Chiral Chemistry
https://doi.org/10.70401/cc.2026.0032

Supplementary information

The odd-even effect in the main-chain chiral azopolyesters

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Materials

5-Bromo-1-pentene, 6-Bromo-1-hexene, 7-Bromo-1-heptene, 8-Bromo-1-octene, 9-Bromo-1-nonene, 10-Bromo-1-decene, 11-bromo-1-undecene (Adamas, 99%), (*R*,*R*)-*N*,*N*'-Bis(3,5-Di-Tert-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(II) (Daicel, ⩾95%), 3-Chloroperoxybenzoic acid (Energy, 85%), Phenol (Macklin, AR), 4-Butoxyaniline (Adamas, ⩾98%), 1,2-Dimethoxyethane (J&K, 99.5%) and all other chemicals and reagents (J&K, TCI and Energy Chemical) were used without further purification. All cyclic anhydrides involved in this study were purchased from Energy Chemical and were purified by sublimation before used. All synthesized epoxide monomers were dried under reduced pressure at 120°C for 12 hours and subsequently used after water removal with CaH_2 in a glove box.

N,*N*'-Bis(3-tert-butyl-5-fluroine salicylidene)-1,2-cyclohexanediamino (Salcy) Co(III)NO_3 and [PPN][NO_3] were synthesized according to the published procedure[1].

Characterization

NMR Experiments: ^1H and ^{13}C NMR spectra were recorded on BRUKER AVANCE III 500 (^1H, 500 MHz) and BRUKER AVANCE NEO 400 MHz (^{13}C, 400 MHz) type spectrometers at ambient temperature. Their peak frequencies were referenced versus an internal standard (TMS) shift at 0 ppm for ^1H NMR and against the solvent, chloroform-*d* at 77.16 ppm for ^{13}C NMR, respectively.

High Performance Liquid Chromatography (HPLC): HPLC was performed on Agilent 1260 Infinity II. Enantiomeric excesses (*e.e. %*) were determined by chiral HPLC analysis on Daicel Chiralpak OD-H and OD-3 columns.

Gel Permeation Chromatography (GPC): Molecular weights and molecular weight distributions of polymers were determined with a PL-GPC equipped with the HP 1260 series pump from Agilent Technologies. The GPC columns were eluted with tetrahydrofuran at 30 °C at 1.00 mL/min. The sample concentration was about 0.1%, and the injection volume was 100 μL. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 to 460000 Da.

CD spectra and UV-vis spectra: CD spectra and UV-vis 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 0.5 nm, a scanning rate of 500 nm/min, and a response time of 1 s. The samples were measured at 25 °C.

Differential Scanning Calorimetry (DSC): DSC was carried out with a NETZSCH DSC 206 thermal analyzer. First cycle: from 30 °C to 100 °C at a heating rate of 10 K/min, and from 100 to 30 °C at a cooling rate of 10 K/min. Second cycle: from 30 to 250 °C at a heating rate of 10 K/min, and from 250 to 30 °C at a cooling rate of 10 K/min. Data was obtained based on second cycle.

Wide Angle X-ray Diffraction (WAXD): Powder X-ray diffraction data were collected on an EMPYREAN diffractometer with Cu KR radiation (λ = 1.54056 Å) over the 2θ range of 5-45º with a scan speed of 0.3333/s and a step size of 0.02º at room temperature.

Small Angle X-ray Scattering (SAXS): SAXS data were measured by Rigaku NANOPIX with CuK α radiation (λ = 0.154 nm).

Polarized Optical Microscope (POM): POM images were measured by Axioscope 5.

2. Experimental Procedures

2.1 The synthesis of azobenzene-containing chiral epoxides

The monomers m*R*-Azo (m = 3, 4, 5, 6, 7, 8 and 9) were synthesized according to the previously reported procedures[2,3]. During the synthesis process, aniline was replaced with 4-butoxyaniline, and the epoxides employed were synthetic chiral epoxides. Chiral epoxides were obtained by the hydrolytic kinetic resolution of the corresponding terminal epoxides catalyzed by chiral salcyCo(III)OAc complexes[4,5].

2.2 Determination of enantimeric purity of azopolyesters

The enantiomeric excess of azo-polyester was determined according to the previously reported method[6].

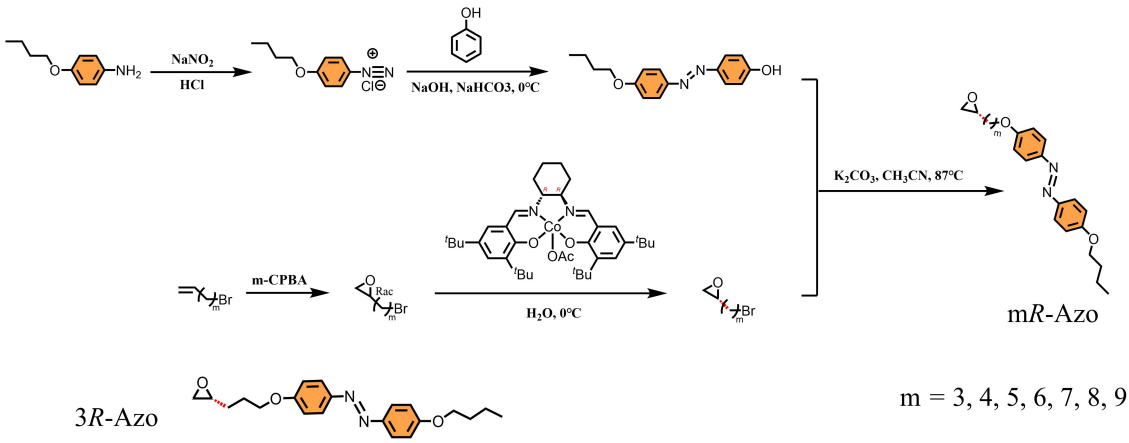
2.3 Preparation of the optically active polymer aggregates in mixed solvents

Taking the preparation of an assembly solution with a volume ratio of THF/EtOH = 0.2/2.8 as an example, the specific procedure is as follows: Under ambient temperature conditions, first prepare a polymer solution at a concentration of 1 mg/mL in tetrahydrofuran (THF). Then transfer 0.1 mL of the prepared polymer-THF solution into a cuvette, followed by adding 0.1 mL of pure THF solvent to ensure a total THF volume of 0.2 mL. Subsequently, slowly add 2.8 mL of ethanol (EtOH) into the same cuvette dropwise. Finally, shake the cuvette gently to form a homogeneous assembly solution. The preparation process for assembly solutions with other volume ratios follows similar procedures, while maintaining a constant azobenzene polymer concentration of 0.1 mg per 3 mL mixed solution. The assemblies were measured after being allowed to stand for 10 h.

