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Cite this article as:

Liu Yi-Jun, Liu Dong, Li Si-Han, Liang Hua-Qing, Zhu Fang-Ming. Investigation on Viscoelasticity of Waterborne Polyurethane with Azobenzene-containing Pendant Groups under Ultraviolet and Visible-light Irradiation[J]. *Chinese J. Polym. Sci.*, 2019, 37(12): 1267-1272. doi: 10.1007/s10118-019-2289-x

View online: <https://doi.org/10.1007/s10118-019-2289-x>

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Investigation on Viscoelasticity of Waterborne Polyurethane with Azobenzene-containing Pendant Groups under Ultraviolet and Visible-light Irradiation

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Abstract In this study, a novel waterborne polyurethane (WPU) with azobenzene-containing (azo-containing) pendant groups was synthesized by isophorone diisocyanate, long-chain diol of polycaprolactone, 2-ethyl-2-methyl-butanoic acid (2,2-dimethylolpropionic acid), 10-(4-(phenyldiazenyl)phenoxy)decyl-3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate, and *N,N*-diethyl-ethanamine (triethylamine). Moreover, the influence of ultraviolet and visible (UV-Vis) light irradiation on the viscoelasticity of azo-containing WPU film in terms of the reversible *trans-cis* photoisomerization of azo-containing pendant groups was investigated by UV-Vis light spectroscopy, atomic force microscopy, and dynamic thermomechanical analysis. The results revealed that the adhesion of azo-containing WPU with single crystal silicon atomic force microscope probe was about 13 nN when irradiated by 450 nm Vis light for 60 s at 25 °C. Subsequently, the adhesion increased to 82 nN after irradiation with 365 nm UV light for 60 s at 25 °C. In addition, the azo-containing WPU presented a photo-induced reversible transition of tensile modulus and $\tan\delta$ in the range from about 2 MPa to 22 MPa and 6000 to 0.35 with UV-Vis light cyclic irradiation for 120 s at 25 °C, respectively.

Keywords Waterborne polyurethane; Viscoelasticity; Photoisomerization; Azobenzene

Citation: Liu, Y. J.; Liu, D.; Li, S. H.; Liang, H. Q.; Zhu, F. M. Investigation on viscoelasticity of waterborne polyurethane with azobenzene-containing pendant groups under ultraviolet and visible-light irradiation. *Chinese J. Polym. Sci.* 2019, 37, 1267–1272.

INTRODUCTION

Azobenzene is a switchable compound based on reversible *cis-trans* photoisomerization.^[1–5] Notably, the *trans-* to *cis-* configuration can be induced by irradiation with ultraviolet and visible (UV-Vis) light.^[6] Given the reversible *cis-trans* photoisomerization, the photo-responsive azobenzene-containing (azo-containing) polymers have been extensively investigated because of the widely potential applications in solid-liquid phase transition materials,^[7,8] liquid crystals,^[9,10] photochromic materials,^[11,12] optical data storage,^[13] non-linear optical materials,^[14] holographic memory,^[15] molecular switches,^[16] regulation of supramolecular chirality^[17–19] and other fields.^[20,21]

Recently, Zhou *et al.* synthesized polyacrylates containing azo-units in side chains.^[22] These resultant polymers exhibited reversible photoswitchable glass transition temperature and solid-to-liquid transitions. Jiang *et al.* prepared photoreactive superhydrophobic azo-containing polyacrylate film formed by self-assembly and investigated its characteristic difference between *cis-* and *trans-* structure.^[23] This film showed higher surface energy and better hydrophilicity

due to the change of surface structure caused by the *cis*-azo groups.

As we all know, waterborne polyurethane (WPU) is an environmentally friendly material,^[24] which has wide range applications in the fields of life, industry, military and so on.^[25] Usually, WPU is mainly synthesized by long-chain polyols, isocyanates and aqueous chain extenders. By adjusting the type and proportion of the raw materials,^[26] WPU shows a variety of different properties and applications. Note that WPU with photo-responsive units is beneficial to developing potential application. Li *et al.* demonstrated the synthesis of azo-containing WPU cationomers which presented the great potential applications in optics and bioengineering due to the responses of pH and UV light.^[27] Ban *et al.* reported a series of new stimulus-responsive shape-memory azo-containing polyurethanes which were capable of UV light-triggered deformation, hydrogen bond-mediated fixation and thermal-induced recovery.^[28]

