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Light-driven Mechanical Property Modulation in Azobenzene-crosslinked Slide-ring Polymers

Xiaoqing Wang[a,b,†], Qimo Mao[a,†], Shiyu Zhao[a], Maolin Wang[a], Chenjuan Yu[a], and Yuping Wang[a,b,c*]

[a] *Stoddart Institute of Molecular Science, Department of Chemistry, Zhejiang University, Hangzhou 310058, China*
[b] *Zhejiang-Israel Joint Laboratory of Self-Assembling Functional Materials, ZJU-Hangzhou Global Scientific and Technological Innovation Center, Zhejiang University, Hangzhou 310058, China*
[c] *State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China*

Electronic Supplementary Information

Abstract The rational design of stimuli-responsive materials exhibiting tunable mechanical properties represents a critical strategy for preventing structural failure and extending service lifetime. Slide-ring polymers with their dynamically mobile crosslinks provide an ideal architectural platform for the development of mechanically adaptive systems. Herein, we fabricate photo-responsive mechanically adaptive slide-ring materials (PSR) employing azobenzene as crosslinkers. Mechanical characterization reveals substantial light-induced enhancement in performance, including breaking strain, tensile strength, and toughness. The materials subjected to photo-irradiation also demonstrate superior energy dissipation and damping efficiency. Through comprehensive mechanical characterization, we reveal a dual photoregulation mechanism in which light-induced *cis*-azobenzene formation (1) enhances interchain hydrogen bonding *via* strong local dipole moments and localized conformational rearrangements, and (2) expands the internal free volume *via* the steric hindrance of the *cis*-isomer, thereby unlocking the mobility of crown ether rings in the slide-ring architecture. This work establishes a new design principle for photoresponsive polymers, whose mechanical properties can be precisely modulated through light-controlled molecular rearrangements.

Keywords Polyrotaxanes; Mechanically interlocked structures; Photoresponsive materials; Azobenzene; Topological mobility

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INTRODUCTION

Nature has perfected dynamic responsive systems through billions of years of evolution, from the sun-tracking movements of sunflowers to the rapid leaf-folding response of Mimosa pudica.[1–4] These biological systems have inspired the development of synthetic materials capable of adaptive mechanical responses, which are crucial for emerging applications in soft robotics, wearable devices, and smart medical implants.[5–8] Among the synthetic candidates, mechanically interlocked polymers have emerged as particularly promising candidates owing to their unique topological architectures and dynamic mechanical bond characteristics.[9–15] Within this class, slide-ring polymers stand out because they incorporate mobile crosslinks that enable exceptional mechanical adaptability through their distinctive sliding dynamics.[16–21]

Current synthetic strategies for slide-ring polymers primarily follow two approaches: direct copolymerization of [2]pseudorotaxane monomers, which offers synthetic simplicity,[22–24] and post-assembly crosslinking of preformed polyrotaxanes, which provides superior architectural control.[25–27] While these methods have successfully established key structure-property relationships through systematic variation of parameters such as macrocycle size,[28,29] quantity,[30] main chain length,[31–33] steric hindrance,[34,35] and crosslinker type,[36–38] they have predominantly focused on optimizing static systems. The critical challenge of incorporating dynamic responsiveness into slide-ring polymer networks remains largely unaddressed, representing a significant gap in this field.

Light-responsive systems offer compelling advantages for dynamic materials owing to their noncontact operation, precise spatiotemporal control, and rapid response characteristics.[39–45] Azobenzene derivatives are particularly attractive as molecular switches and undergo reversible *trans-cis* photoisomerization upon irradiation.[46–48] This molecular-scale transformation induces substantial changes in both the molecular geometry[49,50] and dipole moment[51,52], leading to an increase in free volume and an enhancement of hydrogen-bonding interactions within the polymer network.[53–55] These properties make azobenzene an ideal candidate for engineering photoresponsive behavior in slide-ring polymer networks.

* Corresponding author, E-mail: y.p.wang@zju.edu.cn
† These authors contributed equally to this work.
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In this study, we report the development of photo-responsive slide-ring materials (PSR) that exploit the unique photochemistry of azobenzene to achieve dual-mode mechanical adaptation (Fig. 1). By performing stress-strain tests and dynamic mechanical analyses, we demonstrate that the photoisomerization of azobenzene crosslinkers simultaneously modulates two key aspects of material behavior: first, by controlling the macrocycle mobility through the reversible tuning of the internal free volume *via* photoinduced conformational transitions, and second, by leveraging the strong local dipole moment generated upon isomerization to promote the conformational rearrangement of polar side groups, thereby dynamically optimizing and strengthening the intra- and inter-chain hydrogen-bonding network. This sophisticated control mechanism enables remarkable enhancements in mechanical performance upon irradiation, including a 76% increase in toughness (from 17.00 MJ/m^3 to 29.94 MJ/m^3) and a 43% improvement in energy dissipation capacity (from 7.50 MJ/m^3 to 10.69 MJ/m^3). This study establishes a new strategy for the design of adaptive polymer materials that combines rapid photoresponse with robust mechanical performance. The fundamental insights gained into the relationship between molecular-scale photochemistry and macroscopic material properties provide a foundation for the future development of advanced functional materials with precisely controllable mechanical behaviors.