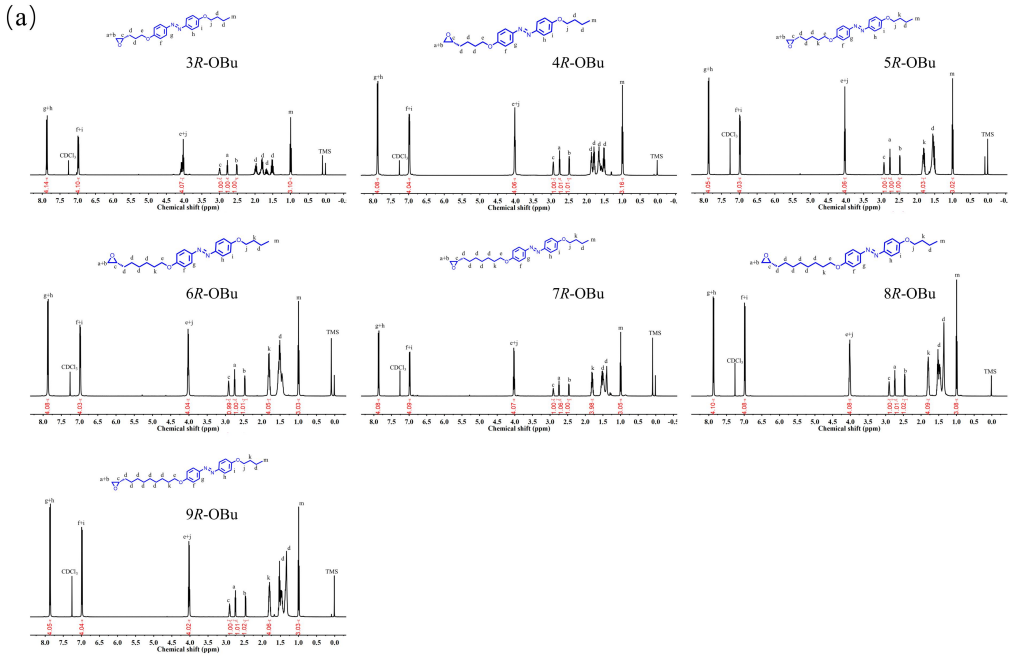
2.4 Cooling treatment of polymer assemblies.

The cooling treatment procedure was as follows: the THF solution containing the polymer and EtOH were separately held at 0 °C for a period of time (10 min), then the two were mixed and kept at that temperature for 10 h before measurement.

3. Synthesis and characteristics of main-chain chiral azopolyesters



Scheme S1. Synthetic routes of chiral azobenzene-containing epoxide monomers with different spacer groups between the chiral stereocenter and the azobenzene chromophore.



(b)

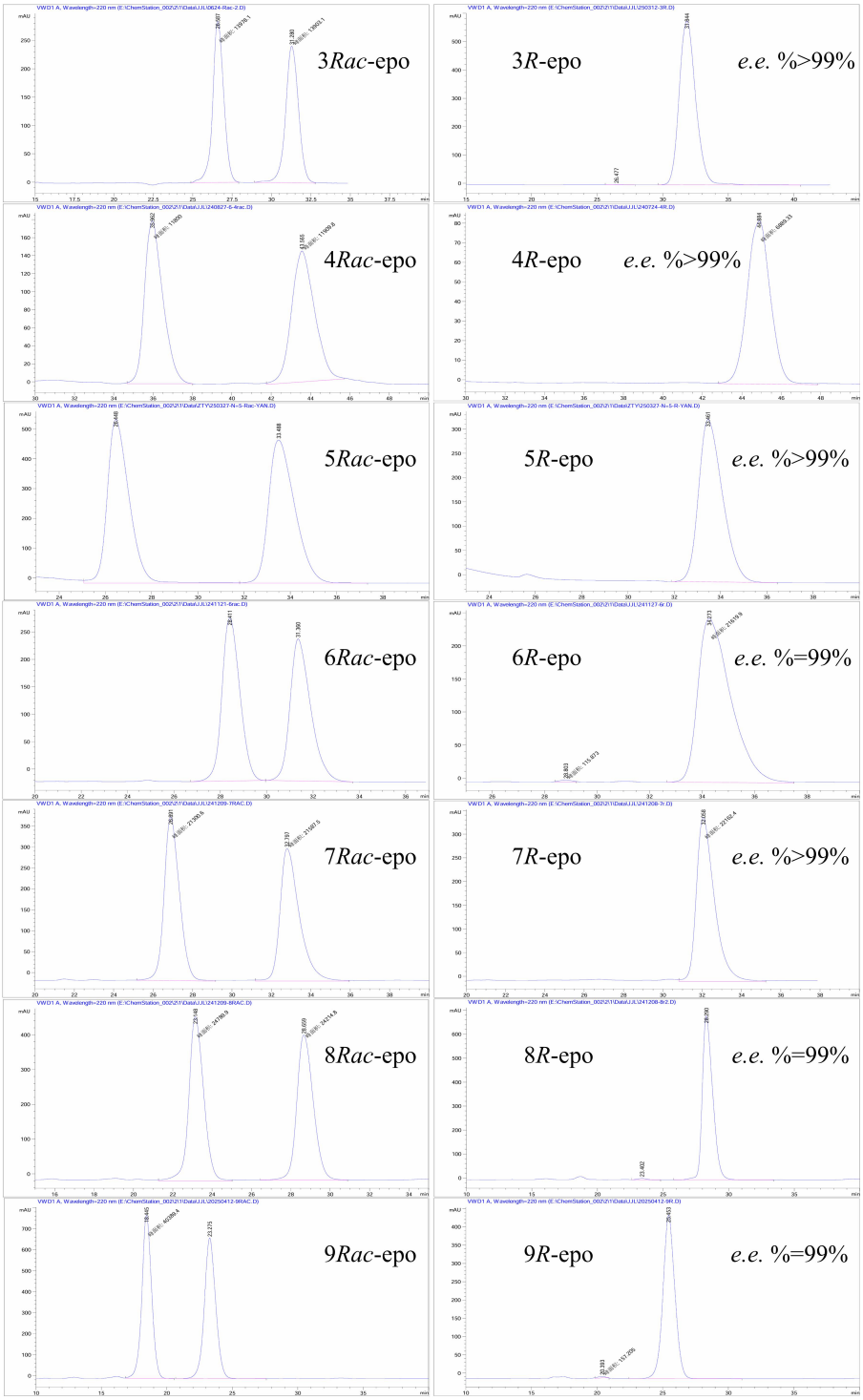
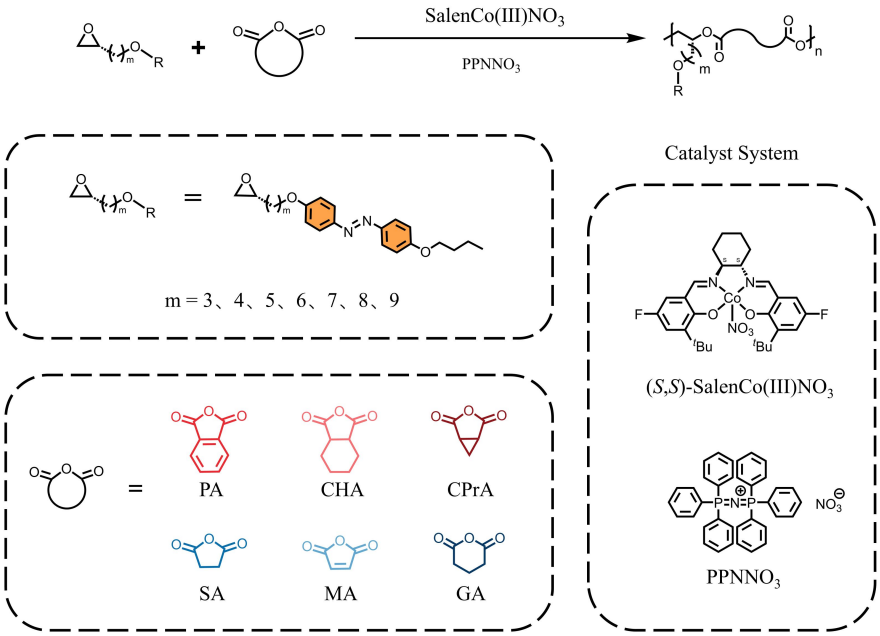


