# Shape memory polyurethanes containing azo exhibiting photoisomerization function†

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A series of azobenzene-containing polyurethanes (azoPU) was synthesized. The structure of the azoPU and the synthesis process were detected by FTIR and nuclear magnetic resonance (NMR), and the transition temperature was determined by differential scanning calorimetry (DSC). Tensile and cyclic thermomechanical experiment results revealed that excellent mechanical properties, shape fixity ($R_f$), and shape recovery ($R_r$) were obtained by the addition of azo to the chain of PU. $R_r$ and $R_f$ of azoPU increased with the increase of hard segment (HS) content. The higher HS content enhanced interaction among polymer chains as the chances of induced dipole–dipole interaction between aromatic rings increased in the presence of azo in the main chain. The materials presented *trans-cis* isomerization under UV irradiation in addition to the shape memory effect. The UV-vis spectrum indicated that photoisomerization occurred both in solution and solid state. It is expected that the work may be helpful in expanding the application of shape memory PU in areas of drug release and optical data storage.

## 1. Introduction

Shape memory polyurethane (SMPU) composed of both reversible phase and fixed phase are attractive candidates for potential smart applications, such as in biomedical fields, because the shape memory polymers can be tailored to exhibit biocompatibilities and body temperature capabilities by introducing special functionalized soft segment (SS) and hard segment (HS) into the polymers.[1] SMPU possesses shape memory effect (SME) due to microphase separation between soft domain and hard domain; the soft domain changes its shape under external stress and then the external stress was released with the subsequent cooling. When reheated to the $T_{trans}$, SMPU recovers its original shape which is controlled by the HS.[2–7] Nowadays, increasing focus has been paid to shape memory polymer, and a variety of new polymers with SME have been studied, such as PCL block segment polymers,[8–11] polyester,[12,13] crosslinked poly(lactic acid),[14] blend polymers,[15–17] biomaterials[18–20] and so on. Additionally, SMPU is widely studied in the bionic field due to its biocompatibility, biodegradation,[21,22] and tunable transition temperature.

In the past few years, a large amount of papers dealing with the alteration of the SMPU architecture have been published, and these contributions mainly focus on the synthesis and characterization of the new function of the SMP. At the beginning, Jeong and Kim studied the SMPU by adjusting the number average molecular weight $M_n$ and the ratio of HS and SS, which could control the transition temperature ($T_s$) and SME.[2,5,23] Recently, more work concentrates on the design of variable groups in the chain. Hu *et al.* tried to introduce the ionomers into SMPU, which has a pyridinium-containing HS, suggesting the new polymer possessed an antibacterial function as well as good SME.[24] Jeng and co-workers have demonstrated that dendritic chains as extender in PU could improve the mechanical and shape memory properties due to the formation of more hydrogen bonds in the PU molecular chains.[25] So far, the other operations that could induce shape recovery of the SMPU have been drawing research interest. For example, Huang *et al.* found that moisture could also trigger the thermal SMPU. The reason for this phenomenon is that the $T_g$ of SMPU samples decreases as the hydrogen bonding among PU chains is weakened due to the bound water.[26]

It is well known that the azo-containing polymers (azopolymers) have the capacity of reversible *trans-cis* isomerization when exposed to UV-vis irradiation.[27–30] The azopolymers are more thermally stable and have better mechanical properties than their respective monomers, which have been used to produce optical sensors. In the present paper, azo was introduced into the PU main chains, and its photoisomerization function was studied. It is expected that this new type of SMPU with azo-groups may find potential applications in the field of medicine, such as drug release and cerebral aneurysm reparation.[9,31,32]

## 2. Experimental section

### 2.1 Materials

Epsilon-caprolactone (CL) and 4,4′-methylenediphenyl diisocyanate (MDI) were received from Acros. 1,4-Butanediol (BDO), 4-nitroaniline, ethylene glycol, dibutyltin dilaurate (DBTDL) and N,N-dimethylformamide (DMF, 99%) were bought from Tianjin Chemical Reagents Company. CL and

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DMF were dried with $CaH_2$ for 24 h and freshly distillated before use.

### 2.2 Preparation of polycaprolactone diols prepolymer PCL-diols (4500)

A certain amount of CL and ethylene glycol with a stoichiometric ratio were mixed in a flask, and then 0.05% stannous octoate was added as catalyst. The reaction was carried out under pure argon at 130 °C for 24 h. The polymer was precipitated in cold diethyl ether and then deterged by methanol. Then the product was dried in vacuum at 30 °C to a constant mass. The molecular weight of the prepolymer was determined by gel permeation chromatography (GPC).

