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To cite this article: Huan Li , Quan Liu , Chongyu Zhu , Jia Wei & Yanlei Yu (2020) Photo-induced bending behaviour of side-on linear liquid crystal polymers with high molecular weight, Liquid Crystals, 47:8, 1154-1161, DOI: [10.1080/02678292.2019.1680755](https://doi.org/10.1080/02678292.2019.1680755)

To link to this article: <https://doi.org/10.1080/02678292.2019.1680755>

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Photo-induced bending behaviour of side-on linear liquid crystal polymers with high molecular weight

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ABSTRACT

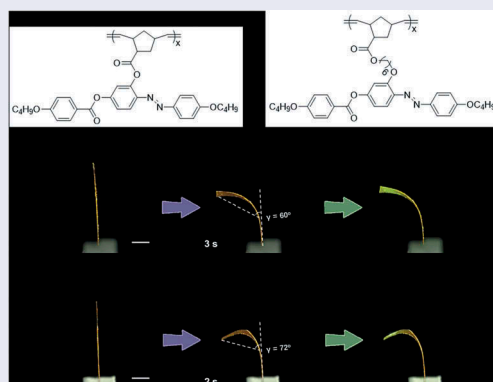
Two photoresponsive side-on linear liquid crystal polymers (SLLCPs) with different spacer lengths have been synthesised through facile ring-opening metathesis polymerisation (ROMP). For the first time, high molecular weight SLLCPs with polynorbornene backbone and azobenzene side chains are obtained and processed into films by the melt shear-induced orientation method. These SLLCP films exhibit fast and large photo-induced bending behaviour, showing bend degree up to 72° in 3 s upon UV irradiation at ambient temperature. The shape of these films remains unchanged under visible light, demonstrating good shape stability against sunlight. Moreover, owing to their linear structure, the SLLCP films are recyclable through traditional melting or solution methods. Possessing these features, these SLLCP films show application prospects in the fields of light-controllable flexible actuators.

ARTICLE HISTORY

Received 30 June 2019

KEYWORDS

Side-on linear liquid crystal polymers; ring-opening metathesis polymerisation; high molecular weight; azobenzene; actuator




1. Introduction

'Smart' polymers whose shape deformation are tunable by external stimuli have shown potential applications in flexible robots [1–3], artificial muscles [4,5], smart surface patterns [6,7] and microfluidic devices [8–10]. Compared to magnetostrictive alloys or piezoelectric ceramics, polymers are under active investigation thanks to their superior properties such as flexibility, lightweight, easy fabrication and low manufacturing cost. Liquid crystal polymers (LCPs) distinguish themselves from other polymers due to their strong combination of mesogen order of liquid crystals (LCs) and entropy elasticity of polymers [11–16]. The LCPs with azobenzene photochromic moieties attract increasing attention since the *trans-cis* isomerisation of azobenzene is accompanied by large changes in size and shape upon irradiation with light [17,18]. Under the cooperative effect

of mesogens and polymers backbone, the nanoscopic molecular motion of azobenzene will be amplified to the whole system resulting in the macroscopic deformation such as contraction/expansion [19], bending [20,21] and even twisting [22]. Among azobenzene-containing LCPs, the side-on LCPs (SLCPs), which mesogenic units are waist-connected to the polymer backbone, acquire considerable attention because high coupling ability between side chains and the main chain impart them with fast response speed and obvious deformation ability [23].

Keller et al. firstly demonstrated a crosslinked azo-containing SLCP films, showing photochemical contraction at 70°C under the UV light [24]. Moreover, they prepared crosslinked azo-containing SLCPs-microstructured surfaces covered with micropillar arrays, showing light-driven contraction of pillars at 60°C and thus contact angle variation of

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water on the surfaces [25]. However, aforementioned SLCPs exhibited high-temperature deformation and poor processability (incompatible with common solution and melt processing) because of chemical crosslinking, severely impeding their practical applications in fabricating diverse actuators. Thus, photodeformable SLCPs with linear structure have been reported by Keller et al. to improve their processing performance. Through atom transfer radical polymerisation, linear SLCPs (SLLCPs) with low molecular weight were synthesised and manufactured into photoresponsive fibres. However, owing to the low molecular weight of these SLCPs, the chain entanglement in this uncrosslinked SLCP fibres is weak; therefore, the *trans-cis* isomerisation of azobenzene was unable to drive the deformation of the whole system. As a result, the photo-induced bending took long time (10 min) and the deformation amplitude (about 45°) was small [26]. Hence, it is necessary to develop photosensitive linear SLCPs with high molecular weight, excellent processing performance, large deformation amplitude and fast response speed.

