

Photoinduced Reversible Solid-to-Liquid Transitions and Directional Photofluidization of Azobenzene-containing Polymers

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Abstract Photoinduced reversible liquefaction and solidification of polymers enable processing and healing of polymers with light. Some azobenzene-containing polymers (azopolymers) exhibit two types of photoinduced liquefaction properties: photoinduced reversible solid-to-liquid transition and directional photofluidization. For the first type, light switches the glass transition temperature (T_g) values of azopolymers and induces reversible solid-to-liquid transitions. For the second type, polarized light guides solid azopolymers to flow along the polarization direction. Here, we compare the two types of photoliquefaction and discuss their mechanisms. Recent progresses and applications based on photoliquefaction of azopolymers are also highlighted.

Keywords Photoresponsive; Polymer; Photoliquefaction; Azobenzene; Photoisomerization

Citation: Liang, S. F.; Nie, C.; Yan, J.; Zhang, Q. J.; Wu, S. Photoinduced reversible solid-to-liquid transitions and directional photofluidization of azobenzene-containing polymers. *Chinese J. Polym. Sci.* 2021, 39, 1225–1234.

INTRODUCTION

Solid-to-liquid transition is essential for polymer processing and repairing. In general, the solid-to-liquid transition of polymers is achieved by heating above glass transition temperature (T_g) values, where polymers change from hard glass states to soft rubber states. If the solid-liquid conversion of polymers is achieved using a non-thermal stimulus, not only could polymer reprocessing be achieved at room temperature, but various applications could be realized by utilizing different properties of the two switchable states of polymers.

Azobenzene-containing polymers (azopolymers) with photoresponsive properties are advantageous in technologies of lithography,^[1–3] actuators,^[4–8] photonics,^[9] solar energy conversion,^[10,11] information storage,^[12,13] etc. Among numerous functional azopolymers, some of them exhibit two types of photoliquefaction properties. For the first type, light can switch T_g values of such polymers and induce reversible solid-to-liquid transitions.^[14,15] For the second type, polarized light can guide solid azopolymers to flow along the polarization direction.^[1] The unique feature of these azobenzene polymers is that light with high spatiotemporal resolution can (re)shape or heal the polymers at room temperature and switch mechanical or other properties of the polymers. So far,

azopolymers exhibiting photoliquefaction have shown promising applications in many emerging fields, including surface relief gratings (SRGs),^[16–19] reversible adhesion,^[20–23] self-healing,^[14,24,25] actuation,^[24,26] nanotechnology,^[3,27] etc.

Over the past decades, there have been many studies on directional photofluidization of azopolymers,^[28] while photoinduced reversible solid-to-liquid transition is a recently developed research field. When the earliest relevant research appeared,^[14] a minireview pointed out there are two types of photoliquefaction for azopolymers.^[29] In this feature article, we discuss the azobenzene types, photoisomerization processes, light wavelengths, flow conditions, liquid presence conditions and mechanisms of the two types of photoliquefaction (Scheme 1), and introduce their latest development and applications.

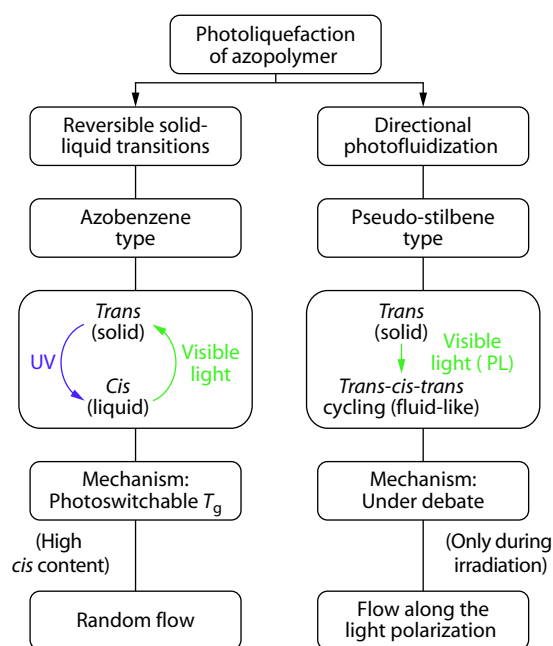
COMPARISON OF TWO TYPES OF PHOTOINDUCED LIQUEFACTION

Azopolymers with photoinduced reversible solid-to-liquid transitions have azobenzene type chromophores (azobenzene derivatives are divided into azobenzene-type, aminoazobenzene-type, and pseudo-stilbene-type in an early review^[30]). *Trans* azopolymers have T_g values above room temperature, while *cis* azopolymers have T_g values below room temperature. These azopolymers are similar to other model polymers with *trans* and *cis* side chains.^[31] In the process of liquefaction, ultraviolet (UV) irradiation induces *trans*-to-*cis* isomerization and liquefaction, while visible light induces *cis*-to-*trans* isomerization and solidification. After photoliquefaction, as long as the

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Special Issue: Self-Healing Polymeric Materials

Received September 9, 2020; Accepted October 12, 2020; Published online November 4, 2020



Scheme 1 Comparison of photoinduced reversible solid-to-liquid transitions and directional photofluidization (PL: polarized light).

content of *cis* azopolymers is high, azopolymers remain liquid even when light is turned off.^[15,29]

