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Photoresponsive polymers with multi-azobenzene groups

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Azobenzene is a switchable compound that exhibits reversible *trans*–*cis* photoisomerization. Photoresponsive polymers have been prepared by incorporating azobenzene groups into polymers. Most of the reported azobenzene-containing polymers (azopolymers) have only one azobenzene group in the repeat unit of the polymers (mono-azopolymers). To improve photoresponsiveness, multi-azobenzene groups have been covalently or non-covalently introduced into the repeat units of azopolymers (multi-azopolymers). In this Perspective, we introduce photoresponsive multi-azopolymers. We summarize the preparation of such polymers and highlight their potential applications in photoactuation, photo-patterning, and photoinduced birefringence. The innovative potential, open questions, and remaining challenges in this field are also discussed.

Introduction

Azobenzene is a photoswitchable compound.¹ Light irradiation can induce reversible *trans*-to-*cis* isomerization.^{2,3} This property enables the use of light to control a variety of properties of azobenzene-containing materials, such as their

polarity,^{4,5} solubility,^{5,6} melting points,^{7–9} glass transition temperature (T_g) values,^{10–12} viscosity,^{13–15} wrinkles,^{16–18} morphology,^{19–23} mechanical properties,^{24,25} etc. In the past, the photophysical and photochemical properties of azobenzene derivatives have been extensively studied. Substituents strongly influence the spectral characteristics and photoswitching behaviors of azobenzene derivatives. Rau divided azobenzenes^{26,27} into three types (Fig. 1): (1) azobenzene-type compounds bearing alkyl, aryl, halide, carbonyl, amide, nitrile, ester, and carboxylic acid substituents. The π – π^* and n – π^* absorption bands of *trans* azobenzene are located in the UV range and visible range, respectively. UV irradiation induces *trans*-to-*cis* isomerization (Fig. 2a). The half-life of *cis* isomers is usually from hours to days. Visible light irradiation

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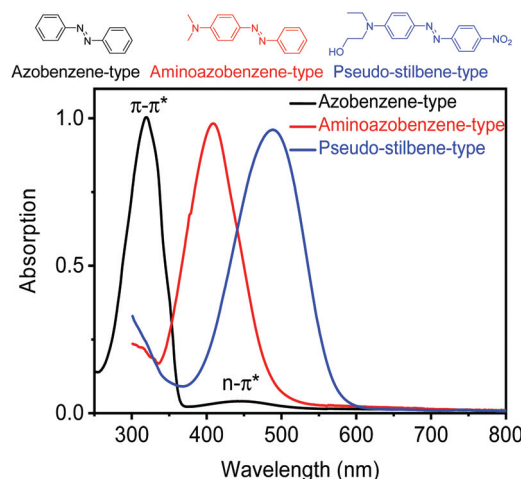


Fig. 1 Typical chemical structures and UV/Vis absorption spectra of three types of azobenzenes.



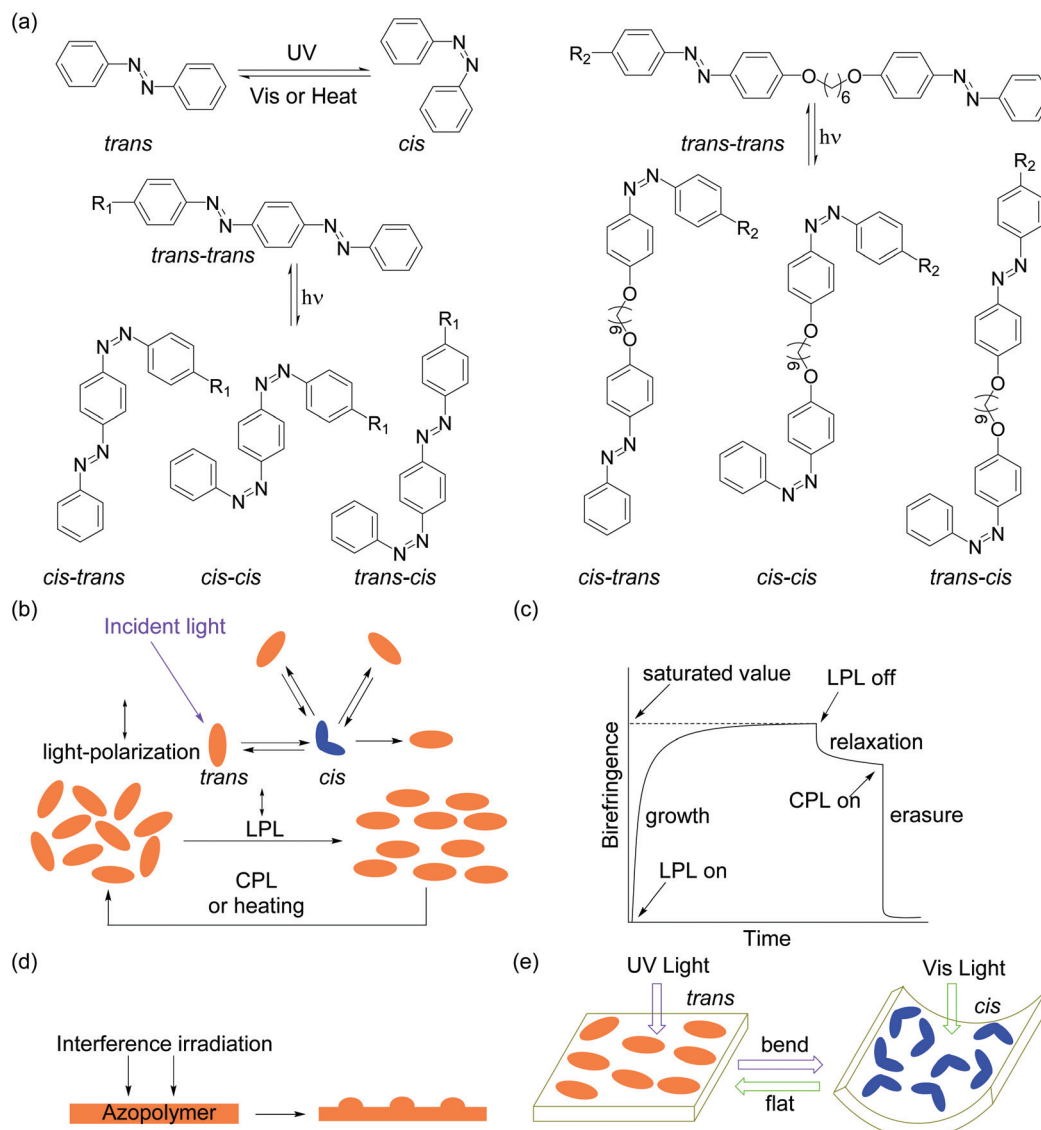


Fig. 2 (a) Photoisomerization of azobenzene and bis-azobenzene derivatives. (b) Schematic illustrations of the photoinduced orientations of azobenzene chromophores in the solid state. (c) Birefringence is induced under LPL irradiation, reaches a saturated value after irradiation for a certain time, relaxes via thermal relaxation when LPL is turned off, and is erased using CPL. (d) Formation of photoinduced SRGs. (e) Schematic illustrations of photoactuation.