Figure S1. a) ^{1}H NMR spectra of chiral azobenzene-containing epoxide monomers;
b) Chiral HPLC analysis of various epoxides.

Table S1. Outcomes of alternating copolymerization of azobenzene-based epoxides with cyclic anhydrides.[a]



Entry	Monomers	M_n [b] [kg/mol]	$Đ$[b]	DP[c]	$T_g/T_c/T_{LC\text{-}iso}$[d] [°C]
1	3*R*-Azo/PA	6.1	1.21	~11	63.3/--/108.9
2	4*R*-Azo/PA	7.6	1.20	~14	65.2/--/85.8
3	5*R*-Azo/PA	6.5	1.24	~12	58.1/--/108.2
4	6*R*-Azo/PA	8.6	1.18	~15	57.7/--/94.8
5	7*R*-Azo/PA	7.2	1.20	~12	48.1/--/107.7
6	8*R*-Azo/PA	6.7	1.21	~11	48.4/-/99.5
7	9*R*-Azo/PA	6.1	1.22	~10	37.6/--/108.4
8	3*R*-Azo/SA	4.8	1.30	~10	--/105.2/123.8
9	4*R*-Azo/SA	6.0	1.19	~12	--/86.2/98.2
10	5*R*-Azo/SA	6.2	1.22	~13	--/94.2/116.1
11	6*R*-Azo/SA	5.3	1.22	~10	--/72.7/104
12	7*R*-Azo/SA	5.4	1.24	~10	--/74.5/114.2
13	8*R*-Azo/SA	6.4	1.25	~11	--/78.1/106.3
14	9*R*-Azo/SA	4.5	1.30	~8	--/69.8/111.8

[a]Reactions were performed under the following conditions: epoxides/anhydrides/catalyst/$PPNNO_3$/DME = 50/50/1/1/1500 (molar ratio), at 30 °C. [b]Number average molecular weights (Mn) and dispersity values were determined by gel permeation chromatography in THF, calibrated with polystyrene. [c]The degree of polymerization of the azopolyester was determined from the corresponding relative molecular weight data. [d]The thermal properties of the azopolyesters were determined using differential scanning calorimetry (DSC).

