Physio- and chemo-dual crosslinking toward thermo- and photo-response of azobenzene-containing liquid crystalline polyester

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ABSTRACT Combining the stability of chemical crosslinking and the processability of physical crosslinking is a well-established strategy to design new materials with desirable stimuli-responsive properties. Herein, a series of azobenzene-based thermotropic liquid crystalline polyesters were synthesized by introducing mesogenic dial named 4,4'-bis(6-hydroxyhexyloxy)azobenzene (BHHAB), 2-phenylsuccinic acid (PSA), and different contents of 1,2,3-propanetricarboxylic acid (PTA) as the chemical crosslinker. All these polyesters showed good thermal stability and smectic liquid crystalline phase. Wide-angle X-ray diffraction (WAXD) and the fluorescence emission spectra confirmed the existence of π - π stacking interactions as the physical crosslinking in the polymer chains, particularly at the lower content of PTA. However, when the PTA content increased, the chemical crosslinking changed the chain conformation, and thus the intensity of physical crosslinking slackened gradually. Combining the physical and chemical crosslinking, these polyesters showed the thermoplastic processability, thermal shape memory, heat-assisted healing and photoresponsive behaviors. Taking advantages of these features, these multiple stimuli-responsive polymers can bring more chances for smart materials such as soft actuator.

Keywords: liquid crystalline polymer, crosslinking, shape memory, photo-response, self healing

INTRODUCTION

Crosslinked liquid crystalline polymers (CLCPs) are developed on the basis of the liquid crystalline polymers (LCPs). Through the moderate density of crosslinking, CLCPs display elasticity either in isotropic state or in

liquid crystal state [1,2]. Attractively, as typical polymer exhibiting the ability to change its shape reversibly after the application of a certain external stimulus [3], CLCPs combine the properties of polymeric elastomers (entropy elasticity) with liquid crystals (self-organization) [4]. Since de Gennes predicted the shape memory properties of CLCPs in 1975 [5], a large amount of CLCPs with different liquid crystalline phases and network structures have been synthesized and characterized, including main-chain smectic [6,7], side-chain smectic [8,9] and nematic [10,11] CLCPs. According to the different structures designed in the CLCPs, the materials can be responsive to different stimuli including heat, light, electricity and so on [12–17].

For shape memory polymers, the fixing phase, such as crystalline phase, intermolecular forces in polymer chains, crosslinking, are the important factors to determine the constant shape of materials [18–21]. As for CLCPs, the crosslinking can be regarded as the fixing phase which ensures the translation of microscopic changes into macroscopic motions and the repeatability of the actuation. In a normal condition, the chemical crosslinking in the CLCPs plays an extremely important role in their shape memory behavior because of its enough strength and stability. However, the chemical crosslinking generally occurs during the synthesis process and could not be changed anymore once synthesized [22,23], which might sacrifice the processability and restrict the practical application of the CLCPs.

In recent years, scientists have paid much attention on finding new modes of crosslinking to replace the normal chemical crosslinking such as the exchangeable covalent

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Scheme 1 Synthetic route and chemical structures of PBHPS- $x\%$ PTA, where 100 and x denote the molar ratio with regard to PSA, not the block length.

bonds or the post-crosslinking method etc. [24–29], where different secondary bonds might be another answer, including hydrogen bond, π – π interaction, coordination linkage, and so on. For example, Ikeda *et al.* [30] prepared azo based liquid crystalline films using hydrogen bond as crosslinking points, obtaining the reversible bending/unbending properties under UV/visible light as well. Zhang *et al.* [31] synthesized azobenzene main-chain LCPs *via* Michael addition polymerization and then studied the photomechanical effects of their supramolecular hydrogen-bonded fibers. Chen *et al.* [32] synthesized a side-chain LCP which showed good thermal shape memory property with the polymer chain columns acting like physical crosslinks. In our previous studies [33–38], two main-chain LCPs with inter-/intra-molecular π – π interaction as crosslinking points were designed and synthesized, and the resulting good shape memory behaviors proved that the π – π interaction could also be an effective modes to build stimuli responsive CLCPs. In summary, physical crosslinking can solve the processibility effectively caused by chemical crosslinking, but these weak intermolecular interactions may be influenced easily by the movement of the polymer chains in some conditions, which also restricted the application of materials.

