

Supporting Information

Construction of the secondary and tertiary chiral structures in side-chain azobenzene polymers with flexible main chains

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S1 Materials and Characterization

Materials.

Methyl (*R*)-(+)-lactate (Adamas, $\geq 98\%$), methyl (*S*)-(-)-lactate (Adamas, $\geq 98\%$), tetrabutylammonium fluoride (Aladdin, 1.0 M in THF), *tert*-butylchlorodiphenylsilane (Amethyst, $\geq 98\%$), 2-chloroethanol, 3-chloro-1-propanol, 4-chloro-1-butanol, 5-chloro-1-pentanol, 6-chloro-1-hexanol (Acros, 95%), phenol (Aladdin, AR), methacryloyl chloride (Aladdin, 95%), 4-aminoanisole (Aladdin, AR), 1,2-triphenylphosphine (Greagent, $>99\%$), diethyl azodicarboxylate (Aladdin, $\geq 97\%$), 4-dimethylaminopyridine (Macklin, 99%), *n*-(3-dimethylaminopropyl)-*n*'-ethylcarbodiimide hydrochloride (Accela, 97%), lithium aluminum hydride (Amethyst, $\geq 97\%$), dichloroethane (DCE) (Aladdin, 99%), methylcyclohexane (MCH) (Adamas, $>99\%$) were used without further purification. 2-Cyanoprop-2-yl-1-dithionaphthalate (CPDN) was synthesized according to the literature.¹ 2,2-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. The monomers MAzo-*m*-L/D (*m* = 3, 4, 6, 7, 10, and 11) were synthesized according to the previously reported procedures.^{2,3}

Characterization.

- ¹H NMR spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz, Bruker, Karlsruhe, Germany) using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard at 25°C.
- Gel permeation chromatography (GPC) measurements were performed using the TOSOH HLC-8320 GPC system (Tokyo, Japan), equipped with refractive index and UV detectors. Two TSKgel SuperMultiporeHZ-N columns (4.6 × 150 mm, 3.0 μm bead size) from Tokyo, Japan, were arranged in series for the analysis. It can separate polymers in the molecular weight range of 500-190k Da. THF was used as the eluent with a flow rate of 0.35 mL/min at 40 °C. The values of the average molecular weight (M_n) and molecular weight distribution (\mathcal{D}) of the polymer were calculated using a polystyrene standard.
- CD spectra were recorded on a JASCO J-1500 spectropolarimeter equipped with a Peltier-controlled housing unit using an SQ-grade cuvette, a single accumulation, a path length of 10 mm, a bandwidth of 2 nm, a scanning rate of 200 nm/min, and a response time of 1 s. The samples were measured at 20°C or -20°C.

4. TEM images were taken with a HITACHI HT7700 operated at an accelerating voltage of 100 kV.
5. The thermal behaviors were measured by TA instrument DSC 250 (New Castle, DE, USA). The heating and cooling rates were both 10°C/min.
6. The monomers were also purified by chiral high-performance liquid chromatography (HPLC). Chiral HPLC was performed on Agilent 1200 Series chromatographs using a Daicel Chiralpak AD-H column (0.46 cm × 25 cm).
7. The IR and VCD spectra of monomers and polymers were recorded with a JASCO FVS-6000 spectrometer using a resolution of 4 cm⁻¹ and a collection time of 1.7 h. The IR and VCD spectra were recorded in THF-*d*₈ and the concentration is about 30 mg/mL in a CaF₂ cell with a 150 μm path length. The samples were measured at -20°C.
8. Polarized optical microscopy (POM) observations were made using an Olympus Corporation BX51-P microscope equipped with a hot stage (Linkam THMS600).

S2 Experimental Procedures

1. Synthesis of side-chain Azo-polymers.

A collection of side-chain Azo-polymers was synthesized through reversible addition-fragmentation chain transfer (RAFT) polymerization, where CPDN and AIBN were used as the RAFT agent and the initiator, respectively. For example, MAzo-6-*L* (282.3 mg, 0.60 mol), CPDN (3.26 mg, 0.012 mmol), AIBN (0.656 mg, 0.004 mmol) and anhydrous THF (1.0 mL) were added into a 5 mL ampoule bottle. The reaction tube was flame-sealed under an argon atmosphere after deoxygenated with three freeze-thaw cycles. Then the polymerization was carried out at 70°C for 4 h. Polymers of other molecular weights were obtained by changing the ratio of monomers and RAFT agents. The naming of polymers is similar to that of monomers. For instance, the polymer synthesized from the monomer MAzo-6-*L* is denoted as PAzo-6-*L*.

2. Preparation of polymer solutions in good solvents.

First, the polymer was dissolved in a good solvent such as THF or 1,2-dichloroethane (DCE), at a concentration of 1 mg/mL. Next, 0.1 mL of the polymer solution was transferred to an SQ-cuvette,

and 3 mL of the good solvent was added. The CD and UV-vis spectroscopy tests were then performed.