or thermal relaxation induces *cis*-to-*trans* isomerization (Fig. 2a); (2) aminoazobenzene-type compounds having at least one amino or hydroxyl group located *ortho* or *para* to the azobenzene group. The π - π^* absorption band of the *trans* isomer is bathochromically shifted to 400–450 nm, partially overlapping with the n - π^* absorption band. The half-life of *cis* isomers becomes shorter, usually from milliseconds to seconds; (3) pseudo-stilbene-type compounds containing a push-pull substitution *para* to the azobenzene group. Their π - π^* absorption band and n - π^* absorption band are both located in the visible range, completely overlapping with each other. These types of azobenzene compounds have a fast rate for photoisomerization. The half-lives of *cis* isomers are usually from milliseconds to seconds.

All these types of azobenzene compounds have been incorporated into polymers that have better processability than small molecules. Polymers provide azobenzene group suited matrices for photoisomerization in the solid state. In addition, besides photoisomerization,^{28,29} azobenzene-containing polymers (azopolymers) show other interesting photoresponsive properties such as photoinduced orientation (Fig. 2b and c),^{30–43} formation of surface relief gratings (SRGs) (Fig. 2d),^{44–48} photoactuation (Fig. 2e),^{49–54} and photo-controlled self-assembly behaviors.^{55–66} When an azopolymer film is irradiated with linearly polarized light (LPL),^{67,68} the azobenzene groups tend to orient perpendicular to the light polarization. Subsequent circularly polarized light (CPL) irradiation or heating can erase the orientation (Fig. 2b).^{30–35} Thus, bire-



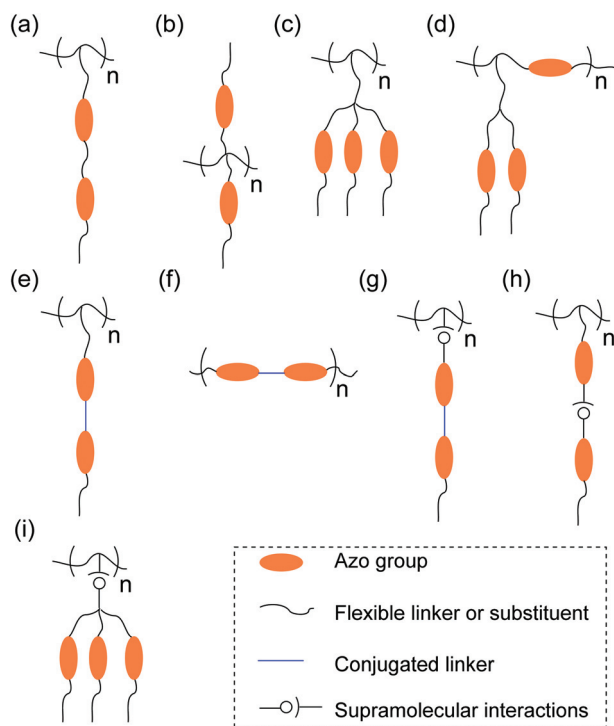


Fig. 3 Schematic illustrations of multi-azopolymers with different structures: (a–d) non-conjugated multi-azopolymers, (e and f) conjugated multi-azopolymers, and (g–i) supramolecular multi-azopolymers.

fringence can be generated and erased by light irradiation (Fig. 2c). When an azopolymer film is irradiated with interference laser beams, SRGs are induced (Fig. 2d).^{69–73} Another photoresponsive behavior of azopolymers is photoactuation. Light irradiation can induce macroscopic motions such as bending and contraction of azopolymers (Fig. 2e).^{74,75} Azopolymers can also undergo self-assembly *via* supramolecular interactions and light can control the physicochemical properties of supramolecular azopolymers.^{76–86} There are comprehensive reviews about the development of azopolymers and the investigations of photoresponsive properties mentioned above.^{67,87–89}

Different from previous reviews, in this Perspective, we focus on azopolymers that have multi-azobenzene groups in the repeat unit. We call these types of polymers multi-azopolymers. Conventional azopolymers have only one azobenzene group in each repeat unit; such mono-azopolymers have been widely studied. The photoisomerization of multi-azobenzene groups results in more types of isomers (Fig. 2a). Multi-azobenzene groups may have a larger aspect ratio than mono-azobenzene groups, exhibiting larger birefringence when oriented. Multi-azobenzene groups also exhibit interesting (liquid) crystallinities. With more azobenzene groups in a repeat unit of polymers, multi-azopolymers show some unique photoresponsive properties.^{90–92} Here, we present the current status of multi-azopolymers, their potential applications, and the challenges, with the aim of highlighting the most relevant literature in this field.