EXPERIMENTAL

The detailed experimental section is provided in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Design, Synthesis, and Structural Characterization

Photo-responsive slide-ring polymers (PSRs) were synthesized through a stepwise process combining supramolecular assembly and covalent polymerization.[24] The initial formation of

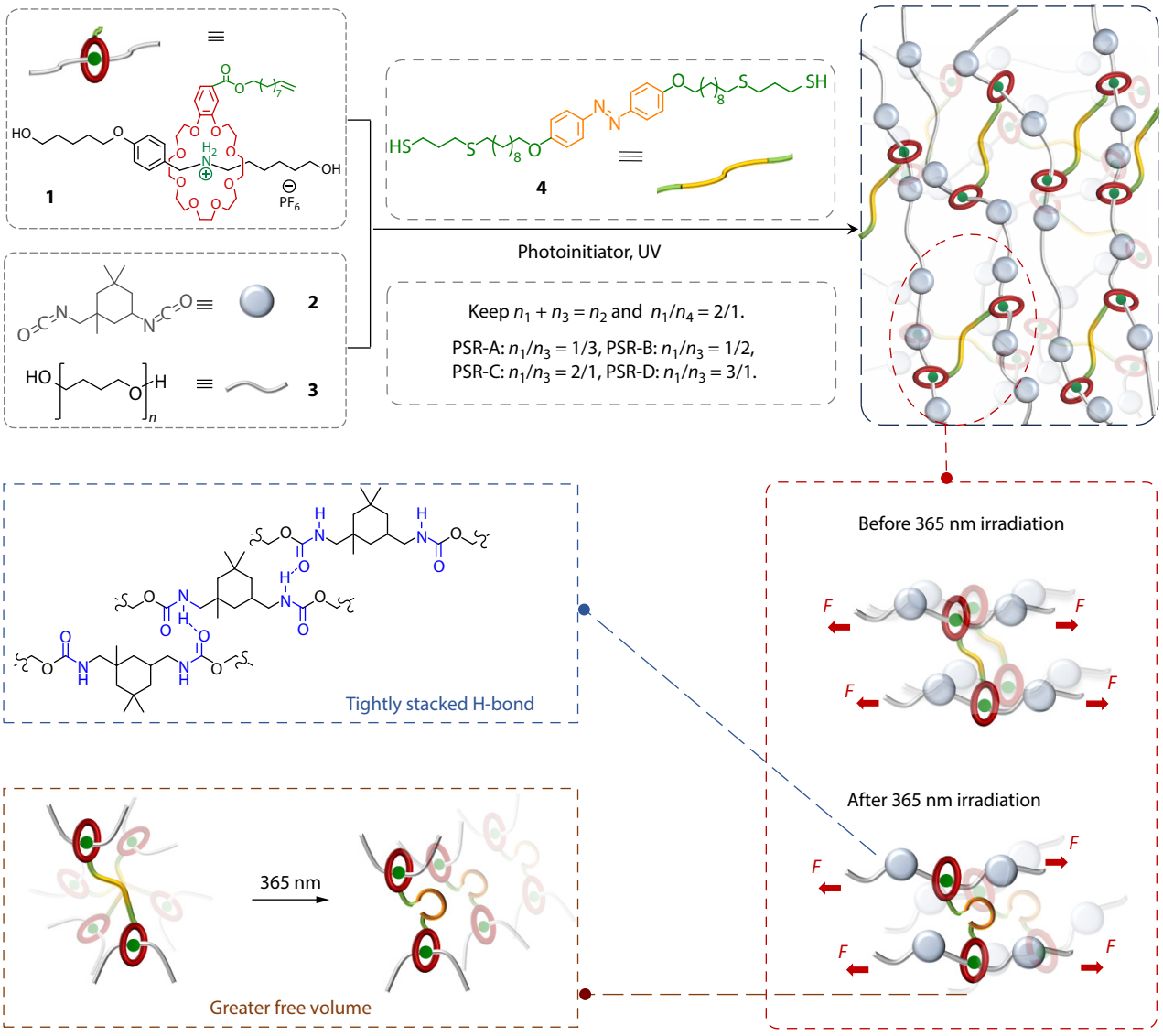


Fig. 1 Schematic representation of the preparation of PSRs and how light irradiation affects their mechanical properties.

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pseudorotaxane **1** was achieved through host-guest complexation between a bis-hydroxyl-functionalized axle and a vinyl-terminated benzo-24-crown-8 (B24C8) macrocycle, as confirmed by the characteristic upfield shifts of the B24C8 aromatic protons in the ^{1}H-NMR spectra (Fig. 2a and Fig. S5 in ESI) and electrospray ionization mass spectrometry (ESI-MS) signals (Fig. S6 in ESI). Subsequent incorporation of this supramolecular building block into a polyurethane backbone *via* step-growth polymerization with **2** and **3** yielded well-defined polyrotaxanes (Fig. 1), with NMR analysis confirming the retention of >80% host-guest complexation and preservation of the vinyl groups on the rings necessary for subsequent crosslinking (Fig. 2a).