Recently, our group applied ring-opening metathesis polymerisation (ROMP), a living and controllable polymerisation with the advantages of mild reaction conditions and fast chain growth rate, and successfully prepared azobenzene-containing linear liquid crystal polymers (LLCPs). The obtained LLCPs have high molecular weight, possessing excellent photodeformability and allowing for solution and melt processing [27].

Herein, we utilised the ROMP method to design and synthesise two photodeformable side-on LLCPs (SLLCPs) with different spacer lengths (Figure 1). Both

SLLCPs were linear structured with high molecular weight, endowing materials with excellent processing performance and facile recycling. Upon 365 nm UV light irradiation, the shear-oriented films showed fast bending behaviour towards the actinic light along the shear direction at room temperature. Moreover, the shape remained under the visible light, implying their good shape stability against sunlight environment.

2. Experimental

2.1. Materials

5-Norbornene-2-carboxylic acid, polyethylene glycol (PEG200), Grubb's second-generation catalyst and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich Inc. Resorcinol, methoxypolyethylene glycols (PEO), 1,4-dioxane, 4-butoxybenzoic acid, *N,N'*-dicyclohexylcarbodiimide (DCC), caesium carbonate were bought from Alfa Aesar Ltd. Tetrahydrofuran (THF) was purified by distilling from sodium benzophenone ketyl under nitrogen. The dichloromethane (DCM) used in the polymerisation was refluxed over calcium hydride and then distilled just prior to use. All other chemicals were commercially available and used without further purification.

2.2. Characterisation

The thermomechanical properties of the polymers were determined by differential scanning calorimetry (DSC; TA, Q2000) at the rate of 10°C min⁻¹. The liquid crystal

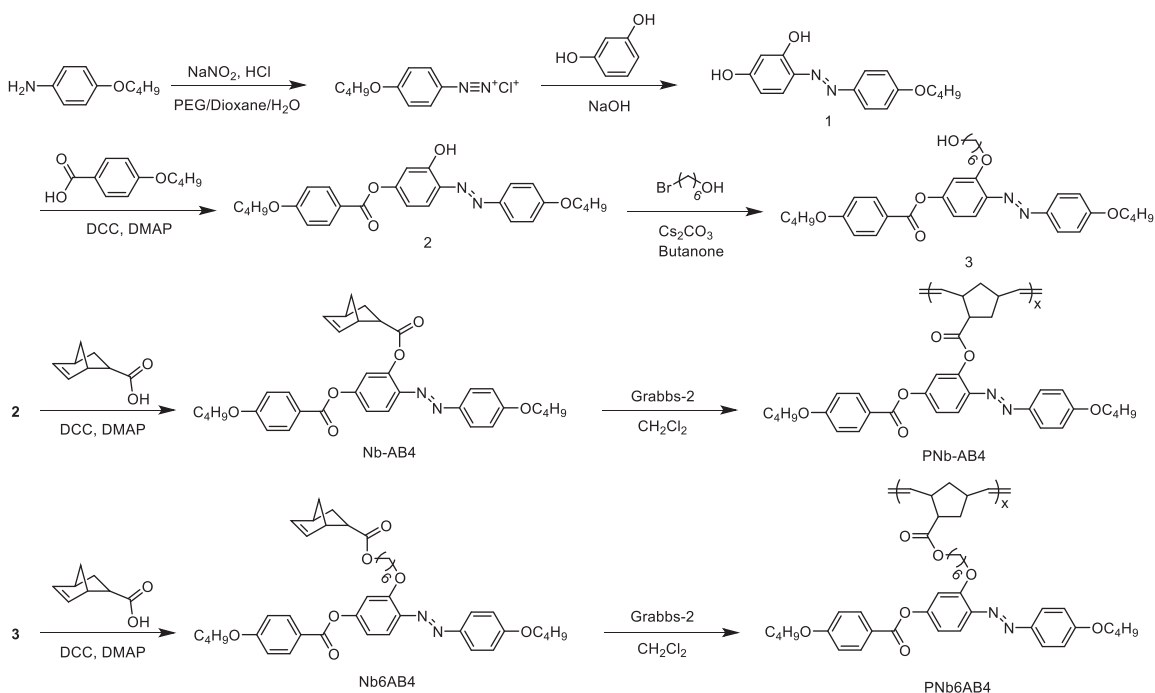


Figure 1. Synthetic routes of side-on mesogenic monomers and the corresponding liquid crystal polymers.