The proton resonance data are in agreement with the expected values: (chloroform-d$_1$): $\delta$ (ppm) 4.24 (s, –O–$CH_2$–$CH_2$–O–)); 4.03 (t, –O–$CH_2$–); 3.62 (t, HO–$CH_2$–$CH_x$–); 2.28 (m, –O–CO–$CH_2$–$CH_x$); 1.58 (m, –$CH_x$–$CH_2$–$CH_x$–); 1.37 (m, –$CH_x$–$CH_2$–$CH_x$–); $T_m = 59.94$ °C, $\Delta H_m = 107.16$ J g$^{-1}$.

### 2.3 Preparation of 4,4′-dihydroxyazobenzene

The diazotization-coupling reaction was conducted according to the methods outlined in the literature.[33] Briefly, 4-hydroxyaminobenzene was firstly dissolved in hydrochloric acid solution, and then the sodium nitrate solution was added dropwise with stirring at 0–5 °C. After the diazotization, the sodium hydroxide solution containing phenol was added to the diazonium salt solution. Meanwhile, the pH value of the mixture was adjusted to 6–7 by adding HCl. Then the orange red precipitate was collected by filtration. The crude product was purified by recrystallization from a mixture of ethanol and ethyl acetate (1 : 1, v/v). $^1$H NMR (DMSO-d$_6$): $\delta$ (ppm) 10.116 (s, 2H); 7.705 (d, 4H); 6.898 (d, 4H); 3.334 (s, $H_2O$); 2.490 (s, DMSO).

### 2.4 Preparation of azo-based PCL-PU [see Scheme 1]

The compositions of PU and its main characteristics are given in Table 1. The following procedure was typical: MDI was dissolved in DMF and PCL with a molecular weight of 4500 g mol$^{-1}$ was added in a dry three-necked tube. The mixture was stirred under nitrogen at 65 °C for 2 h to prepare the pre-polymer. The azo solution in DMF was subsequently added, followed by addition of DBTDL, and then the temperature was adjusted to 110 °C for another 11 h to complete the polymerization.

### 2.5 Film preparation

To prepare the film samples, PU solution in DMF was cast on a Teflon plate and dried at 80 °C for 24 h to evaporate most of the DMF, after which the film samples were further solidified in a vacuum oven at 80 °C for another 24 h. The thickness of the film was controlled to be about 0.2 mm.

### 2.6 Nuclear magnetic resonance (NMR)

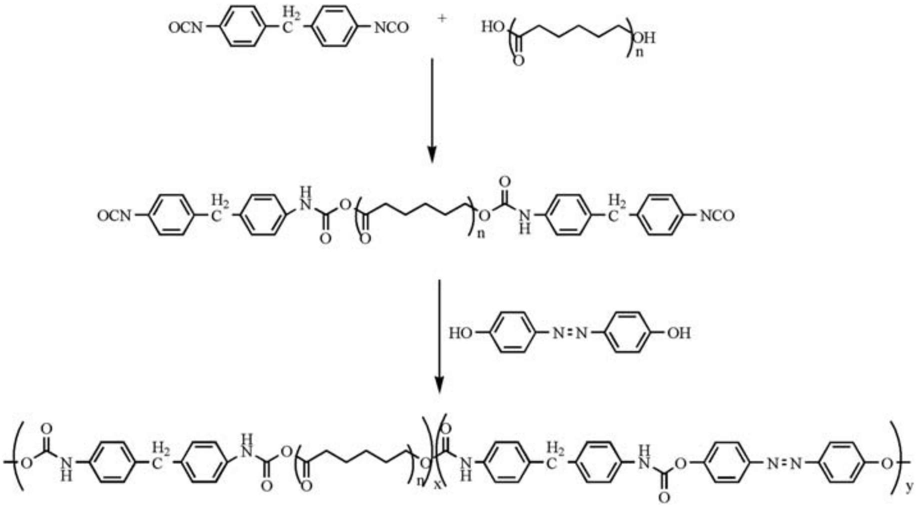
$^1$H NMR (400 MHz) spectra were recorded in DMSO-d$_6$ and $CDCl_3$ as solvent.