The final PSR networks were constructed using UV-initiated thiol-ene click chemistry between the vinyl groups on polyrotaxane and dithiol-functionalized azobenzene **4** (Fig. 1). As the *cis-trans* isomerization of azobenzene shortens the terminal distance of the attached chains, with longer chains showing greater shortening, we chose the alkyl-extended azobenzene **4** as the crosslinker.[56] Systematic variation of the poly(tetramethylene ether)glycol (PTMG) **3** to pseudorotaxane **1** feed ratio (Table S1 in ESI), while maintaining the stoichiometric ratio between thiol and vinyl groups at 1/1, produced four polymer variants (**PSR-A** to **PSR-D**) with graded crosslink densities and the azobenzene-free control polymer **PSR-Ref** (Fig. S13 in ESI). Fourier transform infrared spectroscopy (FTIR) confirmed complete network formation, showing the disappearance of both the vinyl C=C stretch (1652 cm^{-1}) and thiol S—H vibration (2554 cm^{-1}) (Fig. 2b and Fig. S14 in ESI). Detailed experimental procedures and full synthetic characterization data are provided in ESI.

Swelling experiments in DMF demonstrated the interplay between the crosslink density and topological freedom, with swelling ratios ranging from 620% (**PSR-A**) to 318% (**PSR-D**) (Fig. 2c). Notably, even the most densely crosslinked variants (**PSR-D**) maintained swelling ratios greater than 300%, reflecting the unique mobility afforded by the slide-ring architecture.[57] The network integrity was further confirmed by its complete insolubility in THF, acetone, DCM, and acetonitrile (Fig. S15 in ESI). This characterization establishes both the structural precision of the designed synthetic approach and the preservation of the dynamic behavior in the prepared PSRs.

Fundamental Performance Characterizations

With **PSR-A**–**PSR-D** in hand, their thermal and photoresponsive properties were systematically characterized. Thermogravimetric analysis (TGA) reveals excellent thermal stability across all four **PSR** samples, with 5% weight loss temperatures ($T_{d,5\%}$) ex-

