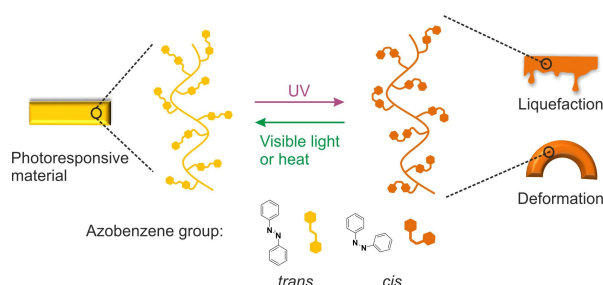


Moving Polymers via Photoisomerization

 Yazhi Liu,^{a,b} Shaodong Sun,^a and Si Wu^{*a,b}

^a CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China
^b Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

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Photoresponsive materials, which can adapt their states and shapes upon light irradiation, have attracted worldwide attention in the past decades. The development of azobenzene-containing polymers (azopolymers) opens up an avenue for controlling their properties and functions with light. These polymers show shape changes and mechanical responses under the stimulation of light via photoisomerization of azobenzene groups. Herein, this report focuses on the growing research on moving polymers via photoisomerization, including their moving mechanisms and various applications.

Background

Stimuli-responsive polymers can respond to particular changes in their surroundings by adopting specific macroscopic properties, such as shape and color.^[1] Moving polymers are defined as a kind of stimuli-responsive polymers, which are able to turn molecular level stimuli-responsiveness into movements on the macro level. Among them, photoresponsive moving polymers are able to turn molecular level stimuli-responsiveness into movements on the macro level via photoisomerization. Therefore, they are highly desirable as smart materials, which can be composed of smart systems. As the most investigated photoresponsive polymers, azobenzene-containing polymers (azopolymers) have attracted

the most attention because of their diversiform applications.^[2] The most intriguing property of azobenzene compounds is the reversible photoisomerization of azo bond (Figure 1a), which can be fast acquired between the thermally stable *trans* form and the meta-stable *cis* form. Thermally stable *trans* form can be converted to the *cis* form by illumination with UV light, and the *cis* form can be converted back to the *trans* form upon irradiation photochemically at visible light or thermally by heating.^[3] Photoisomerization of azo compounds can be used to switch many properties of photoresponsive polymers, such as glass transition temperature, shape, orientation, and polarity.^[4]

Recently, we and other groups developed new azopolymers,

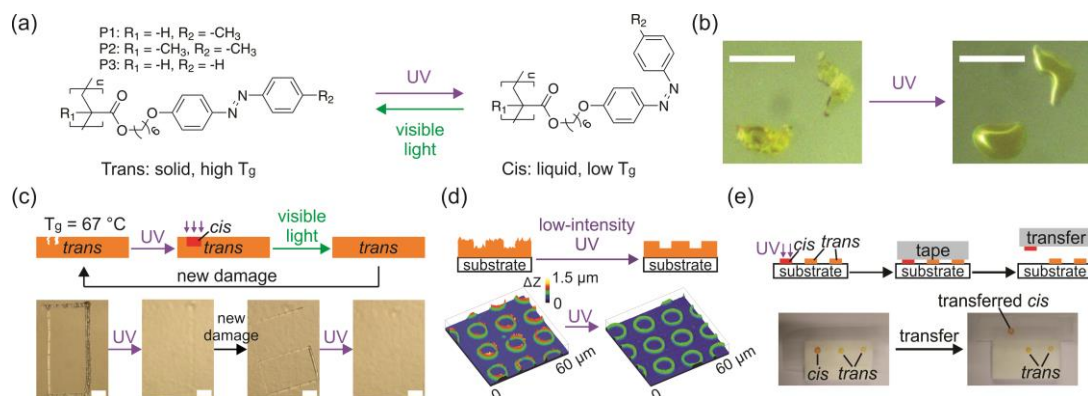


Figure 1 (a) Chemical structures and photoisomerization of azopolymers. (b) Optical microscopy images of azopolymer (P1) powders before and after UV irradiation (365 nm, 67 mW·cm⁻², 30 min). (c) Photoinduced healing of scratches on a film based on high molecular weight azopolymers. (d) Photoinduced reduction of the surface roughness. (e) Transfer printing based on photoinduced solid-to-liquid transitions. Adapted from Ref. [5]. Copyright 2017, Springer Nature.

*E-mail: siwu@ustc.edu.cn

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which show photoinduced moving behaviors. Here, we will discuss the movements of polymers via photoisomerization and introduce their potential applications.