properties were observed using a polarising optical microscope (POM; Leica, DM2500P) equipped with a Mettler hot stage (Models FP-90 and FP-82). The *trans-cis* photoisomerisation of azobenzene in the dichloromethane (DCM) solution of polymers (PNb-AB4, PNb6AB4) were investigated by a UV-vis scanning spectrophotometer (Perkin Elmer, Lambda 650). In this process, a 365 nm UV lamp (OMRON, ZUV-C30H) and a 530 nm visible light lamp (CCS, PJ-1505-2CA, HLV-24GR-3W) were used. The molecular weight of polymers was measured by a gel permeation chromatograph (GPC, SHIMADZU, LC-10ADvp) using THF as the mobile phase. The images of bending behaviours of the films were determined by an ultradepth 3D microscope (Keyence, VHX-1000C).

2.3. Synthesis

2.3.1. Synthesis of side chains

2.3.1.1. Synthesis of 4-butoxy-2',4'-dihydroxyazobenzene (1)

4-Butoxyaniline (5.00 g, 30.0 mmol) and concentrated HCl (5.00 mL, 60.0 mmol) were added into 150 mL of a mixture of PEG200/1,4-dioxane/distilled water (60/30/10, 150 mL) in an ice-bath. A solution of NaNO₂ (2.28 g, 33.0 mmol) in water (10 mL) was added dropwise into the above mixture and stirred at 0–5°C for 1 h to form the diazonium salt. Resorcinol (9.90 g, 91.0 mmol) and NaOH (1.33 g, 33.0 mmol) were dissolved in 150 mL of the mixed solvent (PEG200/1,4-dioxane/distilled water (60/30/10)). The mixture was rapidly added dropwise into the diazonium salt solution. Then appropriately Na₂CO₃ was added to adjust the pH of the mixture to 8–9 and reacted 2 h. After the reaction was completed, HCl was added dropwise to adjust the pH of the mixture to 5–6. The solid product was filtered off, washed with distilled water and dried in vacuum with a yield above 80%.

2.3.1.2. Synthesis of 4-butoxy-4'-(4-butoxybenzoate)-2'-hydroxy azobenzene (2)

4-Butoxy-2',4'-dihydroxyazobenzene (5.80 g, 20.0 mmol), DCC (6.00 g, 30.0 mmol), DMAP (0.40 g, 3.28 mmol) and 4-butoxybenzoic acid (3.80 g, 20.0 mmol) were added into DCM (200 mL) and stirred at room temperature overnight. The solution was distilled to obtain a crude monomer product, which was then separated by column chromatography using DCM to give the pure side chain (2) with a yield above 80%.

2.3.1.3. Synthesis of 4-ethoxy-4'-(4-ethoxybenzoate)-2'-(6-hydroxyhexyloxy) azobenzene (3)

4-Butoxy-4'-(4-butoxybenzoate)-2'-hydroxy azobenzene (2.30 g, 5.0 mmol), 4-butylammonium bromide (0.20 g, 0.6 mmol),

Cs₂CO₃ (3.30 g, 10.0 mmol) and 6-bromo-1-hexanol (0.90 g, 5.0 mmol) were added into *N,N*-dimethylformamide (200 mL) and heated to 110°C for 10 h. After cooling back to room temperature, the mixture was poured into ice water (1 L) to precipitate the (3). The yellow precipitate was filtered then washed with distilled water three times to obtain the side chain (3) with a yield above 60%.

2.3.2. Synthesis of monomers

The synthetic routes of monomers Nb-AB4 and Nb6AB4 were similar; here, the synthetic process of Nb-AB4 was taken as an example.

