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Here we designed a *trans–cis* photoisomerizable achiral side chain azobenzene-containing polymer, poly(6-[4-(4-methoxyphenylazo) phenoxy] hexyl methacrylate (PAzoMA), to investigate the possibility of transferring chirality of chiral solvent molecules to polymers. Preferred chirality in supramolecularly assembled *trans*-azobenzene units of PAzoMA is successfully induced by limonene chirality. This chiral solvation induced chirality arises from superstructural chirality of well-assembled achiral azobenzene units in polymer side chains. The intense bisignated circular dichroism (CD) signals in the UV-vis region disappeared when *trans–cis* photoisomerization of PAzoMA occurred with 365 nm light irradiation. The polymer aggregates solution shows the CD-silent state when the *cis*-PAzoMA solution was conducted with 436 nm light irradiation. The intense CD signals with a ~40 nm red-shift were recovered by heating the polymer aggregates solution to 60 °C and keeping it for 40 mins, then cooling down to room temperature. The successful construction of reversible chiral-achiral switch based on achiral azobenzene-containing side chain polymer will open a new window for production of chiroptical materials.

Introduction

Optically active polymers have attracted intense interest for potential chiro-technological applications in chiral resolution, asymmetric catalysis, enantioselective sensors and opto-electronic materials.[1] Motivated by these considerations, considerable effort has been devoted to design and synthesize chiral polymers, including polyisocyanates,[1f,2] polyisocyanides,[3] polyguanidines,[4] polysilanes,[5] polyacetylenes,[6] polyfluorene[7] and vinyl polymers,[8] by introduction of chiral groups in the polymer structures as the side chains or end groups. Recently the helical main chain poly(quinoxaline-2,3-diyl)s reported by Suginome and coworkers demonstrated interesting chiroptically switching property to external stimulus.[9] In most cases chiral polymers can be prepared by polymerization of enantiomerically pure monomers. Indeed, this approach tends to involve costly and tedious asymmetric synthesis of chiral monomers with relatively complex procedures. Another strategy towards chiral polymers is to expand host-guest chemistry to transfer adjustable chirality of guest to the achiral host via non-covalent interactions, such as hydrogen bonding, ionic bonds, van der Waals forces and π-π interactions. Up to now, chirality transfer from asymmetric reaction field,[1a,1j,10] circularly polarized light (CPL)[11] and chiral solvent[12] to an achiral host polymer have been reported to produce chiral polymer materials.

Chiral solvation has been shown to be a versatile and efficient protocol in inducing chirality of organic molecules, supramolecular systems and polymers. The first successful asymmetric induction experiment by chiral solvation was achieved for benzyl and benzophenone dissolved in *L*-2,3-butanediol by Bosnich in 1967.[12a] The first chiral solvation induced chirality of polymer was demonstrated by Green et al..[12b] As evidenced by circular dichroism (CD) spectra, one of the dynamically interconverting helical senses was preferred when dissolving achiral poly(*n*-hexyl isocyanate) in a series of chiral chlorinated solvents.[12b] Motivated by this pioneering study, chiral solvation was used to produce optically active polymers in aggregation states, such as polysilanes,[12c,d] polyacetylenes,[12e,f] polyfluorene analogs[12g-p] and oligo(*p*-phenylenevinylene).[12q] In these cases, effective aggregation is a key factor in chiral solvation induced chirality of polymers, in which the chirality of solvent could be amplified significantly. These polymers reveal unique (chir)optical properties, e.g., aggregation-induced circular dichroism (AICD) and aggregation-induced CPL (AICPL),[12,13] when the aggregation process is involved. Although this strategy has been well studied in main-chain π- and σ-conjugated polymeric systems,[12b-q] the extension of this concept to side chain polymeric systems is rare reported. The only one example of side chain polymer is syndiotactic polystyrene, which exhibited strong CD signal in the polymer absorption region in film state by solvent vapor and thermal annealing process.[12r] The reason is that the main

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chain π- and σ-conjugated polymers have much stronger interchain interactions and π-π stacking interactions compared with side chain polymers, facilitating formation of ordered helical structures. Therefore, chiral solvation induced chirality of side chain polymers remains a significant challenge due to the relatively weaker π-π stacking interactions from soft unconjugated polymer chains.

Azobenzene-containing polymers have drawn considerable attention in field of photo-switchable molecular systems ascribed to the unique change of mechanical and physicochemical properties upon reversible *trans-cis* photoisomerization.[14] Optically active polymers, including main chain,[12j,15a-d] side chain[15e-h] and supramolecular[15i-k] polymers with a chiral group and azobenzene (Azo) chromophore have been successfully employed to construct chiroptical switches trigged by the reversible *trans-cis* photoisomerization process of Azo. The photoisomerization of the Azo groups can reversibly change the chiral properties of the polymers. However, it is often more expensive or time consuming to attach chiral substituents to these polymers as described above. Thus the construction of chiroptical switches based on achiral Azo-containing polymers would be very interesting. Up to now, CPL[11] and chiral solvation[12] are both elegant strategies for the production of chiroptical switching materials. Recently, Takezoe et al. summarized that CPL-induced chirality can be achieved in Azo-containing main chain or side chain polymers.[11f] The first process arises from individual chirality of chromophores in their main chain backbone, and the latter one originates from superstructural chirality via organization of achiral Azo units in side chains. More recently, we reported the production of optically active poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4'-azobenzene] (F8AZO) aggregates induced by chiral limonene, showing *trans*-origin aggregation and *cis*-disaggregation in the limonene–2-propanol–chloroform tersolvent system.[12j] These promising results motivate us to extend this approach to achiral side chain Azo polymer systems.