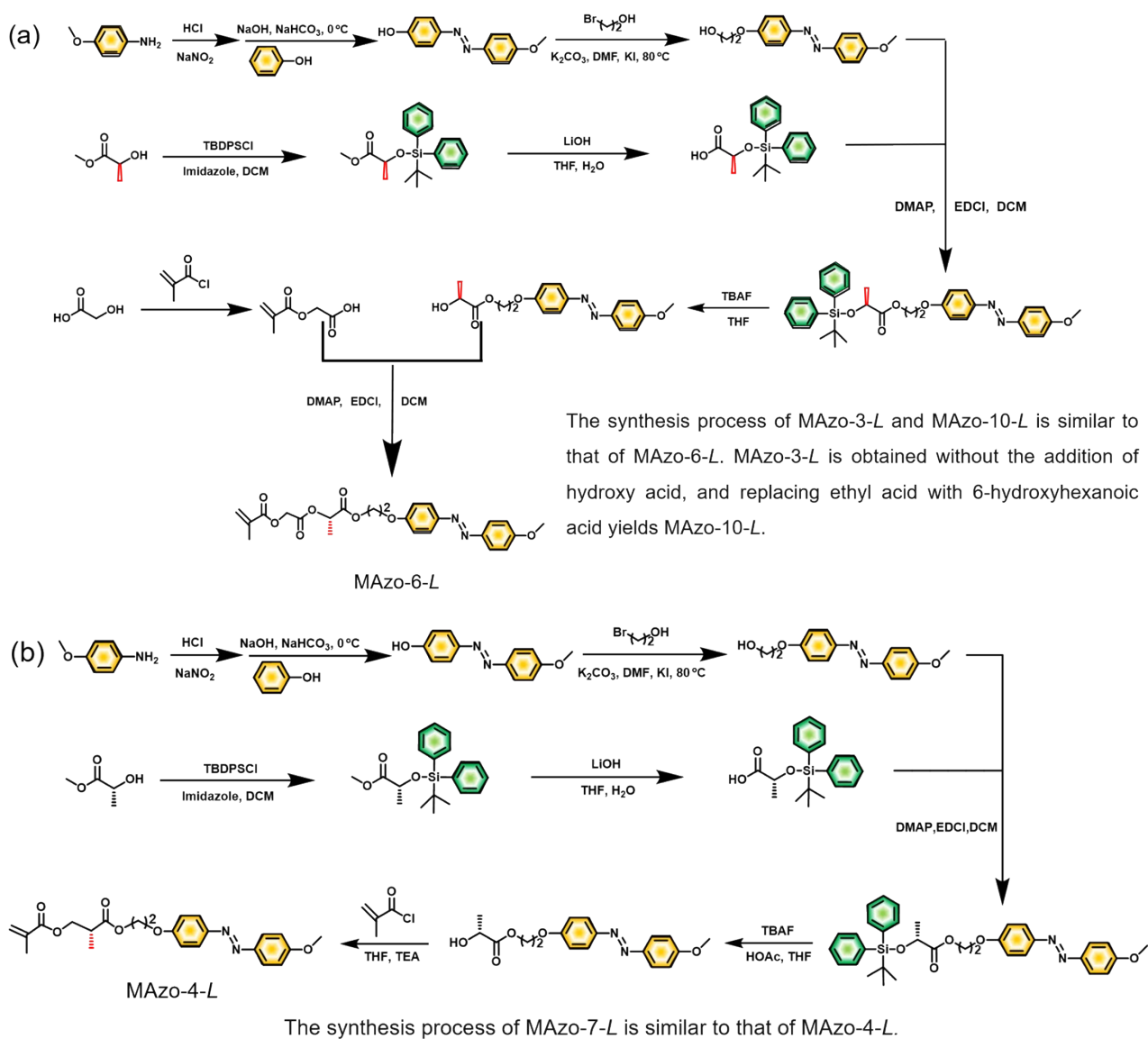
3. Preparation of the optically active polymer aggregates in mixed solvents.

A certain volume of methylcyclohexane (MCH) was added to a DCE solution containing Azopolymers (a total of 0.1 mg of polymer, the volume of DCE varies with the proportion of mixed solvent) in an SQ-cuvette. The total volume of good solvent and poor solvent is 3 mL. After a gentle shaking, the yellow turbid solution of Azo-polymer aggregates was analyzed using the CD/UV-vis spectrometers (if the proportion of good solvent is high, the Azo-polymer will be in a dissolved state). The other polymer aggregates were produced in a similar procedure.

