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

Shuo-Feng Liang, Chen Nie, Jie Yan, Qi-Jin Zhang, and Si Wu

Chinese Academy of Sciences Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at the Microscope, Anhui Key Laboratory of Optoelectronic Science and Technology, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

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,[11–13] 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.[16] 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] actuators,[24,26] nanotechnology,[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.[28] 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 PHOTINDUCED 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.[28]) 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.[29] 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
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...
were reported. 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).\textsuperscript{[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 photoswitchable $T_g$, 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).\textsuperscript{[14]} Especially, trans P1 has an adhesion strength up to 1.02 MPa (substrates: quartz, glued area: 0.375 cm$^2$). After photoliquefaction, the adhesion strength of cis P1 decreased to 0.08 MPa.\textsuperscript{[20]} So, P1 with switchable adhesion can be used for transfer printing (Fig. 2c),\textsuperscript{[14]} and reversible adhesives (Figs. 3a and 3b). Related studies of reversible adhesion of azopolymers have been reported in some works,\textsuperscript{[21−23]} and summarized in a recent review.\textsuperscript{[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 reproprocessable 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).

https://doi.org/10.1007/s10118-021-2519-x
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. Recently, different research groups have studied the properties and applications of these side-chain azopolymers. P2 also showed photoliquefaction. 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. The key of multiple nanopatterning lay in the phototunable mechanical properties of the azopolymer upon photoirradiation with different wavelengths. Chen et al. demonstrated the light-induced nanowetting method for preparing azopolymer nanoarrays with well controlled patterns using designed photomasks.

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 and main chain polymer. Kihara and co-workers reported on an ABA-type triblock copolymer P4 with azopolymer termini. This ABA-type azopolymer had reversible adhesive properties controlled by light. Yu’s group developed a photocontrollable flexible microtube consisting of a copolymer P5 inner layer and outer flexible supporting layer. Benefiting from photoswitchable $T_g$, the damaged P5 layer of microtube was healed with light. 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. 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. SRGs are created upon exposure of interference laser beams on azopolymer films. These works do not specify the flow of...
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.\[46\]
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. Some found that polarization-controlled three-beam interference could produce micro-ellipsoidal cap arrays on P8 films. 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. 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. In recent years, some more complex microstructural techniques have been developed. For example, Lin and co-workers fabricated breath figure arrays of azopolymers 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, 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. This mechanism cannot explain some photofluidization when the films are uniformly illuminated with circularly-polarized or non-polarized light. Pellerin and co-workers put forward a new mechanism: 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). 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. Some works showed that repeated trans-cis-trans cycles cause a decrease of certain mechanical properties upon irradiation, and "photosoften" the polymer matrix and enhance polymer chain mobility. During irradiation, the population of cis-isomers in pseudo-styrene type azopolymers rose, and softening was observed under linearly polarized, circularly

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.

https://doi.org/10.1007/s10118-021-2519-x
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, photosomerization 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-styrene 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 types of stimuli-liquefied polymers? Besides azobenzene, spiropyran and diarylethene also have photosomeration properties. Polymers with these groups are likely to show similar photoliquefation behaviors.

**BIographies**

Qi-Jin Zhang is currently a professor of Polymer Science and Engineering at University of Science and Technology of China. He graduated from University of Science and Technology of China in 1982 and earned his PhD in 1988 at Institute of Chemistry, Chinese Academy of Sciences. His research focuses on photoresponsive polymers, mainly including azobenzene polymers and polymer optical fibers.

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).