Different from reversible solid-to-liquid transitions, the mechanism for directional photofluidization is not clear up to now. The corresponding azopolymers mostly contain pseudo-stilbene type azo chromophores. In addition, some azopolymers containing azobenzene-type and aminoazobenzene-type azo chromophores also have the property of directional photofluidization.^[1] In most cases, polarized light induces *trans-cis-trans* cycles, and guides azopolymers to flow along the direction of polarization. The azopolymers only show fluid property under light irradiation.^[15,29]

PHOTOINDUCED REVERSIBLE SOLID-TO-LIQUID TRANSITIONS

The study of photoinduced reversible solid-to-liquid transitions of azopolymers should be traced back to the small molecule derivatives of azobenzene. In 1937, Hartley discovered that *cis* and *trans* azobenzene isomers had different melting points.^[32] In 2012, Akiyama and Yoshida, and Okui and Han, respectively, observed photoinduced solid-to-liquid transition of azobenzene-containing small molecules at room temperature.^[33,34] After that, more azobenzene small molecules with similar characters

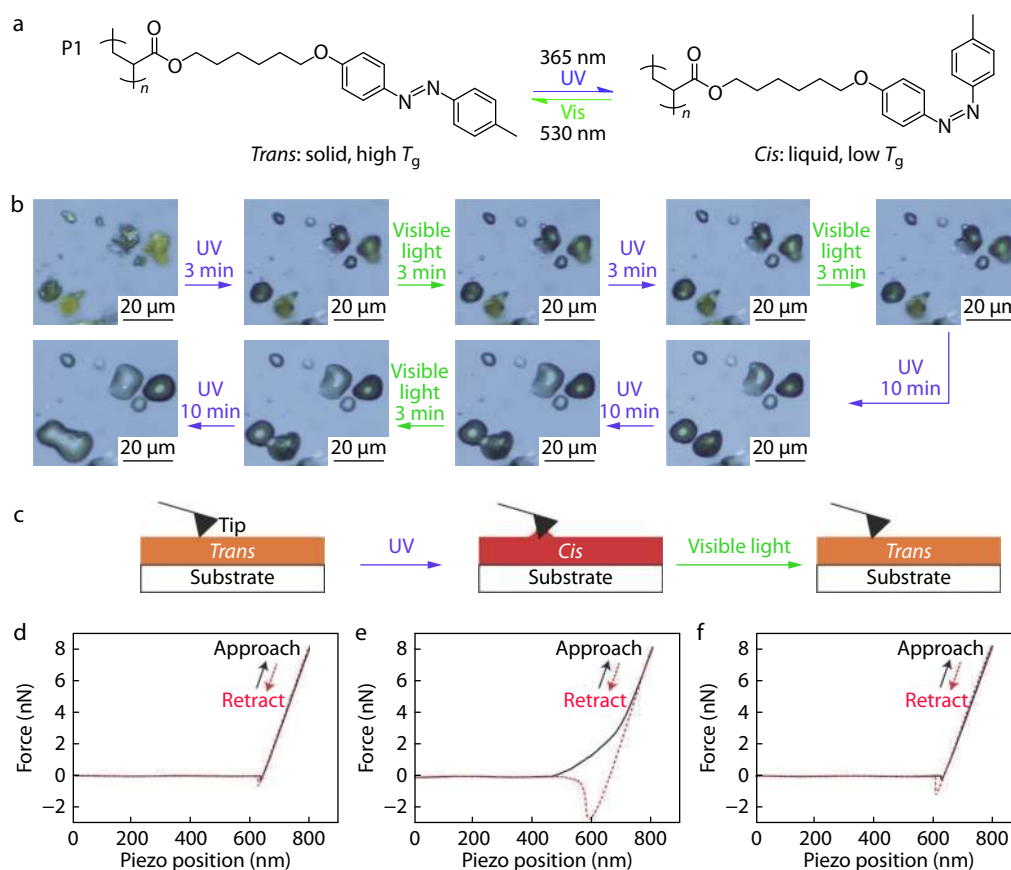


Fig. 1 Photoinduced reversible solid-to-liquid transitions of azopolymer P1. (a) Photoisomerization and chemical structures of P1. P1 is a solid with a high T_g in the *trans* state and is a liquid with a low T_g in the *cis* state. (b) Optical microscopy images of P1 powders under alternating UV (365 nm, 67 mW/cm²) and visible light (530 nm, 5 mW/cm²) irradiation. (c) Scheme of reversible scanning force microscopy (SFM) measurements of P1 film. (d–f) Force-piezo position curves of (d) initial P1 film, (e) after 365 nm light irradiation and (f) after subsequent 530 nm light irradiation (Reprinted with permission from Ref. [14]; Copyright (2017) Springer Nature).

were reported.^[35–37] Because light can change melting points of small molecules, we hypothesized that light may switch T_g values of azopolymers. In 2017, we synthesized a typical azopolymer P1 with photoliquefaction property and demonstrated the photoliquefaction mechanism of P1 (Fig. 1).^[14]

We take P1 as an example to show photoinduced reversible solid-to-liquid transitions. Azopolymer P1 contains azobenzene-type chromophores on its side chains. The azobenzene groups underwent *trans*-to-*cis* isomerization via UV irradiation, and *cis*-to-*trans* isomerization via visible light irradiation. We demonstrated that the T_g of *trans*-azopolymer P1 (48 °C, measured by differential scanning calorimetry) was higher than room temperature and it was solid, while the T_g of *cis* polymer (−10 °C) was lower than room temperature and it was liquid. Therefore, P1 underwent reversible solid-to-liquid transitions upon alternating irradiation of UV and visible light. The transformation of azopolymer P1 from solid powder to liquid droplet was observed using optical microscopy (Fig. 1b). The force-piezo position curves obtained with a spin-coated film of P1 showed reversible signs of a hard surface and a soft surface (Figs. 1c and 1d). The study of photoswitchable T_g provided a new strategy for the application development of photoresponsive polymer. Based on photoinduced reversible solid-to-liquid transitions and photoswitch-

able T_g , we further explored a variety of new functions and applications of azopolymers.