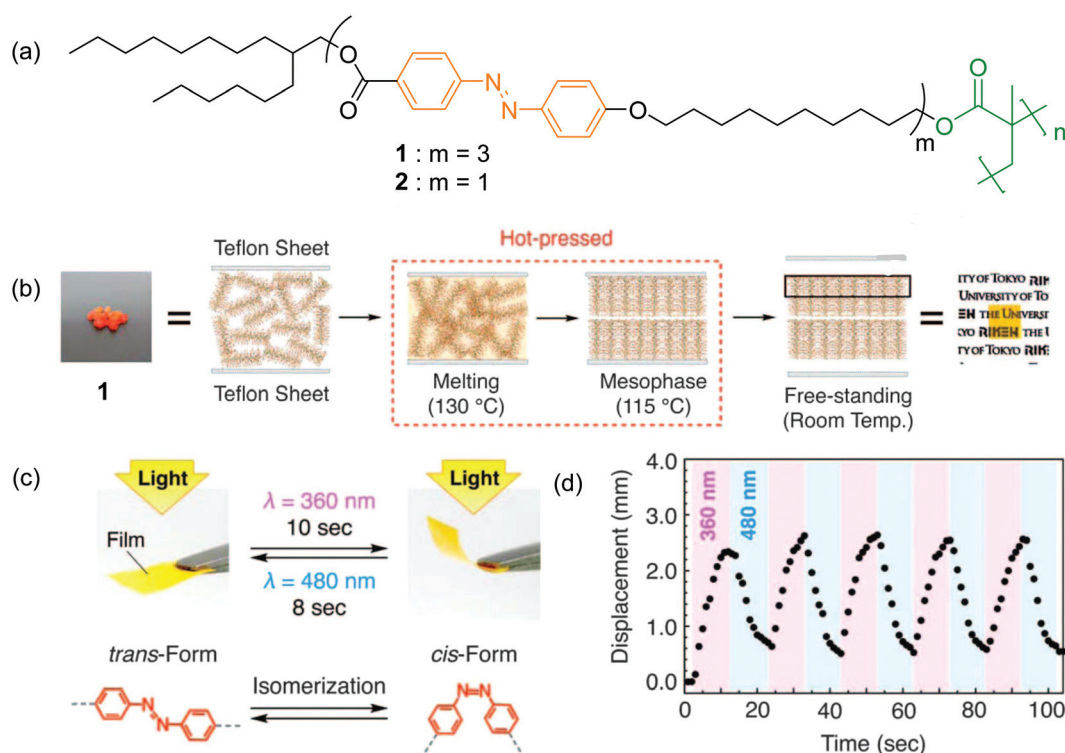


Fig. 4 (a) Chemical architectures of polymers 1 and 2. (b) Schematic illustrations of the preparation of free-standing films *via* hot-pressing. (c) Photographs of a hot-pressed film (5 mm x 6 mm x 10 μm) prepared with parallel-arranged Teflon sheets before (left) and after (right) exposure to UV light (λ = 360 ± 2 nm). The bent film recovered the initial flat shape upon exposure to visible light (λ = 480 ± 2 nm). (d) Time-dependent change in the displacement of the free edge of a hot-pressed film prepared with parallel-arranged Teflon sheets upon alternating irradiation with UV and visible lights. Reproduced with permission from ref. 93, copyright 2010, AAAS.



Types of multi-azopolymers

We summarize a few types of multi-azopolymers in Fig. 3. There is still room for designing new multi-azopolymers based on polymer chemistry, supramolecular chemistry, and organic chemistry. From the polymer chemistry point of view, multi-azobenzene groups can be introduced into polymer side chains, backbones, or both. Because of the diversity of polymer structures, new multi-azopolymers can be designed. From the supramolecular chemistry point of view, multi-azopolymers can be prepared by non-covalently introducing multi-azobenzene groups into polymers. From the organic chemistry point of view, small-molecule multi-azobenzene groups can have different structures (see for example bis-azobenzenes with flexible and conjugated linkers in Fig. 2a). Multi-azobenzene groups can be introduced into a repeat unit of polymers either in parallel or in series. In the following, we introduce different types of multi-azopolymers according to their structures.

Polymers with non-conjugated multi-azobenzene groups

Non-conjugated azobenzene groups mean that two or more azobenzene groups are connected *via* non-conjugated flexible linkers. Non-conjugated multi-azobenzene groups can be

introduced into polymers in series. For example, Aida and co-workers studied a polymer with three azobenzene groups in series in the side chain of each repeat unit (Fig. 4).⁹³ They synthesized a methacrylate monomer with three azobenzene groups and prepared polymer **1** through free radical polymerization (Fig. 4a, $m = 3$). Because of the long side chains, polymer **1** is like a brush. The polymer chains of **1** were oriented homeotropically to the substrates *via* one-step hot-pressing (Fig. 4b). The hot-pressed film exhibited a rapid and reversible photo-mechanical response under the irradiation of UV and visible light (Fig. 4c and d).^{74,94} In contrast, the control sample, polymer **2** (Fig. 4a, $m = 1$), which had only one azobenzene group in each repeat unit, did not show the alignment behavior by hot pressing. These results indicate that the multi-azopolymer forms ordered structures more easily *via* hot pressing than the mono-azopolymer does. On the basis of these interesting findings, the authors demonstrated a design principle for polymers that form 2D homeotropic orders.⁹⁵

Akiyama *et al.* prepared oligo-dendrimer type molecules, multi-azobenzene sugar-alcohol derivatives,^{96–98} in which the multi azobenzene groups were connected in parallel with each other. These kinds of molecules showed photochemically reversible solid-liquid transitions and could be applied to reworkable adhesives.

In 2013, Zhu and Wang reported polymers with two and three azobenzene groups in parallel in the polymer side chains.⁹⁹ These polymers showed reversible photoisomerization. Furthermore, birefringence was induced by LPL

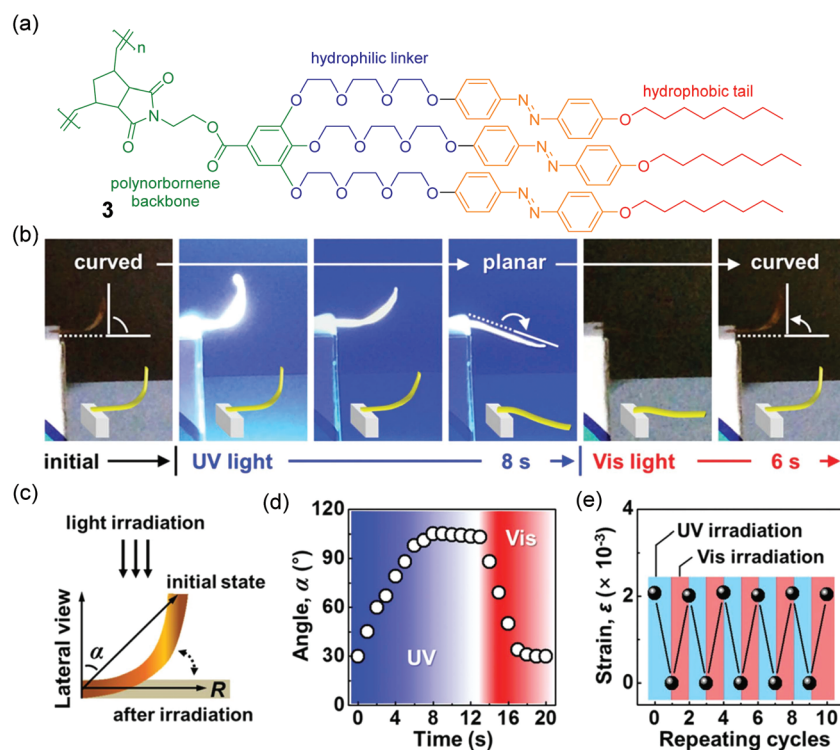


Fig. 5 (a) Chemical structure of polymer **3**. (b) Photo-modulation of a freestanding film of **3** upon UV and visible light irradiation. (c) Schematic illustration of the photomechanical motion. (d) Reversible flexion angle changes with respect to UV and visible irradiation. (e) Repeated experiments of the photo-stimulated bending strain. Reproduced from ref. 100. Copyright (2017) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



irradiation. Multi-azobenzene moieties in each repeat unit of the polymer resulted in larger birefringence.