### 2.7 Differential scanning calorimetry (DSC)

DSC was carried out with a Mettler-Toledo instrument (DSC 822$^e$) with a heating or cooling rate of 10 °C min$^{-1}$. The PU sample was heated to 250 °C and kept at this temperature for 5 min and then cooled to −100 °C in the first run in order to remove the thermal histories. In the second scan, the sample was heated again to 250 °C and cooled to −50 °C, from which the glass transition temperature ($T_g$), melting temperature ($T_m$) and crystal temperature ($T_c$) were determined.

**Table 1** Composition and characterization of polyurethanes

| Polymer code | diols | PCL : MDI : diol | wt% of HS | azo (%) | $T_m$/°C | $T_g$/°C | $X_c$ (%) |
|---|---|---|---|---|---|---|---|
| A | azo | 1 : 6 : 5 | 36.36 | 15.13 | 48.91 | −24.72 | 24.6 |
| B | azo | 1 : 5 : 4 | 31.89 | 12.96 | 49.32 | −32.22 | 29.8 |
| C | azo | 1 : 4 : 3 | 26.75 | 10.45 | 50.27 | −28.42 | 32.5 |
| D | azo | 1 : 3 : 2 | 20.73 | 7.47 | 51.01 | −36.68 | 34.1 |
| E | azo | 1 : 2 : 1 | 13.70 | 4.10 | 50.03 | −37.24 | 37.6 |
| F | BDO | 1 : 5 : 4 | 26.37 | 0 | 52.13 | −48.41 | 26.8 |



**Scheme 1** Synthetic procedure for SMPU.

### 2.8 UV-vis and FTIR

UV-vis spectra were recorded on a Hitachi U-3010 spectrophotometer. IR spectra were measured using a Bruker IFS 66v/s IR spectrophotometer within a range of 4000–400 $\mathrm{cm}^{-1}$.

### 2.9 Atomic force microscope (AFM)

AFM was performed with a Nanoscope IIIa Multimode atomic force microscope (AFM, Digital Instruments) at the tapping mode using FESP probe (curvature radius < 10 nm, 87 kHz). The azoPU was spin-coated onto silicon substrates. The films were allowed to dry in an oven at 80 °C for 24 h, and then annealed in a vacuum oven at 80 °C for another 24 h to obtain the phase equilibrium.

### 2.10 Mechanical and cyclic thermomechanical experiment

Tensile tests were performed on a Shimadzu AG-X. The strain rate was 10 mm $\mathrm{min}^{-1}$. To check the SME of the PU, the test were carried out on a SANS tester (Shenzhen SANS Material Test Instrument Co. Ltd., China) equipped with a controlled thermal chamber. The shape memory test of films was carried out between $T_\mathrm{h}$ and $T_\mathrm{l}$, during which the stress and strain was recorded. Samples were cut to standard dimensions according to ISO 527-2/1BB. The cyclic thermomechanical tensile test was carried out in the following order: (1) heating the sample to $T_\mathrm{h}$ and stretching the sample to 100% extension with a constant crosshead speed of 10 mm $\mathrm{min}^{-1}$ and holding for 5 min; (2) cooling the sample to $T_\mathrm{l}$ with holding the shape, (3) reducing the stress to zero at $T_\mathrm{l}$ and maintain at $T_\mathrm{l}$; (4) raising the temperature from $T_\mathrm{l}$ to $T_\mathrm{h}$ and keeping at $T_\mathrm{h}$ for 5 min and measuring the length of the sample. Under the above conditions, shape retention ($\mathrm{R_r}$) and shape recovery ($\mathrm{R_f}$) are defined as follows:

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100\%$$

$$R_r = \frac{(\varepsilon_m - \varepsilon_p)}{\varepsilon_m} \times 100\%$$

where $T_\mathrm{h} = T_\mathrm{m} + 25$ °C, $T_\mathrm{l} = T_\mathrm{m} - 25$ °C, $\varepsilon_\mathrm{m}$ = strain at 100% elongation, $\varepsilon_\mathrm{u}$ = retention strain at $T_\mathrm{m} - 25$ °C, and $\varepsilon_\mathrm{p}$ = recovery strain at $T_\mathrm{m} + 25$ °C.