The flow property of liquefied *cis* P1 enables the repairing of damaged hard coatings. Scratches on a P1 film were repeatedly healed upon locally and alternately irradiated with UV light and visible light. As a result, the damaged part was converted to the liquid state and the scratch was healed due to capillary flow of the polymer (Fig. 2a). Similarly, the surface roughness of patterns could be effectively reduced by the reversible solid-to-liquid transitions (Fig. 2b).^[14] Especially, *trans* P1 has an adhesion strength up to 1.02 MPa (substrates: quartz, glued area: 0.375 cm²). After photoliquefaction, the adhesion strength of *cis* P1 decreased to 0.08 MPa.^[20] So, P1 with switchable adhesion can be used for transfer printing (Fig. 2c),^[14] and reversible adhesives (Figs. 3a and 3b). Related studies of reversible adhesion of azopolymers have been reported in some works,^[21–23] and summarized in a recent review.^[38] Photo-controlled adhesive P1 was suitable for various kinds of substrates and underwater conditions. Azopolymers with large adhesion force transition are expected to meet the requirement of industrial application. In addition, entangled linear P1 was used as healable and reprocessable photoactuators (Fig. 3c). The photoinduced reversible solid-to-liquid transitions contributed to the photoinduced bend-

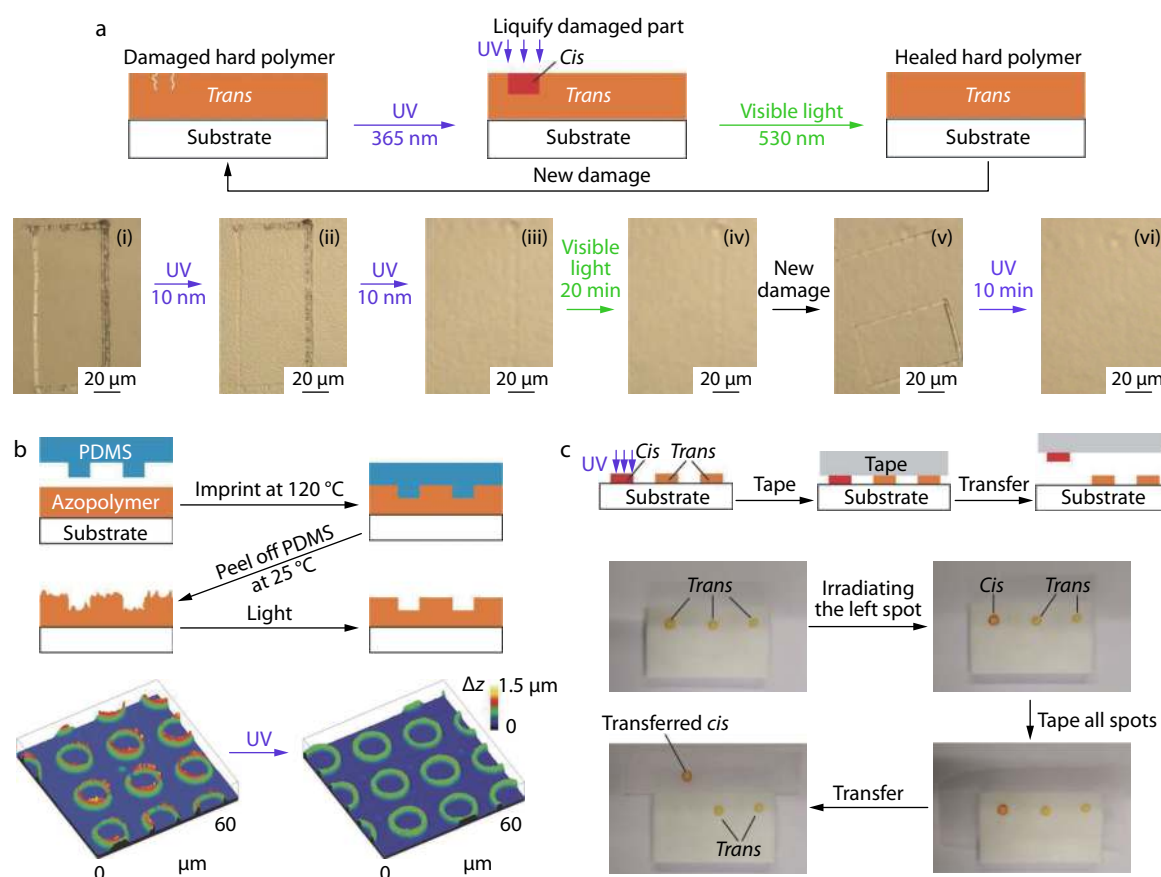


Fig. 2 Various applications of P1 based on photoinduced reversible solid-to-liquid transitions. (a) Light-healable film. The scratches on a P1 film were reversibly healed with light. (b) Light irradiation reduced the surface roughness of microstructures prepared by imprint lithography. (c) Azopolymer P1 was used as ink for transfer printing. (Reprinted with permission from Ref. [14]; Copyright (2017) Springer Nature).