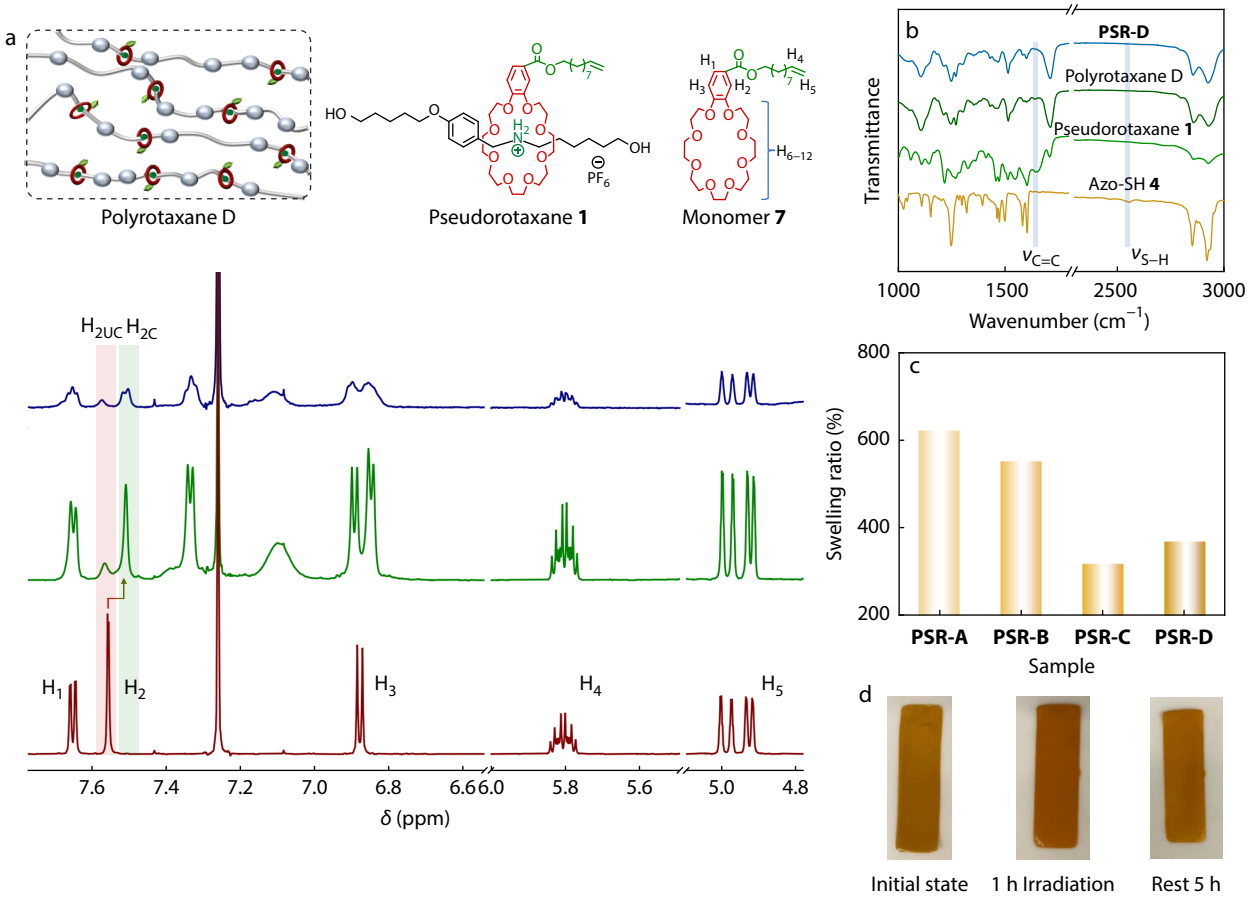


Fig. 2 (a) Comparative ^{1}H-NMR spectra (600 MHz, $CDCl_3$, 25 °C) showing characteristic upfield shifts of crown ether protons (H_2) upon pseudorotaxane formation (middle) and preserved host-guest complexation in polyrotaxane D (upper), with monomer **7** as reference (lower); (b) FTIR spectral evolution demonstrating complete thiol-ene click reaction: disappearance of vinyl (1652 cm^{-1}) and thiol (2554 cm^{-1}) stretches in **PSR-D**; (c) Crosslink density-dependent swelling behavior in DMF (318%–620%); (d) Visual demonstration of photomechanical response in **PSR-D**, showing UV-induced color changes.

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ceeding 210 °C (Fig. S16A in ESI). Differential scanning calorimetry (DSC) further shows that the glass transition temperature (T_g) increased progressively from –6.1 °C (**PSR-A**) to 18.8 °C (**PSR-D**), correlating with the higher azobenzene crosslinker density in the slide-ring system (Fig. S16B in ESI).[58] The markedly elevated T_g values of **PSR-C** and **PSR-D** compared with those of **PSR-A** and **PSR-B** suggest restricted polymer segment mobility owing to their denser crosslinking networks.

To verify the *trans-cis* photoisomerization capability of the azobenzene units in the polymer networks, we examined the photoresponsive behavior of **PSR-D** as a representative sample and compared it to that of monomer **4**. UV irradiation (5 min) of monomer **4** induced complete disappearance of the 362 nm absorption peak and concurrent emergence of a new peak at 448 nm, accompanied by a distinct color change from orange to reddish-orange, confirming successful *trans-cis* photoisomerization (Fig. S17A in ESI).[46–48] This process proved reversible, with visible light exposure (5 h) restoring the original trans-configuration and orange coloration (Fig. S17B in ESI). Importantly, the crosslinked network **PSR-D** exhibited analogous behavior: 365 nm irradiation (1 h) generated an orange-yellow color that gradually reverted to its initial state after 5 h (Fig. 2d and Fig. S17C in ESI), demonstrating that the photoisomerization remains effective when azobenzene units are incorporated into the polymer network architecture.

Mechanical Properties

The facile and reversible isomerization of azobenzene units within **PSRs** enabled systematic investigation of their influence on mechanical properties. Tensile testing of **PSR-A**–**PSR-D** reveals distinct stress-strain behaviors both before and after photoirradiation (Figs. 3a–3d and Table S2 in ESI), whereas the control network **PSR-Ref** exhibits no significant changes in mechanical properties before and after photoirradiation (Fig. S24 in ESI). To evaluate the reversibility of the photoinduced mechanical changes, a UV-irradiated **PSR-D** sample underwent 12-h recovery under ambient visible light. Mechanical testing revealed that **PSR-D** exhibited near-complete recovery of maximum strain (685% versus initial 638%), stress (4.58 versus initial 3.83 MPa), toughness (17.12 versus initial 21.64 MJ/m^3), and elastic modulus (9.89 versus initial 10.87 MPa), likely due to incomplete re-stacking of *trans*-azobenzene hard segments during the relaxation process (Fig. S22 and Table S3 in ESI). Initial characterization of unirradiated samples showed that increasing azobenzene and pseudorotaxane content from **PSR-A** to **PSR-D** led to a marked increase in elastic modulus (0.3 MPa to 7.64 MPa) accompanied by a decreased maximum strain (2813% to 573%), consistent with the enhanced crosslinking density (Figs. 3e and 3f and Table S2 in ESI).[59] Interestingly, while the maximum strain decreased sharply from **PSR-A** to **PSR-C**, the reduction was moderated between **PSR-C** and **PSR-D**. This nonlinear response, coupled with the observed V-shaped toughness trend (Fig. 3f), suggests that the dynamic sliding of crown ether rings provides compensatory mobility that partially offsets the network rigidification at higher crosslink densities.