Reversible photoresponsive surfaces with controllable wettability have attracted enormous attention in recent years due to their importance in surface science and intelligent micro- and nano-devices.^[29] However, many literatures merely focus on the properties of azo-containing WPU dispersion as well as the film wettability,^[30] the influence of photoirradiation on the viscoelasticity of the azo-containing WPU is rarely investigated. In this contribution, we prepared a novel

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Received April 6, 2019; Accepted May 6, 2019; Published online June 26, 2019

azo-containing WPU via prepolymerization of isophorone diisocyanate with polycaprolactone diol and sequent reaction of chain extension by 10-(4-(phenyldiazenyl)phenoxy) decyl-3-hydroxy-2-(hydroxylmethyl)-2-methylpropanoate (AZOD) and hydrophilic extenders of 2-ethyl-2-methylbutanoic acid (2,2-dimethylolpropionic acid, DMPA). Moreover, atomic force microscopy (AFM) and dynamic thermo-mechanical analysis (DMA) were used to characterize the viscoelasticity of the azo-containing WPU.

EXPERIMENTAL

Materials

All reagents were purchased from Aladdin and Innochem. Polycaprolactone diol (PCL, $M_n = 1000$, 112 mgKOH/g) with a hydroxyl value of 1.97 was dried at 105 °C under vacuum for 2 h to remove resident water before use. 1-Isocyanato-2-(isocyanatomethyl)-cyclohexane (isophorone diisocyanate, IPDI), 4-(phenyldiazenyl)phenol, 1,10-dibromononane, 2-ethyl-2-methylbutanoic acid (2,2-dimethylolpropionic acid, DMPA), dibutyltin dilaurate (DBTDL) and *N,N*-diethylethanamine (triethylamine, TEA) were used as received.

Synthesis of 1-(4-((10-Bromononyloxy)phenyl)-2-phenyldiazenyl)phenol (ANB)

The synthesis of ANB was carried out referring to a previously published procedure.^[31] Briefly, as shown in Scheme 1, 4-(phenyldiazenyl)phenol (4.96 g, 25.0 mmol), 1,10-dibromononane (15.0 g, 50.0 mmol) and KOH (1.64 g, 29.0 mmol) were dissolved in 150 mL of ethanol under N_2 atmosphere in a 250 mL two-neck round bottom flask. The reaction mixture was degassed at least 3 times in order to remove oxygen. The solution was refluxed for 12 h at 60 °C and cooled down to room temperature, and the resultant orange precipitate was purified by flash chromatography using silica gel. Elution with 5% ethyl acetate in hexane through the column yielded an orange solid. Molar yield: 70 mol%. ^1H -NMR (400 MHz, CD_3COCD_3 , δ , ppm): 7.95 (d, 2H), 7.89 (d, 2H), 7.60–7.49 (m, 3H), 7.12 (d, 2H), 4.15 (t, 2H), 3.51 (t, 2H), 1.92–1.81 (m, 4H), 1.59–1.32 (m, 12H).

Synthesis of 10-(4-(Phenyldiazenyl)phenoxy)decyl-3-hydroxy-2-(hydroxyl-methyl)-2-methylpropanoate (AZOD)

As shown in Scheme 2, a mixture of DMPA (3.35 g, 25.0 mmol), potassium hydroxide (1.46 g, 28.5 mmol), *N,N*-

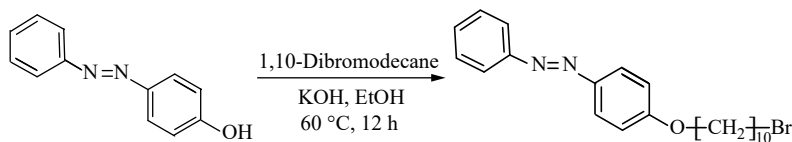
dimethylformamide (DMF, 2 mL) and acetonitrile (18 mL) was heated for 1 h at 100 °C. Then, ANB (8.34 g, 20.0 mmol) and DMF (40 mL) were added to the warm solution, and stirred for 16 h at 100 °C. The system was then cooled down to room temperature and filtered. Finally, the product was lyophilized and recrystallized from methanol to obtain yellow solid. Molar yield: 60 mol%. ^1H -NMR (400 MHz, CD_3COCD_3 , δ , ppm): 7.95 (d, 2H), 7.89 (d, 2H), 7.60–7.49 (m, 3H), 7.12 (d, 2H), 4.15 (t, 2H), 4.08 (t, 2H), 3.80–3.68 (m, 4H), 1.30–1.90 (m, 16H), 1.14 (s, 3H).