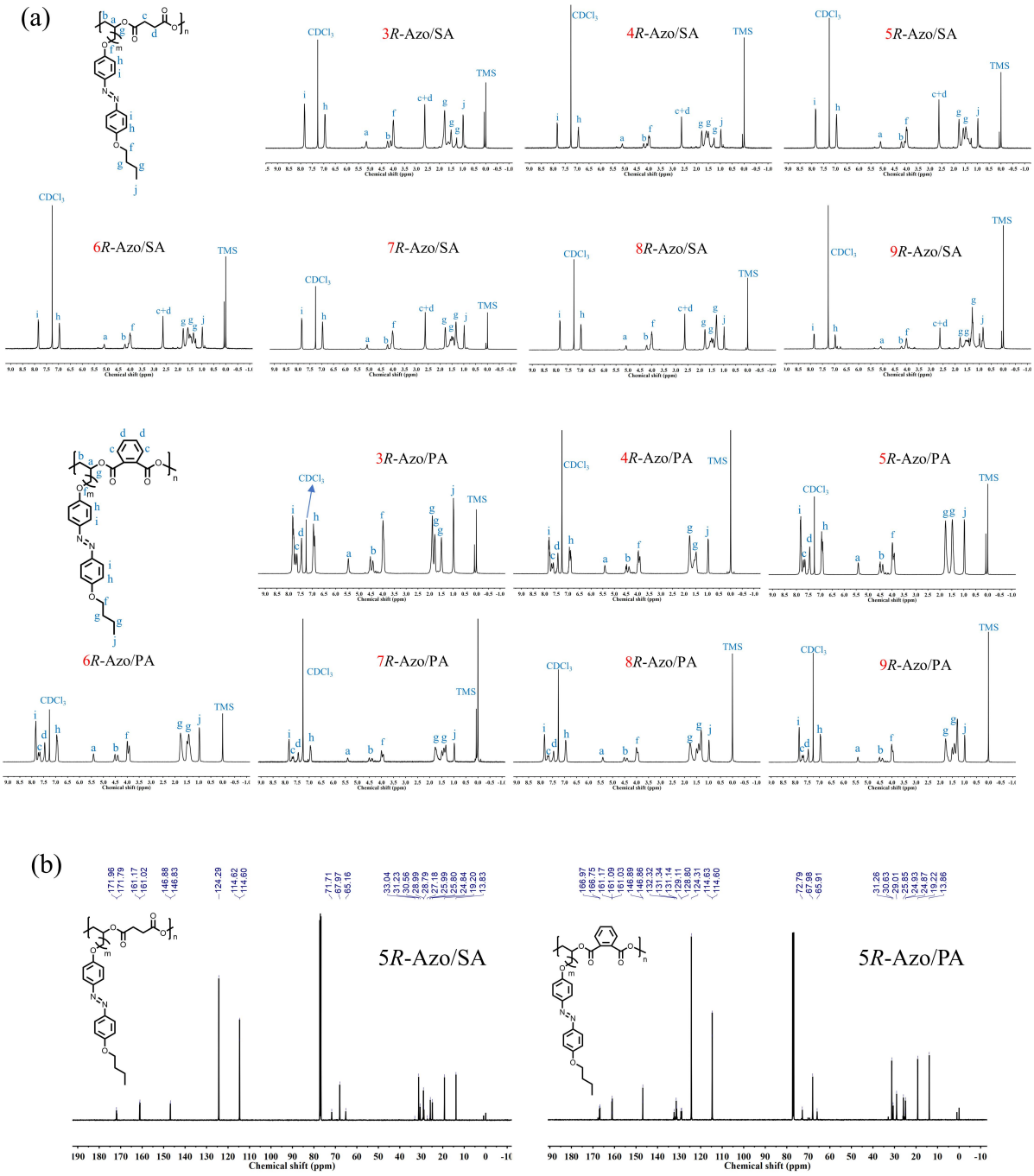


Figure S2. a) ^{1}H NMR spectra of m*R*-Azo/SA and m*R*-Azo/PA; b) ^{13}C NMR spectra of m*R*-Azo/SA and m*R*-Azo/PA (m = 5).

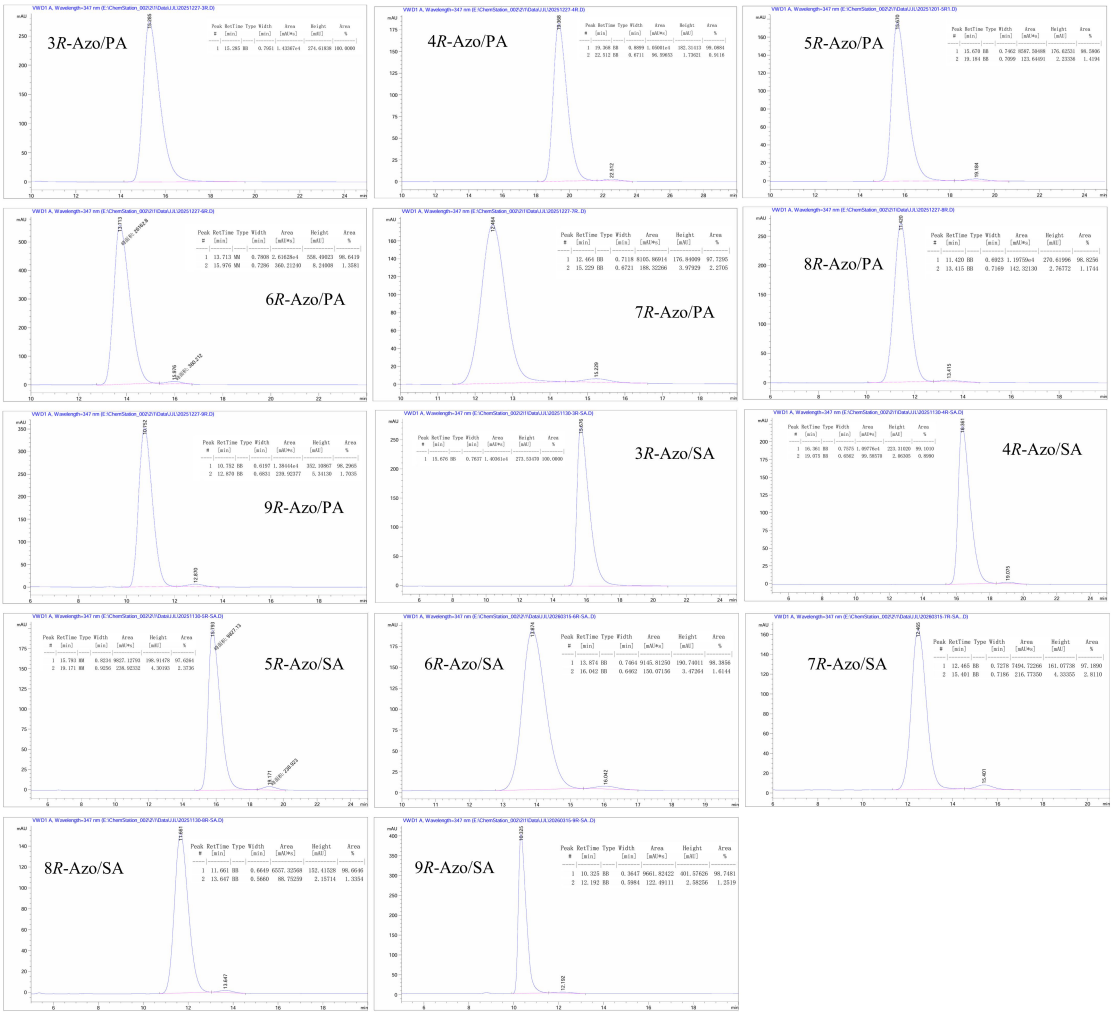


Figure S3. Chiral HPLC analysis of the diols obtained from hydrolysis of the azopolyesters.