Kim *et al.* also prepared polymers with azobenzene groups in parallel in the polymer side chains (Fig. 5).¹⁰⁰ Different from Zhu and Wang's strategy, polymer 3 was synthesized *via* ring opening metathesis polymerization (ROMP). Free-standing films were prepared. The backbone and azobenzene side chains of polymer 3 in the film were perpendicular and parallel to the layer normal, respectively. When the film was exposed to UV light, it quickly bent away from the light source due to *trans*-to-*cis* isomerization (Fig. 5b–d). After subsequent visible light irradiation, the film recovered to its original state because of *cis*-to-*trans* back isomerization. Photoinduced bending and unbending were fully reversible (Fig. 5e). Further investigations showed that such types of multi-azopolymers exhibit photoisomerization¹⁰¹ and photoinduced chirality,¹⁰² and can be used as photoresponsive semiconductors with good photo-fatigue resistance.¹⁰³

Polymers with conjugated multi-azobenzene groups

Some azo groups were connected *via* conjugated linkers. Conjugated multi-azobenzene groups have been introduced into polymer side chains (Fig. 6a). Polymer 4 was prepared by Meng and Natansohn through free radical polymerization.⁹⁰ Compared with 5 that has mono-azobenzene groups (Fig. 6b),¹⁰⁴ 4 showed larger photoinduced birefringence because of the intrinsic higher aspect ratio of the bis-azobenzene group (Fig. 6c and d). In addition, 4 showed a slower rate of photoinduced birefringence and a higher birefringence stability than 5, which is because of the lower mobility of the bis-azobenzene group.

In addition, polymethacrylates with similar structures have been synthesized and their photoresponsive properties, such as photoisomerization,^{91,105–112} photo-alignment,^{106,107,110}

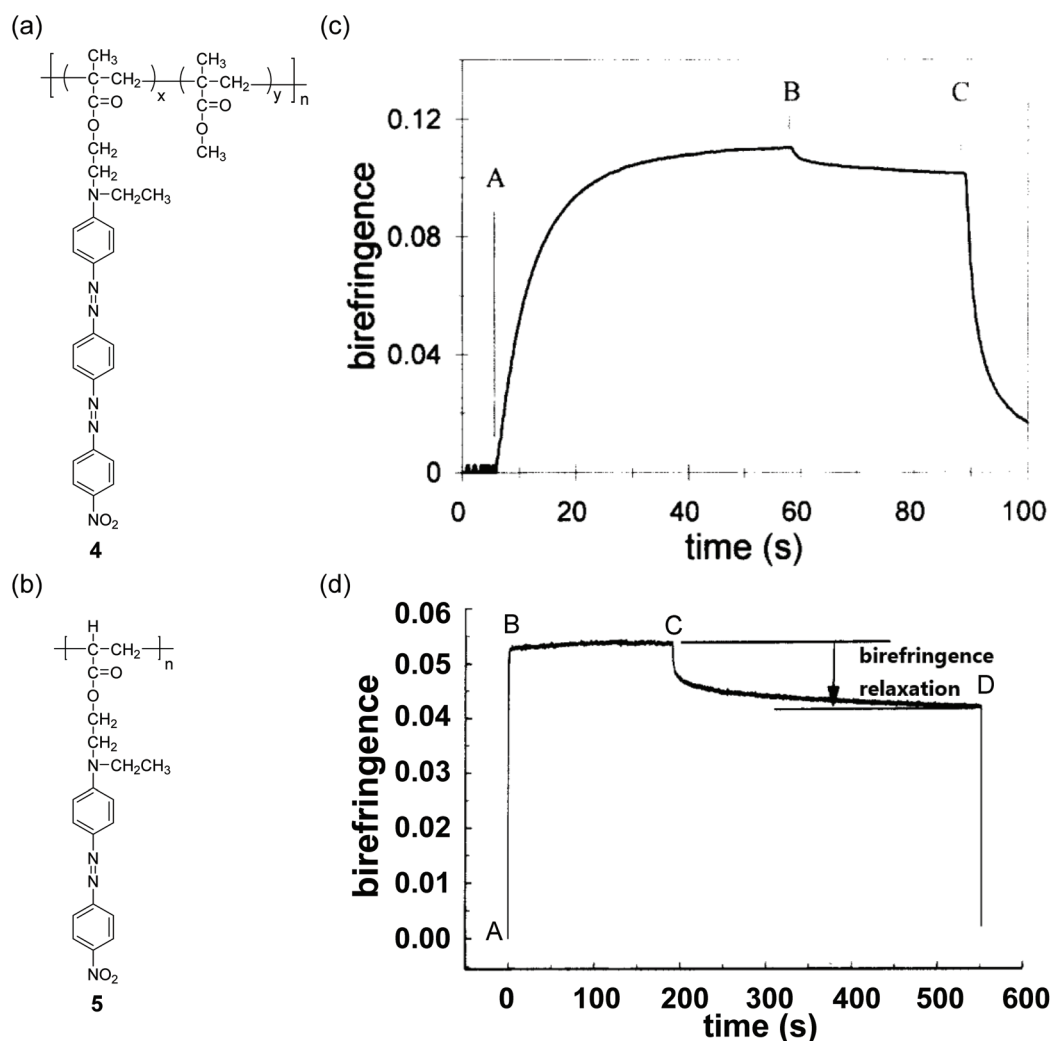


Fig. 6 Chemical structures of (a) 4 and (b) 5. Writing–erasing profile of the photoinduced birefringence of films of (c) 4 and (d) 5. Panel (c) is reprinted from ref. 90. Copyright (1997) with permission from Elsevier. Panel (d) is reprinted with permission from ref. 104. Copyright (1995) American Chemical Society.