Architecturally, combining the stability of chemical crosslinking and the processibility of physical crosslinking might be a good method to endow materials with better comprehensive properties [39,40]. Thus, in this study, a series of azobenzene-containing liquid crystalline polyesters with slight crosslinking were synthesized as shown in Scheme 1. Herein the phenyl group of 2-phenylsuccinic acid (PSA) provided the π – π interaction in the polymer chain as the physical crosslinking points, and the introduction of 1,2,3-propanetricarboxylic acid (PTA) gave the LCPs very slight chemical crosslinking. The thermal shape memory and reversible photo-responsive behaviors were investigated, revealing the relationships

and interactions between physical and chemical crosslinking. The very slight chemical crosslinking could increase the thermo- and photo-responsive properties of the polyesters but did not worsen the thermoplastic processability.

EXPERIMENTAL SECTION

Materials

4-Nitrophenol was manufactured from East China Normal University Chemical Factory (Shanghai, China). 6-Chloro-1-hexanol and 2-phenylsuccinic acid (PSA) were purchased from Aladdin Industrial Corporation (Shanghai, China). 1,2,3-Propanetricarboxylic acid (PTA) was provided by Sinopharm Chemical Reagent Corporation (Chengdu, China). *N,N*-dimethylformamide (DMF, Ke Long Chemical Co. Chengdu, China) was stored over activated 4A molecular sieves before use. All other reagents were commercial and used without further treatment.

Synthesis of PBHPS- $x\%$ PTA

The monomers, including 4,4'-dihydroxyazobenzene (DHAB) and 4,4'-bis(6-hydroxyhexyloxy)azobenzene (BHHAB) were prepared following the procedure reported in the literature [36,41]. All the polyesters were prepared following the same procedure. The typical polymerization procedure of PBHPS-1%PTA was as follows: BHHAB (4.1454 g, 0.01 mol), PSA (1.9418 g, 0.01 mol) and PTA (0.0175 g, 0.0001 mol) were loaded into a 100-mL three-necked flask, which was equipped with nitrogen inlet and nitrogen outlet, a mechanical stirrer, and a distillation trap connected to a vacuum line. In addition, 0.0122 g (0.2 wt%) $\text{Zn}(\text{Ac})_2$ and 0.0183 g (0.3 wt%) Sb_2O_3 were added into the flask as catalyst. Before the reaction, the flask was processed by vacuum pumping and nitrogen protection to remove the oxygen in it. Then, the flask was placed in a 190°C salt bath, the

esterification reaction proceeded and was kept for about 3 h. After that, a low vacuum was employed and the temperature was preserved at 200°C for another 0.5 h. At last, the temperature was kept at 200°C with a high vacuum of 20–40 Pa for about 2.5 h. When the polymerization was completed, the flask was cooled to room temperature under vacuum to obtain the target polymers.

Characterization.

The swelling ratios of polyesters were measured as follow: all the samples were cut into small slices, swelled and extracted by chloroform for 24 h. The gel content ($G(\%)$) was calculated using the equation:

$$G(\%) = \frac{m_1}{m_0} \times 100\%, \quad (1)$$

where m_1 and m_0 represent the mass of dried extracted sample and original sample, respectively. All the data were averaged over three measurements.

Thermogravimetric analysis (TGA) was conducted under a nitrogen atmosphere using a Netzsch TG 209 F1 instrument. The heating rate and flow rate were kept at 10°C min⁻¹ and 60 mL min⁻¹ respectively. In each case, a 3–5 mg sample was examined in a temperature range of 40–700°C.