Herein we present the first production of preferred chirality in supramolecularly assembled *trans*-Azo units in side chains induced by limonene chirality in aggregation state. This supramolecular chirality depends on the polymer structures and volume fractions of each solvent (good solvent and chiral solvent). Furthermore, the *trans-cis* isomerizations of Azo chromophore can disrupt the supramolecular chirality of *trans*-Azo, which would be reversibly recovered by heating-cooling the polymer aggregates solution. The current research will expand not only the design and producing of chiral polymer materials but also construction of chiroptical switching polymer materials.

Experimental section

Materials. Copper (I) bromide (CuBr, Aldrich, 98%) was purified with glacial acetic acid and washed with pure ethanol, then stored under argon before use. Anisole, 1,2-dichloroethane (DCE), tetrahydrofuran (THF), dichloromethane (DCM), chloroform (analytical grade, Shanghai Chemical Reagents Company, China) were distilled prior to use. 1-Chloro-6-hydroxyhexane (Acros, 95%), methacryloyl chloride (Aladdin, 95%), 4-aminoanisole (Aladdin, AR), 4-nitrophenol (Aladdin, analytical grade), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (Aldrich, 97%), ethyl 2-bromoisobutyrate (EBIB) (TCI, 98%), (*R*)-(+)-limonene (1*R*, TCI, >95%, $[\alpha]^{24}_{589}$ = +99.62°) and (*S*)-(-)-limonene (1*S*, TCI, >95%, $[\alpha]^{24}_{589}$ = -97.72°) were used without further purification. Unless otherwise stated, all the other chemicals were obtained from Shanghai Chemical Reagents Company (China) and used as received. The monomer, 6-[4-(4-methoxyphenylazo) phenoxy] hexyl methacrylate (AzoMA), was synthesized according to the previously reported procedures.[16] ^{1}H NMR ($CDCl_3$, 400 MHz), (δ, ppm): 7.86 (m, 4H), 6.99 (m, 4H), 6.10 (s, 1H), 5.55 (s, 1H), 4.15 (t, 2H), 4.03 (t, 2H), 3.88 (s, 3H), 1.95 (s, 3H), 1.82 (m, 2H), 1.71 (m, 2H), 1.49 (m, 4H). Elemental analysis, calculated values for $C_{23}H_{28}N_2O_4$: C, 69.68; H, 7.12; N, 7.07. Found: C, 69.75; H, 7.12; N, 6.96.

Synthesis of Poly(6-[4-(4-methoxyphenylazo) phenoxy] Hexyl Methacrylate (PAzoMA). AzoMA (1.0 g, 2.52 mmol), EBIB (32.8 mg, 0.168 mmol), CuBr (47.8 mg, 0.333 mmol), HMTETA (77.8 mg, 0.333 mmol) and anisole (3 mL) were added to a 5 mL ampoule. The solution was deoxygenated with three standard freeze-pump-thaw cycles and flame-sealed. The ampoule was maintained at 80 ^{o}C for 16 h. The mixture was diluted with 2 mL THF, and then passed through a column of neutral aluminum oxide (Al_2O_3) to remove the catalyst. The resulting polymer was precipitated in a large amount of methanol, filtered, and dried in vacuum at room temperature. The yellow polymer (PAzoMA) was obtained with a yield of 84.6% (0.8460 g).The M_n and M_w/M_n values were found to be 6600 g/mol and 1.22, respectively. The other PAzoMAs with different M_ns were prepared by adjusting the molar ratio of monomer and initiator with the similar procedures.

Synthesis of Random Copolymer of AzoMA and MMA (P(AzoMA-*rans*-MMA)). AzoMA (0.30 g, 0.76 mmol), methyl methacrylate (MMA, 8.4 mg, 0.084 mmol), EBIB (8.2 mg, 0.042 mmol), CuBr (6.1 mg, 0.043 mmol), HMTETA (9.7 mg, 0.042 mmol) and 2 mL anisole were added to a 5 mL ampoule. The mixture was degassed three times by standard freeze-pump-thaw cycles. After flame-sealing, the ampoule was kept at 80 ^{o}C for 16 h. The mixture was diluted with 2 mL THF, passing a column of neutral Al_2O_3, and then precipitated in methanol. The polymer was collected by filtration and dried under vacuum overnight. The copolymer was obtained with a yield of 69.7% (0.209 g). The M_n and M_w/M_n values were found to be 6600 g/mol and 1.18, respectively. The molar ratio of MMA and AzoMA in the final copolymer is determined to be 1/9 by ^{1}H NMR spectrum. The other copolymer (MMA/AzoMA = 1/4) was obtained by changing the MMA and AzoMA ratios under the similar experimental conditions.

Preparation of the Optically Active Polymer Aggregates. 2.5 mL of 1*R* was added to 0.5 mL of a 1,2-dichloroethane solution containing PAzoMA ([repeat unit]$_0$ = 2.52 × 10^{-3} mol/L) in a SQ-cuvette. After being slightly shaken, the yellowish turbid solution of PAzoMA aggregates was used for CD/UV-vis spectroscopic measurements. The other solutions of polymer aggregates were produced in a similar way.