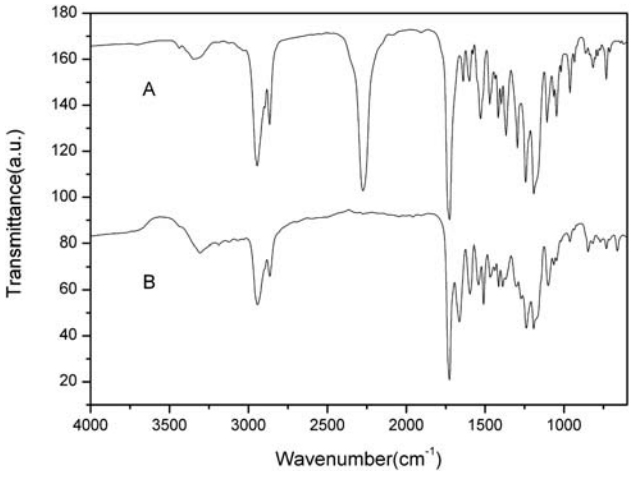


**Fig. 1** FTIR spectrum of prepolymer azoPU (A) and sample A (B).

## 3. Results and discussion

### 3.1 Structural analysis of azoPU

Recently, a series of azo-containing PU were synthesized. The formulations of these PUs with different compositions are shown in Table 1. A series of SMPU extended by diols were previously synthesized by a two-step method. However, due to the relatively low reactivity of phenol in comparison to 1,4-butanediol (BDO), it was difficult to obtain PU extended by phenolic hydroxyl. In the present study, the reaction time was prolonged to 11 h at elevated temperature and in the presence of a catalyst. The FT-IR spectra of (A) prepolymer, (B) sample A are shown in Fig. 1. In Fig. 1A, the peak at 2273 $\mathrm{cm}^{-1}$, corresponding to the isocyanate group stretching vibration, disappeared in the spectra of sample B, indicating the success of the reaction between phenol extender and the residual isocyanate group.[34,35] Fig. 2 shows the $^1$H NMR spectrum of sample A diluted in DMSO. The peaks at 6.88–6.90 ppm and 7.68–7.71 ppm, which could be ascribed to the phenolic hydroxyl (c, f) of azo, confirm the existence of azo groups. Compared to the normal PU, there are two peaks at 10.11 and 9.49 ppm corresponding to the amide group (a, b), which indicates that there are two kinds of group attached to the amidocyanogen.[24] The $^1$H NMR and FTIR spectra confirm the expected structure of the azoPU.

### 3.2 Thermal properties of azo-based PCL-PU

The thermal transitions of azo-based PU were determined by DSC. The curves from the second heating run are shown in Fig. S3, and the $T_\mathrm{m}$ and crystallinity ($\mathrm{X_c}$) are summarized in Table 1. $\mathrm{X_c}$ was calculated according to the follow equation

$$\mathrm{X_c} = (\Delta H_\mathrm{m}/\Delta H_{100\%}) \times 100\%$$

where $\Delta H_{100\%}$ is the theoretical heat of fusion of PCL (135 J $\mathrm{g}^{-1}$).[36,37] As can be seen, the $T_\mathrm{m}$ values of the PU were in the range between 48 and 51 °C, which was lower than that of pure PCL (59 °C) as previously studied. It could be attributed the fact that the introduction of azo and MDI to the molecular chain decreased the crystallinity of the PCL segment and inhibited crystal formation. The speculation was proven by the $\mathrm{X_c}$ values in Table 1. Besides, it can be seen from Table 1 that the transition temperature as well as the $\mathrm{X_c}$ modestly decreases with increasing azo concentration. This is in agreement with the previous PCL systems, which predicted that the incorporation of HS and PCL inhibited the crystal formation and decreased the crystallinity of SS. It is also noticeable that an inconspicuous $T_\mathrm{g}$ was observed between −37 and −24 °C, corresponding to the $T_\mathrm{g}$ of the SS of PCL. In contrast, the azo-PU has higher crystallinity and lower $T_\mathrm{m}$ than those of PU extended with BDO. The difference between these two materials indicated that the chain structure was changed by introduction of azo. With the addition of azo to the main chain, the rigidity increased and the induced dipole–dipole interaction between aromatic rings increased. The crystallinity was improved due to the better combination among the polymeric chains.[2] The $T_\mathrm{g}$ of PU was increased since the local chain mobility was constrained by enhanced interaction among HS.