Thermal transition temperatures of the polyesters were measured using a differential scanning calorimetry (DSC TA Q200 1747) calibrated for both heat flow and temperature using indium and zinc standards. About 5 mg sample was tested under a nitrogen atmosphere at a flow rate of 50 mL min⁻¹. Firstly, it was heated to 150°C directly for 2 min to minimize the adverse influence of thermal history. Then the sample was cooled to -20°C and heated to 150°C again at a heating rate of 10°C min⁻¹. The thermogram was recorded from the first cooling and the second heating cycle.

Liquid crystalline textures of the polyester were observed *via* a Nikon ECLIPSE LV100 POL polarizing optical microscopy (POM) equipped with a hot-stage. The sample was dissolved in chloroform in a concentration of 10 mg mL⁻¹ and then the solution was cast to a glass flat. After the solvent was evaporated at room temperature, the sample was further dried at 100°C for 3 min, and then cooled to 40°C at a cooling rate of 10°C min⁻¹ for observation.

Wide angle X-ray diffraction (WAXD) was carried out with a Philip X' Pert X-ray diffractometer. The samples were firstly under an isothermal process at 50°C for 30 min before test.

Fluorescence spectra were recorded on an F-7000

fluorescence spectrometer (Hitachi, Japan) at the fluorescence emission wavelength of 250 nm. All the samples were dissolved in chloroform to obtain solutions with concentration of 5 mg mL⁻¹ respectively, and then the solution was cast to an optical glass flat. The spectra were recorded after the solvent evaporated at room temperature.

Shape memory behaviors of the polyesters were conducted with dynamic mechanical analysis (DMA, TA Q800). The sample was cut into a rectangular shape with dimensions of approximately 20 mm × 5 mm × 0.5 mm to test.

UV-vis absorption spectra were recorded on a Varian Cary® 50 UV-Vis Spectrophotometer (Varian Co., USA). The photochemical isomerization of the polymer solution was investigated by irradiating it first with a 365 nm UV lamp until the photostationary state was reached and then with a 550 nm visible light lamp. This lamp was also utilized to test the bending and unbending properties of the samples.

The heat-assisted healing process of the scratched polyester films was carried out on the hot stage at 60°C and was observed *via* Nikon ECLIPSE LV100 POL POM. The healing efficiency was tested by tensile test. Two PBHPS-2%PTA strips of a knife-scratched depth of about 0.1 mm and an undamaged strip with an average thickness of 0.50 mm and a width of 3 mm were prepared. Then, one of the damaged strips was put into an oven for 5 h at 60°C. After that, all the strips were tested by INSTRON 3366 Testing Machine under a 100 N load cell and uniaxially stretched to a displacement at 5 mm min⁻¹. The healing efficiencies (R) have been assessed by the equations below [42]. Here σ refers to the tensile strength and ε denotes the elongation at break.

$$R(\sigma) = \frac{\sigma_{\text{healed}}}{\sigma_{\text{initial}}} \quad (2)$$

$$R(\varepsilon) = \frac{\varepsilon_{\text{healed}}}{\varepsilon_{\text{initial}}} \quad (3)$$

RESULTS AND DISCUSSION

Polymerization

The slightly crosslinked liquid crystalline polyesters PBHPS- $x\%$ PTA were synthesized by melting polycondensation. When the temperature reached 190°C, BHHAB, PSA and PTA melted together into a dilute solution with small bubble. The esterification reaction was kept for about 3 h, and during this time, nitrogen was kept flowing to protect the reaction system from thermal