Recent Advances

Recently, we demonstrated that light can induce reversible solid-to-liquid transitions of the azopolymers by switching the glass transition temperatures (T_g s).^[5] The photo-controlled mechanical properties of polymers are illustrated by making use of the reversible *cis-trans* photoisomerization abilities exhibited by azobenzene groups (Figure 1a). The T_g of *trans* azopolymers is above room temperature, whereas the T_g of *cis* azopolymers is below room temperature. UV and visible light irradiation are able to induce reversible solid-to-liquid transitions (Figure 1b). The *cis* azopolymers show a known property of liquid, which can move, providing ample opportunities for versatile applications.

There are some applications based on photoinduced reversible solid-to-liquid transitions of azopolymers. Healable hard coatings can be prepared by using our azopolymers. UV light is used to liquefy the damaged area on the surface of coatings. The polymer chains flowed across the area to repair the damaged coating, followed by visible light illumination to solidify it to heal the scratch (Figure 1c). Light can also reduce the roughness of the surface of azopolymer films by almost 600%. The rough microstructures became smooth after irradiation due to solid-to-liquid transitions

(Figure 1d). Our azopolymers can also be used for transfer printing upon light irradiation because of the property of liquefied *cis* azopolymer. High-resolution transfer printing technique could be developed based on this photo process (Figure 1e).

To further develop the processibility of azopolymers, our group fabricated a reprocessable and healable photoactuator using entangled high-molecular-weight azopolymers (Figure 2a).^[6] Unlike the crosslinked networks of traditional photoactuators, the freestanding azopolymer films fabricated by our azopolymers are noncrosslinked, which exhibit good processibility. The entangled high-molecular-weight azopolymers are more suitable than low-molecular-weight azopolymers to fabricate actuators due to their ascendant mechanical properties (Figures 2b, c). The flexible and stretchable actuators revealed photoinduced reversible bending due to the photoinduced reversible solid-to-liquid transitions (Figures 2d, e). This photoactuator can also be reprocessed and reshaped by common methods, such as heating or solution processes. The combination of polymer chain entanglements and photoswitching of T_g provides a new strategy for fabricating healable and reprocessable actuators.

Moreover, azopolymers with photoinduced reversible solid-to-liquid transitions can be also used as photoswitchable adhesives, which are important for industrial applications (Figure 3).^[7] The mechanism of switchable adhesive we fabricated is also based on photoinduced reversible solid-to-liquid transitions of azopolymers (Figure 3a). The mechanism of molecular level of this photo-