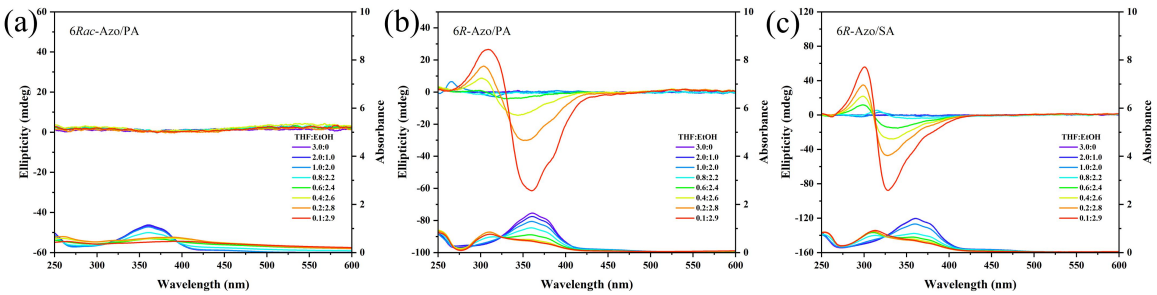


Figure S4. CD and UV-vis spectra of atactic azopolyester (a, 6*Rac*-Azo/PA) and isotactic azopolyester (b, 6*R*-Azo/PA and c, 6*R*-Azo/SA) in mixed solvents with different THF/EtOH volume ratios.

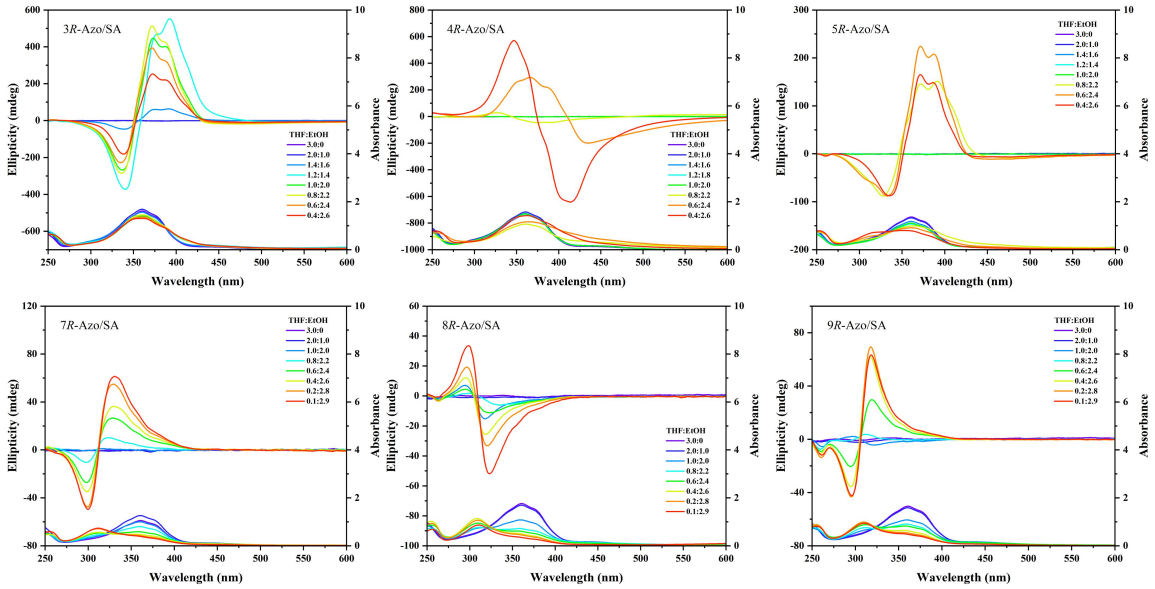


Figure S5. CD and UV-vis spectra of azopolyesters (m*R*-Azo/SA, m = 3, 4, 5, 7, 8, 9) in mixed solvents with different volume ratios of THF/EtOH.

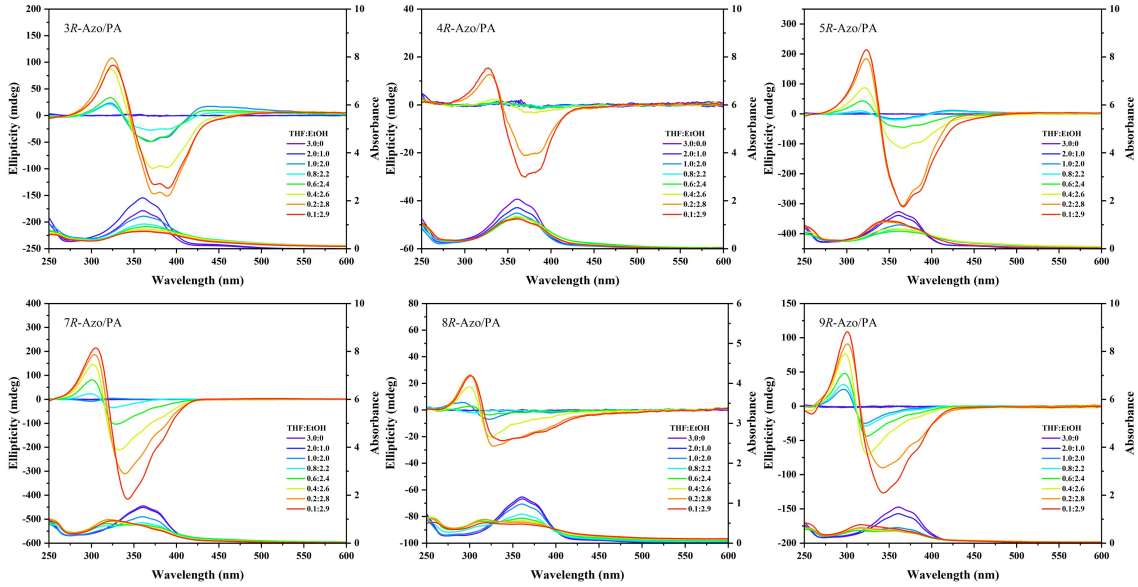


Figure S6. CD and UV-vis spectra of azopolyesters (m*R*-Azo/PA, m = 3, 4, 5, 7, 8, 9) in mixed solvents with different volume ratios of THF/EtOH.