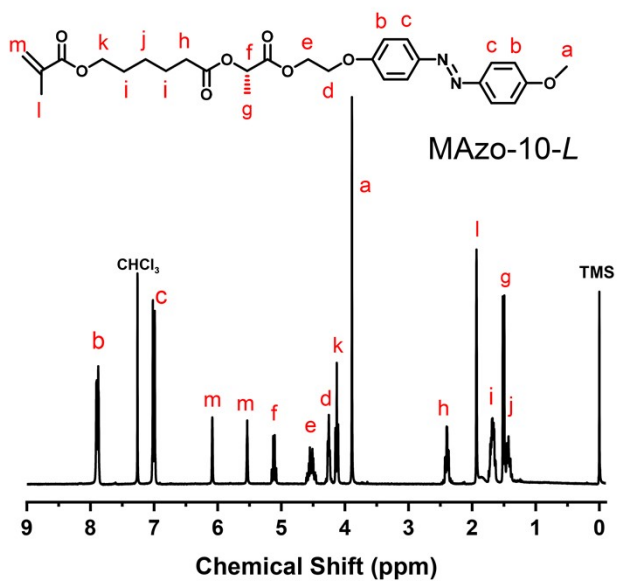
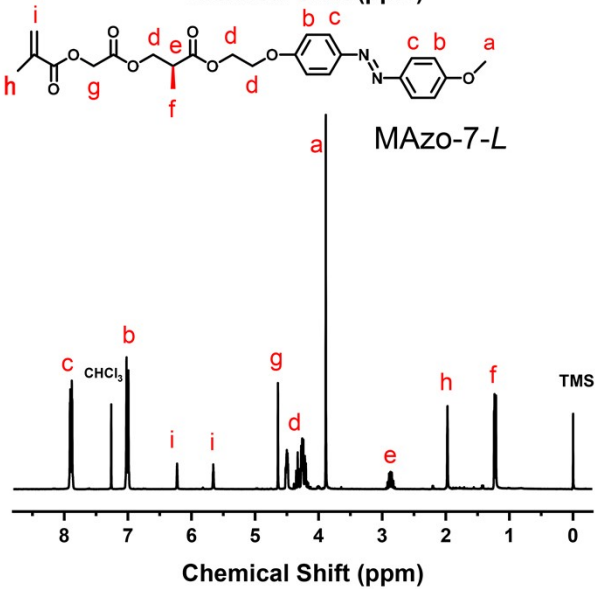
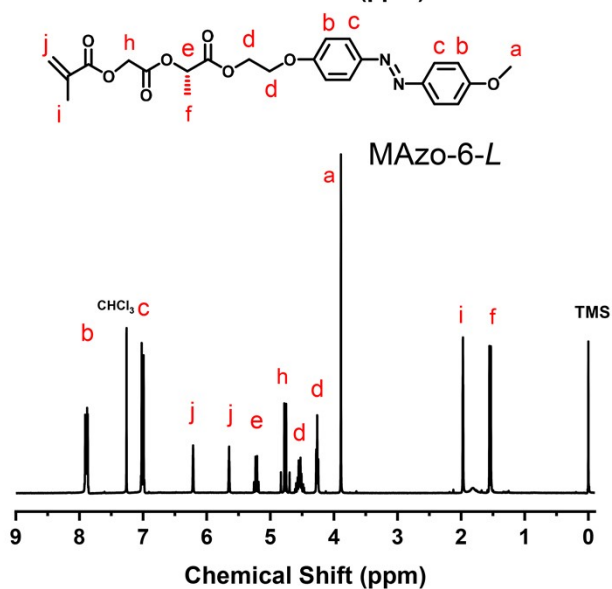
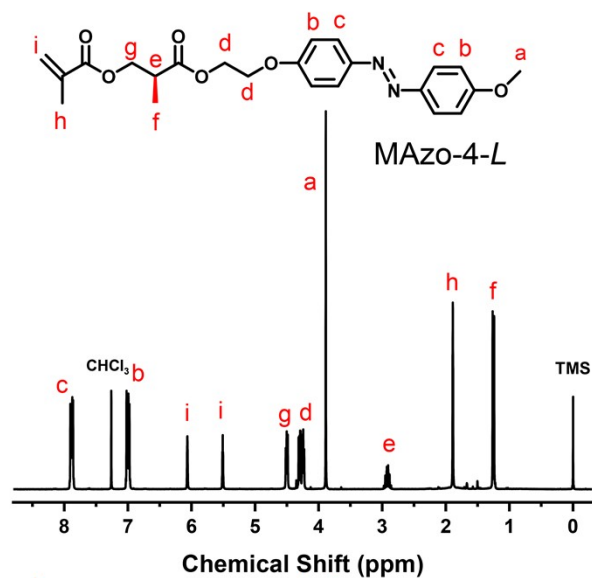
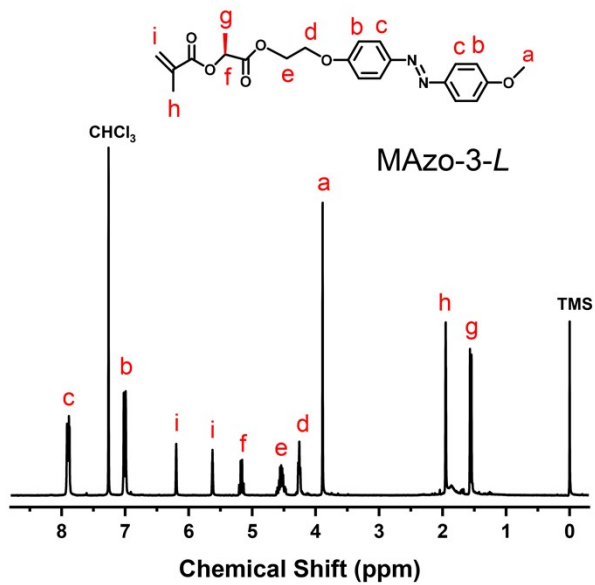
4. Heating treatment of polymer assemblies.

The heating-cooling (H-C) treatment process is to first heat up from 20°C to 80°C (30°C/min), hold for a period of time (10 min), and then cool down to 20°C (20°C/min).

S3 Supporting Figures.



Scheme S1. Synthetic routes of chiral Azo monomers with different distances from chiral stereocenter to the carbon-carbon double bond.