**References**

1. Lee, S.; Kang, H. S.; Park, J. K. Directional photofluidization lithography; micro/nanostructural evolution by photofluidic motions of azobenzene materials. *Adv. Mater.* 2012, 24, 2069–2103.
2. Kravchenko, A.; Shevchenko, A.; Ovchinnikov, V.; Priimagi, A.; Kaivola, M. Optical interference lithography using azobenzene-functionalized polymers for micro- and nanopatterning of silicon. *Adv. Mater.* 2011, 23, 4174–4177.
3. Yang, B.; Cai, F.; Huang, S.; Yu, H. Athermal and soft multi-nanopatterning of azopolymers: phototunable mechanical properties. *Angew. Chem. Int. Ed.* 2020, 59, 4035–4042.
4. Yu, H.; Ikeda, T. Photoccontrollable liquid-crystalline actuators. *Adv. Mater.* 2011, 23, 2149–2180.
5. Pang, X.; Lv, J. A.; Zhu, C.; Qin, L.; Yu, Y. Photodeformable azobenzene-containing liquid crystal polymers and soft actuators. *Adv. Mater.* 2019, 31, 1904224.
6. Ge, F.; Zhao, Y. Microstructured actuation of liquid crystal polymer networks. *Adv. Funct. Mater.* 2019, 30, 1901890.
7. Jiang, Z. C.; Xiao, Y. Y.; Yin, L.; Han, L.; Zhao, Y. "Self-lockable" liquid crystalline Diels-Alder dynamic network actuators with room temperature programmability and solution reprocessability. *Angew. Chem. Int. Ed.* 2020, 59, 4925–4931.
8. Qin, C.; Feng, Y.; Luo, W.; Cao, C.; Hu, W.; Feng, W. A supramolecular assembly of cross-linked azobenzene/polymers for a high-performance light-driven actuator. *J. Mater. Chem. A* 2015, 3, 16453–16460.
9. Priimagi, A.; Shevchenko, A. Azopolymer-based micro- and nanopatterning for photonic applications. *J. Polym. Sci., Part B: Polym. Phys.* 2014, 52, 163–182.
10. Dong, L.; Feng, Y.; Wang, L.; Feng, W. Azobenzene-based solar thermal fuels: design, properties, and applications. *Chem. Soc. Rev.* 2018, 47, 7339–7388.
11. Saydjari, A. K.; Weis, P.; Wu, S. Spanning the solar spectrum: azopolymer solar thermal fuels for simultaneous UV and visible light storage. *Adv. Energy Mater.* 2017, 7, 1601622.
12. Ikeda, T.; Tsutsumi, O. Optical switching and image storage by means of azobenzene liquid-crystal films. *Science* 1995, 268, 1873–1875.
13. Wu, S.; Duan, S.; Lei, Z.; Su, W.; Zhang, Z.; Wang, K.; Zhang, Q. Supramolecular bisazopolymers exhibiting enhanced photoinduced birefringence and enhanced stability of birefringence for four-dimensional optical recording. *J. Mater. Chem.* 2010, 20, 5202–5209.
14. Zhou, H.; Xue, C.; Weis, P.; Suzuki, Y.; Huang, S.; Koykov, N.; Auerhammer, G. K.; Berger, R.; Butt, H. J.; Wu, S. Photoswitching of glass transition temperatures of azobenzene-containing polymers induces reversible solid-to-liquid transitions. *Nat. Chem.* 2017, 9, 145–151.
15. Xu, W. C.; Sun, S.; Wu, S. Photoinduced reversible solid-to-liquid transitions for photoresponsive switchable materials. *Angew. Chem. Int. Ed.* 2019, 58, 9712–9740.
16. Ahmed, R.; Priimagi, A.; Faul, C. F.; Manners, I. Redox-active, organometallic surface-relief gratings from azobenzene-containing polyferrocenylsilane block copolymers. *Adv. Mater.* 2012, 24, 926–31.
17. Morikawa, Y.; Nagano, S.; Watanabe, K.; Kamata, K.; Iyoda, T.; Seki, T. Optical alignment and patterning of nanoscale microdomains in a block copolymer thin film. *Adv. Mater.* 2006, 18, 883–886.
18. Zettu, N.; Ogawara, T.; Mizoshita, N.; Nagano, S.; Seki, T. Photo-triggered surface relief grating formation in supramolecular liquid crystalline polymer systems with detachable azobenzene unit. *Adv. Mater.* 2008, 20, 516–521.
19. Gao, J.; He, Y. N.; Liu, F.; Zhang, X.; Wang, Z. Q.; Wang, X. G. Azobenzene-containing supramolecular side-chain polymer films for laser-induced surface relief gratings. *Chem. Mater.* 2007, 19, 3877–3881.
20. Zhou, Y.; Chen, M.; Ban, Q.; Zhang, Z.; Shuang, S.; Koykov, N.; Butt, H. J.; Kong, J.; Wu, S. Light-switchable polymer adhesive based on photoinduced reversible solid-to-liquid transitions. *ACS. Macro Lett.* 2019, 8, 968–972.
21. Akiyama, H.; Fukata, T.; Yamashita, A.; Yoshida, M.; Kihara, H. Reversible adhesives composed of photoresponsive azobenzene polymer for glass substrates. *J. Adhes.* 2016, 93, 823–830.
22. Ito, S.; Yamashita, A.; Akiyama, H.; Kihara, H.; Yoshida, M. Azobenzene-based (meth)acrylates: controlled radical polymerization, photoresponsive solid-liquid phase transition behavior, and application to reworkable adhesives.
Liang, S. F. et al. / Chinese J. Polym. Sci. 2021, 39, 1225–1234