Pbotoisomerization Process of Polymer Solution. Photoisomerization of Azo-containing polymer solutions in mixed solvent (DCE/(1*R* or 1*S*) = 0.5/2.5, v/v) was conducted using a 500-W high-pressure mercury lamp (Ushio (Tokyo, Japan), Optiplex SX-UID and 502HUV), and the wavelengths (365 and 436 nm) were obtained through narrow bandpass filters (Sigma Koki, Shanghai, China). The irradiation intensities were 2000 μW cm^{-2} at 365 nm and 880 μW cm^{-2} at 436 nm, respectively (Ophir Optronics with

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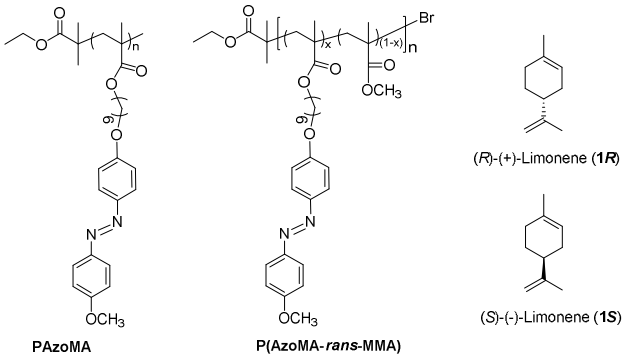
Nova with photodiode head PD300-UV (Tel-Aviv, Israel)). For the chiroptical switch experiment, the sample was kept at 60 °C for 40 mins and cooled down to room temperature.

Characterization. Gel-permeation chromatography (GPC) measurements were conducted on a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2412), using HR1 (pore size: 100 Å, 100−5000 Da), HR2 (pore size: 500 Å, 500−20,000 Da), and HR4 (pore size 10,000 Å, 50−100,000 Da) columns (7.8 × 300 mm^2, 5 μm beads size) with molecular weights ranging from 10^2 to 5 × 10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. GPC samples were injected using a Waters 717 plus auto sampler and calibrated with poly(methyl methacrylate) (PMMA) standards. Transmission electron micrograph (TEM) images were taken with a HITACHI HT7700 operated at an accelerating voltage of 150 kV. Dynamic light scattering (DLS) measurements were performed with a Zetasizer Nano ZS instrument (Malvern (Malvern, Worcestershire, UK)) at 25 °C. ^{1}H NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard at 25 °C. Elemental analyses (C, H and N) were measured with an EA1110 CHNO-S instrument. The UV-vis spectra were recorded on a UV-2600 spectrophotometer (Shimadzu (Nakagyo-ku, Kyoto, Japan)). The CD spectra were recorded on a JASCO J-815 spectropolarimeter (JASCO China, Shanghai, China) equipped with a Peltier-controlled housing unit using an SQ-grade cuvette, with a path length of 10 mm, a scanning rate of 100 nm/min, a bandwidth of 2 nm and a response time of 1 s, using a single accumulation at 25 °C. The magnitude of the circular polarization at the ground state is defined as $g_{CD} = 2 \times (\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$, where ε_L and ε_R denote the extinction coefficients for left and right circularly polarized light, respectively. Experimentally, g_{CD} value is defined as $\Delta\varepsilon/\varepsilon$ = [ellipticity/32,980]/absorbance at the CD extremum.



Scheme 1 Chemical structures of poly(6-[4-(4-methoxyphenylazo) phenoxy] hexyl methacrylate (PAzoMA), random copolymer of AzoMA and MMA, (*R*)-(+)-limonene (1*R*) and (*S*)-(-)-limonene (1*S*).

Results and discussion

Prior to inducing chirality of side chain Azo-containing polymers by chiral solvation, the homopolymer of AzoMA (PAzoMA) and random copolymer of AzoMA and methyl methacrylate (MMA) (P(AzoMA-*rans*-MMA)) (Scheme 1) were prepared by atom transfer radical polymerization (ATRP)[16] with controlled molecular weight (M_n) and relatively low molecular weight distribution (M_w/M_n) (Fig. S1). As presented in Table 1, three PAzoMAs with different M_ns (6600, 11000 and 14700 g/mol) and relatively narrow M_w/M_n (1.22−1.30) were easily achieved by regulating the molar ratio of monomer AzoMA and the initiator EBiB. Two P(AzoMA-*rans*-MMA)s with different AzoMA contents (90% and 80%), determined by ^{1}H NMR spectra (Fig. S2), were also successfully obtained in good yields by adjusting the molar ratio of AzoMA and MMA monomers.

Table 1 Molecular weight characteristics of the PAzoMAs and P(AzoMA-*rans*-MMA)s.

Entry	Ratio[a]	Conv[b] (%)	$M_{n(th)}$[c] (g/mol)	$M_{n(GPC)}$[d] (g/mol)	M_w/M_n[e]	AzoMA/MMA[f] (molar ratio)
$PAzoMA_1$	15:1:2:2	84.6	5200	6600	1.22	-
$PAzoMA_2$	35:1:2:2	78.7	11100	11000	1.26	-
$PAzoMA_3$	50:1:2:2	78.8	15800	14700	1.30	-
RC_1	2:18:1:2:2	69.7	5300	6600	1.18	9/1
RC_2	4:18:1:2:2	58.9	4400	6400	1.17	4/1

[a]Polymerization ratio: $[AzoMA]_0/[EBIB]_0/[CuBr]_0/[HMTETA]_0$ for the homopolymerization and $[MMA]_0/[AzoMA]_0/[EBIB]_0/[CuBr]_0/[HMTETA]_0$ for the copolymerization. [b]Determined gravimetrically. [c]Caculated by $M_{n(th)}$ = ($[Monomer]_0/[EBiB]_0$) × $M_{w,Monomer}$ × conversion%. [d,e]Determined by GPC according to PMMA standards in THF. [f]Estimated by ^{1}H NMR spectra. RC_1 and RC_2 are P(AzoMA-*rans*-MMA)s with different AzoMA/MMA ratios. Polymerization time is 7 h for all of experiments.

