure 6, the UV-Vis spectra of azobenzene monomer A44V6 and polymer PMMS-A44V6 dispersed in THF with a concentration of ca. 1.0 × 10⁻⁴ mol/L were obtained using a TU-1810 ultraviolet-visible spectrophotometer. Similar to A44V6/THF solution sample, PMMS-A44V6 has a strong absorption peak in the UV region centred at 365 nm. These peaks are attributed to the \( \pi-\pi^* \) electronic transitions of the trans-azobenzene chromophore.[43]

The UV-triggered photo-response behaviour of polymer PMMS-A44V6 was studied using a 365 nm UV-light (LUYOR LP-20A) at 50°C. According to DSC, POM and WAXS results, the polymer PMMS-A44V6 formed a nematic phase before the UV-irradiation because the straight azobenzene moieties in the LCP system were in the trans-conformation and tended to line up to reduce free volume. It is well known that the molar absorption coefficient of azobenzene moiety is very high under 365 nm UV-light, and the trans-azobenzene absorbs the photons to form its geometric isomer, cis-azobenzene. The cis-azobenzene bends and cannot line up with each other, meanwhile disrupts the nematic phase of LCP, resulting in a nematic-to-isotropic phase change.

POM was used to monitor this nematic-to-isotropic phase change of polymer PMMS-A44V6 under the UV irradiation. The images of the birefringent textures were captured using a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software. Figure 7(a) showed an ambiguous birefringence of a nematic phase without UV-light irradiation. As time went on, the colour of whole image turned to blue and dark, meanwhile that the birefringent textures were petering out as shown in Figure 7(b–e). Figure 7(d–e) showed that the isotropization process took place in the both centre and corner of the screen and the isotropic areas gradually expanded. Figure 7(f) presented no birefringence in the exposed area, which indicated

![Figure 7.](image-url)
the accomplishment of the isotropization process. The red, green, and blue 24-bit colour intensities of these POM images were evaluated for each pixel, and the overall colour intensity of the entire picture was summed by multiplying the total pixels using Photoshop software. This colour intensity is plotted as a function of time as shown in Figure 8. The colour intensity first exhibits a linear decrease feature with a rate of $-6.5 \times 10^5$ intensity/s, and later enters into an exponential decrease regime. Nevertheless, the decrease speed is not as fast as that of previous photo-responsive nematic systems,[44–48] which might be caused by the applied low-power UV-light source.

Previously, many reported research works were related to the linear phase growth kinetics of nematic formation process.[49–52] In contrast, in this work we pay attention on kinetic studies of the nematic-to-isotropic transition process of such a nematic azobenzene-containing LCP material PMMS-A44V6. As shown in Figure 8, at the first stage, the isotropization rate of PMMS-A44V6 was linear decrease, which was consistent with the azobenzene's isomerization according to first-order kinetics.[51] When UV light was introduced, the nematic phase began to be disrupted. The trans-azobenzene moieties started an isomerization process from the domain boundaries and moved inward, leading to linear kinetics. Meanwhile, the bent cis-azobenzene moieties acted as bulky impurities in the nematic phase to lower its clearing point ($T_{iso}$) and destroy nematic phase at a temperature below the original $T_{iso}$. At the second stage, the exponential regime was correlated with the kinetics of a nematic phase. As analysed in previous literatures,[31,53,54] there is a distribution of nematic domains in the beginning. With the disappearance of individual domains, the exposed area was supersaturated with cis-azobenzene moieties, accompanied with the convergences of growing isotropic domains. Meanwhile, the convergences of growing isotropic domains implied a decreasing number of growing isotropic domains and a decreasing isotropization rate, leading to the exponential kinetics. Besides, according to Imrie’s work,[55] the transitional properties of this azobenzene-containing LCP material PMMS-A44V6 were likely to be in the molecular weight dependent regime. After irradiation of visible light or heating, the cis-azobenzene returned to its original state. In accordance with expectation, the two stages of nematic-to-isotropic transition were repeatedly observed in the next UV-irradiation process.

4. Conclusion

In summary, we successfully prepared a nematic azobenzene-containing LCP material PMMS-A44V6 via a facile thiol-ene click chemistry approach by grafting a side-on azobenzene monomer A44V6 onto PMMS backbone. Taking advantage of the low $T_g$, low $T_{iso}$ and azobenzene’s trans-cis isomerization effect, the photo-responsive LCP material PMMS-A44V6 could perform a UV-induced isotropization response in the temperature range of 30–75°C. Under UV irradiation, the trans-azobenzene moieties started an isomerization process with a linear decrease feature and finished in an exponential decrease manner to form cis-azobenzene structure, corresponding to the decrease of the nematic domains and combination of the growing isotropic domains. The functional temperature range of PMMS-A44V6 is around room temperature, which might endow this novel azobenzene-containing LCP material with potential applications in control devices.

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