Nb-AB4: 4-Butoxy-4'-(4-butoxybenzoate)-2'-hydroxy azobenzene (5.00 g, 10.82 mmol), 5-norbornene-2-carboxylic acid (1.5 g, 10.82 mmol), DCC (3.00 g, 15 mmol) and DMAP (0.20 g, 1.64 mmol) were added into DCM in an ice bath, stirring for 10 h at room temperature. After evaporation of the solvent, the residue was purified by chromatography on silica gel using DCM as eluent. The product was recrystallised from ethanol with a yield above 80%. ¹H NMR (CDCl₃): 0.99 (m, 6H, CH₃), 4.05 (m, 4H, CH₂-O), 6.08 (m, 2H, CH=CH), 6.22 (m, 2H, CH=CH), 6.97–8.13 (m, 11H, arom).

2.3.3. Synthesis of polymers

The synthetic routes of polymers PNb-AB4 and PNb6AB4 were similar; here, the synthetic process of PNb-AB4 was taken as an example.

PNb-AB4: Nb-AB4 (1.00 g, 1.72 mmol) was added into a Schlenk-type flask (50 mL). After the reactant was degassed and exchanged with nitrogen gas for three times, second generation Grubb's catalyst (1.0 mg) in 1 mL of re-distilled DCM was injected into the Schlenk flask with a syringe. The mixture was stirred at 50°C for 4 h. After the reaction was completed, the mixture was diluted with a small amount of DCM and then precipitated into methanol twice, filtered and dried in vacuum to obtain the desired PNb-AB4 with a yield of 98%. ¹H NMR (CDCl₃): 0.99 (m, 6H, CH₃), 4.05 (m, 4H, CH₂-O), 6.02 (m, 2H, CH=CH), 6.97–8.13 (m, 11H, arom).

2.4. Preparation of shear-oriented SLLCP films

Polymer was heated to T_c on a clean glass substrate placed on a hot stage, which was kept at that temperature until it became fully melted, and then quickly sheared with a blade along one direction and rapidly cooling to fix the orientation. The free-standing SLLCP films were obtained after being peeled from the glass substrates and cut into any wanted shapes using a sharp knife.

3. Results and discussion

3.1. Characterisation of PNb-AB4 and PNB6AB4

The molecular structure of monomers and polymers was characterised by $^1\text{H-NMR}$ (Figure S1), in which the difference of chemical shift reflected the successful polymerisation. The molecular weight and polymer dispersity indices (PDIs) of the SLLCPs were confirmed by GPC and summarised in Table 1. The linear polymer PNb-AB4 has a number-average molar mass (M_n) of 13.7×10^4 g/mol; meanwhile, the M_n of PNB6AB4 is 15.2×10^4 g/mol. The molecular weight of polymers is an order of magnitude higher than those of the previously reported side-on liquid crystal polymers. High molecular weight can improve the mechanical properties and processing performance of materials.

The mesomorphic properties of PNb-AB4 and PNB6AB4 were investigated by both DSC and POM equipped with a hot stage. PNb-AB4 and PNB6AB4 exhibit glass transition around 58.3°C and 35.2°C ,

Table 1. Molecular weight and polymer dispersity indices (PDIs) of side-on LLCs measured by GPC.

Samples	M_n ($\times 10^4$ g mol $^{-1}$)	M_w ($\times 10^4$ g mol $^{-1}$)	PDIs
PNb-AB4	13.7	29.6	2.16
PNb6AB4	15.2	19.0	1.25

respectively (Figure 2(a,c)), allowing room-temperature operation. PNB-AB4 shows phase transition at 160°C in the heating process and 158.8°C in the cooling process. The POM photograph of PNB-AB4 shows the bright Schlieren texture at 150°C (Figure 2(b)). However, there is no obvious phase transition of PNB6AB4 in the heating and cooling process, while the POM photograph of PNB6AB4 at 35°C shows LCs texture revealing the presence of LC phases (Figure 2(d)). On the basis of DSC and POM experiments, we found that the glass transition temperature (T_g) of PNB6AB4 is lower than that of PNB-AB4 because the flexible spacer in PNB6AB4 decouples motions of the main chain and side chain and alleviates steric hindrance [28]. Moreover, it was observed that PNB-AB4 has high phase transition temperature. This may be due to the azobenzene mesogen directly surrounds the polymer chain to form the mesogen-jacketed effect, which makes liquid crystal phase more stable and phase transition temperature much higher [29].