Typically the chiral tersolvent system composed of good solvent, chiral solvent and poor solvent is needed to produce the optically active polymer aggregates from achiral conjugated polymers.[12c-p] It is noted that, good, chiral and poor solvents play respective roles, *e.g.* dissolving the polymer, the chiral source and implementation of aggregation, respectively. In current study, chiral limonene (1*R* and 1*S* in Scheme 1) is selected as chiral solvent because it is naturally occurring hydrocarbon solvent with good stability and nontoxicity.[12e-p] Considering the poor solubility of PAzoMA in 1*R* or 1*S*, PAzoMA was first dissolved in dichloroethane (DCE), and then 1*R* or 1*S* was added into solution as chiral transducer and a poor solvent to produce optically active polymer aggregates. The intense circular dichroism (CD) signals related to the π-π* electronic transition of the *trans*-Azo chromophore shown in Fig. S3 indicated that the optically active PAzoMA aggregates were successfully produced by chiral solvation of limonene. Almost intense mirror-image CD spectra were obtained (Fig. S3) when 1*R* were replaced by 1*S*. Interestingly, limonene can act as a chiral solvent and poor solvent simultaneously in current system due to the relatively poor solubility of PAzoMA in limonene, which would facilitate producing optically active polymer aggregates and studying its mechanism. Previous studies indicated that the volume fraction of cosolvents (good solvent and chiral solvent in this study) is a very important factor in chiral solvation induced chirality of π-conjugated polymers.[12c-p] The similar results were also observed as displayed in Fig. 1a. The maximum absolute CD amplitude of PAzoMA aggregates solution was observed when DCE/(1*R* or 1*S*) is 0.5/2.5 (v/v). The absolute CD amplitude first increased steeply with an increase of

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DCE/(1*R* or 1*S*) volume fraction, and then decreased after reaching its maximum absolute amplitude. Considering the effect of absorbance in solutions with various DCE/(1*R* or 1*S*) volume fractions, the dependence of g_{CD} value on DCE/(1*R* or 1*S*) volume fraction was further studied, showing the similarly changing trend to that of CD amplitude. The reason is that the production of loose polymer precipitates resulted from lower volume fraction of good solvent, and relatively weaker π-π stacking of Azo units in polymer side chains due to higher volume fraction of good solvent.[12g-p] This phenomenon is supported by the corresponding UV-vis spectra as recorded in Figs. 1b and S4. UV-vis spectra of polymer aggregates show two absorption bands ranged from 300 nm to 425 nm and from 425 nm to 550 nm, which are attributed to the π-π* electronic transition of the *trans*-Azo chromophore and *n*-π* electronic transition of the *cis*-Azo chromophore in polymer side chains. The apparent narrowing of the π-π* band with the increase of DCE/(1*R* or 1*S*) volume fraction demonstrates a weaker tendency to π-π stacking of Azo units. Appearance of the shoulder at 342 nm indicates that the organization of Azo units dominates with *H*-aggregates in aggregation state. This conclusion was supported by the dynamic light scattering (DLS) data recorded in different DCE/(1*R* or 1*S*) volume fractions. The DLS data demonstrate that the polymer aggregate size becomes bigger ranging from 8 nm to 773 nm for DCE/1*R* and from 1 nm to 655 nm for DCE/1*S* respectively, with the decrease of DCE/(1*R* or 1*S*) volume fraction (Figs. 2 and S5),

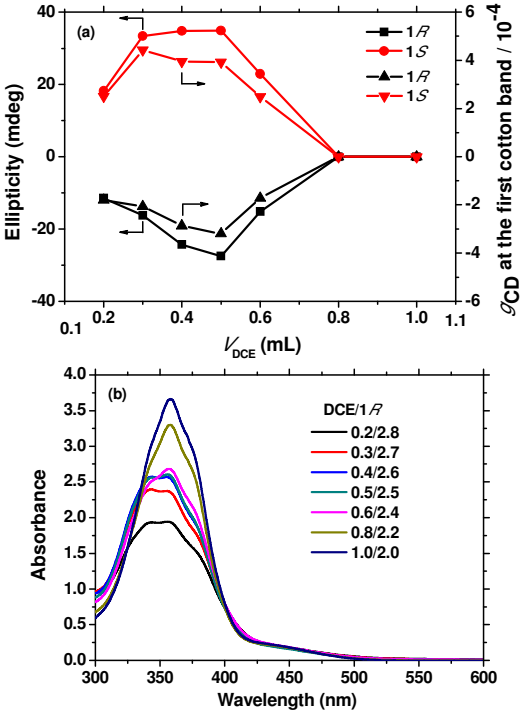

Fig. 1 (a) The maximum CD and g_{CD} values (360 nm) of PAzoMA aggregates with different DCE/(1*R* or 1*S*) volume fractions and (b) UV-vis spectra of PAzoMA aggregates with different DCE/1*R* volume fractions. The concentration of polymer repeating unit is 1.26×10^{-4} mol/L. The molecular weight of PAzoMA determined by GPC is 11000 g/mol.

implying stronger aggregation in mixed solvents with lower DCE/(1*R* or 1*S*) volume fractions.