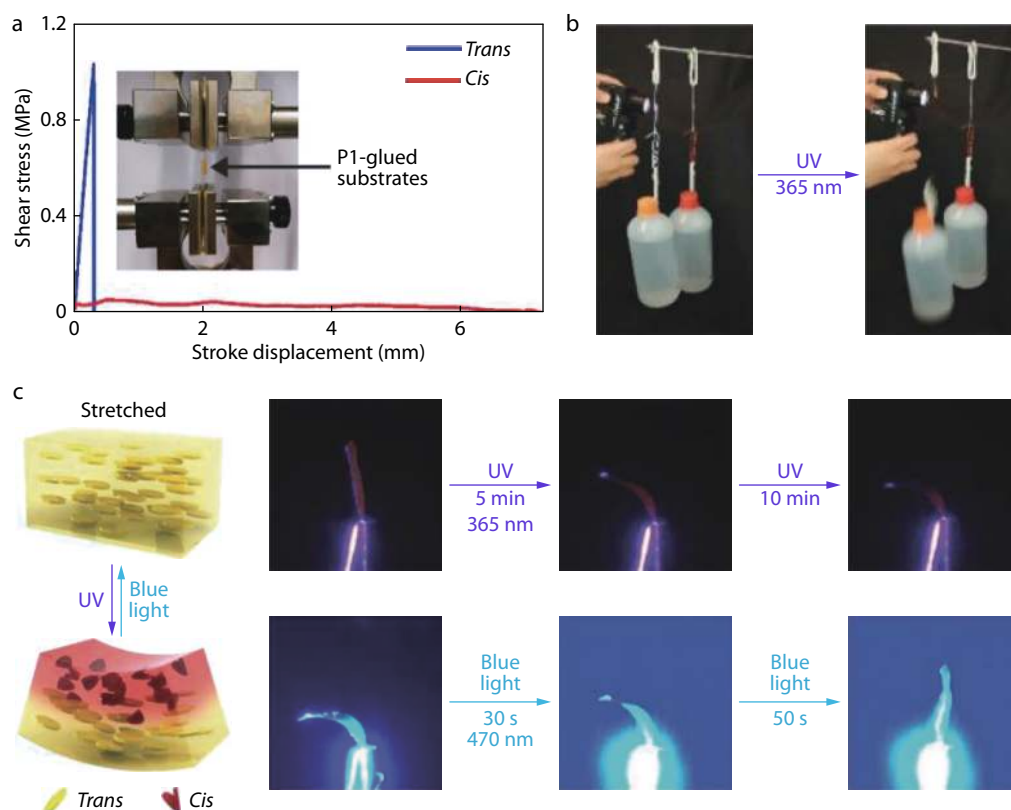


Fig. 3 Various applications of P1 based on photoinduced reversible solid-to-liquid transitions: (a) light-switchable polymer adhesives, where P1 had a strong shear stress in the *trans* state and a weak shear stress in the *cis* state; (b) after UV irradiation, *trans* P1 between two quartz substrates was liquefied and the bottle fell. (Reprinted with permission from Ref. [20]; Copyright (2019) American Chemical Society). (c) Photoactuation. Stretched P1 film (100 kg/mol) bent towards the UV light source and bent away from the visible light source. (Reprinted with permission from Ref. [24]; Copyright (2019) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

ing of the nonaligned azopolymer films.^[24]

As a side-chain azobenzene polymer, structure of P1 presented a typical design reference. Azopolymers could retain the solid-to-liquid transition property after properly changing the length of spacer group and tail group.^[21,39] Recently, different research groups have studied the properties and applications of these side-chain azopolymers. P2 also showed photoliquefaction (Figs. 4a and 4b). The thermal conductivity of P2 changed after liquefaction.^[40] In addition, precise control of the micro-nano structures was achieved by utilizing the high spatial resolution of light. Yu's group presented a facile fabrication method of multiple nanopatterns in azopolymer P3 film by combining athermal nanoimprint lithography and photolithography.^[3] The key of multiple nanopatterning lay in the phototunable mechanical properties of the azopolymer upon photoirradiation with different wavelengths (Figs. 4c and 4d). Chen *et al.* demonstrated the light-induced nanowetting method for preparing azopolymer nanoarrays with well controlled patterns using designed photomasks.^[27]

In addition to the typical side chain azobenzene homopolymers, some other types of azopolymers also exhibited photoinduced solid-to-liquid transition properties, including side chain copolymers^[23,25] and main chain polymer.^[41] Kihara and co-workers reported on an ABA-type triblock copolymer P4

with azopolymer termini.^[23] This ABA-type azopolymer had reversible adhesive properties controlled by light (Figs. 5a and 5b). It had a higher flexibility than the corresponding homo-azopolymer. Yu's group developed a photocontrol-lable flexible microtube consisting of a copolymer P5 inner layer and outer flexible supporting layer.^[25] Benefiting from photoswitchable T_g , the damaged P5 layer of microtube was healed with light (Figs. 5c and 5d). With the combination of athermal and high spatiotemporal resolution of light irradiation, photoinduced reversible solid-to-liquid transition at room temperature is a new frontier field in the study of stimuli-responsive materials.