The optical anisotropy in the representative shear-oriented PNB6AB4 film was evaluated by placing them between crossed polarisers. Typical polarised optical micrographs are shown in Figure 3(a). Periodic changes in the dark (0°) and bright (45°) images under the POM (with crossed polariser and analyser) are clearly

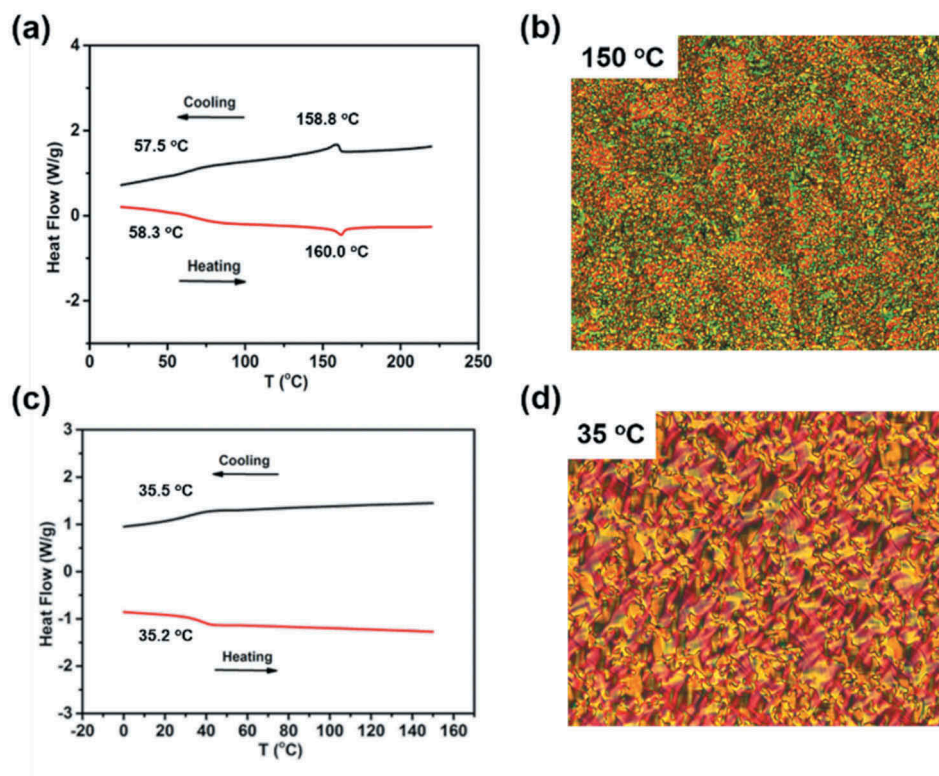


Figure 2. (Colour online) (a) DSC curves of PNB-AB4, (b) POM photograph of PNB-AB4 at 150°C , (c) DSC curves of PNB6AB4 and (d) POM photograph of PNB6AB4 at 35°C .

observed upon rotating the film sample with respect to the analyser. These results reveal that the mesogens preferentially orient to the shearing direction. Then, 2D-XRD was used to investigate the LC phase structure of oriented SLLCP films. From the 2D-XRD diffraction pattern of both shear-oriented PNB-AB4 and PNB6AB4 film (Figure 3(b,c)), no diffraction peak appears in the low angle region but two diffuse diffraction arcs paralleling to the shear direction are shown in the high angle region, implying that these two polymers all present nematic phase.

3.2. Photochemical isomerisation of monomers and polymers

The azobenzene mesogens undergo π - π^* and n - π^* transitions upon the irradiation of the UV and visible light. The UV-Vis spectra of PNB-AB4, PNB6AB4 in DCM

with an azobenzene concentration of $ca\ 4.0 \times 10^{-5}$ mol/L were recorded by an UV-vis spectrophotometer. In Figure 4, both PNB-AB4 and PNB6AB4 samples show a strong trans isomers π - π^* absorption peak decreases under 365 nm UV light, indicating the *trans-to-cis* transformation, while a strong trans isomers π - π^* absorption peak increases under 530 nm visible light, implying the *cis-to-trans* transformation.