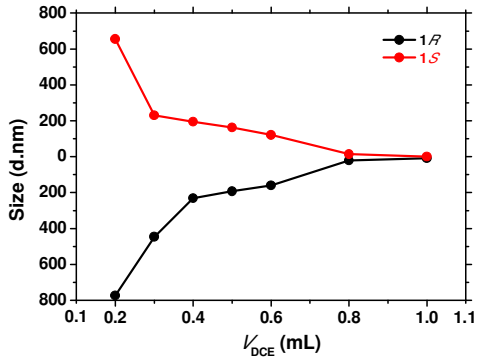

Fig. 2 The dependence of polymer aggregates size on the DCE/(1*R* or 1*S*) volume fractions. These data are taken from Fig. S5. The concentration of polymer repeating unit is the same as in Fig. 1.

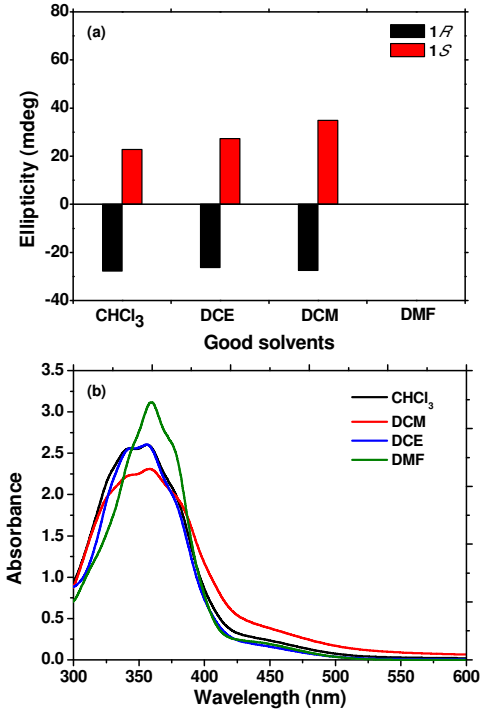

Fig. 3 The maximum CD (360 nm) values (a) and UV-vis spectra (b) of PAzoMA aggregates in mixed solvents with different good solvents. Good solvent/(1*R* or 1*S*) = 0.5/2.5 (v/v) for (a) and Good solvent/1*R* for (b). The concentration of polymer repeating unit is the same as in Fig. 1.

The aggregation experiment was also conducted in DCE and DCE/CH_3OH to verify that the chiral aggregation of Azo units in polymer chains was really induced by limonene solvation. As evidenced by Fig. S6, the similar broad UV-vis spectrum was observed when the polymer aggregate dispersed in the mixed DCE/CH_3OH (0.5/2.5, v/v), indicating the similar aggregation behaviour as that in DCE/(1*R* or 1*S*). However, no detectable CD

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signal was observed, demonstrating that the preferential helicity of the Azo stacks was driven by limonene solvation.

The effect of good solvent was also investigated with chloroform ($CHCl_3$), dichloromethane (DCM) and dimethylformamide (DMF) as the good solvent in place of DCE respectively (Fig. 3). The maximum CD value in ($CHCl_3$ or DCM)/(1*R* or 1*S*) is similar to that in DCE/(1*R* or 1*S*) (Fig. 3a), however, it almost disappeared in DMF/(1*R* or 1*S*). In addition, Figs. 3b and S7 show that UV-vis spectra in DMF/(1*R* or 1*S*) is much more narrower than that employed $CHCl_3$, DCM or DCE as good solvent respectively. The absorption intensity in DMF/(1*R* or 1*S*) is also high, with respect to the other three good solvents cases. It can be concluded that the effect of good solvent greatly affected the π-π stacking of Azo units in polymer side chains.

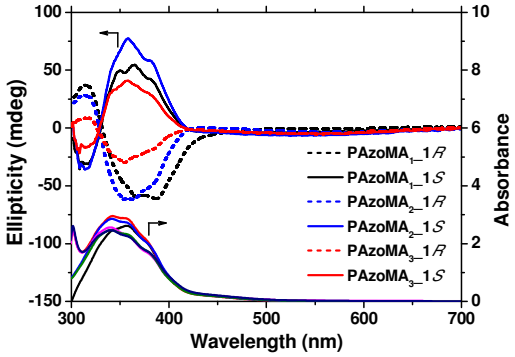

Fig. 4 UV-vis and CD spectra of PAzoMA aggregates with different molecular weights in mixed solvents. DCE/(1*R* or 1*S*) volume fraction and the concentration of polymer repeating unit is the same as in Fig. 3.

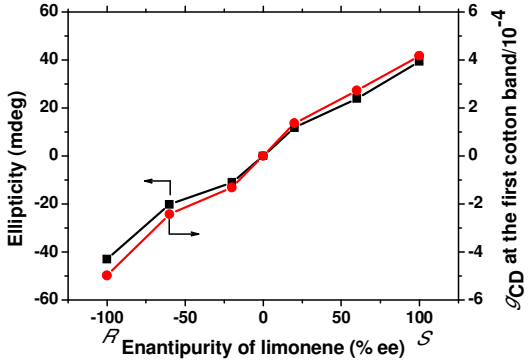

Fig. 5 The maximum CD (360 nm) and g_{CD} values of PAzoMA aggregates in mixed solvents with different 1*R*/1*S* enantiopurities. DCE/(1*R*+1*S*) = 0.5/2.5 (v/v). The concentration of polymer repeating unit is the same as in Fig. 1.