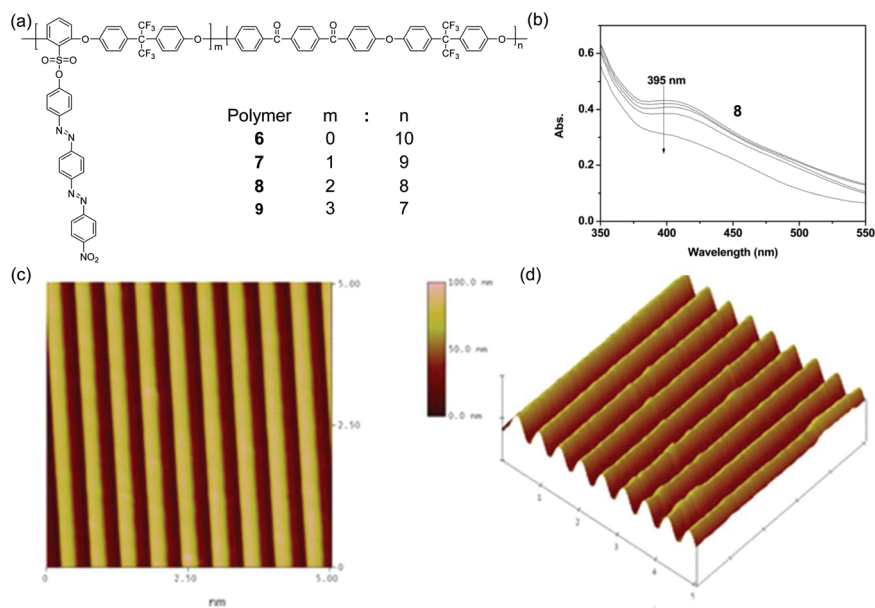


Fig. 7 (a) Chemical structures of **6**, **7**, **8** and **9**. (b) Changes in the UV-Vis absorption spectra of **8** in DMF induced by 405 nm light irradiation. (c) AFM plane view of the SRGs and (d) AFM 3-D view of the SRGs. Reprinted with permission from ref. 119. Copyright (2016) SAGE Publications.

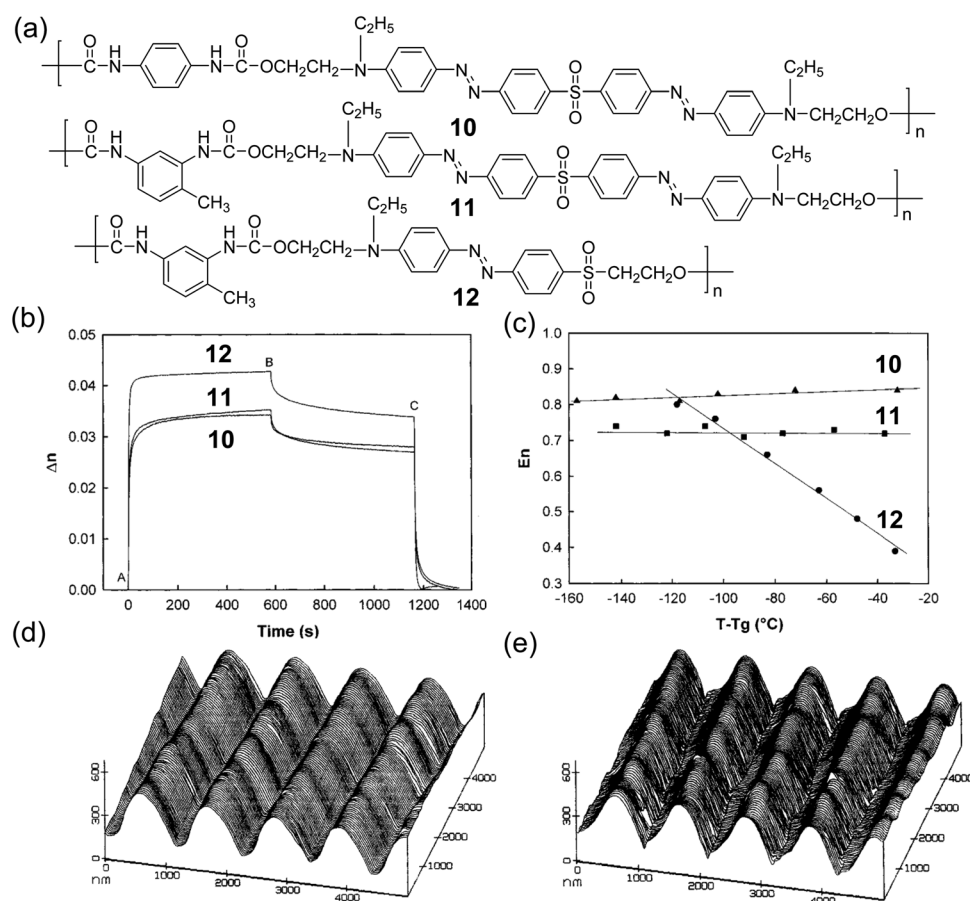


Fig. 8 (a) Chemical structures of **10**, **11**, and **12**. (b) Typical birefringence curves for **10**, **11**, and **12** films. LPL is turned on at point A and turned off at point B; CPL is turned on at point C. (c) Long-term stable birefringence, E_n , which is denoted as the ratio of birefringence conserved for a very long time to saturated birefringence, as a function of reduced temperature. The lines are only a guide to the eye. ▲, **10**; ■, **11**; ●, **12**. AFM surface grating profile of **11** observed before (d) and after (e) thermal treatment at 182 °C for 90 min. Reprinted with permission from ref. 120. Copyright (2001) American Chemical Society.



photoinduced birefringence,^{91,105,106,108–110,113} information storage,¹¹² and the induction of helical chirality,^{111,114,115} have been investigated. The rate of photoinduced birefringence for the bis-azopolymers was slower than that for mono-azopolymers,^{90,91} while the birefringence values for bis-azopolymers were higher and the birefringence stability for bis-azopolymers was better than those for mono-azopolymers.^{90,91,108,109} However, there was an exception, where both the rate and the level of photoinduced birefringence for the bis-azopolymers were better than those for mono-azopolymers.¹⁰⁵ In addition to multi-azopolymers with a poly(meth)acrylate backbone, multi-azopolymers with other types of backbones have also been studied, such as polymethacrylamides showing photoinduced birefringence¹¹⁶ and polyurethane anionomers showing photoisomerization.¹¹⁷

Besides photoinduced birefringence, multi-azopolymers are also suited for photoinduced SRGs. In an early example, Wang *et al.* reported the inscription of SRGs on polymers with conjugated bis-azobenzene groups on polymer side chains.¹¹⁸ Recently, Zhang *et al.* synthesized poly(aryl ether)s **6**, **7**, **8**, and **9** (Fig. 7) *via* polycondensation.¹¹⁹ Polymers **6**, **7**, **8**, and **9** had

high glass transition temperature (T_g) values and good thermal stability.¹¹⁹ These polymers also showed photoisomerization (Fig. 7b) and photoinduced SRGs under the irradiation of interference beams (Fig. 7c and d), which have potential applications in optical data storage.