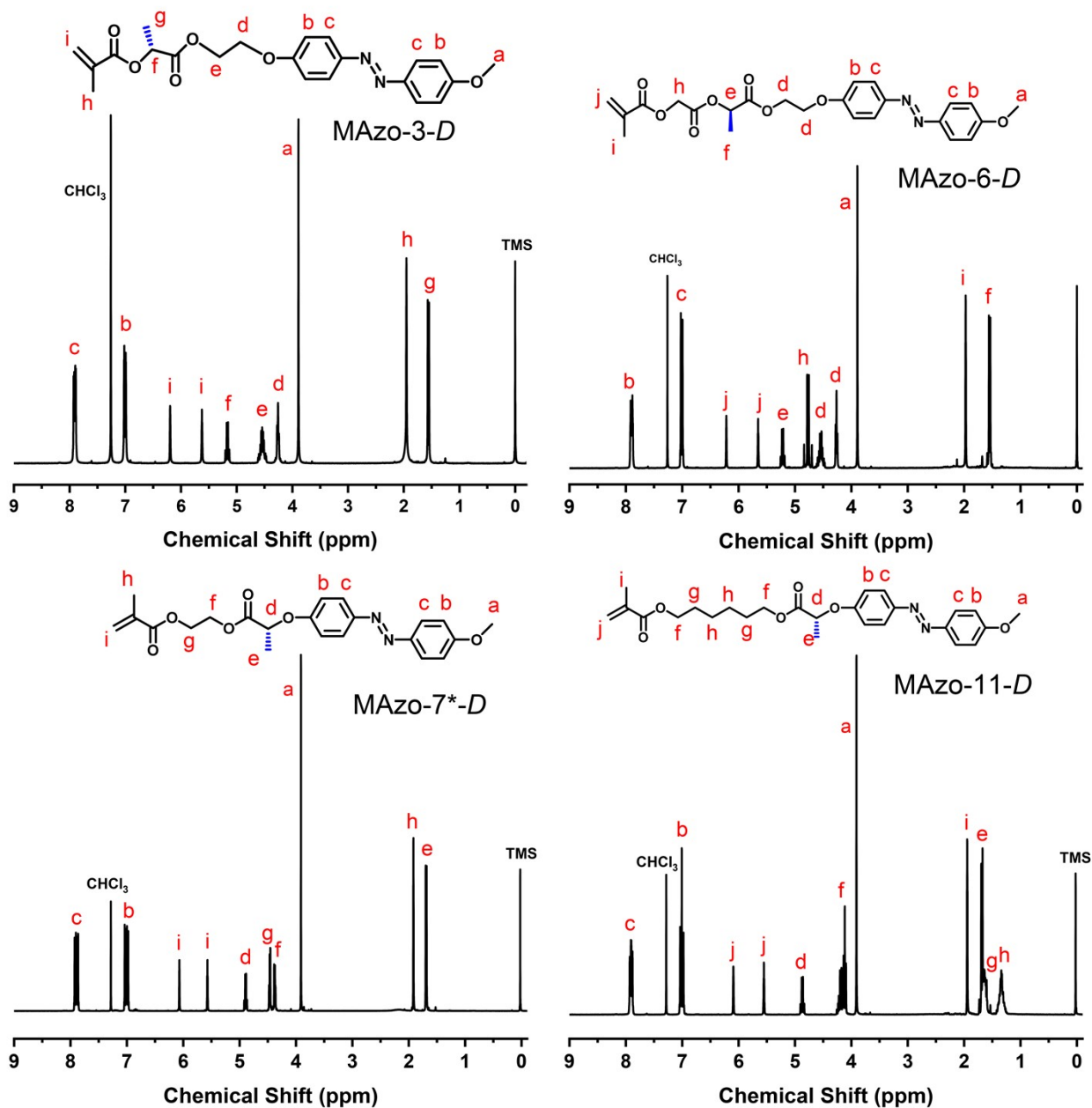


Figure S1. ^1H NMR spectra of the chiral Azo monomers.

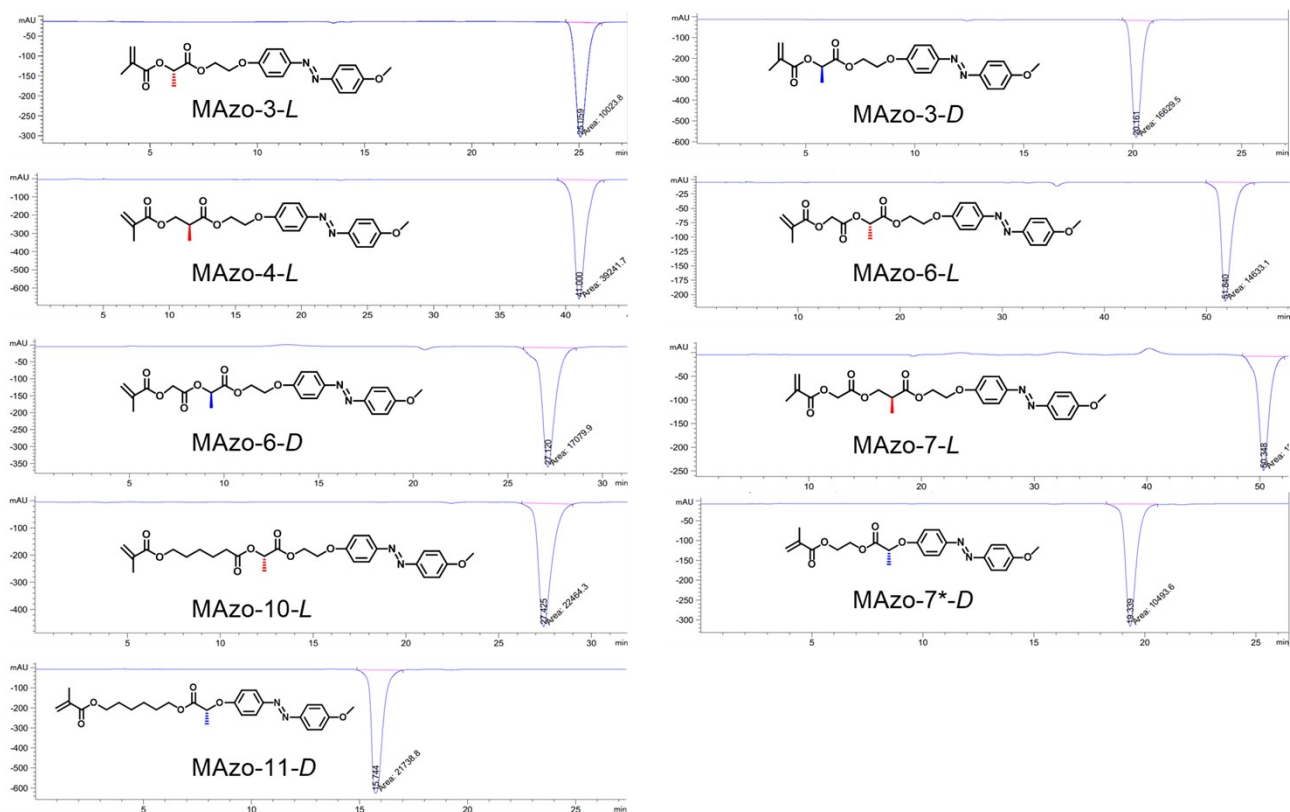


Figure S2. HPLC spectra of the chiral Azo monomers.