DIRECTIONAL PHOTOFLUIDIZATION

Directional photofluidization has been studied for more than 15 years, which has been summarized by some reviews.^[1,28,42] In this section, we will focus on the characteristics of liquid-like behaviors in directional photofluidization. We summarize its developments, new progresses, and differences with photoinduced reversible solid-to-liquid transitions.

The first two interrelated reports about directional photofluidization are photoinduced SRGs on azopolymers.^[43,44] SRGs are created upon exposure of interference laser beams on azopolymer films. These works do not specify the flow of

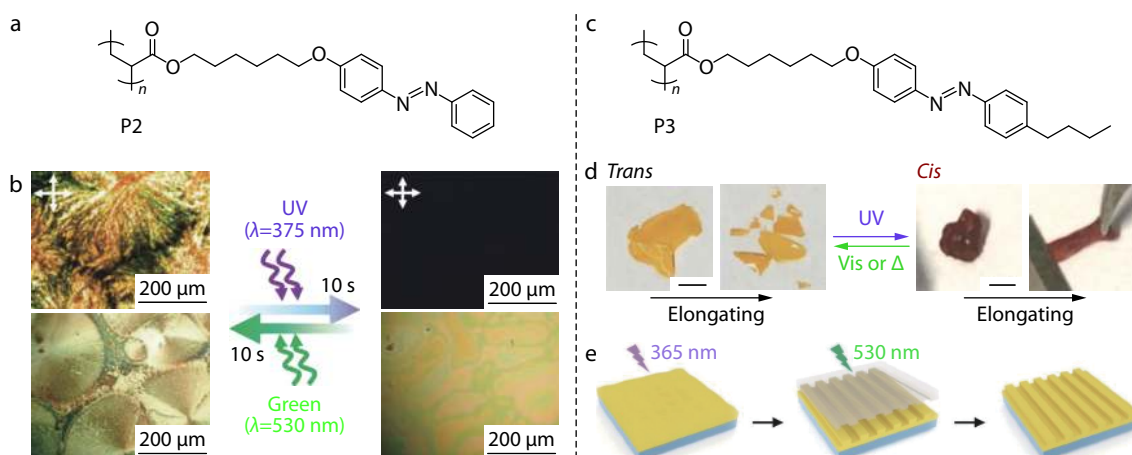


Fig. 4 (a) Chemical structure of azopolymer P2; (b) Cross-polarized optical microscopy images of P2 film under reversible UV and visible light irradiations. (Adapted from Ref. [40]; Copyright (2019) National Academy of Sciences). (c) Chemical structure of azopolymer P3; (d) Photographs of *trans*-rich P3 and *cis*-rich P3 (scale bars, 5 mm); (e) Photolithography of P3 through UV irradiation, imprint and visible light irradiation. (Adapted from Ref. [3]; Copyright (2020) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