3.3. Photo-induced bending behaviour of SLLCP films

The *trans-cis* photoisomerisation of the azobenzene units changes the shape of molecules and disturbs the arrangement of LC mesogens, thus the conformational of polymer chains changes under the synergistic effect of LC molecules and polymer chains. In the present system, azobenzene mesogens near the surface facing the light

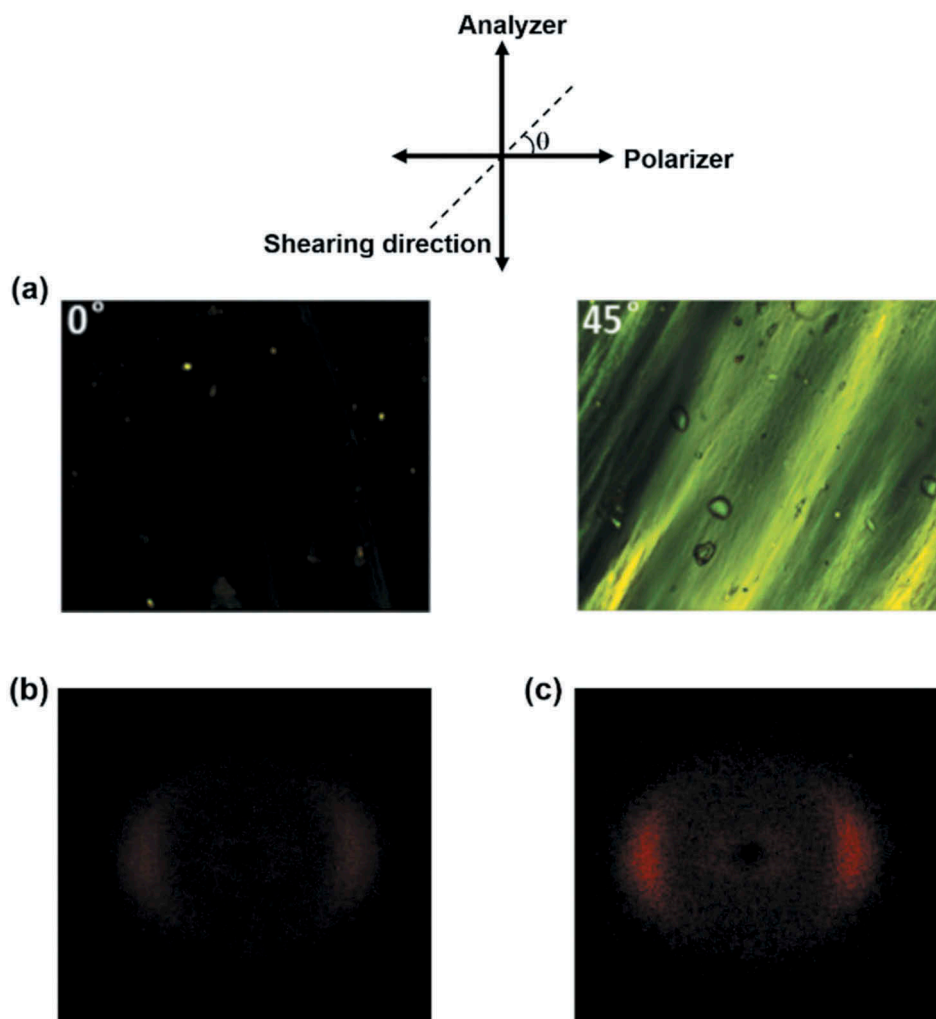


Figure 3. (Colour online) POM photographs of sheared PNB6AB4 film (a) in two directions ($\theta = 0^\circ$ and 45°). The black arrows indicate the directions of optical axes of the two polarisers, while the dashed line shows the shearing direction. 2D-XRD pattern of (b) shearing PNB-AB4 film and (c) shearing PNB6AB4 film.