The CD intensity of the polymer aggregates is slightly affected by the molecular weight. As presented in Fig. 4, three polymers with different molecular weights all shows strong mirror image Cotton effect, although $PAzoMA_2$ (M_n = 11000 g/mol) give slightly stronger CD intensity compared to the other polymers with different M_ns.

The possibility of chiral amplification in the aggregation of Azo units in polymer side chains was investigated by changing the enantiopurity (*ee*) of limonene, while keeping the total volume fraction of DCE and limonene as constant ((1*R*+1*S*)/DCE = 2.5/0.5, v/v). The plot of CD intensity and g_{CD} value at 360 nm presents a linear dependence on the enantiopurity of limonene (Fig. 5), demonstrating that the helical sense of the Azo stacks is linearly controlled by excess enantiomer of the chiral solvent. Several similar enantiopurity dependencies of the chiral solvents for the chiral solvation induced chiral aggregation of the CD-silent main chain π-conjugated polymers were also found.[12g-p] The possible reason may be that the right- and left-handed Azo stacks were predominantly produced proportionally to the corresponding ratio of 1*R* and 1*S*, when the mixture of them was added into polymer solution simultaneously as chiral inducer and poor solvent.

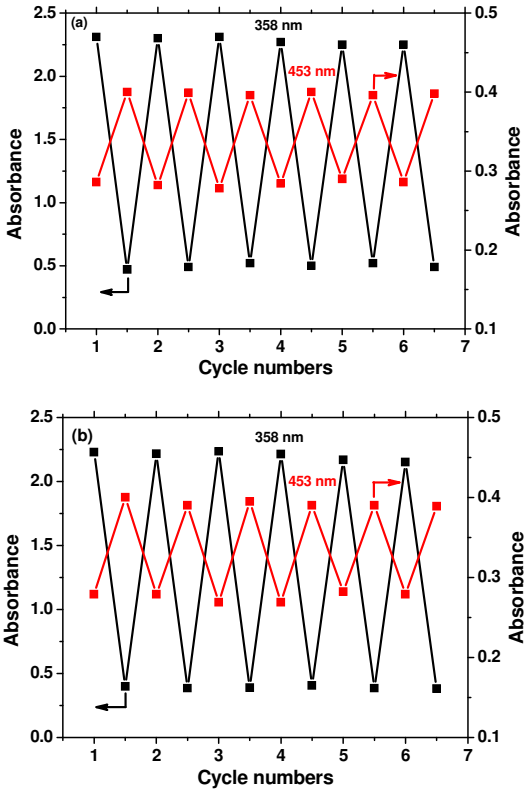

Fig. 6 Photoisomerization switching of the UV-vis spectra ((a) DCE/1*R* and (b) DCE/1*S*) of PAzoMA aggregates by alternating irradiation with 365 nm and 436 nm light. The irradiation times for 365 nm light and 436 nm light are both 2 min. The absorbance change for *trans*- and *cis*-form is taken from 358 nm (black) and 453 nm (red), respectively. DCE/(1*R* or 1*S*) volume fraction and the concentration of polymer repeating unit is the same as in Fig. 3.

The *trans-cis* photoisomerization of PAzoMA aggregates in mixed solvent DCE/(1*R* or 1*S*) (0.5/2.5, v/v) were investigated, as displayed in Figs. 6 and S8. Expectedly the strong absorption band attributed to a π-π* electronic transition of the *trans*-Azo chromophore centered at 358 nm rapidly decreased upon 365 nm light irradiation, while the weak absorption at 453 nm due to *n*-π* electronic transition of the *trans*-Azo chromophore increased, regardless of limonene chirality. As a result, the absorption at 358 nm increased

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along with the decrease of the absorption at 453 nm with 436 nm light irradiation, indicating that the *cis*-*trans* photoisomerization was achieved. The reversible photoisomerization process can be conducted many times by alternative 365 /436 nm light irradiation, as shown in Fig. 6.

Our previous study demonstrated that the repeated photoisomerization of Azo chromophore trigged the reversible chiroptical response from the *trans*-origin chiral aggregation and *cis*-origin achiral disaggregation of main chain polymers.[12j] This interesting result prompts us to study the chiroptical response to the reversible photoisomerization of side chain Azo polymer aggregates. As presented in Fig. 7, the intense CD signals in *trans*-PAzoMA in DCE/(1*R* or 1*S*) immediately disappeared after 365 nm light irradiation for 2 min, indicating the chiral aggregation of Azo groups in polymer side chain was destroyed in *cis*-PAzoMA. It is well known that the coplanar structure of Azo unit will be distorted from *trans*-form to *cis*-form, which will disorganize the orderly assembled structure of *trans*-Azo.[14c,f,17] Bobrovsky and co-workers reported that the *trans*-*cis* photoisomerization process resulted in the decrease of CD values of chiral Azo polymers, deriving from disrupting elements of helical order by *cis*-form.[15e] As clearly seen in Fig. 8, the energy-mimized structure of *trans*-form of PAzoMA side chain shows better coplanar property than that of *cis*-form, indicating that the chirality of PAzoMA aggregates are definitely due to the supramolecular helical structures of PAzoMA side chains.