Macromolecules 2018, 51, 3243–3253.
23 Ito, S.; Akiyama, H.; Sekizawa, R.; Morì, M.; Yoshida, M.; Kihara, H. Light-induced reworkable adhesives based on ABA-type triblock copolymers with azopolymer termini. ACS Appl. Mater. Interfaces 2018, 10, 32649–32658.
24 Chen, M.; Yao, B.; Kappi, M.; Liu, S.; Yuan, J.; Berger, R.; Zhang, F.; Butt, H. J.; Liu, Y.; Wu, S. Entangled azobenzene-containing polymers with photoinduced reversible solid-to-liquid transitions for healable and reprocessable photoactuators. Adv. Funct. Mater. 2019, 30, 1906752.
25 Xu, B.; Zhu, C.; Qin, L.; Wei, J.; Yu, Y. Light-directed liquid manipulation in flexible bilayer microtubes. Small 2019, 15, 1901847.
26 Yue, Y.; Norikane, Y.; Azumi, R.; Koyama, E. Light-induced mechanical response in crosslinked liquid-crystalline polymers with photoswitchable glass transition temperature. Nat. Commun. 2018, 9, 1–8.
27 Lin, K. T.; Chen, Y. J.; Huang, M. R.; Karapala, V. K.; Ho, J. H.; Chen, J. T. Light-induced nanowetting: erasable and rewritable polymer nanoarrays via solid-to-liquid transitions. Nano Lett. 2020, 8, 5853–5859.
28 Natansohn, A.; Rochon, P. Photoinduced motions in azo-containing polymers. Chem. Rev. 2002, 102, 4139–4175.
29 Weis, P.; Tian, W.; Wu, S. Photoinduced liquefaction of azobenzene-containing polymers. Chem. Eur. J. 2018, 24, 6494–6505.
30 Rau, H. in Photochemistry and photophysics. Vol. II, Ed. by Rabek, J. F.; Scott, G. W. CRC, Boca Raton, 1990, p. 119–141.
31 Pipertzis, A.; Hess, A.; Weis, P.; Papamokos, G.; Koyov, K.; Wu, S.; Floudas, G. Multiple segmental processes in polymers with cis and trans stereoregular configurations. ACS Macro Lett. 2017, 7, 11–15.
32 Hartley, G. S. J. N. The cis-form of azobenzene. Nature 1937, 140, 281–281.
33 Okui, Y.; Han, M. Rational design of light-directed dynamic spheres. Chem. Commun. 2012, 48, 11763–11765.
34 Akiyama, H.; Yoshida, M. Photochemically reversible liquefaction and solidification of single compounds based on a sugar alcohol scaffold with multi azo-arms. Adv. Mater. 2012, 24, 2353–2356.
35 Uchida, E.; Sakaki, K.; Nakamura, Y.; Azumi, R.; Hirai, Y.; Akiyama, H.; Yoshida, M.; Norikane, Y. Control of the orientation and photoinduced phase transitions of macrocyclic azobenzene. Chem. Eur. J. 2013, 19, 17391–17397.
36 Hoshino, M.; Uchida, E.; Norikane, Y.; Azumi, R.; Nozawa, S.; Tomita, A.; Sato, T.; Adachi, S.; Koshihara, S. Y. Crystal melting by light: X-ray crystal structure analysis of an azo crystal showing photoinduced crystal-melt transition. J. Am. Chem. Soc. 2014, 136, 9158–9164.
37 Norikane, Y.; Uchida, E.; Tanaka, S.; Fujiwara, K.; Koyama, E.; Azumi, R.; Akiyama, H.; Kihara, H.; Yoshida, M. Photoinduced crystal-to-liquid phase transitions of azobenzene derivatives and their application in photolithography processes through a solid-liquid patterning. Org. Lett. 2014, 16, 5012–5015.
38 Xu, G.; Li, S.; Liu, C.; Wu, S. Photoswitchable adhesives using azobenzene-containing materials. Chem. Asian J. 2020, 15, 547–554.
