Electronic Supplementary Information

Photoinduced Deformation of Amorphous Polyimide Enabled by

Improved Azobenzene Isomerization Efficiency

Xuejie Sun, Jia Wei,* and Yanlei Yu*

Department of Materials Science and State Key Laboratory of Molecular Engineering

of Polymers, Fudan University, 220 Handan Road, Shanghai, 200433, China.

1. Synthesis and characterization

Synthesis of intermediate product A3: A2 (0.02 mol), dichloromethane (50 mL) and triethylamine (0.04 mol) were added to 100-mL flask and cooled in ice-water. Then, the dichloromethane solution (10 mL) containing 3,5-dinitrobenzoyl chloride (0.024 mol) was added to the above flask drop by drop, followed by reaction for 6 h. After chromatographic separation, the product A3 was obtained.

Synthesis of DAC3AB-PI film: The DAC3AB-PI film was synthesized according to the literature.¹



Fig. S1 Synthesis route of DAC3AB-PI.



Fig. S2 ¹H NMR spectrum of s-DAC11AB.

The FT-IR spectrum: the characteristic peaks at 1787 cm⁻¹ and 1730 cm⁻¹ correspond to the symmetric and asymmetric vibration of carbonyl group (C=O). The absorption peak at 1353 cm⁻¹ corresponds to the asymmetric vibration of C-N. The characteristic peak around 3300 ~ 3500 cm⁻¹ corresponding to the carboxyl group (-COOH) disappeared, indicating that the polyimide was successfully synthesized and the imidization processing was completed.



Fig. S3 FT-IR spectrum of s-DAC11AB-PI.

2. Results and Discussions

The glass transition temperature (T_g) of the s-DAC11AB-PI film measured by differential scanning calorimetry (DSC) is ~ 147 °C which measured by dynamic mechanical analysis (DMA) is ~ 167 °C. The storage modulus (E') of the s-DAC11AB-PI film was evaluated by DMA. As shown in Fig. S5, the storage modulus reached 1.35 GPa at 25 °C and decreased with increasing temperature, when the temperature increased to T_g , the storage modulus decreased sharply due to the free motions of the molecular chains in high elastic state.



Fig. S4 (a) DSC and (b) DMA curves of the s-DAC11AB-PI film.

The isotropic characteristic of the s-DAC11AB-PI film was also confirmed by POM photographs. When rotating the s-DAC11AB-PI sample, there was no periodic bright and dark change, indicating the random arrangement of molecular chains in the film.



Fig. S5 POM photographs of the s-DAC11AB-PI film. There was no periodic change from dark to bright field at the polarization angle of 0°, 45° and 90°.



Fig. S6 WXRD curves of the s-DAC11AB-PI film before and after UV light irradiation.



Fig. S7 Photoinduced deformation of the unstretched DAC3AB-PI film under unpolarized UV light irradiation. The sample size: 5 mm \times 1 mm \times 20 μ m.¹



Fig. S8 UV-vis absorption spectra of the DAC3AB-PI film under the UV light (365 nm, 35 mW/cm²) irradiation. The film thickness: ~ 3 μ m.



Fig. S9 The relationship of bending angle and irradiation time of the s-DAC11AB-PI film under the UV (365 nm, 70 mW/cm²) and visible (530 nm, 80 mW/cm²) light irradiation.



Fig. S10 The thermal relaxation of the s-DAC11AB-PI film in the darkness.

3. References

(1) P. P. Zhang, Z. X. Lan, J. Wei and Y. L. Yu, ACS Macro Lett., 2021, 10, 469-475.