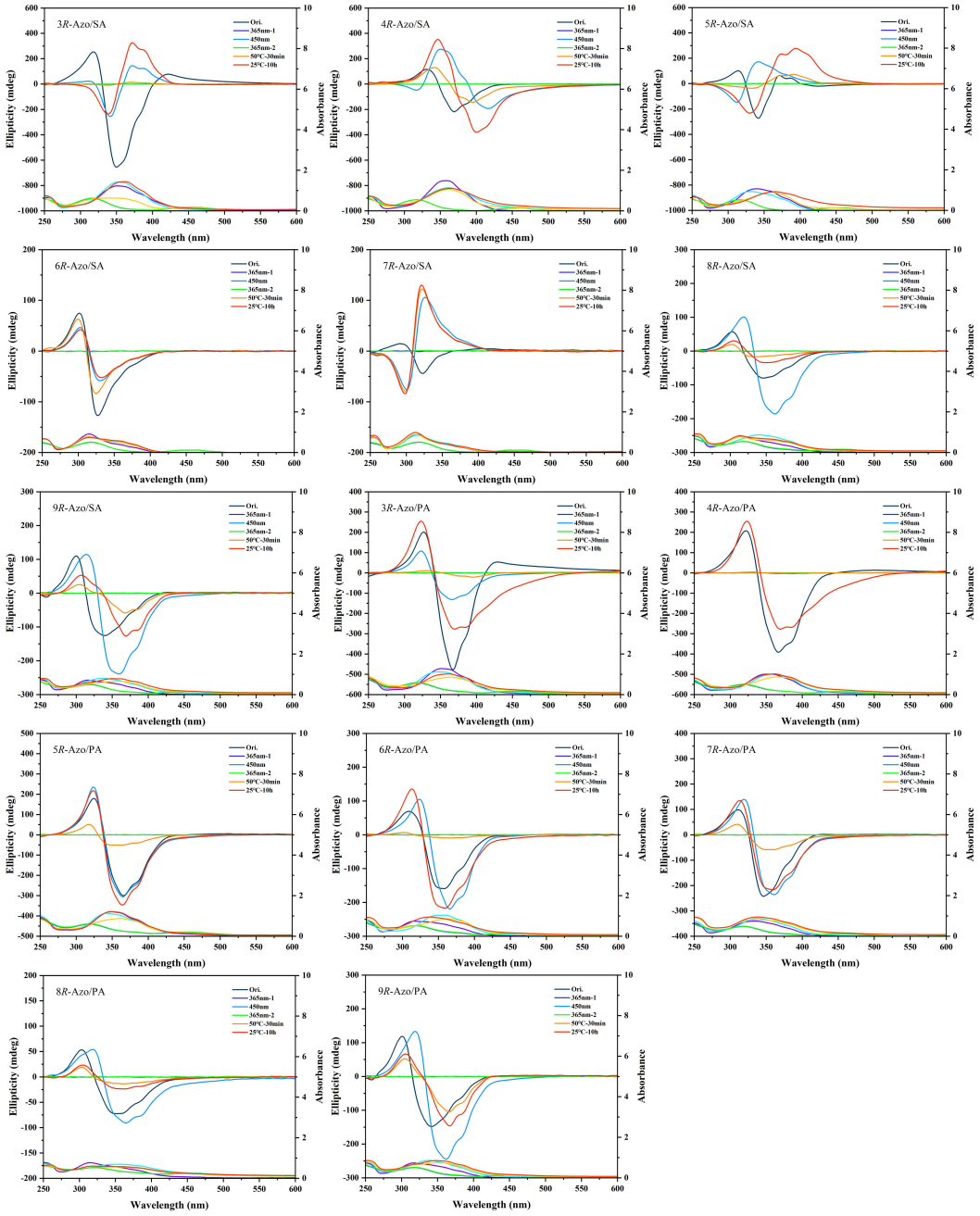


Figure S7. CD and UV-vis spectra of m*R*-Azo/SA and m*R*-Azo/PA (m = 3, 4, 5, 6, 7, 8, 9) in a THF/EtOH mixture (0.1/2.9, v/v) after light irradiation or thermal recovery.

Table S2. Outcomes of alternating copolymerization of azobenzene-based epoxides with cyclic anhydrides.[a]

Entry	Monomers	M_n[b] [kg/mol]	$Đ$[b]	DP[c]	$T_g/T_c/T_{LC\text{-}iso}$[d] [°C]
1	6*R*-Azo/MA	7.3	1.36	~14	--/66.2/110.7
2	7*R*-Azo/MA	7.0	1.38	~13	--/59.8/117.7
3	6*R*-Azo/GA	7.1	1.36	~13	--/74.6/98.3
4	7*R*-Azo/GA	6.3	1.22	~11	--/73.2/109.4
5	6*R*-Azo/CHA	5.2	1.34	~9	37.7/--/70.7
6	7*R*-Azo/CHA	6.1	1.34	~11	44.9/--86.0
7	6*R*-Azo/CPrA	9.6	1.37	~18	42.7/--/103.5
8	7*R*-Azo/CPrA	9.8	1.50	~18	--/107.4/113.8

[a]Reactions were performed under the following conditions: epoxides/anhydrides/catalyst/$PPNNO_3$/DME = 50/50/1/1/1500 (molar ratio), at 30 °C. [b]Number average molecular weights (Mn) and dispersity values were determined by gel permeation chromatography in THF, calibrated with polystyrene. [c]The degree of polymerization of the azopolyester was determined from the corresponding relative molecular weight data. [d]The thermal properties of the azopolyesters were determined using differential scanning calorimetry (DSC).