39 Weis, P.; Hess, A.; Kircher, G.; Huang, S.; Aeumhammer, G. K.; Koyov, K.; Butt, H. J.; Wu, S. Effects of spacer on photoinduced reversible solid-to-liquid transitions of azobenzene-containing polymers. Chem. Eur. J. 2015, 21, 10946–10953.
40 Shin, J.; Sung, J.; Kang, M.; Xie, X.; Lee, B.; Lee, K. M.; White, T. J.; Leaf, C.; Sottos, N. R.; Braun, P. V.; Cahill, D. G. Light-triggered thermal conductivity switching in azobenzene polymers. Proc. Natl. Acad. Sci. USA 2019, 116, 5973–5978.
41 Kuenstler, A. S.; Clark, K. D.; de Alainiz, J. R.; Hayward, R. C. Reversible actuation via photoisomerization-induced melting of a semicrystalline poly(azobenzene). ACS Macro Lett. 2020, 9, 902–909.
42 Seki, T. Meso- and microscopic motions in photosensitive liquid crystalline polymer films. Macromol. Rapid Commun. 2014, 35, 271–290.
43 Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. Laser-induced holographic surface relief gratings on nonlinear optical polymer films. Appl. Phys. Lett. 1995, 66, 1166–1168.
44 Rochon, P.; Batalla, E.; Natansohn, A. Optically induced surface gratings on azaaromatic polymer films. Appl. Phys. Lett. 1995, 66, 136–138.
45 Li, Y.; He, Y.; Tong, X.; Wang, X. Photoinduced deformation of amphiphilic azo polymer colloidal spheres. J. Am. Chem. Soc. 2005, 127, 2402–2403.
46 Karageorgiev, P.; Neher, D.; Schulz, B.; Stiller, B.; Pietsch, U.; Giersig, M.; Brehmer, L. From anisotropic photo-fluidity towards nanomanipulation in the optical near-field. Nat. Mater. 2005, 4, 699–703.
47 Wang, J.; Wang, X.; He, Y. Fabrication of fluorescent surface relief patterns using AIE polymer through a soft lithographic approach. J. Polym. Sci., Part B: Polym. Phys. 2016, 54, 1838–1845.
48 Koskela, J. E.; Liljestrom, V.; Lim, J.; Simanek, E. E.; Ras, R. H.; Primagi, A.; Kostiainen, M. A. Light-fuelled transport of large dendrimers and proteins. J. Am. Chem. Soc. 2014, 136, 6850–6853.
49 Gao, F.; Yao, Y.; Wang, W.; Wang, X.; Li, L.; Zhuang, Q.; Lin, S. Light-driven transformation of bio-inspired superhydrophobic structure via reconfigurable PAzOma microarrays: from lotus leaf to rice leaf. Macromolecules 2018, 51, 2742–2749.
50 Kong, X.; Wang, X.; Luo, T.; Yao, Y.; Li, L.; Lin, S. Photomanipulated architecture and patterning of azopolymer array. ACS Appl. Mater. Interfaces 2017, 9, 19345–19353.
51 Wang, W.; Yao, Y.; Luo, T.; Chen, L.; Lin, J.; Li, L.; Lin, S. Deterministic reshaping of breath figure arrays by directional photomanipulation. ACS Appl. Mater. Interfaces 2017, 9, 4223–4230.
52 Huang, J.; Wu, S.; Beckemper, S.; Gillner, A.; Zhang, Q.; Wang, K. All-optical fabrication of ellipsoidal caps on azobenzene functional polymers. Opt. Lett. 2010, 35, 2711–2713.
53 Huang, J.; Beckemper, S.; Wu, S.; Shen, J.; Zhang, Q.; Wang, K.; Gillner, A. Light driving force for surface patterning on azobenzene-containing polymers. Phys. Chem. Chem. Phys. 2011, 13, 16150–16158.
54 Lee, S.; Shin, J.; Lee, Y. H.; Park, J. K. Fabrication of the funnel-shaped three-dimensional plasmonic tip arrays by directional photofluidization lithography. ACS Nano 2010, 4, 7175–7184.