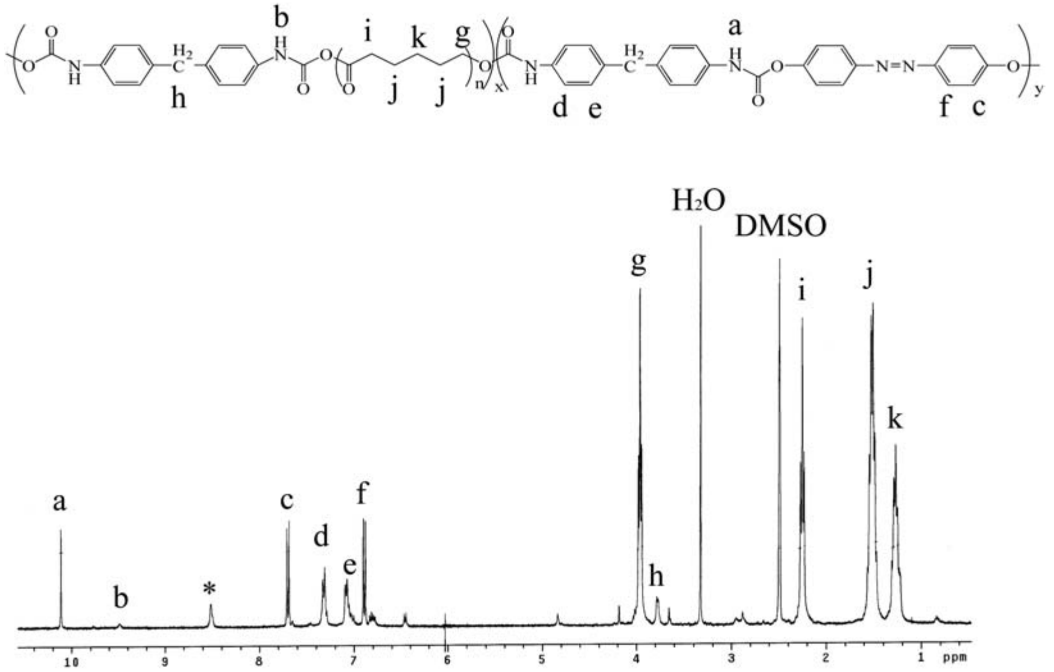


**Fig. 2** $^1$H NMR spectrum of azoPU (sample A) in DMSO-$d_6$ (signal * existed also in the $^1$H NMR spectrum of pure MDI).[34]

### 3.3 Mechanical and shape-memory properties of azo-based PCL-PU

As described in the experimental section, the mechanical property of PU was examined by tensile tests at room temperature, and the results are summarized in Table 2.

As can be seen from Table 2, Young's modulus (E) increased and elongation at break ($\varepsilon_R$) decreased with increasing HS, while the maximum tensile strength ($\sigma_m$) remained almost constant with values around 20–30 MPa. E was found to be strongly influenced by the content of HS. With the azo increased from 4.10% to 15.13%, E was increased over a large range from 58 to 181 MPa, which can be ascribed to the enhancement of the rigidity. However, it was not the case for $\varepsilon_R$, which decreased from 791% to 460%. Comparing azo-PU B with BDO-PU, relatively higher E and $\sigma_m$ were observed for B in the presence of azo, due to the enhanced rigidity and interaction between the molecules as mentioned above after the introduction of azo groups in the main chains.

The $R_f$ and $R_r$ of samples A–F are shown in Table 2. In the previous studies, the shape memory properties of SMPU with different kinds and variable content of SS and HS have been studied, and the results indicated that the key factors influencing SME were the molecular weight of SS and relevant content of SS.[2] In this paper, we choose PCL (4500) as the SS, which exhibits an obvious $T_m$ and acts as switch segment. The shape fixity was negligibly influenced by the varying amounts of HS content since the $R_f$ is determined by the SS, except for sample E, all the samples have a high $R_f$ above 96% with changing HS content from 13.7% to 36.36% it indicates that the $R_f$ was negligibly influenced by varying the amount of HS. In Table 2, it is found that the shape recovery decreases gradually with the decrease of HS content. When HS content increases from 13.70% to 36.36%, the $R_r$ increased from 80% to 99.9%. As the HS content increased, the ability to maintain a permanent shape is increased by physical crosslinking. Sample A exhibited a perfect ability to fix the temporary deformed shape and recover the permanent shape. This excellent SME is attributed to the enhancement of phase separation because of the strong interaction among HS caused by azo. Lee *et al.* suggests that the domain formation is helpful to the SME.[2] For example, the shape deformation and recovery process for azoPU sample A is shown in Fig. 3.