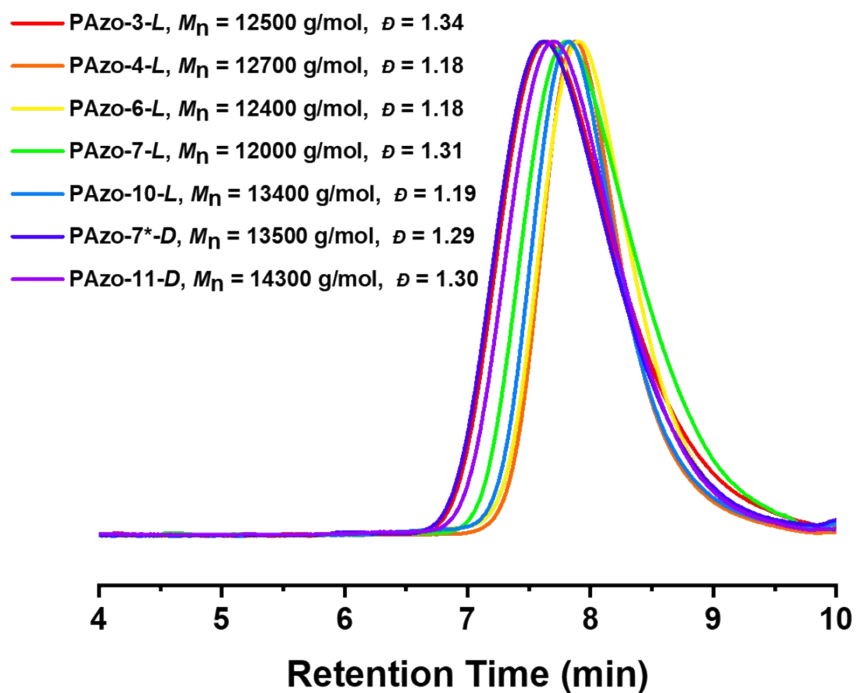


Figure S3. GPC curves of side-chain Azo-polymers.

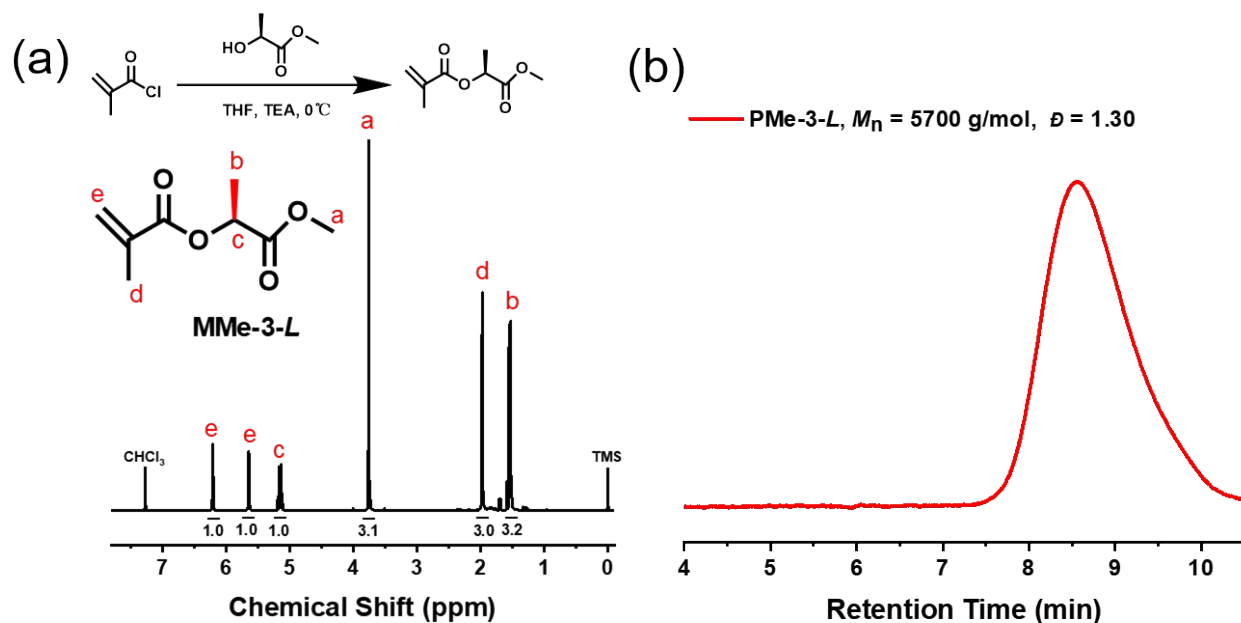


Figure S4. (a) Synthetic routes and ^1H NMR of MMe-3-L; (b) GPC curves of PMe-3-L.

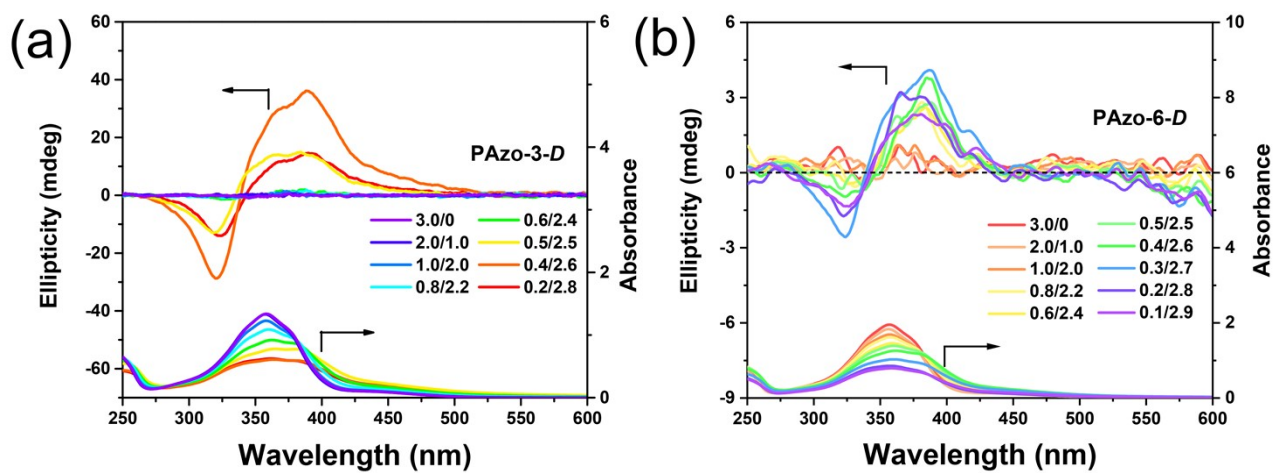


Figure S5. CD and UV-vis spectra of Azo-polymers in mixed DCE/MCH solvents with different volume ratios. (a) PAzo-3-D; (b) PAzo-6-D.