Preparation of the Azo-containing WPU Film

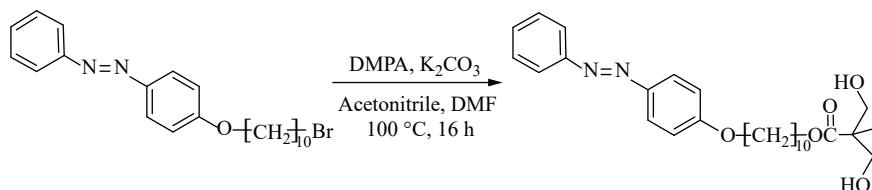
As shown in Scheme 3, PCL-1000 (18.0 g) was added into flask and kept at 85 °C in a N_2 atmosphere under continuous stirring (300 $r \cdot min^{-1}$). Then, IPDI (8.67 g, 39.0 mmol) and DBTDL (12.6 mg, 0.02 mmol) were added into the container and kept at this temperature for ~30 min until the amount of residual NCO groups reached the desired value (determined by di-*n*-butylamine back titration). After this step, DMPA (1.74 g, 13.0 mmol) and AZOD (0.94 g, 2.0 mmol) in 30 mL of acetone were added to the reactor for 6 h at 60 °C. Then, 90 mL of acetone was added into the reactor to reduce viscosity, and the reaction mixture was subsequently neutralized by TEA (1.32 g, 13.0 mmol) for 1 h at 45 °C. After that, 40 mL of deionized water was added to the flask with a high shearing rate (1500 $r \cdot min^{-1}$) for 1 h at 25 °C. As a result, the azo-containing WPU dispersion was obtained after the acetone was removed by a decompression rotary evaporator. Finally, AZO-WPU dispersion was poured into a Teflon dish and dried for 12 h at 85 °C to obtain AZO-WPU film.

Characterization

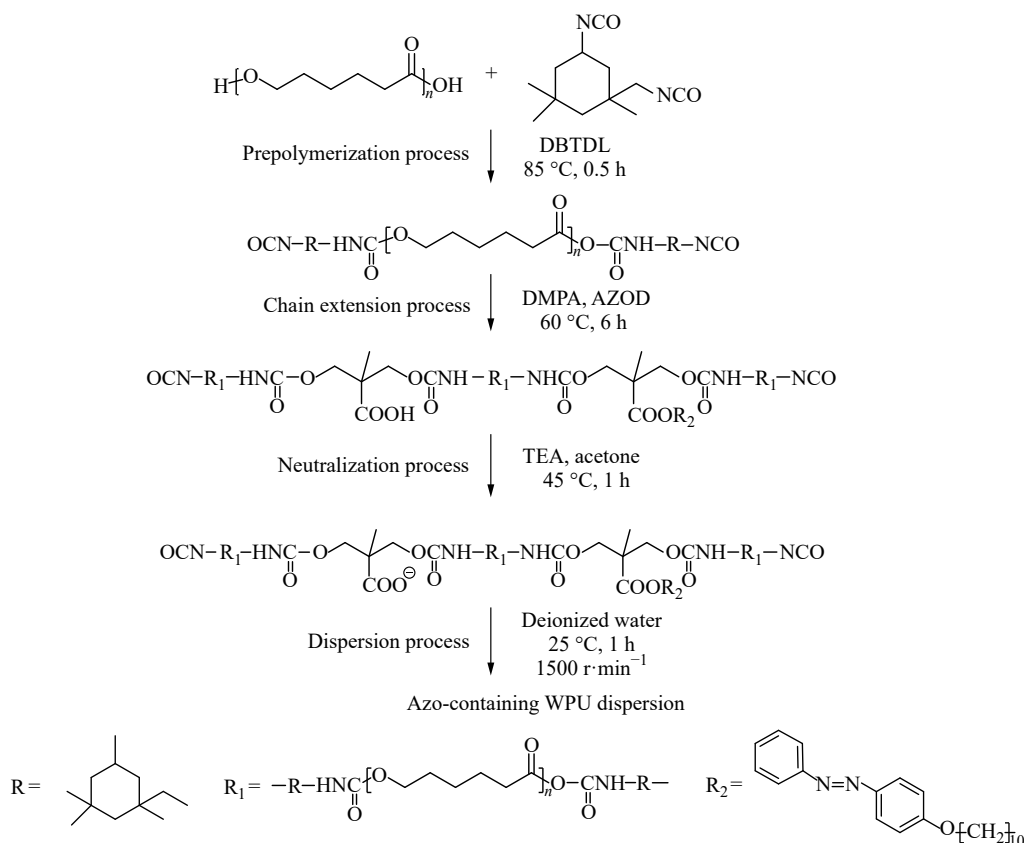
^1H -NMR (400 MHz) spectra were recorded in CD_3COCD_3 at 25 °C on a Varian Unity Inova 400 spectrometer. UV-Vis spectra of AZOD and azo-containing WPU were recorded by a UV-3600 spectrometer, with the scanning range of 250–500 nm and a slow scan mode. Molecular weight and molecular weight distribution (M_w/M_n) of azo-containing WPU were determined by gel permeation chromatography (GPC) against polystyrene standards with narrow molecular weight distribution on a Waters 2414 refractive index detector at 40 °C using DMF as the eluent. The surface morphology and adhesion of the azo-containing WPU films were measured by an atomic force microscope (AFM, Dimension Fastscan) with peakforce quantitative nanomechanics mode