Besides polymers with conjugated multi-azobenzene groups on side chains, polymers with conjugated multi-azobenzene groups on polymer backbones were also reported. Wu *et al.* reported a series of main-chain type bis-azopolyurethanes (**10** and **11**) (Fig. 8).¹²⁰ The mono-azopolyurethane (**12**) was also studied for comparison. Polymers **10**, **11**, and **12** had T_g values at 182 °C, 167 °C, and 143 °C, respectively.¹²⁰ All of them showed photoinduced birefringence (Fig. 8b). Polymers **10** and **11** displayed smaller birefringence than polymer **12** due to the bent V shape of the bis-azobenzene groups that did not generate large birefringence. Wu *et al.* quantitatively investigated the stability of birefringence with parameter E_n , where E_n is defined as the ratio of birefringence conserved for a very long time to saturated birefringence. A higher value of E_n meant higher stability. They found that the birefringence of **10** and **11** showed higher stability than that of **12** at high tempera-

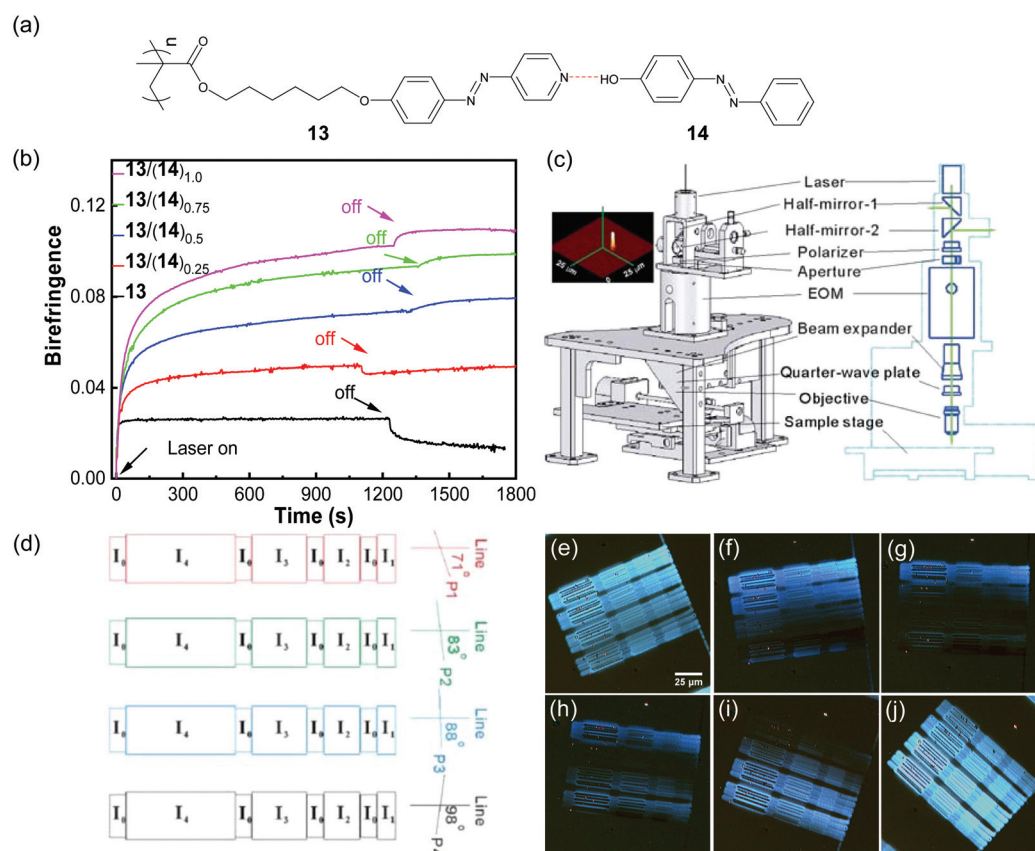


Fig. 9 (a) Chemical structures of **13**, **14**, and the supramolecular polymer. (b) Photoinduced birefringence of the spin-casting films of **13** and **13/(14)_x** (x is the molar ratio of **14/13**). (c) Schematic model of the laser direct writing system for optical recording. The energy distribution of the laser around the focal plane is shown in the upper left. (d) Schematic model of the four-dimensional patterns with 5 different writing powers and 4 different polarization directions. $I_0 = 2$ mw, $I_1 = 4$ mw, $I_2 = 6$ mw, $I_3 = 8$ mw and $I_4 = 10$ mw. Polarized optical microscopy images of four-dimensional patterns with different angles: (e) 65°, (f) 80°, (g) 90°, (h) 95°, (i) 107°, and (j) 130°. Reproduced with permission from ref. 80, copyright 2010, the Royal Society of Chemistry.



tures, even close to T_g (Fig. 8c), which was attributed to the following two reasons: (1) the bulky bis-azobenzene groups with lower mobility enhanced the stability of the orientation; (2) the special architectures of V-shaped bis-azobenzene groups might result in higher relative stability of the photo-induced birefringence. The SRG formed in polymer **11** could be only partly erased by heating (Fig. 8d and e), which was distinct from thermally erasable SRGs reported in other literature studies.^{121,122} Based on this work, the authors further investigated photoinduced birefringence and SRGs in polyurethane elastomers with bis-azobenzene groups in the hard segment.¹²³

Another type of main-chain conjugated multi-azopolymer, which contained azobenzene crown ether moieties, has been studied by Ardeleanu *et al.*^{124,125} This type of multi-azopolymer also showed good thermal stability and reversible photoisomerization behavior.

In addition, a novel organo-phosphonate with bis-azobenzene moieties in the main chain has been reported by Homocianu *et al.*¹²⁶ The new structure endowed the polymers with reversible dual stimuli response, such as light and pH.

Supramolecular multi-azopolymers

In the above two sections, multi-azobenzene groups were introduced into polymers covalently. In contrast, multi-azobenzene groups can also be introduced into polymers *via* supramolecular interactions. Supramolecular multi-azobenzene groups can be introduced into polymers in series or in parallel.