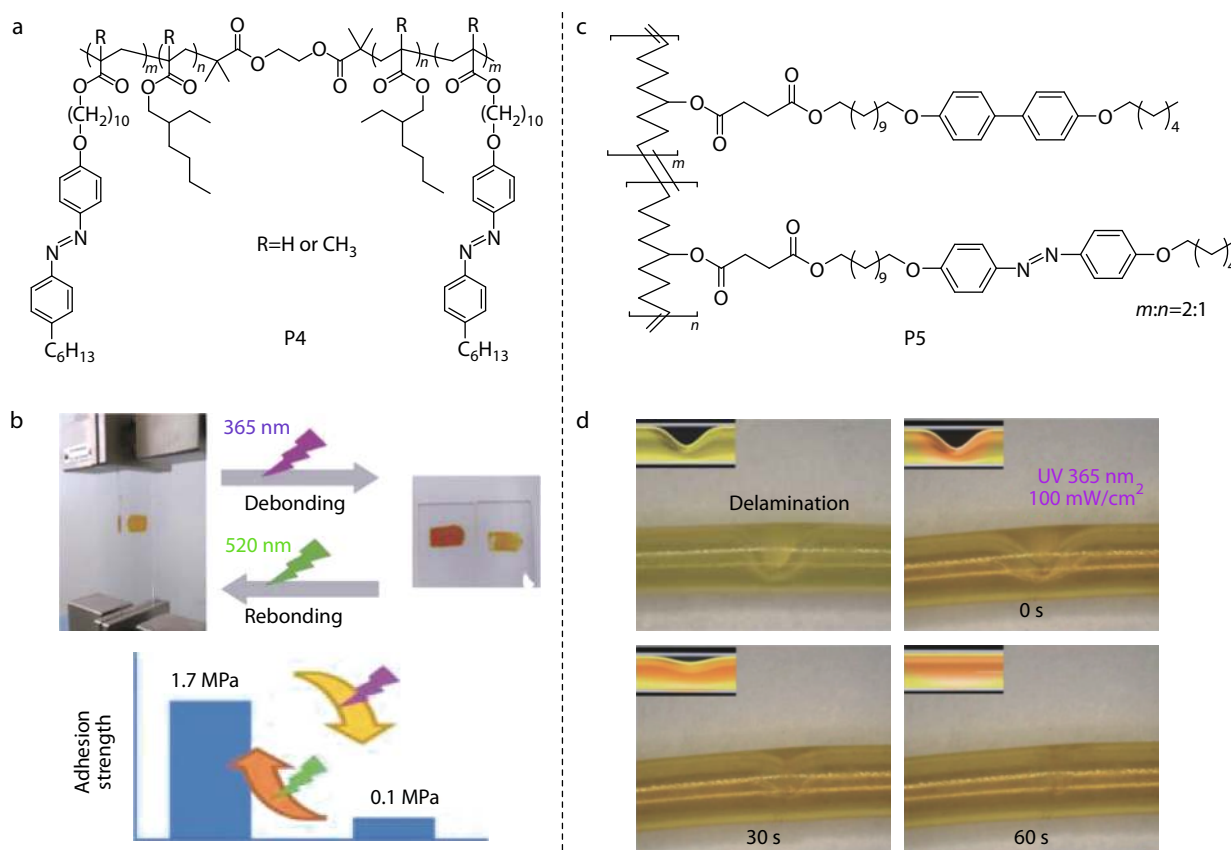


Fig. 5 (a) Chemical structure of azopolymer P4; (b) Bonding and debonding of P4 under reversible UV and visible light irradiations. (Reprinted with permission from Ref. [23]; Copyright (2018) American Chemical Society). (c) Chemical structure of azopolymer P5; (d) The microtube of P5 healed under UV irradiation. (Adapted from Ref. [25]; Copyright (2019) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

azopolymers, but set a precedent. In 2005, two pioneering works demonstrated the fluid-like properties of azopolymers under light irradiation. Wang and co-workers found that colloidal spheres of the azopolymer P6 stretched after being exposed to interfering polarized Ar⁺ laser beams (Figs. 6a–6e).^[45]

Karageorgiev *et al.* reported a light-induced isothermal transition of azopolymer P7 film from an isotropic solid to an anisotropic liquid state (Figs. 6f–6h). In both works, the flow direction of the azopolymers was along the light polarization direction.^[46]

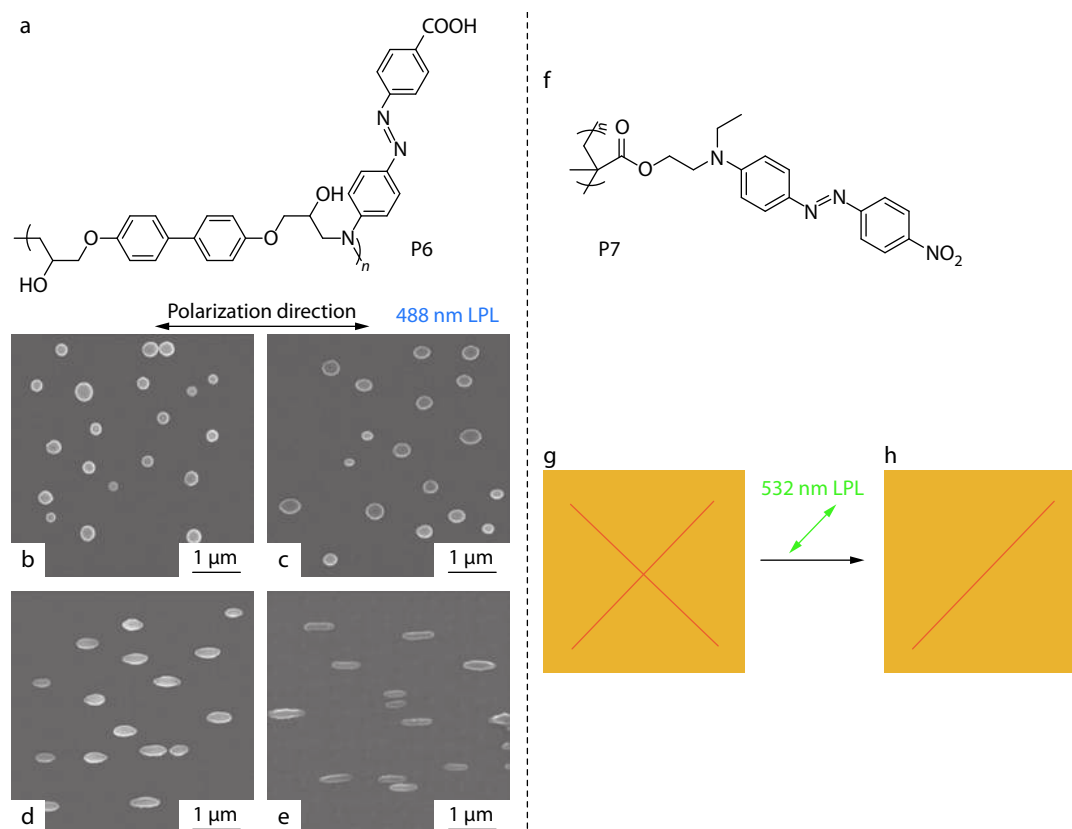


Fig. 6 (a) Chemical structure of azopolymer P6; (b–e) SEM images of colloidal spheres (b) before irradiation and after irradiation with 488 nm linearly polarized light (LPL) for (c) 5 min, (d) 12 min, and (e) 15 min. (Reprinted with permission from Ref. [45]; Copyright (2005) American Chemical Society). (f) Chemical structure of azopolymer P7; (g, h) Scheme of directional photofluidization of P7: (g) two perpendicular scratches produced by SFM lithography presented on P7 film and (h) scheme of the surface irradiation with 532 nm linearly polarized light.