Scheme 1 Synthesis route to ANB



Scheme 2 Synthesis route to AZOD



Scheme 3 Synthesis route to azo-containing WPU dispersion

and single crystal silicon AFM probe. Young's modulus and loss tangent ($\tan\delta$) were tested using a dynamic thermomechanical analyzer (DMA, DMA-25) at ambient temperature and with tensile mode.

RESULTS AND DISCUSSION

Preparation of Azo-containing WPU

In the case, AZOD was utilized as a chain extender and incorporated into WPU. Fig. 1 shows the ^1H -NMR spectrum of azo-containing WPU. The resonances with the chemical shifts at 7.95, 7.55 and 7.15 ppm are the characteristic signals of the protons in the benzene ring of AZOD units. In addition, the characteristic signal of methylene protons adjacent to the hydroxyl group in AZOD monomer at 3.71 ppm completely disappears in the azo-containing WPU, implying the successful incorporation of AZOD monomer into the WPU molecular chain. As a result, the content of AZOD can be estimated by the feed ratio as about 3.20%. Furthermore, a representative GPC profile of azo-containing WPU is displayed in Fig. 2. The weight-average molecular weight and molecular weight distribution are 1.33×10^5 and 1.80, respectively.

Optical Performance of AZOD and Azo-containing WPU

Fig. 3 shows the UV-Vis absorption spectra of azo-containing WPU and AZOD in DMF solution at 25 °C. The spectra of both nascent AZOD (up) and azo-containing WPU (bottom) reveal a significant absorption at about 350 nm attributed to *trans*-azo group and the characteristic absorption

peak of *cis*-azo group at about 440 nm. As shown in Fig. 3, irradiated by 365 nm light for 1 min, the absorption peak decreases at about 350 nm, and the absorption value increases at about 440 nm. When AZOD and azo-containing WPU were again irradiated with 450 nm light for 1 min, the absorption peak at about 350 nm reappears clearly and the absorption value at about 440 nm decreases. Compared with AZOD, azo-containing WPU shows significantly hypsochromic shift in the dispersion, which results from the larger $\pi-\pi^*$ band gap and H-aggregation of azo-units.^[27] These results indicate the reversible *trans*-to-*cis* photoisomerization of azo group. Further, the formation of isosbestic point depends on the relative concentration of *trans*/*cis* isomer during isomerization. In addition, the occurrence of isosbestic point indicates that the long alkane chain of AZOD and the polymer molecules did not hinder the isomerization process.^[32]

Effect of light irradiation with two different wavelengths on the viscoelasticity of azo-containing WPU was investigated by DMA. In the case, alternate cyclic irradiations were implemented using 450 nm Vis light and 365 nm UV light with a period of 120 s at 25 °C. As shown in Fig. 4, the Young's modulus and $\tan\delta$ were 22 MPa and 0.35 respectively, during the Vis light (450 nm) irradiation period. However, during the UV light (365 nm) irradiation period, the Young's modulus of WPU reduced to 2 MPa, whereas the $\tan\delta$ rapidly increased to 6000. Due to the photoisomerism of azobenzene, AZOD exhibited *cis* or *trans* isomer under the different wavelengths. As a consequence, it is suggested that the AZOD units in azo-containing WPU possessed a similar