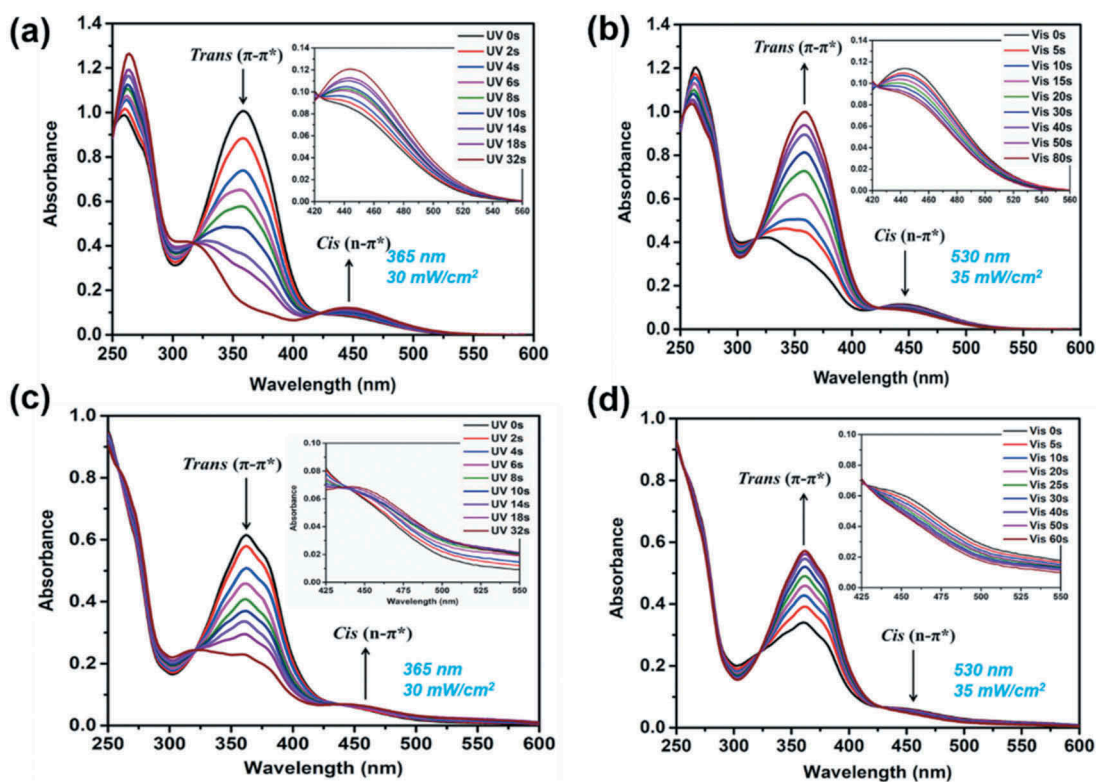


Figure 4. (Colour online) Changes in UV-vis absorption spectra over time of linear polymer in DCM solution at 25°C. (a) PNB-AB4 upon irradiation with 365 nm light (30 mW/cm²), (b) PNB-AB4 upon irradiation with 530 nm light (35 mW/cm²) at the photostationary state, (c) PNB6AB4 upon irradiation with 365 nm light (30 mW/cm²) and (d) PNB6AB4 upon irradiation with 530 nm light (35 mW/cm²).

source aligned along the shearing direction of the film due to the shear-induced orientation method. Moreover, UV light is mostly absorbed near the surface of the film facing the incident light because of the large extinction coefficient of azobenzene groups, causing shrinkage of the surface layer of the film. Therefore, the SLLCP films bent towards the incident direction of the UV light along the LCs alignment direction. As shown in Movie S1, S2 and Figure 5, PNB-AB4 and PNB6AB4 films bent to 60° and 72° in 3 s and 2 s under UV light, respectively. PNB6AB4 with longer spacer groups has faster bending speed and larger bending degree thanks to the coupling effect of main chains and azobenzene groups is reduced. The bent SLLCP films could be reprocessed into new films by melt shear-induced orientation method owing to their linear structure and melttable properties. The repaired films exhibited photoinduced bending behaviours similar to the initially prepared films, demonstrating that the SLLCPs reported in this paper are recycled and reconstructed (Figure S2).