While light exposure had a negligible influence on **PSR-A** owing to its low azobenzene content, photoirradiation induced significant mechanical property changes in **PSR-B**–**PSR-D** systems. The most pronounced photoresponse occurred in **PSR-D**, which exhibited an increased breaking strain

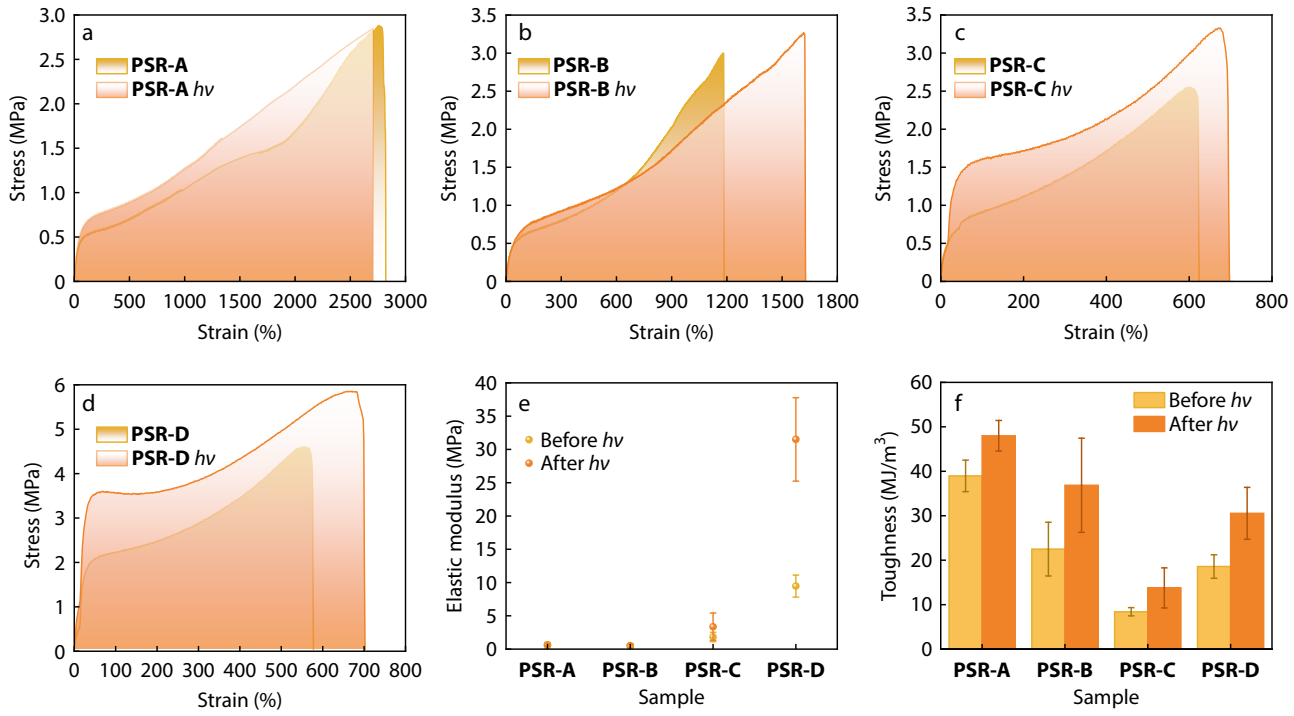


Fig. 3 Photomechanical switching of slide-ring polymers. (a–d) Stress-strain curves showing UV-induced enhancement in mechanical performance across **PSR-A**–**PSR-D** (100 mm/min, 25 °C), with **PSR-D** exhibiting pronounced fracture strain increase and tensile strength boost; (e, f) Quantitative comparison of elastic modulus and toughness, revealing consistent light-triggered (e) elasticity modulus increase and (f) toughness amplification, regardless of crosslink density (n>3).

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(573% to 700%), elastic modulus (7.64 MPa to 26.58 MPa), maximum stress (4.60 MPa to 5.85 MPa), and toughness (17.00 MJ/m^3 to 29.94 MJ/m^3). This multifaceted enhancement can be attributed to two complementary microscopic mechanisms triggered by photoisomerization: first, the steric hindrance of the *cis*-isomer expands the internal free volume of the network, increasing ring mobility and consequently improving the maximum strain. Second, the strong local dipole moment generated by the *cis*-configuration acts as a crucial electrostatic driving force, which, combined with the localized motional freedom afforded by network loosening, promotes the conformational rearrangement of polar side groups and strengthens the intermolecular hydrogen-bonding network, thereby boosting the stiffness and strength of the polymer network.[56,60–62] These findings demonstrate successful light-induced mechanical reinforcement through azobenzene incorporation.

Dynamic mechanical analysis (DMA) of **PSR-D** with maximal azobenzene content further validated this photomechanical coupling. Frequency-dependent measurements reveal marked light-induced stiffening, with irradiated samples showing substantially elevated storage moduli (*G*') at frequencies above 1.0 Hz (Fig. S18 in ESI). The excellent correlation between DMA and the tensile data confirms that azobenzene photoisomerization can effectively and reversibly modulate the bulk mechanical properties of these slide-ring polymers, establishing their potential for advanced photoresponsive applications.