Table 1 The swelling test results and TGA data of polyesters

Sample	G (%)	$T_{5\%}$ (°C)	$T_{\max}$ (°C)	Residue at 700°C (%)
PBHPS	Complete dissolution	344.0	351.6	17.8
PBHPS-1%PTA	5.9±2.0	343.7	353.6	15.8
PBHPS-2%PTA	12.6±0.6	344.2	354.9	17.0
PBHPS-3%PTA	59.4±9.7	348.0	355.7	17.5

oxidation and remove the by-product water. As the time went on, the reaction system became viscous and the water could not be taken away by nitrogen, leading the reversible polycondensation to equilibrium. Therefore, the vacuum system was introduced to remove the by-product and keep the reaction to the positive direction. Then, the polyester became more viscous. For the PBHPS and PBHPS-1%PTA, the melt adhered to the flask wall finally, but the 2% and 3% PTA samples became an elastic substance adhering to the stirring pole. This part of the reaction was kept for about 2 or 3 h with a high vacuum of 20–40 Pa according to the different reactive phenomena. Finally, the target product was obtained after cooling the system to room temperature under high vacuum. The swelling test was performed to evaluate the efficiency of the crosslinking, and the results are listed in Table 1. As the contents of PTA increased, the gel contents increased as expected, meaning the density of chemical crosslinking increased.

Thermal properties and liquid crystalline behaviors

Fig. 1 shows the TGA and DTG curves of the PBHPS- x %PTA samples, and the specific data are summarized in Table 1. All the testing polyesters had one single degradation process. The temperatures of 5 wt% loss ($T_{5\%}$, defined as the initial decomposition temperature) and $T_{\max}$ were nearly the same, indicating that the incorporation of PTA caused a slight chemical crosslinking

Figure 1 TGA and DTG curves of liquid crystalline polyesters in N_2 .

but did not affect the thermal stability of the polyesters.

Fig. 2 illustrates the DSC curves of the PBHPS- x %PTA samples in the first cooling scan (a) and the second heating scan (b) at a rate of $10^\circ\text{C min}^{-1}$ under N_2 atmosphere. The relevant thermal parameters and their corresponding values are summarized in Table 2. The samples, except PBHPS-3%PTA, had nearly the same glass transition temperatures (T_g) and isotropic temperatures (T_i) at about 22°C and 70°C in the first cooling process, which meant that the incorporation of low

Figure 2 DSC curves of the polyesters on (a) first cooling and (b) second heating at a rate of $10^\circ\text{C min}^{-1}$ under N_2 atmosphere.

Table 2 DSC data of the polyesters at a rate of $10^{\circ}\text{C min}^{-1}$ under N_2 atmosphere

Sample	First cooling			Second heating		
	T_g ($^{\circ}\text{C}$)	T_i ($^{\circ}\text{C}$)	ΔH_i (J g^{-1})	T_g ($^{\circ}\text{C}$)	T_i ($^{\circ}\text{C}$)	ΔH_i (J g^{-1})
PBHPS	22.3	71.5	7.1	26.9	75.8	7.0
PBHPS-1%PTA	21.9	70.5	7.6	25.6	73.8	7.6
PBHPS-2%PTA	22.6	70.0	8.0	25.2	73.3	7.9
PBHPS-3%PTA	24.6	76.2	8.4	27.7	79.2	8.4

contents of PTA did not influence the phase transition temperatures. However, when the content of PTA increased to 3%, both T_g and T_i slightly increased to 24.6°C and 76.2°C , respectively. This was reasonable because the relative high density of crosslinking would restrict the movement of the polymer chains, thus increasing the relevant temperatures.

It was noteworthy that all the polyesters with PTA crosslinking still showed the isotropic temperatures, meaning that the crosslinking did not negatively affect the melting processability. For further confirming the thermoplasticity of these polyesters, PBHPS-2%PTA and PBHPS-3%PTA samples with higher crosslinking density were chosen to undergo a 5 time cooling and heating cycles by using DSC respectively. As shown in Fig. 3, during the multiple cooling and heating process, the tested samples exhibited the T_g and T_i , and these phase transition temperatures were kept the same all the time, which further confirmed the slight crosslinking did not influence the thermoplasticity of the resulting polyesters.