It is worth noting that the bent SLLCP films remained their shape upon irradiation of 530 nm light, which is different from the conventional photodeformable liquid crystal polymers [30]. As we all know, the presence of an appropriate level of crosslinking in

photodeformable systems has proven to be indispensable for their macroscopic motions because it is responsible for the accumulation of the photomechanical force (generated from azo isomerisation) across the entire network. Based on their different crosslinking mechanisms, photodeformable azo liquid crystal polymer systems can be divided into chemically and physically crosslinked systems [31]. In LLCs, the physically crosslinked systems are especially important for the photodeformable behaviour [27]. However, the SLLCPs reported in this paper present nematic phase, which do not have layered structure as physical crosslinking. Therefore, the SLLCPs were unable to revert to original state under the 530 nm light, endowing the actuators stability against sunlight (Figure S2).

4. Conclusion

In this work, we used ring-opening metathesis polymerisation (ROMP) method to synthesise the novel photoresponsive side-on linear liquid crystal polymers (SLLCPs) with polynorbornene as main chain. The high molecular weight SLLCPs without crosslinked structure, provides excellent mechanical properties and facile recycling for the present system. By melt shear-

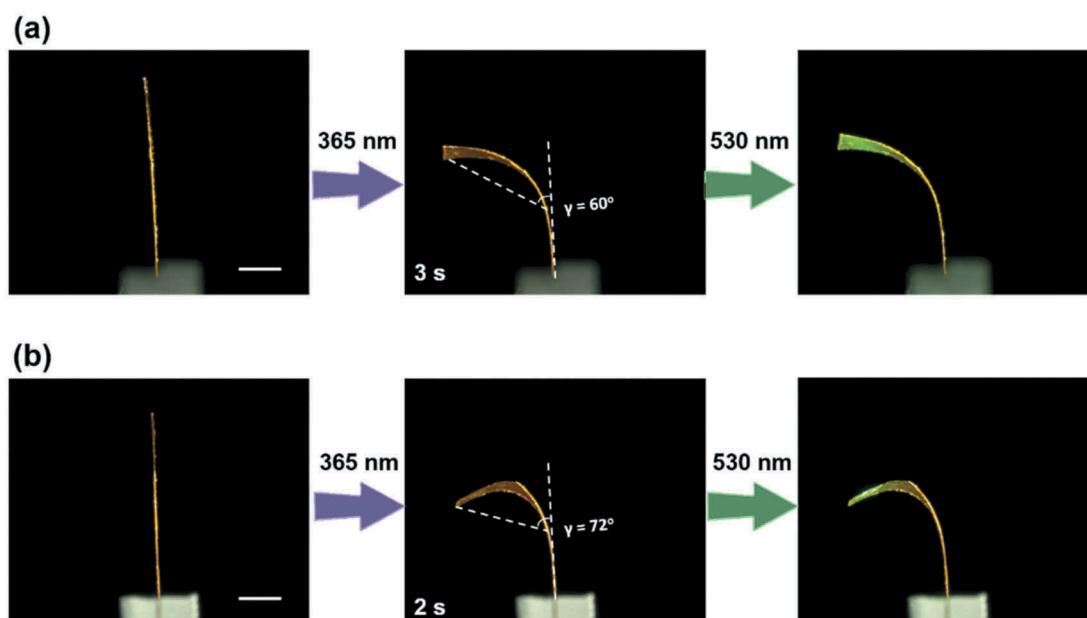


Figure 5. (Colour online) Photo-deformation behaviour of (a) PNb-AB4 and (b) PNB6AB4 sheared films. The films are bent upon irradiation of 365 nm UV light (80 mW/cm^2), while the bending remains under visible light. The maximum bending angles of PNb-AB4 and PNB6AB4 reach 60° and 72° , respectively. The size of the films is $10 \text{ mm} \times 2 \text{ mm} \times 20 \text{ }\mu\text{m}$, and the scale bar is 2.5 mm.

induced orientation method, the obtained SLLCP films underwent fast three-dimensional bending behaviours upon irradiation of UV light at ambient temperature, which is significantly faster than previous reported SLCPs. Meanwhile, the bending remained under visible light, indicating that the SLLCPs have good shape stability. In short, the obtained SLLCP films possess many intriguing merits thus numerous applications of the light-driven soft actuators on a large scale are possible.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported financially from the National Natural Science Foundation of China [21734003]; the National Key R&D Program of China [2017YFA0701302]; Innovation Program of Shanghai Municipal Education Commission [2017-01-07-00-07-E00027] and Science and Technology Commission of Shanghai Municipality [17JC1400200].

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