**Table 2** Mechanical properties and shape memory properties of polyurethanes

| Polymer code | $R_f$ | $R_r$ | E/MPa | $\sigma_m$/MPa | $\varepsilon_R$ (%) |
|---|---|---|---|---|---|
| A | 100 ± 0.1 | 99.90 | 181.07 ± 5.10 | 21.74 ± 0.86 | 468 ± 24 |
| B | 98.52 ± 3.5 | 95.17 | 164.11 ± 3.05 | 31.68 ± 1.20 | 780 ± 12 |
| C | 97.03 ± 0.1 | 87.50 | 100.73 ± 1.02 | 20.01 ± 0.20 | 677 ± 53 |
| D | 96.31 ± 2.2 | 85.00 | 66.48 ± 2.30 | 24.06 ± 1.56 | 709 ± 67 |
| E | 83.79 ± 0.4 | 80.00 | 58.25 ± 2.86 | 21.51 ± 2.22 | 791 ± 90 |
| F | 95.02 ± 0.3 | 90.00 | 80.30 ± 4.52 | 21.41 ± 1.57 | 611 ± 32 |

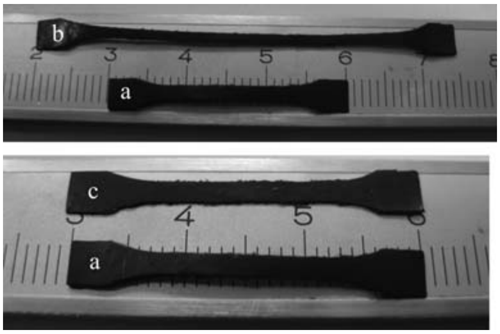


**Fig. 3** azoPU (sample A) showing shape memory effect at 75 °C: (a) initial state; (b) deformed state (stretched at 75 °C and fixed at 25 °C); (c) recovered state after heating in oven at 75 °C.

### 3.4 UV absorption and photochromic properties of azoPU

Polymers containing azo units exhibited special strong absorption bands in the UV-vis spectra, which would be changed when the isomerization occurred.[38–40] The UV-vis spectra are often used to characterize the *trans-cis* isomerization of azo. The azoPU in chloroform solution was irradiated with UV light ($\lambda =$ 254 nm) in 10 min intervals, shown in Fig. 4(a). The absorption intensity of the $\pi \rightarrow \pi^*$ transition band at 360 nm decreased and the $n \rightarrow \pi^*$ intensity of the transition band at 500 nm increased with increasing irradiation time, which indicated the transformation from *trans* form to *cis* form. To investigate the UV-vis spectra and photochromic properties of the polymers in the solid state, thin films of azoPU were prepared by spin-coating of 5% w/w azoPU DMF solution onto clean glass plates (2 × 2 cm). For comparison, films of sample A were subjected to UV irradiation for 5 min under a temperature of 80 °C (30 °C above the $T_m$), and the UV-vis absorption spectra of film A is reported in Fig. 4 (b). A significant shift of absorption peak was observed compared to the sample in solution. It was inferred that the blue shift in chloroform was probably due to the solvent effect. Under UV irradiation at 254 nm for 5 min, the spectra change corresponding to isomerization was exhibited. The *cis* form of the azo which is thermodynamically instable was induced by UV light due to the absorbed energy. When the macromolecules were linked to the azo group, the isomerization would induce the macroscopic change of the polymers. This result indicates that the azo in azoPU can undergo *trans-cis* reversible photoisomerization both in solution and in the solid state.

Fig. 5 shows the phase image of azoPU films before and after UV irradiation. Before irradiation, the surface displayed phase separation at the nanometre scale, while a more homogeneous phase image was seen after the UV irradiation at 80 °C (30 °C above the $T_m$). The results revealed that UV irradiation led to reformation of phase structure of the film. The bright regions could be related to the HS due to its high modulus, which was consistent with previous studies,[41,42] and it became more homogeneous under the UV irradiation. The change of morphology indicated a high sensitivity of the film to UV light. The *trans-cis* isomerization should change the length of the chain or dipole moment, induced by the UV light, heat or other stimuli.[43] Many azopolymer films can form surface relief gratings induced by a laser, which can be erased by laser or heating. This attracted considerable attention for potential applications such as holographic gratings, optical information storage, and so on.[44] The reversible change between hydrophilicity and hydrophobicity arising from *trans-cis* isomerization could induce dissociation and aggregation, which has potential applications in drug formulation.[45]