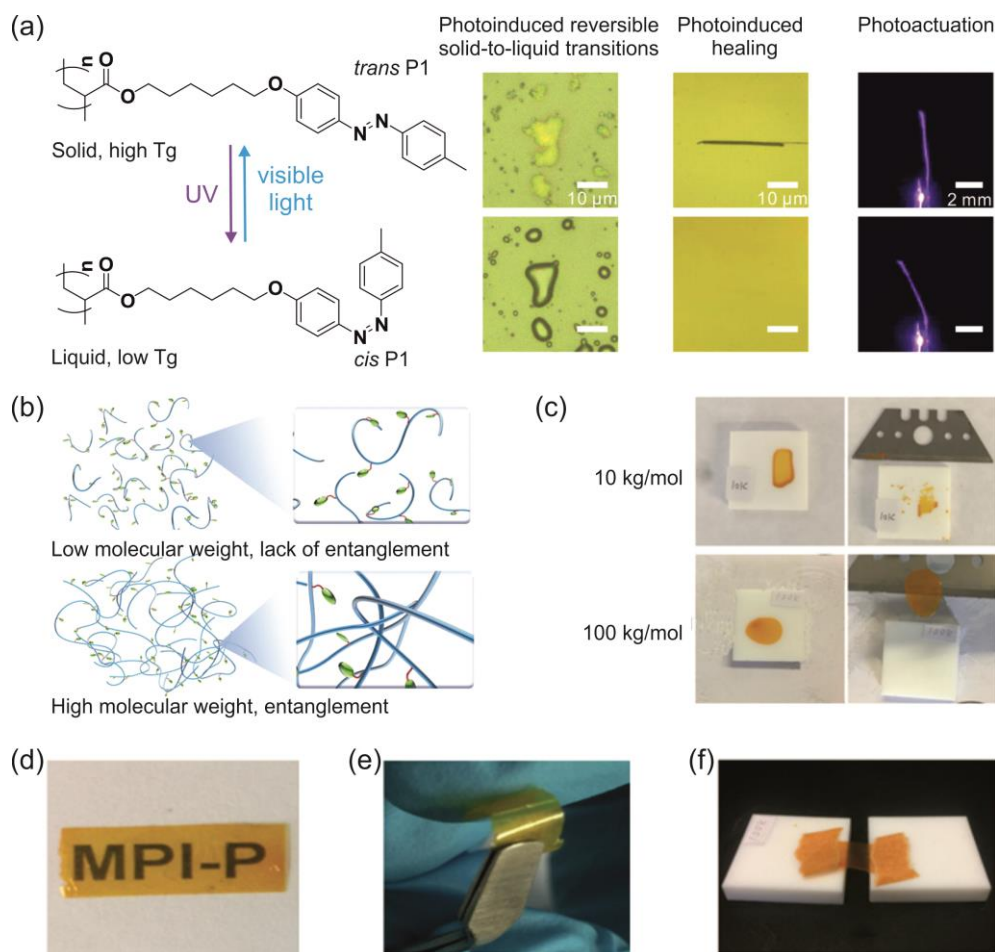


Figure 2 (a) The chemical structure and photoisomerization of P1. Photoisomerization induced the solid-to-liquid transitions of P1 powders, the healing of scratches on a P1 film, and the bending of a freestanding P1 film. (b) Schematic illustration: polymer chains of a low-molecular-weight P1 hardly entangle, while polymer chains of a high-molecular-weight P1 entangle. (c) Peeling off the azopolymer films P1-10k and P1-100k from Teflon substrates. The freestanding film of P1-100k was highly transparent (d), flexible (e) and stretchable at 90 °C (f). Adapted under the terms of the Creative Commons Attribution License, Ref. [6]. Copyright 2019, The authors, published by Wiley-VCH.

switchable adhesive is that chain mobility of azopolymer in the solid state cannot move freely to separation. On the contrary, the liquid state has sufficient chain mobility for separation. According to the photoswitchable T_g s, *trans* azopolymer is a solid, which can bond two substrates firmly while *cis* azopolymer is a liquid, which facilitates the separation of the substrates (Figure 3b). The adhesion strength was ~ 1.02 MPa, which is higher than that of small-molecule azobenzene adhesives (Figure 4a). *Cis-trans* transitions can be easily controlled by UV and visible light irradiation. Thus, the adhesion of azopolymer-glued substrates can be switched by light due to photoinduced reversible solid-to-liquid transitions (Figure 4b). Unlike other reversible adhesives, this photoswitchable adhesive does not need surface treatment of substrates, which provides a simple and efficient strategy to bond and debond surfaces reversibly. In addition, light has a high spatiotemporal resolution and can control adhesion precisely without contact. This adhesive is also reusable due to photoinduced reversible solid-to-liquid transitions (Figure 4c). Hence, this work provides a new way for designing up-to-date switchable adhesives. The photoinduced reversible solid-to-liquid transitions further improve the recyclability of materials. This photoswitchable adhesive makes automated production processes become possible due to reversible bonding and debonding.

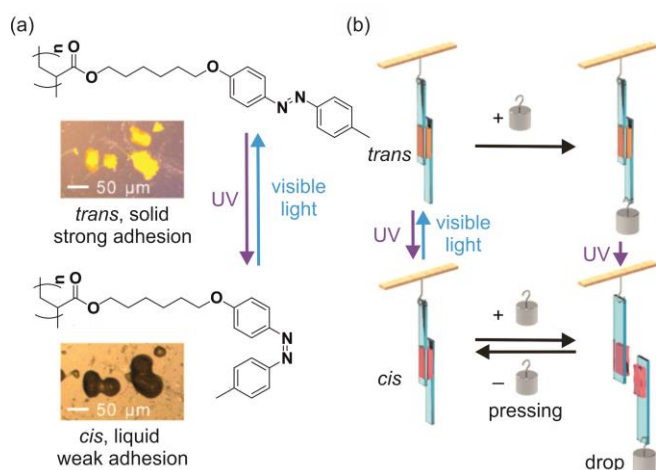


Figure 3 (a) Photoisomerization and solid-to-liquid transition of the azopolymer P1. The insets are optical microscopy images of azopolymer powders before and after UV irradiation. (b) Schematic illustration of the photoswitchable adhesion of P1-glued substrates. *Trans* P1 has strong adhesion that can sustain the load. In contrast, *cis* P1 has weak adhesion, and photoisomerization causes the load to fall. Adapted under the terms of the Creative Commons Attribution License, Ref. [7]. Copyright 2019, The authors, published by American Chemical Society.