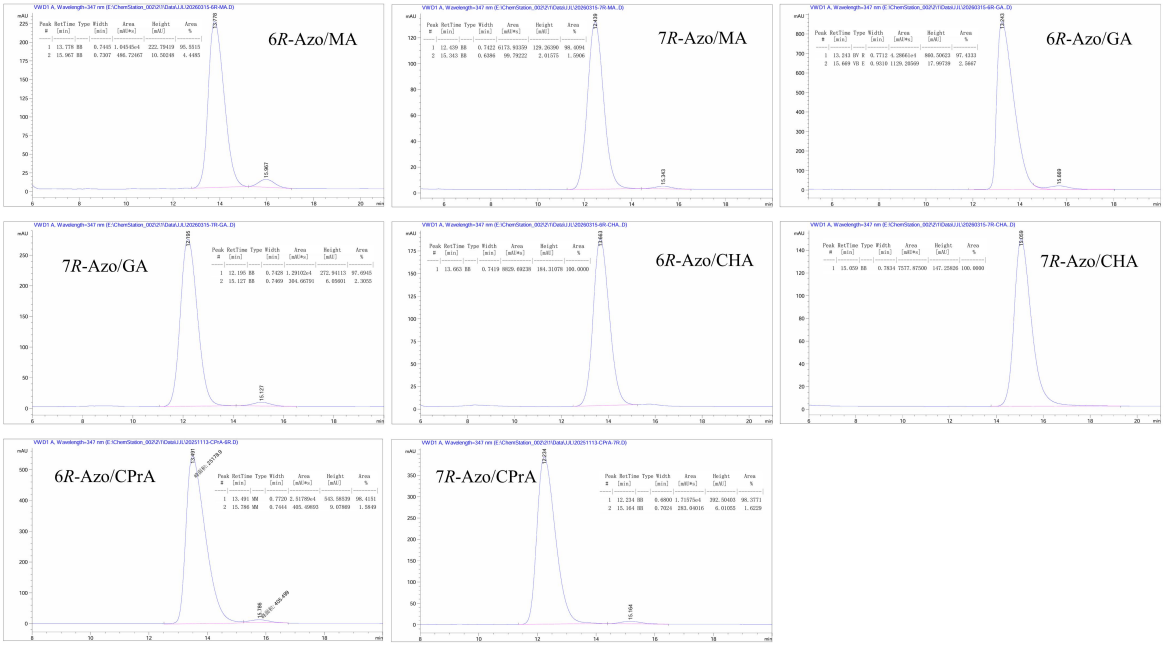


Figure S8. HPLC spectra of diols obtained after hydrolysis of azopolyesters with different main-chain structures.

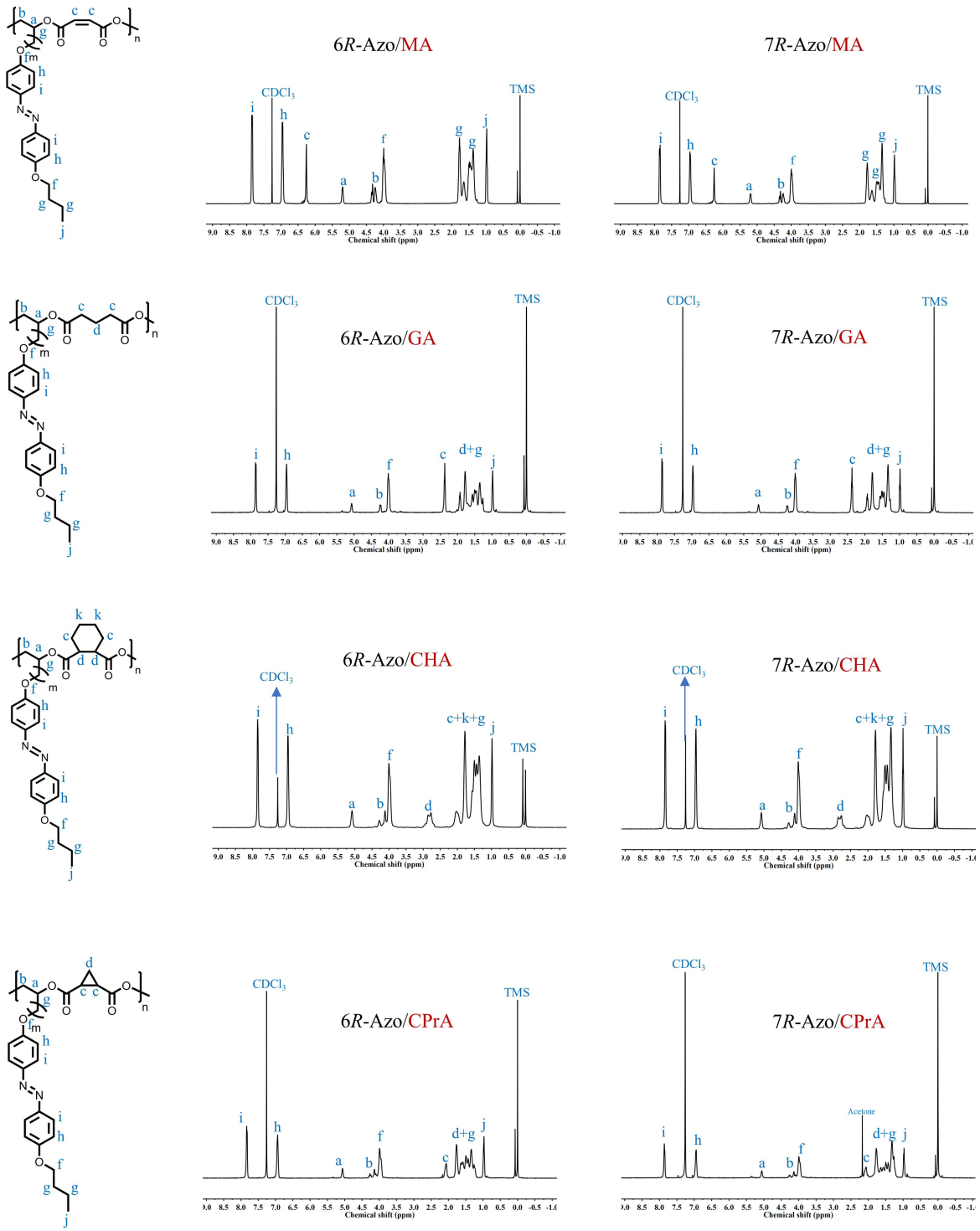


Figure S9. ^{1}H NMR spectra of azopolyesters with different main-chain structures.