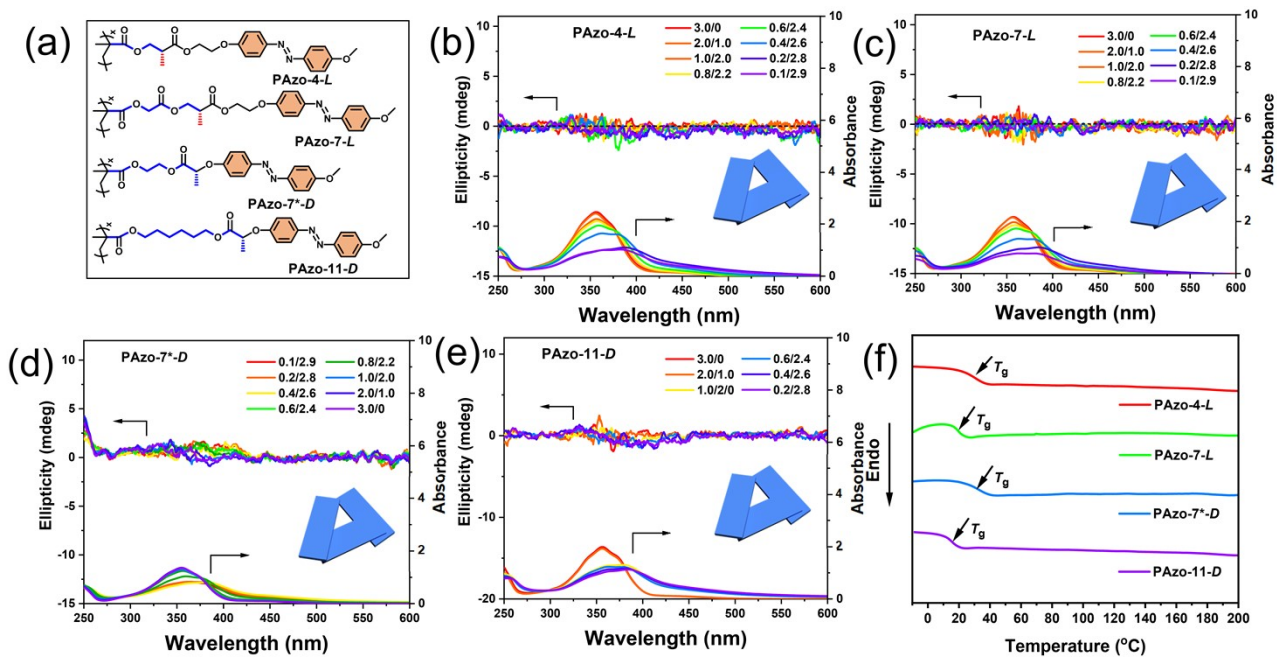


Figure S6. (a) The structural formula of Azo-polymers; (b-e) CD and UV-vis spectra of Azo-polymers in mixed DCE/MCH solvents with different volume ratios. (f) The second heating DSC curves of Azo-polymers.