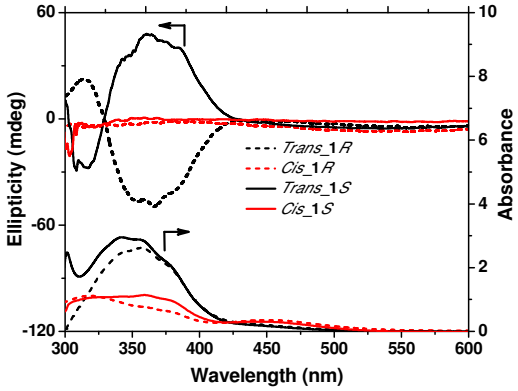


Fig. 7 Changes in CD and UV-vis spectra of *trans*- and *cis*-form of PAzoMA aggregates in mixed solvents. DCE/(1*R* or 1*S*) volume fraction and the concentration of polymer repeating unit is the same as in Fig. 3.

Nevertheless, no obvious CD signals were recorded when the PAzoMA aggregates in DCE/(1*R* or 1*S*) underwent from *cis*-form to *trans*-form by 436 nm light irradiation for 2 min. In order to explain this observation, the monomer AzoMA and random copolymers of AzoMA and methyl methacrylate (MMA) with different MMA ratios, (P(AzoMA-*rans*-MMA)s) (Scheme 1 and Table 1), were dissolved in DCE/(1*R* or 1*S*) (0.5/2.5, v/v), respectively. No detectable CD signals were observed in AzoMA solution (DCE/(1*R* or 1*S*)) (Fig. S9a) because the AzoMA is molecularly dissolved in this mixed solvent and no obvious aggregation occurred. Meanwhile, the CD signals of the polymer aggregates weakened with the increase of MMA contents in P(AzoMA-*rans*-MMA), and disappeared when MMA contents is 20% (Fig. S9b). It means that the randomly inserted MMA units in P(AzoMA-*rans*-MMA) chain will impede the assembly process of Azo to helical stacks. Based on these data, a chiral supramolecular assembly process was proposed in Scheme 2, in which the chiral signals of PAzoMA aggregates deriving from the Azo units in the polymer side chain were induced by limonene chirality. Then the supramolecular helical Azo stacks aggregated into particles. It is noted that the polymethacrylic chain is not involved in a helical organization. This well-organized supramolecular structure is easily to be disorganized by *trans*-*cis* photoisomerization of Azo units or incorporating MMA units into polymer chains, resulting in the CD-silent polymer aggregates. The unrecovered chiral aggregation of PAzoMA in above mixed solvents may be attributed to the uncompleted *cis*-to-*trans* transformation of Azo units or the formation of imperfect supermolecular assemblies, especially in aggregation state, althrough it can not be strongly supported by the UV-vis spectra.

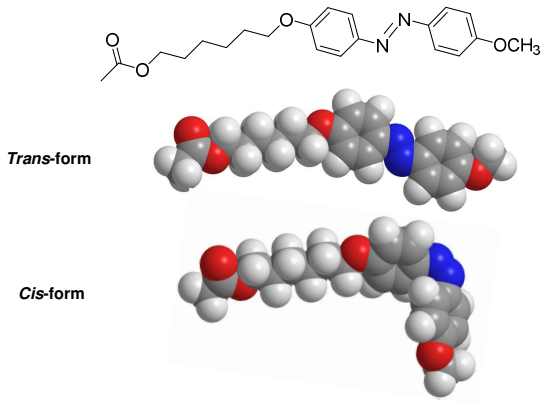
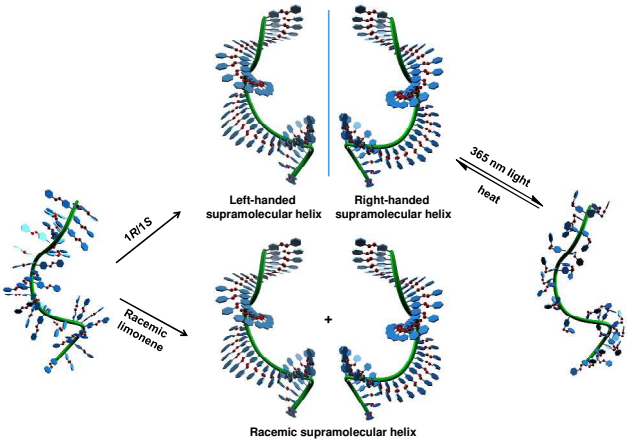


Fig. 8 The energy-mimized models of *trans*- and *cis*-form of PAzoMA side chain.



Scheme 2 Illustration of the supramolecular helical structure of PAzoMA induced by chiral limonene and construction of chiroptical switch. Limonene molecules and methoxyl group in Azo units are omitted for clarity. The polymethacrylic chain is not involved in a helical organization.

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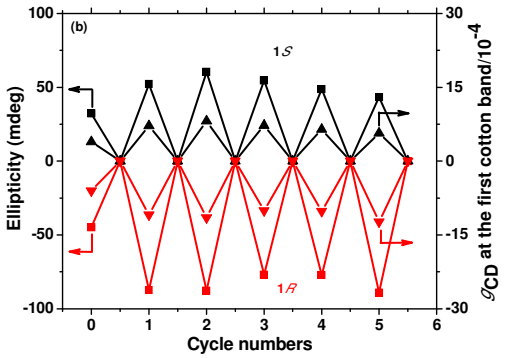

Fig. 9 (a) Change of the maximum CD and g_{CD} values of PAzoMA aggregates in mixed solvents during 365 nm light irradiation and heating-cooling treatment. These data are taken from Fig. S10. DCE/(1*R* or 1*S*) volume fraction and the concentration of polymer repeating unit is the same as in Fig. 3.