Photoinduced reversible solid-to-liquid transitions of azopolymers open up an avenue for photoresponsive materials. Besides that, photoinduced actuation of azopolymers has also attracted a dramatic growth of interest. Recently, Yu and colleagues investigated a photodeformable microactuator, which can manipulate liquids precisely by photo-induced asymmetrical deformation of tubular microactuators (TMAs).^[8] Liquid can be propelled by capillary forces, which is induced by the deformation of polymers. This kind of polymer shows asymmetrical deformation upon illumination by 470 nm light with an intensity gradient along the TMAs; such illuminated TMAs can thus control liquid movement by light. While the TMAs are illuminated by unpolarized 470 nm light, the azobenzene groups can be re-oriented along the propagation direction after repeating of *trans-cis-trans* isomerization cycles, which is known as a Weigert effect. The thickness of the TMA wall decreases and the perimeter of the TMA elongates

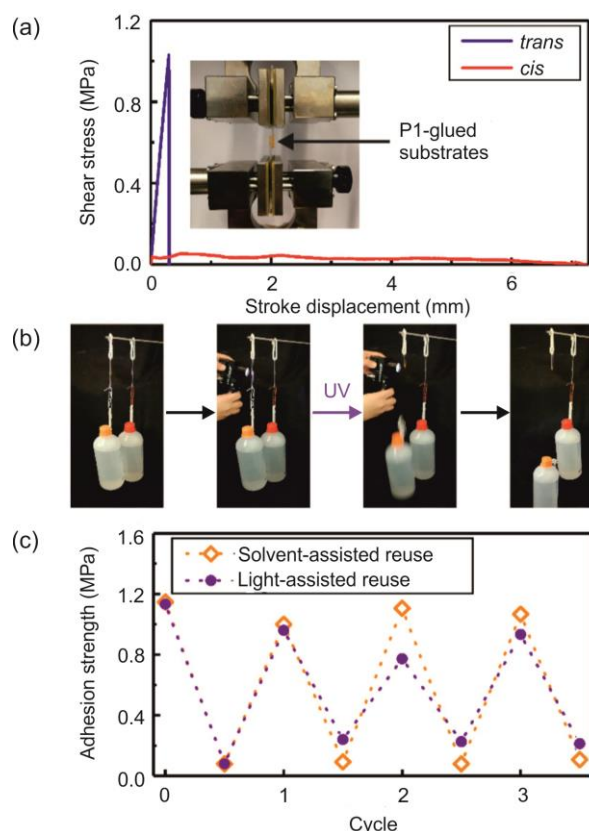


Figure 4 (a) Lap joint shear strength tests with two quartz substrates glued with *trans* (blue) and *cis* (red) P1. (b) Snapshots show photocontrolled adhesion. Sample on the left: *trans*-P1-glued quartz substrates holding a bottle of water (~ 500 g). The bottle fell after UV irradiation. Sample on the right: a control experiment showing that the P1-glued substrates held the bottle of water when P1 was not irradiated. (c) Light-assisted and solvent-assisted reuse of the adhesive. Adapted under the terms of the Creative Commons Attribution License, Ref. [7]. Copyright 2019, The authors, published by American Chemical Society.

because of this photoinduced reorientation. Hence, the TMA deforms to an asymmetrical cone-like geometry, which propel liquids in the attenuation direction of light by capillary force.

This photodeformable microactuator is able to not only manipulate various kinds of liquids over a long distance with controllable rate and direction, but also mix and combine multiphase liquids. Hence, this microactuator has potential applications in many fields, such as micro-reactors, laboratory-on-a-chip settings and micro-optomechanical systems.

Potential and Challenges

In brief, we have illustrated that reversible photoisomerization of azobenzene can switch T_g s of azopolymers along with reversible solid-to-liquid transitions. On this basis, we further used entangled azopolymers to develop healable and reprocessable photoactuator. This photoactuator also shows photoinduced reversible solid-to-liquid transitions. Moreover, photoswitchable adhesives based on our azopolymers were also fabricated due to photoinduced solid-to-liquid transitions. According to the photoinduced reorientation of azobenzene groups, Yu's group investigated photodeformable TMAs, which are excellent candidates for microactuators to manipulate liquids precisely.

However, the knowledge about the influencing factors of photo-induced reversible solid-to-liquid transitions is lacking, which impedes the development of photoresponsive materials. To give an insight into designing azopolymers, we have reported the

influence of different lengths of spacers between the polymer backbone and the azobenzene group on photoresponsive behavior of azopolymers.^[9] However, the effect of the length of chain on the end of azobenzene group has not been investigated. In addition, the thermal stability of such photoresponsive materials is also a big challenge that should be addressed as the *cis* azopolymer can be converted to *trans* azopolymer easily by heating.

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