One of us designed supramolecular bis-azopolymers by connecting a side-chain azopolymer with azobenzene small molecules *via* hydrogen bonding (Fig. 9a).⁸⁰ Compared with the mono-azopolymer (**13**, Fig. 9a), the supramolecular polymers **13(14)_x** showed larger photoinduced birefringence and better stability when the content of **14** increased (Fig. 9b). These results are attributed to higher concentrations of azobenzene groups, a higher aspect ratio of the chromophores, and more ordered structures based on chromophore–chromophore interactions. In addition, by using a newly designed laser direct writing system (Fig. 9c), the supramolecular polymer **13(14)_{1.0}** was used for four-dimensional optical recording by integrating the polarization and the intensity of the laser and the planar two dimensions (Fig. 9d), which had an information density 20 times that of a normal DVD. Fig. 9(e–j) show the polarized

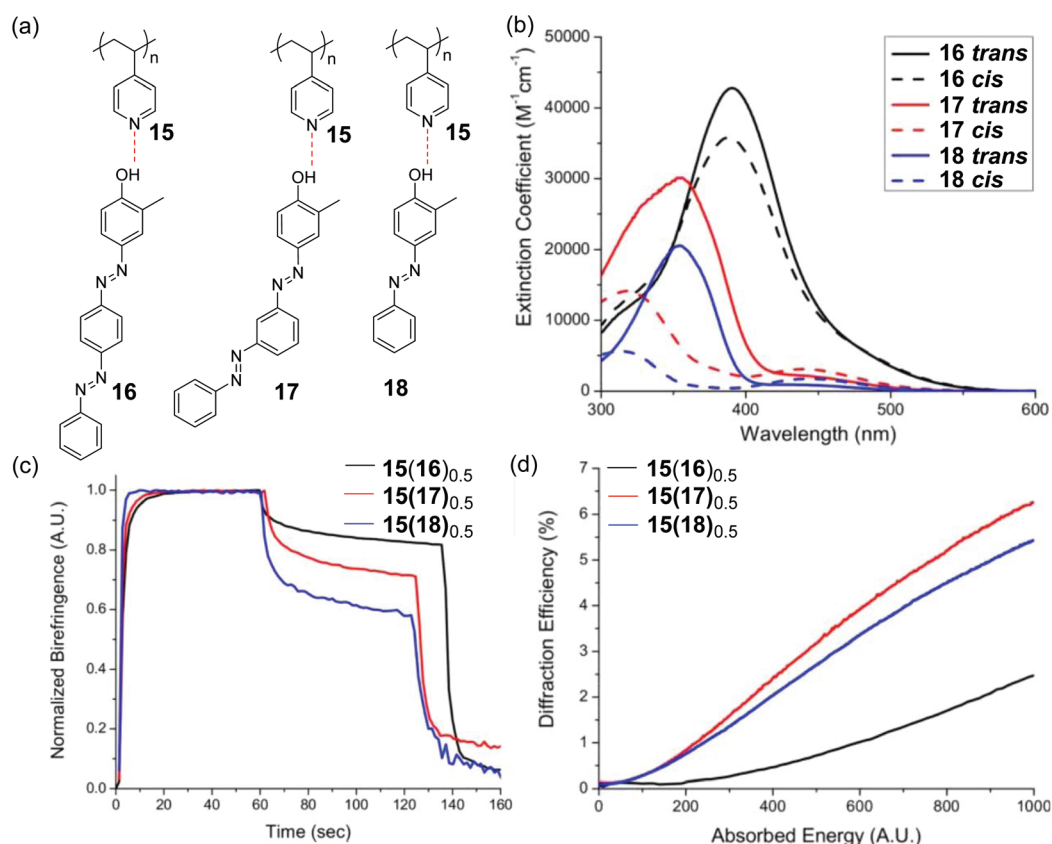


Fig. 10 (a) Chemical structures of **15**, **16**, **17**, and **18** and hydrogen-bonded supramolecular polymers constructed using these compounds. (b) UV–Vis absorption spectra of **16**, **17**, and **18** in THF. (c) Normalized birefringence for thin films of **15(16)_{0.5}**, **15(17)_{0.5}**, and **15(18)_{0.5}** induced by 488 nm light, where 0.5 means the average number of azobenzene chromophores per polymer repeat unit. (d) First-order diffraction efficiencies of **15(16)_{0.5}**, **15(17)_{0.5}** and **15(18)_{0.5}** during SRG inscription under 488 nm light irradiation as a function of absorbed energy. Reprinted with permission from ref. 92. Copyright (2014) American Chemical Society.



optical microscopy images of the microstructure at different angles. These types of supramolecular bis-azopolymers have better solubility and processability than the covalent bis-azopolymers.

Priimagi *et al.* reported another type of supramolecular bis-azopolymer by connecting poly(4-vinylpyridine) (P4VP) with bis-azobenzene small molecules *via* hydrogen bonding.^{127–129} They prepared SRGs on the supramolecular bis-azopolymers. Furthermore, Vapaavuori *et al.* compared the photoresponsive properties of supramolecular polymers with bis-azobenzene and mono-azobenzene groups (Fig. 10).⁹² Supramolecular multi-azopolymers showed better photoinduced birefringence (Fig. 10c). Supramolecular bis-azopolymers **15**(**17**)_{0.5} exhibited more efficient photoinduced SRG formation (Fig. 10d). A few investigations based on similar supramolecular azopolymers were reported.^{129–132}

Besides hydrogen-bonded supramolecular multi-azopolymers, supramolecular multi-azopolymers based on other supramolecular interactions such as host–guest interactions¹³³ and ionic interactions⁸⁴ have also been investigated. These polymers formed supramolecular hydrogels with multi-stimuli responsive properties¹³³ and were used for photoinduced SRGs.⁸⁴

The above-mentioned examples showed that supramolecular multi-azobenzene groups can be introduced into polymers in series, while del Barrio *et al.* demonstrated supramolecular polymers that had hydrogen-bonded multi-azobenzene groups in parallel (Fig. 11).¹³⁴ The photoinduced orientations of these supramolecular multi-azopolymers were studied (Fig. 11a–c). The supramolecular multi-azopolymers showed large and stable photoinduced birefringence even at low contents of the azobenzene compounds (Fig. 11b–d), which were superior to the systems previously reported.¹³⁵ Additionally, other studies based