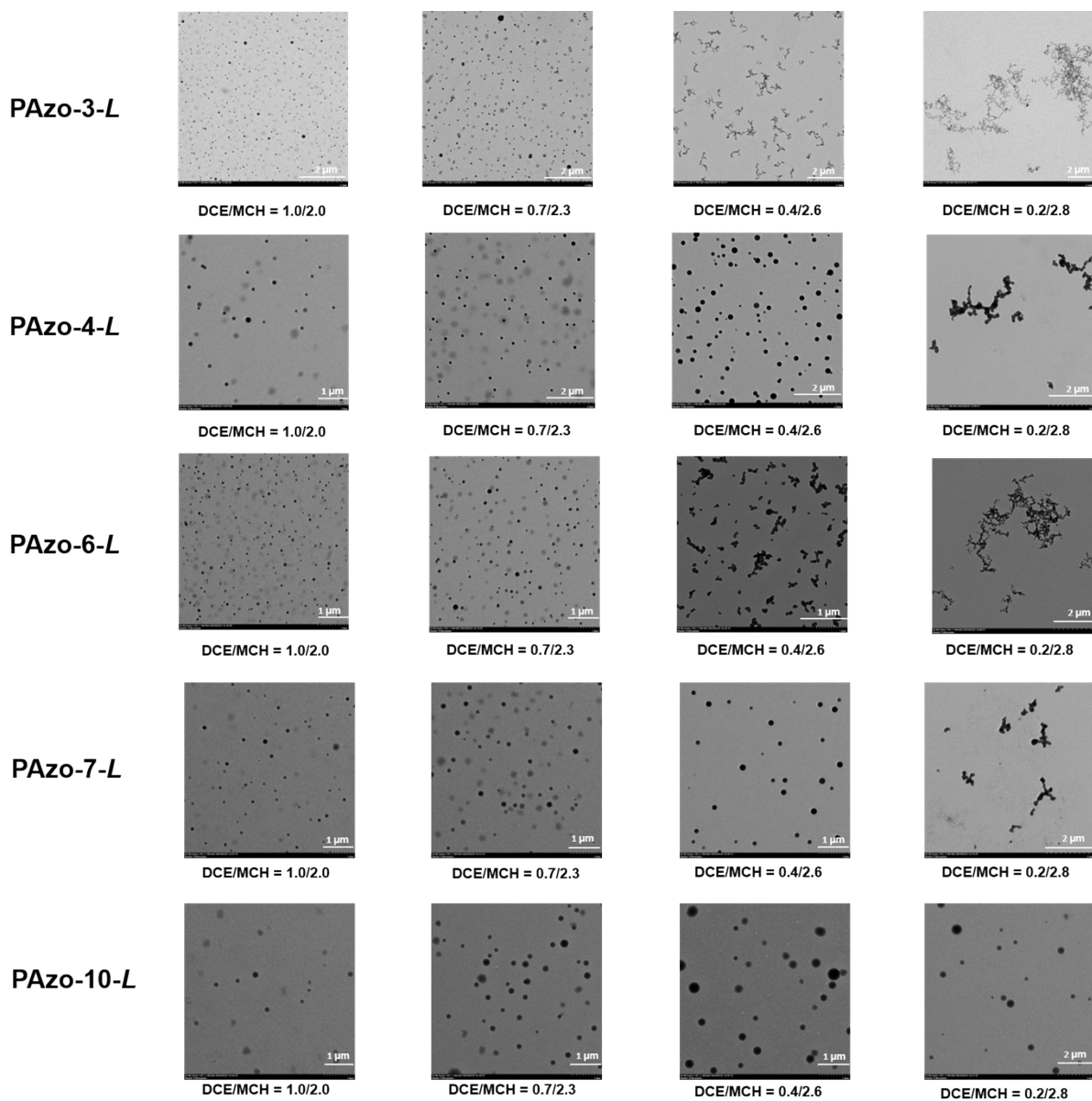


Figure S7. TEM images of Azo-polymer assemblies in DCE/MCH mixed solvents.

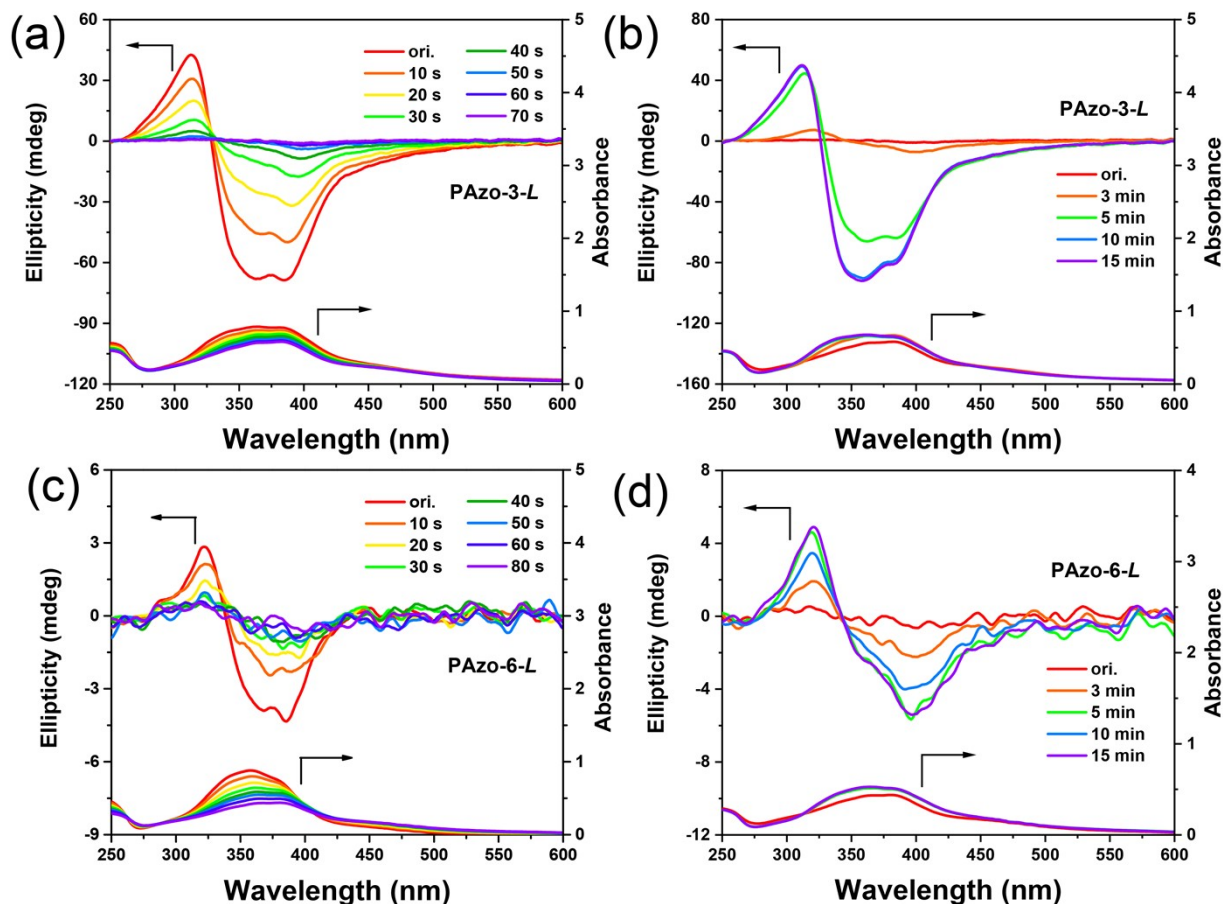


Figure S8. (a) CD and UV-vis spectra of PAzo-3-*L* when irradiated with 365 nm light in mixed solvent (DCE/MCH = 0.4/2.6); (b) CD and UV-vis spectra of PAzo-3-*L* during recovery by heating in mixed solvent (DCE/MCH = 0.4/2.6), (c) CD and UV-vis spectra of PAzo-6-*L* when irradiated with 365 nm light in mixed solvent (DCE/MCH = 0.3/2.7), (d) CD and UV-vis spectra of PAzo-6-*L* during recovery by heating in mixed solvent (DCE/MCH = 0.3/2.7).

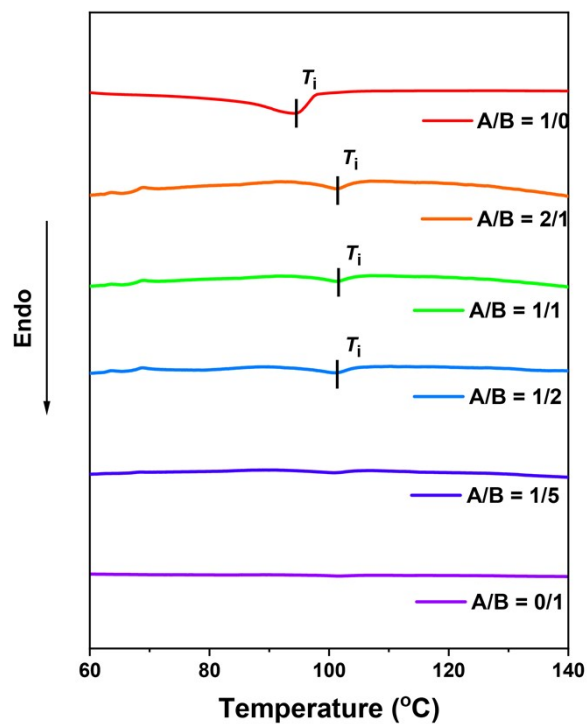


Figure S9. DSC curves of Azo copolymers formed by monomer A (MAzo-3-*L*) and monomer B (MAzo-10-*L*) at different copolymerization ratios.