After the discovery of directional photofluidization, it has attracted a lot of attention by researchers. Some groups utilized this property to develop micro and nanostructures.^[47–51] Some found that polarization-controlled three-beam interference could produce micro-ellipsoidal cap arrays on P8 films.^[52,53] The arrays deformed along the polarization direction of the incident light (Figs. 7a and 7b). Lee and co-workers developed photofluidization lithography based on directional photofluidization.^[54–56] Combined with micro-moulding in capillaries, large-area, high resolution nanostructures were generated on P9 film with the aid of directional photofluidization (Figs. 7c and 7d). In addition, Lee *et al.* also made use of polarized light to achieve the repairing of wearable electrical conductors.^[57] In recent years, some more complex microstructural techniques have been developed. For example, Lin and co-workers fabricated breath figure arrays of azopolymers^[58,59] and found that polarized light with different directions converted P10 arrays into different structures (Figs. 7e–7j).

Although directional photofluidization has been studied by researchers for more than 15 years, the mechanism of photoliquefaction is still under debate. Some underlying mechanisms have been summarized in a previous review,^[1] but none of the proposed mechanisms could explain the

existing phenomena perfectly. Recently, some new opinions have been presented. Saphiannikova *et al.* disagreed with the concept of photofluidization and proposed the view that anisotropic light-induced stress contributed to the structure changes of azopolymers.^[60] This mechanism cannot explain some photofluidization when the films are uniformly illuminated with circularly-polarized or non-polarized (lamp) light.^[57] Pellerin and co-workers put forward a new mechanism:^[61] upon visible light irradiation, P11 underwent repeated *trans-cis-trans* isomerization (Fig. 8). Such a molecular motion is equivalent to the increase of local environment temperature of the azo groups (some simulation approaches reproduced relatively well the behavior observed using the real azobenzene molecule^[62–64]). When the local temperature exceeded T_g of *trans*-P11, photofluidization occurred. However, why the flow direction is polarization-dependent is difficult to understand. Another possible mechanism is that *trans-cis-trans* cycling could decrease T_g of azopolymers.^[65] Some works showed that repeated *trans-cis-trans* cycles cause a decrease of certain mechanical properties upon irradiation,^[66–68] and “photosoften” the polymer matrix and enhance polymer chain mobility.^[69] During irradiation, the population of *cis*-isomers in pseudo-styrene type azopolymers rose, and softening was observed under linearly polarized, circularly