Cyclic Tensile Behavior and Energy Dissipation Characteristics

The dynamic mechanical characteristics of **PSR-D** were thoroughly investigated through cyclic tensile testing and recovery experiments under both pristine and photoactivated conditions. Wide-strain cyclic testing (100%–500%) reveals that **PSR-D** maintained excellent energy dissipation capacity regardless of the irradiation state, with a linear correlation between dissipated energy and maximum strain (Fig. 4a and Fig. S19 in ESI).[63] Notably, photoactivated samples consistently demonstrated about 1.5 MJ/m^3 greater energy dissipation across all strain levels, attributable to the *cis*-azobenzene configuration's dual effect of enhancing ring mobility while strengthening interchain hydrogen bonding. This confirms successful photoregulation of the mechanical properties through strategic azobenzene incorporation in the slide-ring architecture.

A more detailed analysis at a fixed strain of 400% shows significant hysteresis in both the irradiated and non-irradiated states during the initial loading-unloading cycles (Fig. 4b), arising from the combined effects of hydrogen bonding and the characteristic pulley mechanism. Photoirradiation further improved the energy dissipation (10.69 versus 7.50 MJ/m^3) and damping efficiency (91% versus 89%) (Fig. 4c). These improvements are consistent with the strain-dependent results and confirm the dual-tuning mechanism, where *cis*-azobenzene simultaneously strengthens intermolecular interactions while enhancing ring mobility. The cyclic stress-strain tests also revealed distinct recovery properties; when immediately retested, both systems showed diminished hysteresis (Figs. 4d and 4e) due to kinetic limitations in dynamic bond reformation. After 60-min recovery, the non-irradiated samples regained 51% of their initial configuration compared with only 27% of the irradiated specimens (Fig. 4f). This substantial dif-

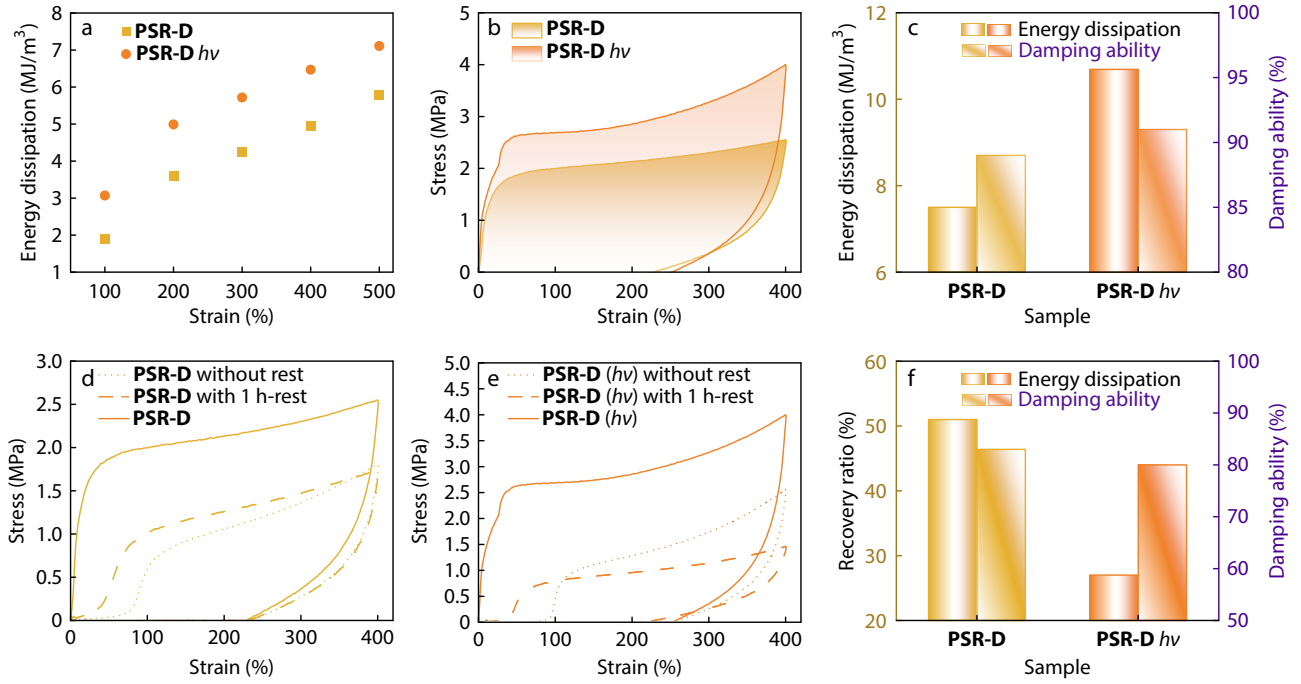


Fig. 4 Photomodulated energy dissipation in **PSR-D**. (a) Strain-dependent energy dissipation comparison showing UV-induced enhancement; (b) Representative cyclic tensile curves demonstrating improved hysteresis loop area post-irradiation; (c) Quantitative analysis revealing simultaneous increase in both energy dissipation and damping ability; (d, e) Cyclic performance with/without 60 min recovery intervals, highlighting the interplay between photoresponsiveness and self-recovery; (f) Comparison of recovery ratio and damping ability of irradiated and non-irradiated **PSR-D** after stretching and 1 h rest.

ference arises because light-activated ring mobility allows crown ethers to slide beyond effective host-guest recognition distances, thereby slowing molecular repositioning. Remarkably, despite these recovery differences, both systems maintained exceptional damping performance (>75%) after relaxation, highlighting their robust energy-dissipation characteristics regardless of the photostate.