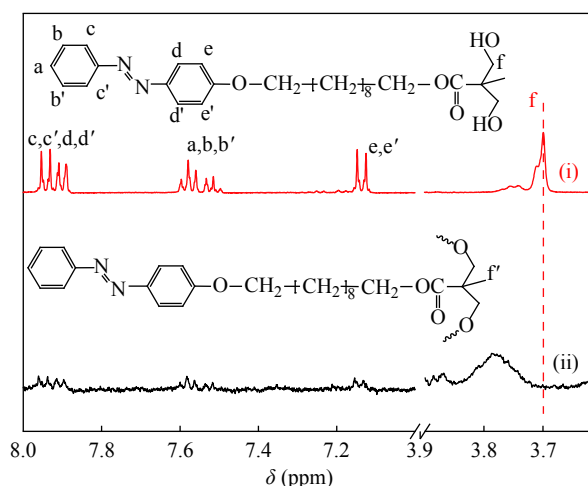


Fig. 1 ^1H -NMR spectra of AZOD monomer (i) and azo-containing WPU (ii)

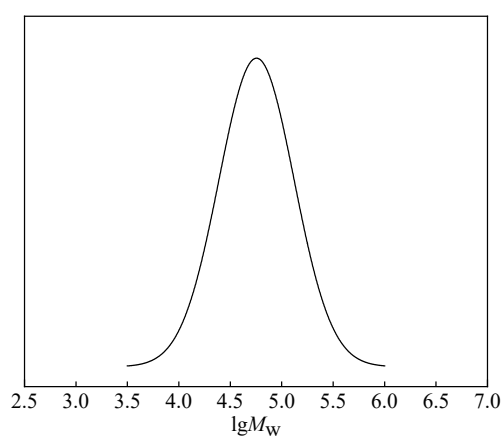


Fig. 2 A representative GPC profile of azo-containing WPU

behavior of photoisomerism. Moreover, photo-tuned property of azo-containing WPU was strongly dependent on the *cis* or *trans* structure of AZOD units under the different wavelengths. These results indicate that because of the photoisomerization of azo-pendant groups, the azo-containing WPU presented lower hardness and higher viscosity irradiated by UV light of 365 nm, while presented higher hardness and lower viscosity with Vis light of 450 nm. The images of azo-containing WPU film under the irradiation of Vis and UV are further displayed in Fig. 5.

Surface Morphology and Adhesion Performance of Azo-containing WPU Film

The AFM height image (Fig. 6) can express the influence of *trans-cis* photoisomerization of azo-pendant groups on the surface morphology and root mean square roughness (R_q) of azo-containing WPU film.^[33] After irradiation with 450 nm Vis light for 1 min, R_q reached higher value of 14.3 nm, indicating that the surface was rough. Subsequently, the film was irradiated by 365 nm UV light for 1 min and R_q decreased to 3.26 nm, implying that the surface became smooth. When the azo-containing WPU film was irradiated by 365 nm UV light, its surface roughness decreased. The decreased hardness and promoted viscosity resulted from the conversion within *trans* azo-pendant groups to *cis* isomerism. On