55 Lee, S.; Shin, J.; Lee, Y. H.; Fan, S.; Park, J. K. Directional photofluidization lithography for nanoarchitectures with controlled shapes and sizes. Nano Lett. 2010, 10, 296–304.
56 Lee, S.; Kang, H. S.; Park, J. K. High-resolution patterning of various large-area, highly ordered structural motifs by directional photofluidization lithography: sub-30-nm line, ellipsoid, rectangle, and circle arrays. Adv. Funct. Mater. 2011, 21, 1770–1778.
57 Kang, H. S.; Kim, H. T.; Park, J. K.; Lee, S. Light-powered healing of a wearable electrical conductor. Adv. Funct. Mater. 2014, 24, 7273–7283.
58 Wang, W.; Du, C.; Wang, X.; He, X.; Lin, J.; Li, L.; Lin, S. Directional
photomanipulation of breath figure arrays. Angew. Chem. Int. Ed. 2014, 53, 12116–12119.
59 Wang, W.; Shen, D.; Li, X.; Yao, Y.; Lin, J.; Wang, A.; Yu, J.; Wang, Z. L.; Hong, S. W.; Lin, Z.; Lin, S. Light-driven shape-memory porous films with precisely controlled dimensions. Angew. Chem. Int. Ed. 2018, 57, 2139–2143.
60 Saphiannikova, M.; Toshchevikov, V. Optical deformations of azobenzene polymers: orientation approach vs. photofluidization concept. J. Soc. Inf. Disp. 2015, 23, 146–153.
61 Vapaavuori, J.; Laventure, A.; Bazuin, C. G.; Lebel, O.; Pellerin, C. Submolecular plasticization induced by photons in azobenzene materials. J. Am. Chem. Soc. 2015, 137, 13510–13517.
62 Teboul, V.; Rajonson, G. Breakdown of the scallop theorem for an asymmetrical folding molecular motor in soft matter. J. Chem. Phys. 2019, 150, 144502.
63 Ciobotarescu, S.; Hurdus, N.; Teboul, V. How does the motion of the surrounding molecules depend on the shape of a folding molecular motor? Phys. Chem. Chem. Phys. 2016, 18, 14654–14661.
64 Juan, M. L.; Plain, J.; Bachelot, R.; Royer, P.; Gray, S. K.; Wiederrecht, G. P. Multiscale model for photoinduced molecular motion in azo polymers. ACS Nano 2009, 3, 1573–1579.
65 Yager, K. G.; Barrett, C. J. in Light-induced nanostructure formation using azobenzene polymers. Vol. 0, Ed. by Nalwa, H. S. American Scientific, New York, 2006, p. 1–38.
66 Vapaavuori, J.; Mahimwalla, Z.; Chromik, R. R.; Kaivola, M.; Primagi, A.; Barret, C. J. Nanoindentation study of light-induced softening of supramolecular and covalently functionalized azo polymers. J. Mater. Chem. C 2013, 1, 2806–2810.
67 Harrison, J. M.; Goldbaum, D.; Corkery, T. C.; Barret, C. J.; Chromik, R. R. Nanoindentation studies to separate thermal and optical effects in photo-softening of azo polymers. J. Mater. Chem. C 2015, 3, 995–1003.
68 Sorelli, L.; Fabbri, F.; Frech-Baronet, J.; Vu, A.; Fafard, M.; Gacoin, T.; Lahlil, K.; Martinelli, L.; Lassailly, Y.; Peretti, J. A closer look at the light-induced changes in the mechanical properties of azobenzene-containing polymers by statistical nanoindentation. J. Mater. Chem. C 2015, 3, 11055–11065.
69 Kumar, J.; Li, L.; Jiang, X. L.; Kim, D.; Lee, T. S.; Tripathy, S. Gradient force: the mechanism for surface relief grating formation in azobenzene functionalized polymers. Appl. Phys. Lett. 1998, 72, 2096.