In order to confirm this assumption, the polymer aggregates solution above was heated and kept at 60 °C for 40 min, and then cooled down to the room temperature. It is interesting to find that the strong CD signals appeared again after heating-cooling cycle, however, accompanied by red shifted from the original 360 nm (absolute maximum value position) to 410 nm, regardless of limonene chirality. The similar result can be achieved only by heating-cooling assisted *cis-trans* isomerization of Azo units, without 436 nm light irradiation, as depicted in Figs. S10a and S10c. This reversible chiral-achiral switch can be repeated at least six times by alternating 365 nm light irradiation and heating-cooling process (keeping 60 °C for 40 min), as shown in Fig. 9. No significant changes were detected in the UV-vis spectra (Figs. S10b and S10d).

TEM were employed to monitor the changes in the size and morphology of polymer aggregates during the reversible chiral-achiral switch experiments. As presented in Fig. 10, polymer aggregates composed by nanoparticles were observed in DCE/(1R or 1S) system (Fig. 10a). The relatively big nanoparticles (about 500 nm in diameter) were obtained when the polymer aggregates solution was irradiated for 2 min with 365 nm light (Fig. 10b). In *cis*-form, the ordered supramolecular structure was destroyed and much more polymer chains aggregated together, resulting the much larger particles.[14f,16b] After heating-cooling treatment, the particles mixed with different sizes (about 30 and 1000 nm) (Figs. 10c and 10d). The particles with about 500 nm in diameter were obtained again when above solution was irradiated 2 min with 365 nm light again (Fig. 10e). Similar changes in the size and morphology of polymer aggregates were also observed in DCE/1S system (Fig. 10f-j). These changes in size and morphology of polymer aggregates during the reversible chiral-achiral switching processes may be partly contributed to the red-shift in their CD spectra.

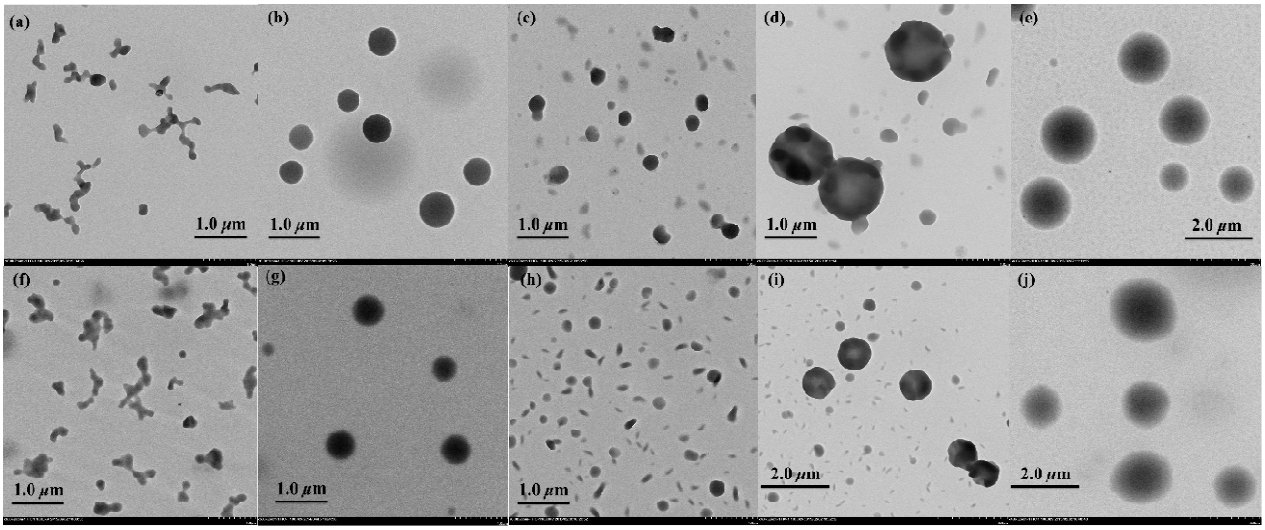

Fig. 10 TEM images of polymer aggregates during the chiral-achiral switching process. (a-e for 1*R*/DCE and f-j for 1*S*/DCE). The original *trans*-form (a and f), after the first 2 min 365 nm light irradiation (b and g), after the heating-cooling treatment (c,d and h, i), after the second 2 min 365 nm light irradiation (e and j). DCE/(1*R* or 1*S*) volume fraction and the concentration of polymer repeating unit is the same as in Fig. 3.

Conclusions

In summary, chiral solvation induced chirality transfer from limonene molecules to achiral side chain Azo-containing polymers (PAzoMAs) in aggregation state is achieved. The chirality originated from the supramolecularly assembled *trans*-azobenzene units of PAzoMA is affected by types of good solvents, volume fraction of

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good and chiral solvents, enantiopurity of limonene. No apparent effect of molecular weights of PAzoMAs on chiral aggregation behaviour is observed. This supermolecular chirality will be destroyed by *trans-cis* photoisomerization process due to noncoplanar structure of *cis*-Azo unit, however, it can be recovered by heating-assisted reorganized process. This reversible chiral-achiral switching process can be repeated more than six times. The mechanism of current system is different from our previous studied Azo-containing π-conjugated polymer system. The current study will facilitate producing not only chiroptical materials from achiral polymers, but also studying the mechanism of chirality transfer induced by chiral solvation.

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