Temperature-dependent dynamic mechanical analysis provided additional insights into the damping performance. Both irradiated and non-irradiated **PSR-D** exhibit thermomechanical stability from −60 °C to 100 °C, with storage modulus consistently exceeding loss modulus (Figs. 5a and 5b). The tanδ profiles revealed broad effective damping windows (tanδ>0.3)[64] of 33–72 °C (non-irradiated) and 35–73 °C (irradiated), with peak values increasing from 0.77 to 0.82 upon irradiation (Fig. 5c). In the DMA experiment, only a small deformation was applied to the material; therefore, the minor change in the tanδ peak primarily reflects the local network structural changes induced by the *cis-trans* isomerization of the azobenzene units. Conversely, large-strain cyclic tensile tests (Fig. 4f) show that there was a significant difference in energy dissipation before and after photoirradiation. Under large deformations, the slide-ring crosslinking points underwent extensive sliding. This significant difference between the small-strain and large-strain states proves that the photoisomerization of azobenzene acts as a structural switch, thereby effectively enhancing the sliding capability of rotaxane rings under macroscopic large deformations.

Photo-regulated Mechanical Properties

To elucidate the photoregulation of the bulk mechanical properties, we conducted comprehensive DMA studies on **PSR-D**, including stress relaxation experiments and creep recovery at ambient temperature. The results of stress relaxation are shown in Fig. 5(d). After light exposure, **PSR-D** exhibits a relatively more rapid stress relaxation response. This result is consistent with the energy dissipation behavior. These findings implied that azo-crosslinked **PSR-D** could exploit the photoresponsive behavior of azobenzene to modulate its mechanical properties.

Creep and recovery experiments were performed to further understand the mechanical properties of **PSR-D**. Under different stresses (0.5−1.0 MPa), **PSR-D** exhibits similar creep-recovery behavior before and after light exposure, notably with a rapid increase in creep strain under higher stress conditions (1.0 MPa) (Fig. S20 in ESI). Interestingly, at low stress (0.5 MPa), non-irradiated samples exhibited greater creep compliance but comparable recovery to irradiated specimens, whereas under high stress (1.0 MPa), photoactivated **PSR-D** demonstrated significantly enhanced creep strain and recovery capacity (Fig. 5e and Fig. S21 in ESI). This observed stress-dependent response presumably stems from a fundamental competition between two distinct molecular mechanisms that govern the network behavior under different loading conditions. In the low-stress regime, the mechanical properties are primarily dictated by hydrogen-bonding interactions within the network, where the *cis*-azobenzene configuration plays a crucial role in strengthening these intermolecular connections. The enhanced hydrogen bonding in this photostate effectively restricts chain mobility, thereby improving the resistance of the material to creep deformation. Conversely, under high-stress conditions, the mechanical response shifts to being dominated by the mobility of the crown ether rings within the slide-ring architecture. In this regime, the *cis*-azobenzene configuration becomes particularly significant because its non-planar, bulky structure increases the internal free volume of the network. This endows the crown ether rings with higher dynamics, thereby reduc-