Fig. 4 shows the liquid crystalline textures of PBHPS and PBHPS- $x\%$ PTA on the first cooling process, which were observed and captured at 40°C by using a POM. All the slightly crosslinking samples showed the typical focal conic textures as PBHPS did [26], which implied the small quantity of PTA incorporated into the PBHPS chains did not change the molecular mobility and regular packing, as illustrated in DSC test. WAXD analysis was also used to determine the microstructure of the polyesters. As shown in Fig. 5a, in the small angle region, except PBHPS-3%PTA, there were two distinct peaks at 6.3° (1.39 nm) and 12.5° (0.71 nm), suggesting the existence of the layer structure in the liquid crystalline chain. For PBHPS-3%PTA, the peaks in the small angle range were negligible, because the relative high content of PTA influenced the chain folding or arrangement, thus destroyed the orderly structure between the layers. For PBHPS, there was a peak at the angle of 28.1° (0.32 nm) which indicated the π - π interactions between the phenyl rings existing in the polymer chains as reported previously

Figure 3 DSC curves of PBHPS-2%PTA (a) and PBHPS-3%PTA (b) in five cooling and heating cycles at a rate of $10^{\circ}\text{C min}^{-1}$ under N_2 atmosphere.

Figure 4 POM pictures of PBHPS (a), PBHPS-1%PTA (b), PBHPS-2%PTA (c) and PBHPS-3%PTA (d) at 40°C.

[23,26]. When 1% of PTA was incorporated, peaks in this area still existed, implying the π - π interactions remained in PBHPS-1%PTA. However, the peaks at about 28° for the polyesters PBHPS-2%PTA and PBHPS-3%PTA decreased obviously, which meant the π - π interactions might be weakened or broken. To further reveal the relation between the PTA (chemical crosslinking) and the π - π interactions (physical crosslinking), fluorescence spectra test was performed to study the intensity of π - π interactions—the fluorescence emission means there exists conjugation in the system [35,43]. As shown in Fig. 5b, the intensity of the fluorescence emission spectra decreased with increasing the contents of PTA, meaning the π - π interactions were decreased even disappeared gradually. This process could suggest that the physical crosslinking was replaced by the chemical crosslinking slowly but surely.

Thermally induced shape memory properties

In this part, the thermally induced shape memory prop-

erties of the polyesters were characterized by a well-established four-step thermo-mechanical cycling method conducted *via* DMA. All the samples were stretched at 40°C firstly and then the strain was ramped to about 50% gradually (deformation). After that a rapid cooling procedure was executed, during which the force was kept constant until the temperature reached 10°C. In the third step, the stress was gradually released to witness the strain fixing at 10°C. In the fourth step, the strain recovery occurred by heating to 60°C at the rate of 10°C min⁻¹ (recovery). According to the Equations (4) and (5), where ε_m , ε_μ , ε_p and N represent the strain before unloading, the strain after unloading, the permanent (residual) strain after heat induced recovery and the number of cycles, respectively, the fixing ration (R_f) and the recovery ratio (R_r) were calculated to assess the shape memory property.

$$R_f = \frac{\varepsilon_\mu(N) - \varepsilon_p(N-1)}{\varepsilon_m(N) - \varepsilon_p(N-1)} \times 100\% \quad (4)$$

$$R_r = \frac{\varepsilon_\mu(N) - \varepsilon_p(N)}{\varepsilon_\mu(N) - \varepsilon_p(N-1)} \times 100\% \quad (5)$$

Typically, Fig. 6e presents the thermally induced shape memory results of PBHPS-2%PTA sample investigated by cyclic thermomechanical analysis, while those of others were provided in Fig. S1. The corresponding data are summarized in Table 3. Generally, the results recorded within the first cycle were strongly dependent on the residual stresses of samples resulting from processing history. The R_f and R_r were therefore calculated from the data determined within the 2nd to the 4th cycle. All the samples had good shape fixing ratios about 98%: as the temperature came to 10°C, all the polyesters were at glassy state and lost their chain mobility, and the storing elastic energy was frozen at the same time. However, the recovery ratios were significantly different with different

Figure 5 XRD patterns of the polyesters at room temperature (a). The intensity of the fluorescence emission spectra (b) of the polyesters.