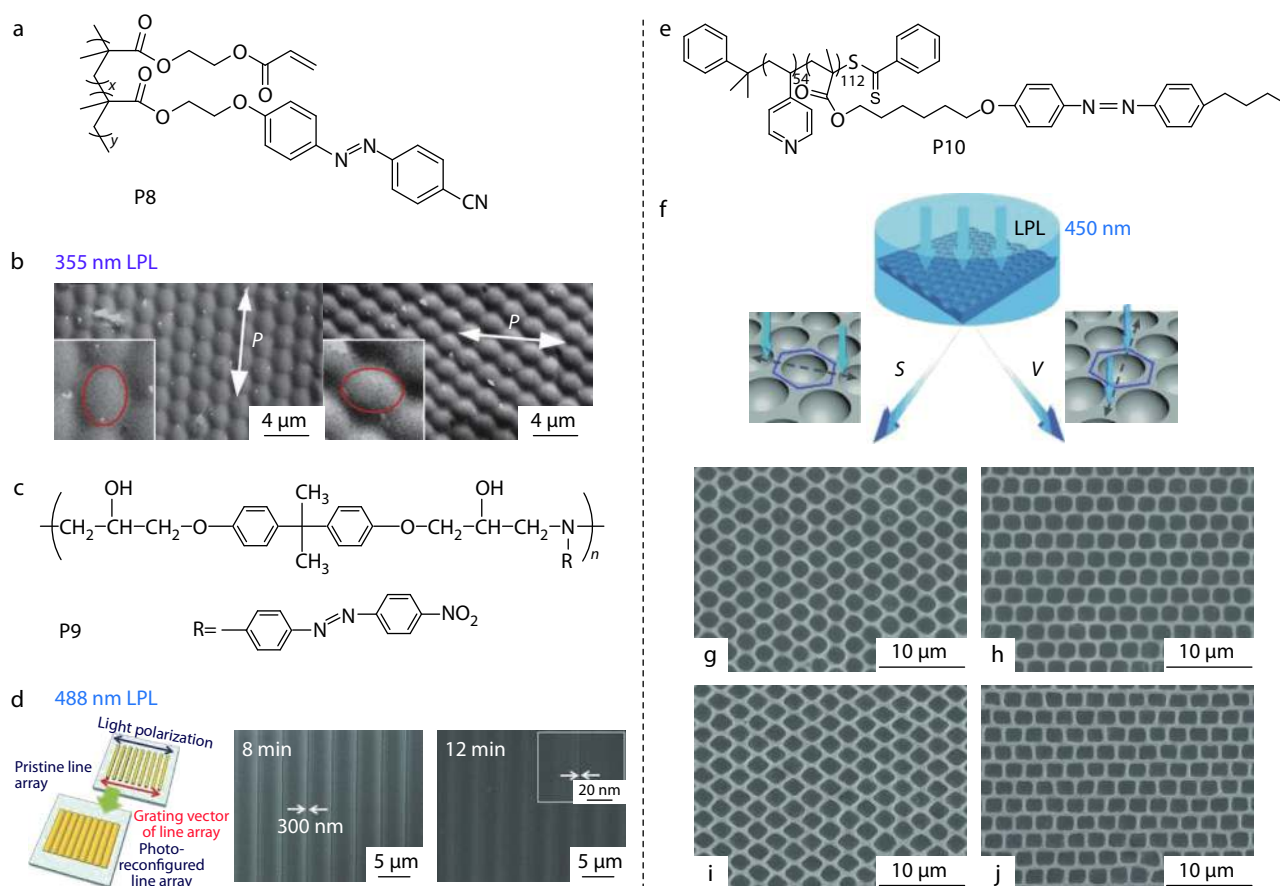


Fig. 7 (a) Chemical structure of azopolymer P8; (b) Deformed microcaps fabricated by irradiating the microcaps with 355 nm linearly polarized light. (Reprinted with permission from Ref. [52]; Copyright (2010) The Optical Society). (c) Chemical structure of azopolymer P9; (d) Directional photofluidization of P9 line arrays. (Adapted from Ref. [56]; Copyright (2011) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). (e) Chemical structure of azopolymer P10; (f) Schematic diagram of arrays prepared by breath figure after 450 nm linearly polarized light irradiation (The arrows deformed along the polarization directions of the light); (g–j) Photo-reconfiguration of patterns *via* irradiation along the S direction (from the center of the pore to the side of the honeycomb hexagon) and the V direction (from the center of the pore to the vertex of the honeycomb hexagon) for (g, h) 10 min and (i, j) 30 min. (Adapted from Ref. [58]; Copyright (2014) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

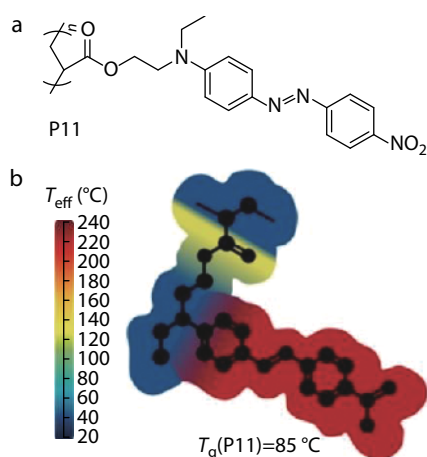


Fig. 8 (a) Chemical structure of azopolymer P11; (b) Effective temperature (T_{eff}) of each moiety of P11 was assigned by infrared spectroscopy. Local environment temperature of the azo groups exceeded T_g of *trans*-P11 upon visible light irradiation (520 nm, 100 mW/cm²). (Reprinted with permission from Ref. [65]; Copyright (2015) American Chemical Society).

polarized and nonpolarized visible illumination.^[1] Decreased T_g may contribute to flow/softening of azopolymers and directional fluidization is correlated with the light polarization. However, the T_g values of pseudo-stilbene type azopolymers under irradiation are difficult to measure because the short half-lives of *cis* pseudo-stilbene azo groups and insufficient light penetration hinder the measurement of T_g . In a word, the mechanism of directional photofluidization needs further exploration.

CONCLUSIONS

In summary, recent progresses on two types of photoliquefaction of azopolymers are reviewed. We presented their differences in azobenzene type, photoisomerization processes, light wavelength, flow condition, the conditions for liquefaction and mechanisms. We also highlighted their applications. Regarding the future perspective of photoliquefaction of azopolymers, there are several notable challenges and questions: (1) How to clarify the mechanism of directional photofluidization? If the two types of liquefaction have similarity in mechanism (*trans*-

to-*cis* isomerism and *trans-cis-trans* cycling both decrease T_g values of azopolymers and induce liquefaction), how to monitor the T_g of pseudo-stilbene type azopolymers during rapid isomerism? (2) Whether the applications of these azopolymers could be expanded by combining with other functional materials? Composites made up of azopolymers and nanoscale materials could still have photoliquefaction properties. (3) Moreover, could we design new photoliquefied polymers based on other photoresponsive groups or design other forms of stimuli-liquefied polymers? Besides azobenzene, spiropyran and diarylethene also have photoisomerization properties. Polymers with these groups are likely to show similar photoliquefaction behaviors.

BIOGRAPHIES

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Si Wu is a full professor at the University of Science and Technology of China (USTC). He studied polymer chemistry at USTC and obtained bachelor's degree in 2005. He was supported by the joint doctoral promotion programme working at USTC and the Max Planck Institute for Polymer Research (MPIP). After obtained PhD in 2010, he worked as a postdoctoral fellow at MPIP and was promoted to a group leader in 2012. He headed a research group at MPIP from 2012 to 2018. In 2018, he joined USTC as a full professor. His research focuses on photoresponsive polymers.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51973204) and the Thousand Talents Plan and Anhui Provincial Natural Science Foundation (No. 1908085MB38).

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