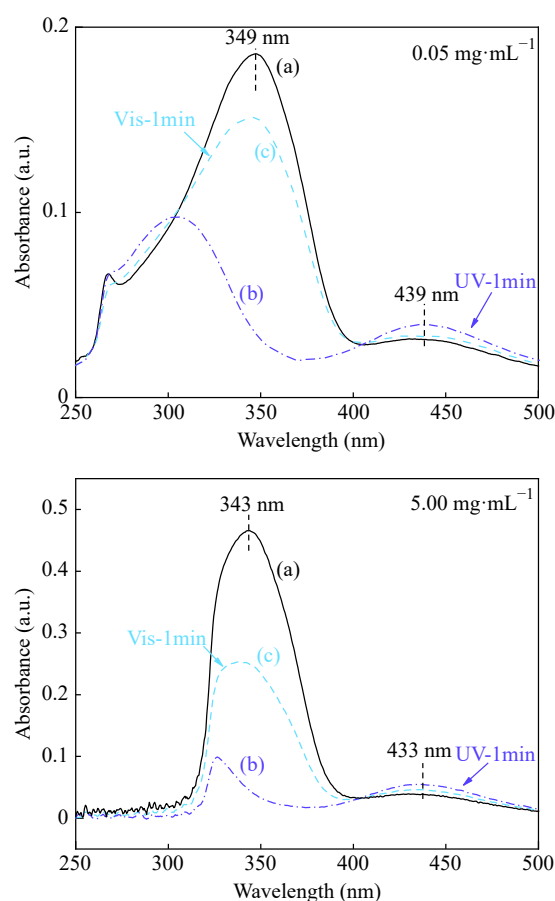


Fig. 3 UV-Vis absorption spectra of AZOD (up) and azo-containing WPU (bottom) in DMF solution at 25 °C: (a) Nascent AZOD and azo-containing WPU, (b) irradiation with 365 nm UV light ($100 \text{ mW}\cdot\text{cm}^{-2}$) for 1 min, and (c) radiation with 450 nm Vis light ($50 \text{ mW}\cdot\text{cm}^{-2}$) for 1 min

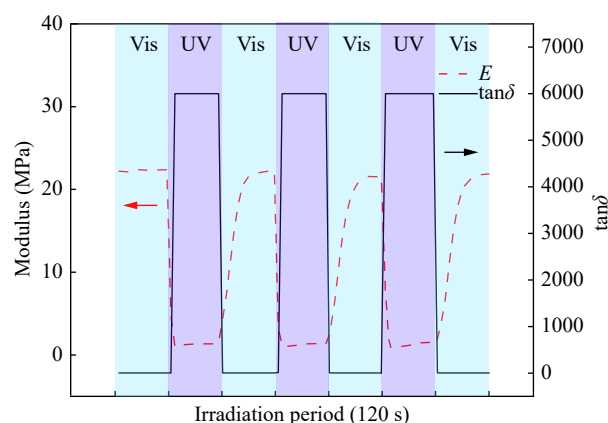


Fig. 4 DMA curves of modulus and $\tan\delta$ as a function of irradiation period for azo-containing WPU film (film thickness 31 nm) irradiated by 450 nm Vis light ($50 \text{ mW}\cdot\text{cm}^{-2}$) and 365 nm UV light ($100 \text{ mW}\cdot\text{cm}^{-2}$) for 120 s at 25 °C respectively

the contrary, after irradiation with the 450 nm Vis light, the *cis* azo-pendant groups converted to *trans* isomerism resulting in the increase of hardness and decrease of viscosity for azo-containing WPU. As reported by Zhou *et al.*,^[22] the changes of glass transition temperature (T_g) and viscous flow temperature (T_f) were able to give a reasonable explanation.

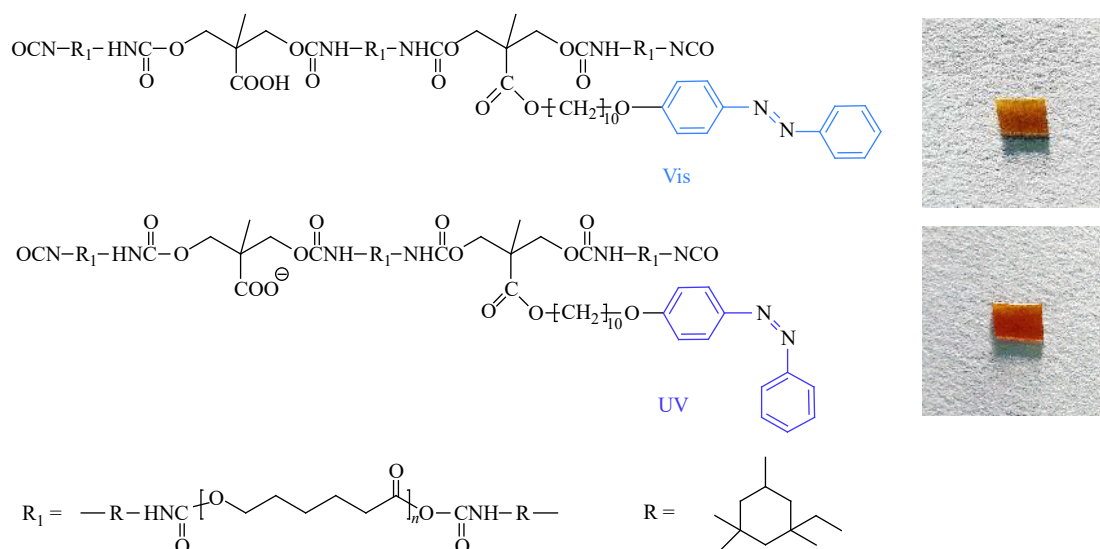


Fig. 5 The chemical structures and corresponding images of azo-containing WPU film under the irradiation of Vis (450 nm) and UV (365 nm)