Figure 6 Digital photograph of shape memory process of polyesters: (a) PBHPS, (b) PBHPS-1% PTA, (c) PBHPS-2% PTA and (d) PBHPS-3% PTA. Programmed cyclic thermomechanical curves of PBHPS-2%PTA obtained by DMA (e).

Table 3 Fixing and recovery ratio of the polyesters obtained by DMA

Sample	Fixing ratio (%)	Recovery ratio (%)
PBHPS	98.6±0.4	94.4±0.9
PBHPS-1%PTA	97.9±0.2	85.3±1.1
PBHPS-2%PTA	97.9±0.4	94.0±2.6
PBHPS-3%PTA	99.5±0.1	98.6±0.4

content of PTA. When the content of PTA was 1%, the recovery ratio of PBHPS-1%PTA dropped obviously to about 85.3%. As the introduction of PTA, the chemical crosslinking strongly influenced the chain conformation. As a consequence, some physical crosslinking (π - π interactions) did not form effectively, and the intensity of physical crosslinking became weak. However, when the PTA content was relatively low, the introduced chemical crosslinking was not strong enough to force the deformed sample to recover, resulting in a sharply decline of the recovery ratio. As the amount of PTA increased sequentially, the recovery ratio of the polyesters rose again. The recovery ratio of PBHPS-3%PTA reached 98.6%. With relative high content of PTA, the chemical crosslinking became more dominant than the physical crosslinking in the system, thus making the shape memory properties much better. Fig. 6 shows digital photographs of the recovery process of these polyesters. The samples were firstly stretched and then recovered in the hot stage at 60°C. The results of all these polyesters' shape memory properties were in accordance with the DMA tests.

Photo-responsive behavior

The photo-responsive properties of all these polyesters were investigated by UV-vis spectroscopy in DMF solu-

tion under irradiation of 365 nm light and 550 nm light, as illustrated in Fig. 7 (PBHPS-2%PTA). When irradiated at 365 nm, the solution underwent *trans* to *cis* photoisomerization until a photostationary state was eventually reached. The intensity of the π - π^* transition band around 360 nm decreased with the irradiation time, whereas that of the n - π^* transition band around 450 nm slightly increased. Then the *cis* to *trans* back-isomerization process happened when the samples were irradiated at visible light ($\lambda=550$ nm). The π - π^* transition band increased and the n - π^* transition band decreased back. However, the finally recovered absorbance of the *trans*-isomer was lower than that before UV irradiation. This phenomenon was reported before [31] but the reason was not clear yet. One possible explanation is that when the *cis* to *trans* photochemical back-isomerization was performed, there was also a weak absorption from the *trans*-isomer at the same wavelength, which led to an equilibrium between these two isomers during the isomerization process under the same visible light after most of the *cis*-isomer returned to the *trans*-isomer. The other three polyesters displayed the similar properties under the irradiation of UV light and visible light, and the results were given in the supporting information (Fig. S2).

The macroscopical photo-mechanical properties of all these polyesters were then studied. The simple melt stretching method was used to get the vimineous samples with a relatively high order of mesogen along the stretch direction for the test [31,37]. Fig. 8 shows the photo-induced bending and unbending behaviors of these polyesters upon irradiation with UV light and visible light, respectively. It was seen clearly that the PBHPS bent to the UV light source direction when it was exposed to 365 nm UV light (15 mW cm^{-2}) from above of the sam-

Figure 7 UV-vis spectral changes with time for the solution of PBHPS-2%PTA in DMF at room temperature upon irradiation with 365 nm UV light (a) and upon irradiating the polymer solution at the photostationary state with 550 nm visible light (b).