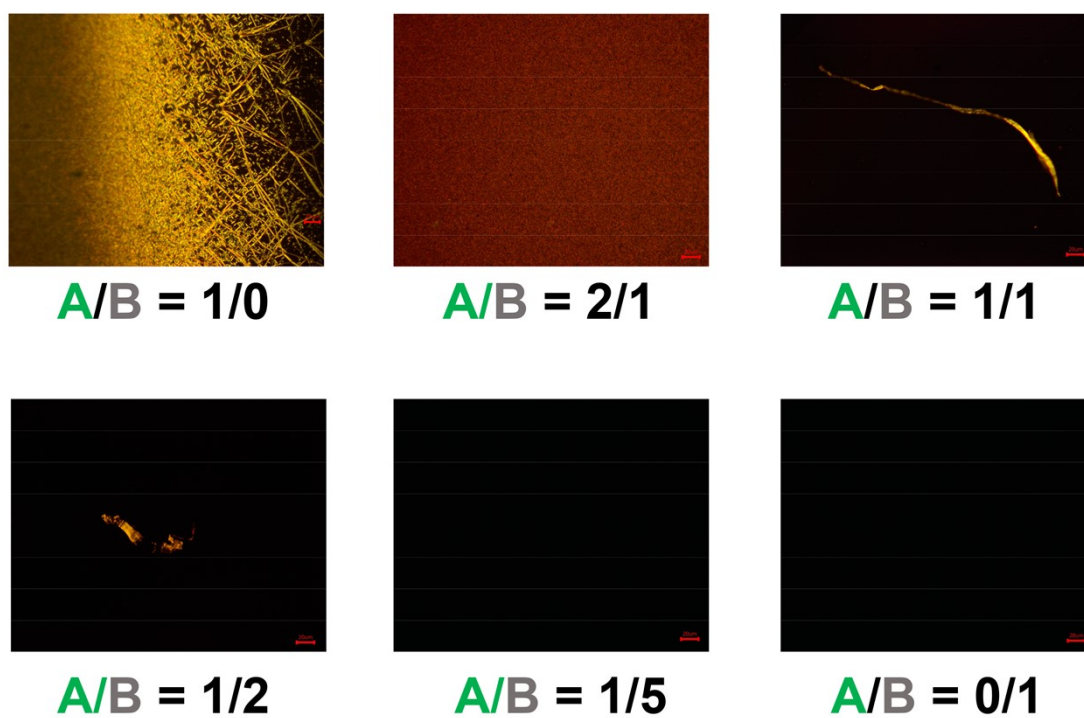


Figure S10. POM images of Azo copolymers formed by monomer A (MAzo-3-*L*) and monomer B (MAzo-10-*L*) at different copolymerization ratios.

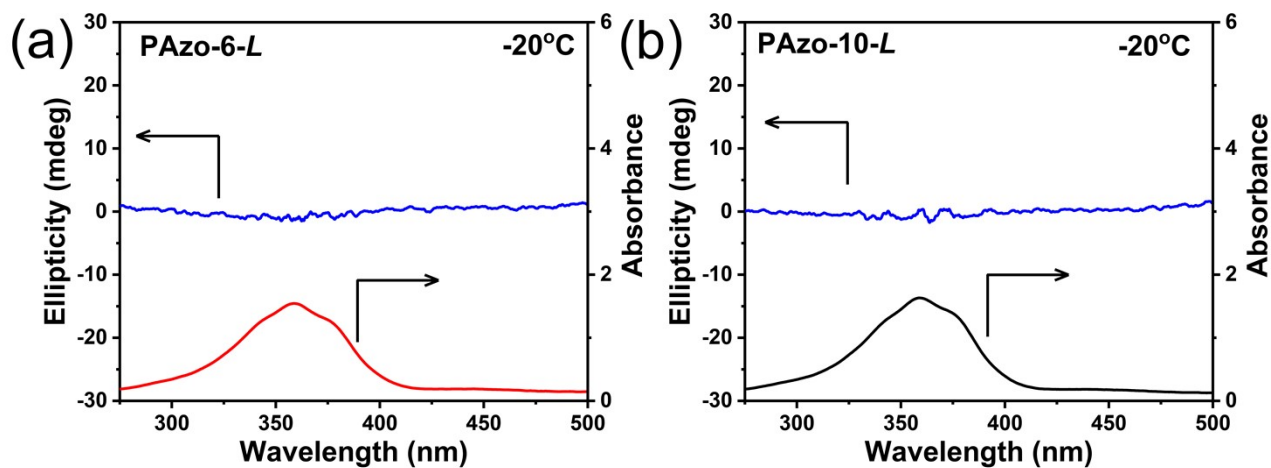


Figure S11. CD and UV-vis spectra of Azo-polymers in DCE. (a) PAzo-6-L; (b) PAzo-10-L. The concentration of all samples is 0.033 mg/mL, and the test temperature is -20°C.

S4 References

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2. W. Q. Xie, B. Zou, D. Q. Pei and D. W. Ma, *Org. Lett.*, 2005, **7**, 2775-2777.
3. J. del Barrio, R. M. Tejedor, L. S. Chinelatto, C. Sánchez, M. Piñol and L. Oriol, *J. Mater. Chem.*, 2009, **19**, 4922-4930.