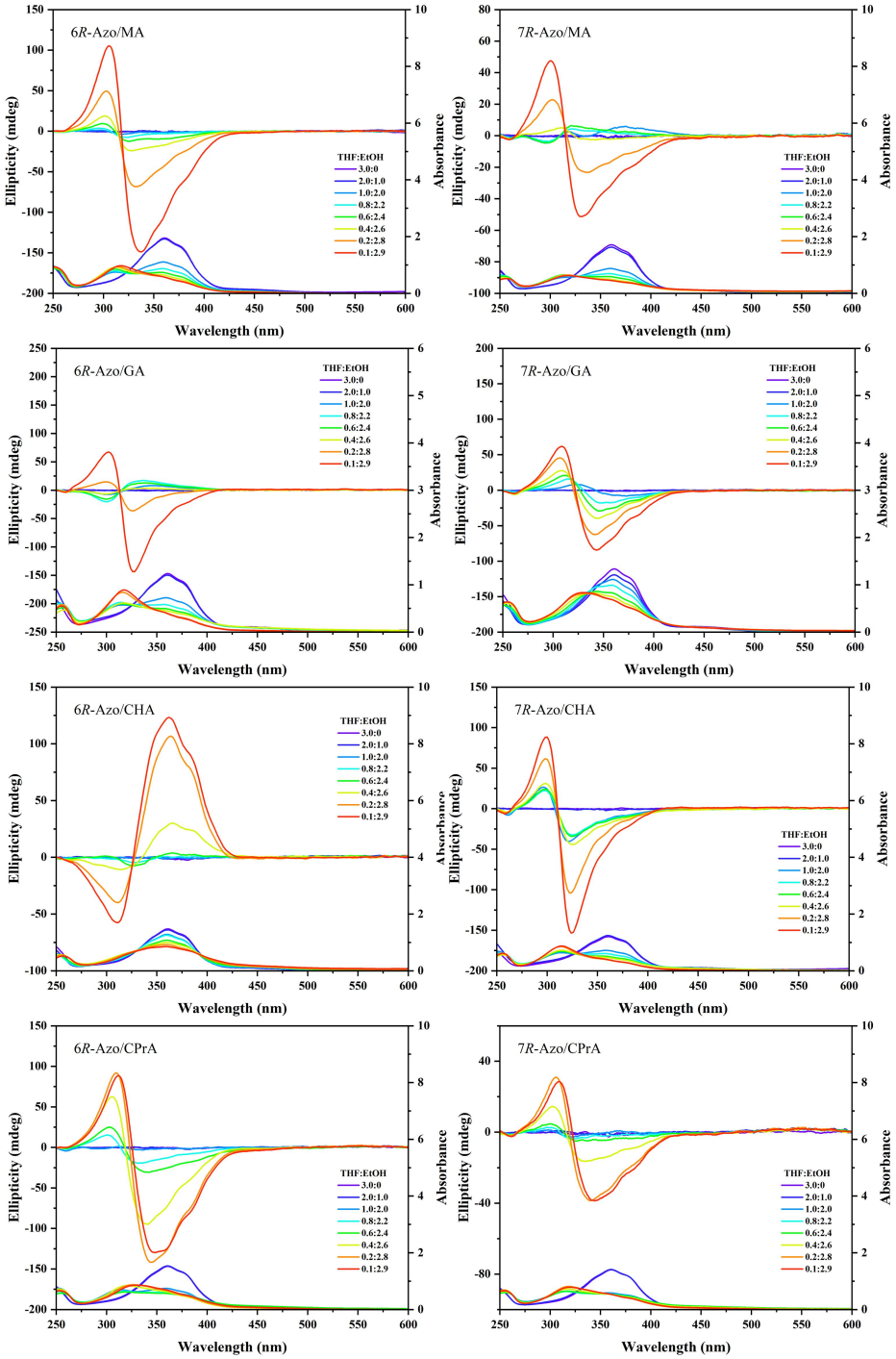


Figure S10. CD and UV-vis spectra of azopolyesters with different main-chain structures (m = 6 and7) in mixed solvents with different volume ratios ofTHF/EtOH.

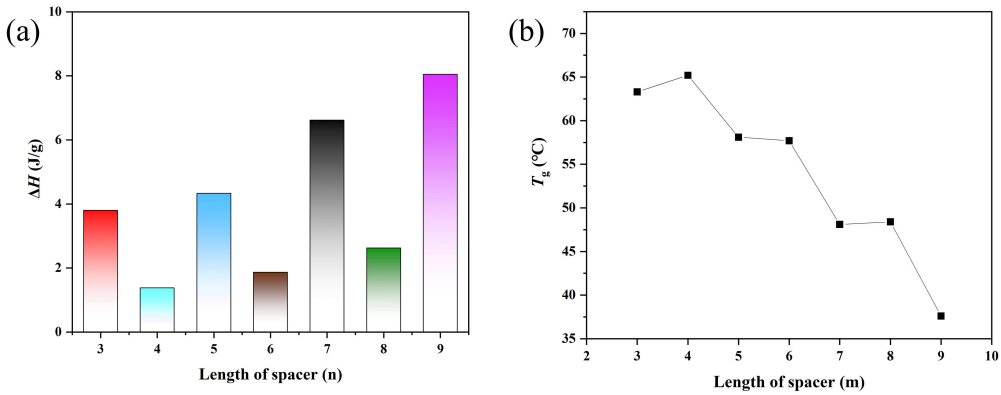


Figure S11. The enthalpy (a) and T_{LC-iso} (b) of m*R*-Azo/PA in DSC.

4. References

1. DiCiccio AM, Longo JM, Rodríguez-Calero GG, Coates GW. Development of highly active and regioselective catalysts for the copolymerization of epoxides with cyclic anhydrides: an unanticipated effect of electronic variation. J Am Chem Soc. 2016;138(22):7107-7113. [DOI:10.1021/jacs.6b03113]
2. Peris S, Tylkowski B, Carles Ronda J, Garcia-Valls R, Reina JA, Giamberini M. Synthesis, characterization, and photoresponsive behavior of new azobenzene-containing polyethers. Journal of Polymer Science Part A: Polymer Chemistry. 2009;47(20):5426-5436. [DOI:10.1002/pola.23592]
3. Li J, Zhang QY, Lu XB. Azopolyesters with intrinsic crystallinity and photoswitchable reversible solid-to-liquid transitions. Angew Chem Int Ed. 2023;62(46):e202311158. [DOI:10.1002/anie.202311158]
4. Tokunaga M, Larrow JF, Kakiuchi F, Jacobsen EN. Asymmetric catalysis with water: efficient kinetic resolution of terminal epoxides by means of catalytic hydrolysis. Science. 1997;277(5328):936-938. [DOI:10.1126/science.277.5328.936]
5. Li J, Ren BH, Wan ZQ, Chen SY, Liu Y, Ren WM, et al. Enantioselective resolution copolymerization of racemic epoxides and anhydrides: efficient approach for stereoregular polyesters and chiral epoxides. J Am Chem Soc. 2019;141(22):8937-8942. [DOI:10.1021/jacs.9b02722]
6. Wan ZQ, Longo JM, Liang LX, Chen HY, Hou GJ, Yang S, et al. Comprehensive understanding of polyester stereocomplexation. J Am Chem Soc. 2019;141(37):14780-14787. [DOI:10.1021/jacs.9b07058]