Figure 8 Digital pictures of the polyester films motion in the presence of UV light (365 nm, 15 mW cm^{-2}) and visible light (550 nm, 15 mW cm^{-2}).

ple. However, the PBHPS sample did not revert to its initial straight state upon irradiation with visible light (550 nm, 15 mW cm^{-2}). This was because the aromatic structure in the PBHPS chain slipped during the isomerization process of the azobenzene groups under the UV light, resulting in losing the physical crosslinking points in the system. As the bending process finished, a kind of new π - π stacking formed, fixing the deformed bending shape. When irradiated by the visible light, the newly formed π - π stacking was broken again as the *cis* to *trans* isomerization happened. However, the final alignment of *trans* azobenzene mesogens were different from the original ones in the absent of some hard segment to restrict the movement of the polymer chain. Thus, the PBHPS sample could not recover to its original straight state. For the sample PBHPS-1%PTA, the introduction of 1% PTA did not afford enough chemical crosslinking as a

Figure 9 The schematic drawing of the oriented samples PBHPS (a) and PBHPS-PTA (b) during the isomerization process under the UV light and visible light.

hard segment, and thus the photo-mechanical property of PBHPS-1%PTA was similar to that of PBHPS. A schematic drawing of this process is shown in Fig. 9a. When more PTA was incorporated to form chemical crosslinking, the reversible photo-induced bending and unbending properties were improved. Also shown in Fig. 8, the PBHPS-2%PTA samples could bend under the UV light irradiation, and revert to their straight state upon the irradiation with the 550 nm visible light with a recovery ratio of 85.6%, although the bending angles were decreased, which could be attributed to the chemical crosslinking in the polymer chains. Since the chemical crosslinking did not response to the UV light and restricted the mobility of the azobenzene groups, these crosslinking points (fixing phase) remained during the isomerization of azobenzene groups under UV light, and then forced the polymer chains back to the initial align-

Figure 10 Self-healing process of the scratched polyesters observed by POM at 60°C: (a) PBHPS, (b) PBHPS-1%PTA, (c) PBHPS-2%PTA and (d) PBHPS-3%PTA. Stress versus strain curves for the original, scratched and healed state of PBHPS-2%PTA (e).

ment under the visible light. The schematic drawing of this process is shown in Fig. 9b. However, as the PTA chemical crosslinking became dominant in the polymer chains, the mechanical properties were enhanced (Fig. S3) and the movement of the polymer chains were restricted gradually, causing the bending angles of the crosslinked polyesters to decrease obviously. Even the PBHPS-3%PTA sample could not bend when induced by the UV light.

Heat-assisted healing behavior

In our previous work [36,37], the azobenzene based main-chain liquid crystalline polyester PBHPS showed heat-assisted healing behavior due to the π - π interaction in the chain as the physical crosslink. When crosslinker PTA is introduced into PBHPS to form some slight chemical crosslink, would the chemical crosslink influence the healing behaviors? Firstly, the scratch healing behaviors of the polyesters were studied by using POM. The scratched polyester films were put on the 60°C hot stage and the heat-assisted healing process was recorded by the digital camera equipped on the POM. The snapshots were captured at different time. As shown in Fig. 10, the PBHPS-1%PTA sample with lower content of PTA showed similar healing behavior as PBHPS because of the relatively strong π - π interaction in the polymer chains. When the healing process occurred at 60°C, the polyesters were in liquid crystalline phase, making the π - π stacking reformed at the presence of the position order of the mesogenic units. When the content of PTA increased, some π - π stacking physical crosslink did not form effectively which was proved by WXAD and fluorescence emission spectra above. Thus, the heat-assisted healing properties of PBHPS-2%PTA and PBHPS-3%PTA decreased. For PBHPS-2%PTA, there still existed a blurred

scratch after healing 60 min. The PBHPS-3%PTA shrank did not heal at the temperature of 60°C, proving the π - π interaction played an important role in heat-assisted healing behavior indirectly.