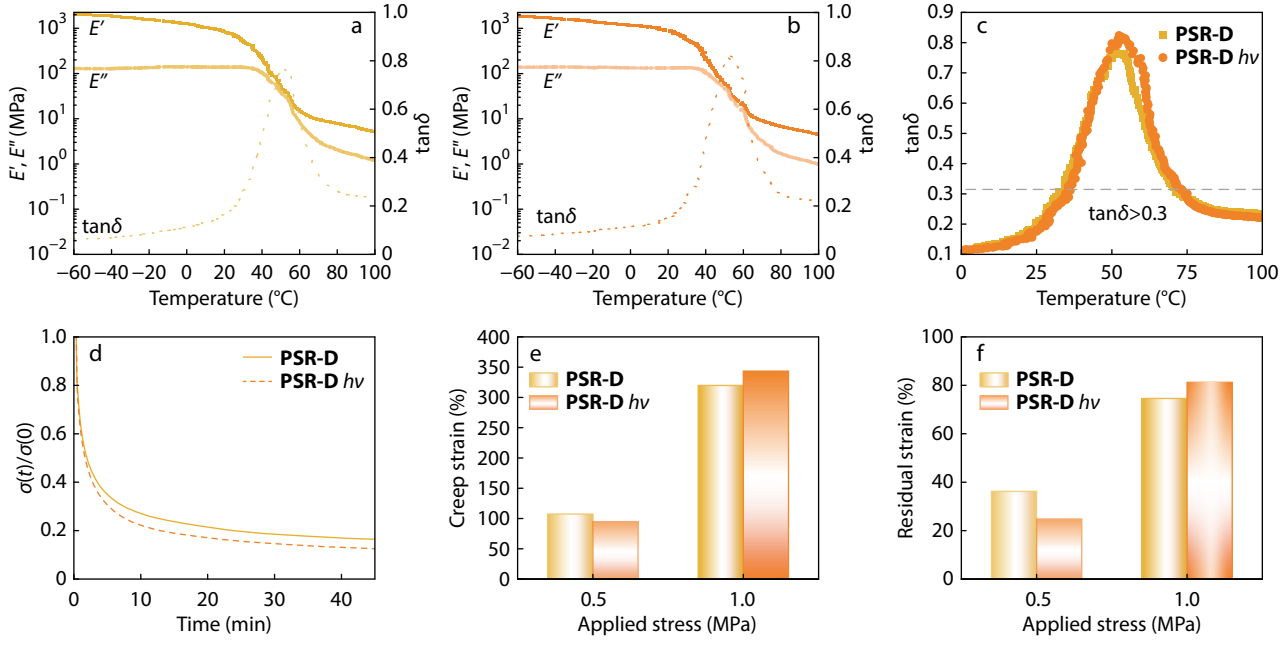


Fig. 5 (a, b) DMA curves of **PSR-D** recorded during the heating process from −60 °C to 100 °C with a heating rate of 5.0 °C/min; (c) DMA analysis reveals UV-induced shifts in tanδ peaks, indicating enhanced energy dissipation capability after irradiation; (d) Stress relaxation profiles of **PSR-D** before and after photoirradiation at room temperature; (e) The change in creep strain of **PSR-D** before and after illumination exhibits different trends under varying stresses; (f) The residual strain of **PSR-D** at 1.0 MPa is greater than that at 0.5 MPa.

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ing the creep resistance of the material under high stress. The residual strain analysis further supported this interpretation, where hydrogen bond-mediated deformations exhibit superior elastic recovery (<40% residual strain), whereas ring-sliding-dominated deformations show a more pronounced permanent set (>70% residual strain) (Fig. 5f). Therefore, the overall working process of the azo-crosslinked **PSR-D** was well demonstrated by the creep and recovery results.

CONCLUSIONS

In this study, we successfully developed a novel class of photoresponsive slide-ring polymers by strategically incorporating azobenzene units as dynamic crosslinkers. Through comprehensive mechanical characterization, we demonstrated that UV irradiation triggers substantial property enhancements in the optimized **PSR-D** system, including a 22% increase in maximum strain (573%→700%), 27% improvement in tensile strength (4.60 MPa→5.85 MPa), 76% boost in toughness (17.00 MJ/m^3→29.94 MJ/m^3), and 43% greater energy dissipation capacity (7.50 MJ/m^3→10.69 MJ/m^3). These improvements stem from a unique dual-regulation mechanism: the formation of cis-azobenzene strengthens intra- and interchain hydrogen bonding, while simultaneously liberating crown ether mobility by expanding the internal free volume of the material.

By combining the topological benefits of slide-ring architectures with molecular photoswitches, we established a new approach for designing smart materials with photo-tunable mechanical performance. This work not only advances the fundamental understanding of structure-property relationships in dynamic polymer networks but also opens exciting possibilities for developing next-generation photoresponsive materials for applications ranging from adaptive damping systems to soft robotics. The demonstrated principles of molecular-scale photomechanical control provide a versatile platform for creating stimulus-responsive materials with precisely adjustable properties.

Conflict of Interests

The authors declare no conflict of interest

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-026-3815-2.

Data Availability Statement

All relevant data supporting the findings of this study are included within the article (DOI: 10.1007/s10118-026-3815-2) and its ESI. Additional data are available from the corresponding author upon reasonable request.

ACKNOWLEDGMENTS

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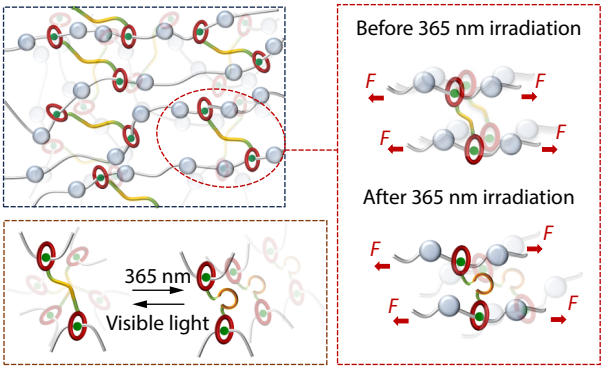
Graphical Abstract

Light-driven Mechanical Property Modulation in Azobenzene-crosslinked Slide-ring Polymers

Xiaoqing Wang, Qimo Mao, Shiyu Zhao, Maolin Wang, Chenjuan Yu, and Yuping Wang

Zhejiang University; Sichuan University

In this study, azobenzene-crosslinked photoresponsive slide-ring networks were constructed using photoisomerization as a topological switch to simultaneously boost strength, ductility, and toughness. Under large strains, expanded free volume unlocks ring mobility, boosting energy dissipation and adaptive damping.



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