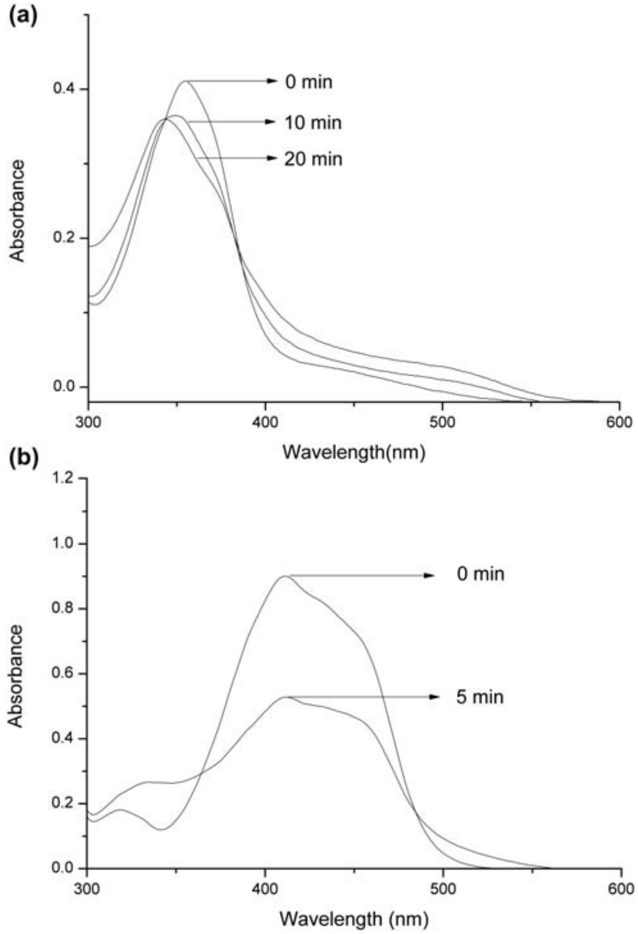


**Fig. 4** UV-vis spectra of azoPU (sample A) with UV irradiation at 254nm, in chloroform solution (a) and film sample (b).

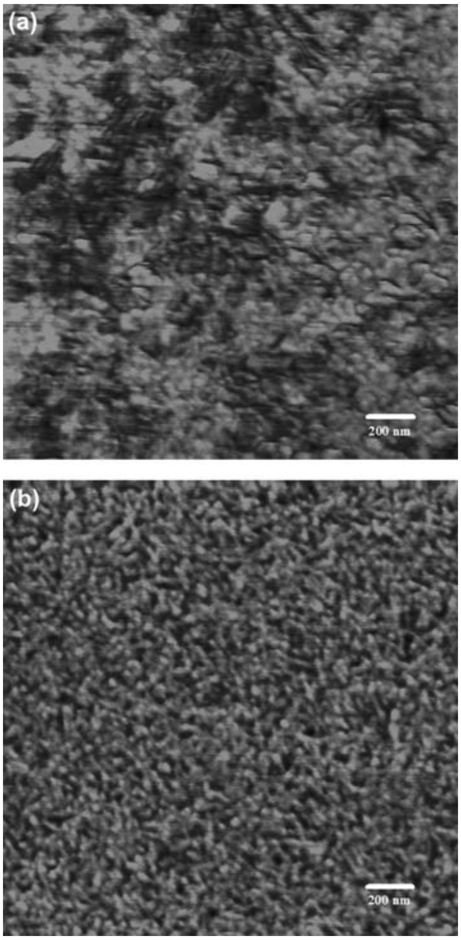


**Fig. 5** AFM phase image for azoPU film spin-coated on a silicon wafer: films prior to UV irradiation (a) and the same film after UV irradiation (254 nm) (b).

## 4. Conclusions

Shape memory PU with azo as hard segments were synthesized and characterized in the present study. Due to the increased interaction, especially the induced dipole–dipole between the chains, high strength and $R_f$ and $R_r$ of almost 99.9% were obtained. The data presented suggest that the design of PU with azo as chain extender can achieve excellent mechanical properties and shape memory effect. Photoisomerization was observed both in chloroform solution and the solid state. The *trans-cis* photoisomerization of the shape memory polyurethane is expected to have very promising applications in specific fields. The light-triggered shape memory polymers will be studied in the future.

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