Herein, the PBHPS-2%PTA was chosen to study the healing efficiency. The healing efficiency of scratched healing method was measured by tensile test, as shown in Fig. 10e. The tensile stress and the elongation at break of the original PBHPS-2%PTA was 15.5 MPa and 928.9%, respectively; and the scratched one decreased to 8.3 MPa and 107.9%, where the testing sample fractured precisely at the scratch trace. After 5 h healing process at 60°C and without the compression stress, the tensile stress of the healed one recovered to 11.1 MPa and 529.8%, thus the healing efficiency was 71.6% (for strength) and 57.0% (for elongation), respectively.

CONCLUSION

In conclusion, a series of azobenzene-containing liquid crystalline polyesters combining physical and chemical crosslinking were synthesized successfully. All of these polyesters showed good thermal stability and their thermal decomposition temperature was higher than 340°C. DSC showed that all these crosslinked samples had a relative low phase transition temperatures with thermoplastic processability. With POM and XRD results, these polyesters showed smectic liquid crystalline phase. Furthermore, there also exist strong π - π stacking interactions in the polymer chains with low content of PTA as the crosslinking agent. When PTA content increased, as illustrated in XRD and fluorescence emission spectra, the chemical crosslinking negatively influenced the original physical crosslinking (π - π interaction) among the polymer chains. The thermally induced shape memory behaviors of these polyesters were evaluated by DMA: all

these samples exhibited expected fixing ratios about 98%; however, the recovery ratios changed obviously with different content of PTA. The chemical crosslinking also influenced the photo responsive performance of these polyesters. At the absence of chemical crosslinking, the oriented sample (PBHPS) could be bent under the irradiation of UV light; however, since the isomerization process of azobenzene groups broke the π - π interactions in the polymer chains, the bent sample could not revert straight under the irradiation of visible light. At the presence of slight chemical crosslinking, thanks to the inert response of the crosslinking to the UV light, such problem was solved by restricting the mobility of the azobenzene groups, then forcing the polymer chains back to the initial alignments under the visible light. As a consequence, the reversible bending and unbending behaviors of the slightly crosslinked polyesters were achieved. The heat-assisted healing properties of these polyesters were achieved as the physical crosslinking dominated in the chains. Therefore, this main-chain azobenzene-containing liquid crystalline polyester could be utilized as a kind of smart polymer and exhibits its own value in the industry field.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Shape memory tests of polyesters by DMA, UV-vis spectra of PBHPS, PBHPS-1%PTA and PBHPS-3%PTA solution in DMF and the storage modulus of these polymers tested by DMA are available in the online version of the paper.

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物理、化学双重交联偶氮液晶聚合物的合成及其光热双重响应性能

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摘要 结合化学交联提供的稳定性和物理交联提供的可热塑加工性可设计得到具有多种刺激响应行为的新材料. 本文以偶氮苯二氧己醇(BHHAB)为液晶基元, 与苯基丁二酸(PSA)和丙三羧酸(PTA)本体聚合得到一系列液晶聚合物PBHPS-*x*%PTA, 其中PTA作为化学交联, 而取代苯基与介晶基元之间的 π - π 相互作用可提供物理交联. 热分析结果显示这些聚合物具有高的热稳定性并表现出近晶型液晶行为. 广角X射线衍射(WAXD)和荧光光谱证实了分子间具有可作为物理交联点的 π - π 相互作用; 并且随着PTA含量的增加, 化学交联会逐渐影响分子链构象, 最终破坏物理交联作用. 轻度的化学交联保留了液晶聚合物的可热塑加工性, 而在物理交联与化学交联的共同作用下, 液晶聚合物具有可逆光致形变, 热致形状记忆及自修复性能, 在智能高分子材料领域表现出一定的应用前景.