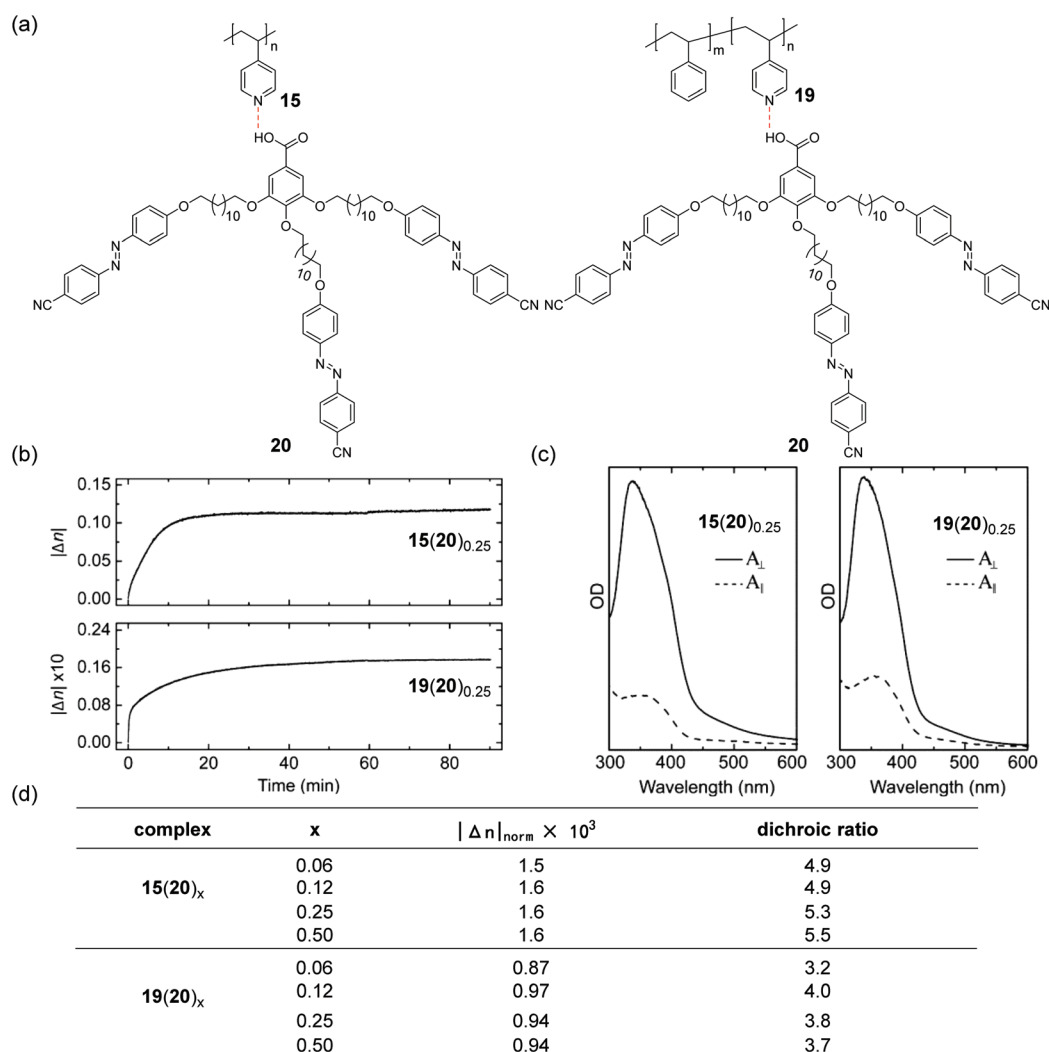


Fig. 11 (a) Chemical structures of **15**, **19**, **20**, and supramolecular polymers constructed using these compounds. (b) Evolution of the photoinduced birefringence in the thermally treated films of **15**(**20**)_{0.25} and **19**(**20**)_{0.25} under the irradiation of 488 nm LPL (films were irradiated between $t = 0$ and $t = 60$ min). (c) Stable polarized absorption spectra of **15**(**20**)_{0.25} and **19**(**20**)_{0.25} recorded at room temperature after irradiation with 488 nm LPL for 60 min and subsequent evolution in the dark for 30 min at the same temperature. (d) Values of $|\Delta n|_{\text{norm}}$ after the irradiation and relaxation periods and the equilibrium dichroic ratio. Reprinted with permission from ref. 134. Copyright (2014) American Chemical Society.



on hydrogen-bonded polymers with supramolecular multi-azobenzene groups in parallel have been reported. Photoinduced anisotropy,¹³⁶ orientation,^{136,137} or birefringence^{136,137} and the photoinduced deformation¹³⁸ of these supramolecular multi-azopolymers have been investigated.

Conclusions and perspective

We introduced multi-azopolymers that exhibit interesting photoresponsive properties. Both side-chain and main-chain multi-azopolymers have been investigated. The photoisomerization of multi-azobenzene groups resulted in more types of isomers. Because multi-azobenzene groups usually have a larger aspect ratio than mono-azobenzene groups, they exhibit larger photoinduced birefringence. Multi-azobenzene groups can be introduced into polymers *via* supramolecular interactions. This supramolecular strategy may simplify the route for the preparation of multi-azopolymers.¹³⁹ Moreover, the composition of supramolecular complexes can be adjusted easily by changing the ratio of azobenzene components and polymer matrices.

Although multi-azopolymers have been extensively studied, we believe that the full potential of multi-azopolymers has not been realised yet. Some key areas in photoresponsive polymers remain to profit from designing multi-azopolymers. Some challenges with regard to multi-azopolymers should be addressed to take this field forward.

First, multi-azobenzene groups, especially the conjugated ones, have poorer solubility than their mono-azobenzene counterparts, which makes the synthesis and processing of multi-azopolymers more difficult. Decoupling the conjugation of multi-azobenzene groups *via* supramolecular interactions may improve solubility and address the issue of processing.

Second, almost all the reported multi-azopolymers have linear architectures. A field that awaits exploration is the combination of interesting photoresponsiveness of multi-azobenzene groups with a variety of polymer topologies, such as stars, branches, and dendrimers. Such a design will result in new photoresponsive polymers.

Thirdly, hydrogen bonding, host-guest interactions¹³³ and ionic interactions⁸⁴ have been used to construct supramolecular multi-azopolymers. Supramolecular multi-azopolymers constructed using other supramolecular interactions such as halogen bonding^{140,141} and coordination^{81–83} are still awaiting exploration.

Fourth, multi-azobenzene small molecules with heterogenic azobenzene groups showed orthogonal photoswitching by light with different wavelengths.^{85,142,143} Such heterogenic multi-azobenzene groups can be switched between more than 2 states. Multi-azopolymers with heterogenic azobenzene groups have not been explored yet and can be controlled with light of different colors.

Conflicts of interest

There are no conflicts to declare.

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