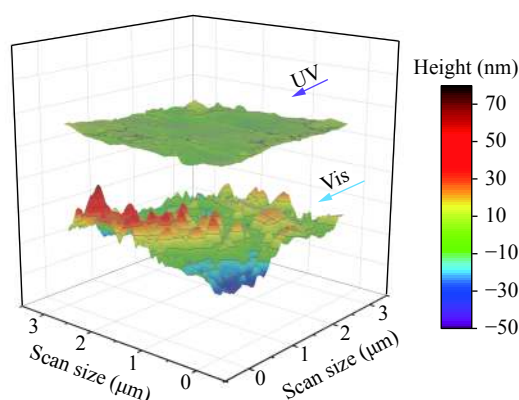


Fig. 6 AFM height image of azo-containing WPU film (film thickness 30 nm) after irradiation with 365 nm UV light (top, 100 mW·cm⁻²) and 450 nm Vis light (bottom, 50 mW·cm⁻²) for 1 min at 25 °C

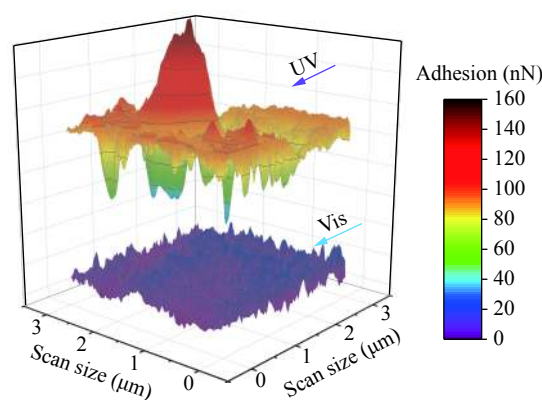


Fig. 7 AFM adhesion images of azo-containing WPU film (film thickness 30 nm) after irradiation with 365 nm UV light (top, 100 mW·cm⁻²) and 450 nm Vis light (bottom, 50 mW·cm⁻²) for 1 min at 25 °C

Since the *cis* isomer required more free volume,^[34] the distance between molecular chains increased after UV irradiation, leading to higher $\tan\delta$ and lower T_f . So, the surface of azo-containing WPU became very soft and flat, which gave lower roughness. As a consequence, the surface roughness of azo-containing WPU film was photo-switchable under the UV-Vis light.

The adhesion of azo-containing WPU with single crystal silicon AFM probe can also be determined by AFM using peakforce quantitative nanomechanics mode.^[35] As shown in Fig. 7, the mean value of adhesion was 13 nN by irradiation with 450 nm light for 1 min at 25 °C, but it increased rapidly to 82 nN when irradiated with 365 nm light for the same time and at the same temperature. These results suggest that the interaction force between azo-containing WPU and single crystal silicon probe was weaker by irradiation with 450 nm light resulting from the increase of hardness and decrease of viscosity of WPU. By contrast, the interaction force increased rapidly due to much higher viscosity of WPU by irradiation with 365 nm light.

CONCLUSIONS

In conclusion, WPU containing pendant azo-groups was synthesized using 10-(4-(phenyldiazenyl)phenoxy)decyl-3-hydroxy-2-(hydroxyl-methyl)-2-methylpropanoate as chain extender. The effect of reversible *trans-cis* photoisomerization of the azo-containing pendant groups on the viscoelasticity of azo-containing WPU was investigated by AFM and DMA. The azo-containing WPU exhibited reversible stimuli-responsive smart properties of viscoelasticity with UV-Vis light irradiation. Moreover, the azo-containing WPU would likely be applied in the field of smart materials and microsensors.

ACKNOWLEDGMENTS

This work was financially supported by the Guangzhou Science and Technology Plan Project (No. 201607010348).

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