

The conformationally supramolecular chirality prevails over configurational point chirality in side-chain liquid crystalline polymers

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1. Materials and Method

1.1. Materials

4-Cyanopentanoic acid dithiobenzoate (CPADB, 97%, Aladdin), 4,4'-azobis(4-cyanovaleric acid) (ACVA, 98%, J&K Chemical), 1,1,3,3-tetramethylguanidine (TMG, 99%, Macklin), 2-bromoethanol (95%, Acros), 1-chloro-6-hydroxyhexane (95%, Acros), *p*-nitrophenol (> 99%, Aladdin), phenol (AR, Aladdin), tin(II) chloride (98%, Energy Chemical), methacryloyl chloride (95%, Aladdin), diisopropyl azodicarboxylate (98%, 3A Chemicals), triphenylphosphine (> 99%, Greagent), benzyl chloride (99%, Macklin), (*R*)-(-)-2-octanol and (*S*)-(+)-2-octanol (> 99%, TCI) were used as received without further purification. Methylacrylic acid (MAA, 99%, Aladdin) was purified by passing through a basic alumina oxide column prior to storage at -10 °C. The chiral Azo-containing monomers (Azo2MA-8*R/S*, Azo6MA-8*R/S*) were synthesized as described previously.^{S1}

1.2. Characterization

1. ¹H NMR spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz, Bruker, Kalsruhe, Germany) using 75/25% (w/w) CDCl₃/DMSO-*d*₆ mixtures as the solvent and tetramethylsilane (TMS) as the internal standard at 25 °C.
2. Gel permeation chromatograph (GPC) measurements were conducted on the TOSOH HLC-8320 gel permeation chromatograph (GPC) (Tokyo, Japan), which was equipped with a refractive index and UV detectors using two TSKgel SuperMultiporeHZ-N (4.6 × 150 mm, 3.0 μm beads size) columns (Tokyo, Japan) arranged in a series. 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 (*D*) of the polymer (have been fully esterified using benzyl chloride with TMG as a promoter) was calculated with PMMA standard.
3. CD spectra were recorded on a JASCO J-1500 spectropolarimeter equipped with a Peltier-controlled holder using a SQ-grade cuvette, with identical parameters (1 accumulation, 10 nm path length, 2 nm bandwidth, 200 nm/min scan rate, 1 s response time). All samples were measured at 25 °C unless otherwise specified. The magnitude of the circular polarization at the ground state was defined as $g_{CD} = 2 \times (\epsilon_L - \epsilon_R) / (\epsilon_L + \epsilon_R)$, where ϵ_L and ϵ_R denoted the extinction coefficients for left and right circularly polarized light, respectively. Experimentally, the g_{CD} value was defined as $\Delta\epsilon/\epsilon = [\text{ellipticity}/32,980]/\text{absorbance}$ at the CD extremum. UV-vis spectra were recorded on a UV-2600 spectrophotometer (Shimadzu (Nakagyo-ku, Kyoto, Japan)).
4. TEM images were taken with a HITACHI HT7700 operated at an accelerating voltage of 120 kV.

5. SAXS data were measured by Anton Paar SAXSess MC2 diffractometer with Cu K α radiation ($\lambda = 0.154$ nm). POM images were measured by CNOPTec BK-POL microscope fitted with a CNOPTec BK-RDY thermo-control system (Chongqing, China). WAXD data were obtained on an X'Pert-Pro MPD X-ray powder diffractometer (Panalytical, Holland) equipped with a copper target, at a scan speed of $0.375151^\circ \text{ s}^{-1}$ and at a scattering angle range of $2\theta = 10\text{-}50^\circ$. Experimentally, a small aliquot mixture after PICSA was filtered directly at room temperature to remove ethanol, and then the LC property of the sample was measured.

6. The enantiomeric excess of chiral monomers were measured by chiral high performance liquid chromatography (HPLC). Chiral HPLC was performed on an Agilent 1200 Series chromatographs using a Daicel Chiralpak AD-H column ($0.46 \text{ cm} \times 25 \text{ cm}$).

2. Experimental Procedures

2.1. Synthesis of PMAA₅₁ macro-CTA via RAFT solution polymerization

For a typical polymerization system, MAA (5.16 g, 60.0 mmol), CPADB (0.28 g, 1.0 mmol), EtOH (10.32 g) and ACVA (56.1 mg, 0.2 mmol) with the molar ratio of [MAA]₀/[CPADB]₀/[ACVA]₀ = 60/1/0.2 were added into a 25 mL round bottomed flask equipped with a magnetic bar. The reaction medium was purged with argon for 30 min at 0 °C to remove oxygen. After three freeze-thaw-pump cycles, the flask was sealed and placed in an oil bath at 70 °C. After 5 h, the flask was cooled to room temperature with ice-water. The mixture was diluted with EtOH, precipitated in *n*-hexane 3 times. PMAA macro-CTA was purified via dialysis (MWCO 3000 g/mol) in EtOH for 3 days. Then dry under vacuum at 35 °C. The product obtained was a pink solid (4.32 g, monomer conversion: 84%). The DP was 51 measured by ¹H NMR in DMSO-*d*₆. The *M*_n (9000 g/mol) and *D* (1.08) were measured by GPC after chemical modification of the carboxylic acid groups by benzyl chloride.^{S2}

2.2. Synthesis of random PMAA₅₁-*b*-P(Azo6_{1-n}-*co*-Azo2_n) copolymer assemblies via RAFT dispersion polymerization

A typical RAFT dispersion polymerization for the synthesis of the random PMAA₅₁-*b*-P(Azo6_{1-n}-*co*-Azo2_n) copolymer assemblies at 10 wt% total solid content was carried out as follows. Taking *R*-type Azo assemblies as an example, the random PMAA₅₁-*b*-P(Azo6_{1-n}-*co*-Azo2_n) copolymer assemblies with the DP of 60 and the ratio of Azo2 units *n* = 0.20 (DP = 60, *r*-0.20-*R*) was prepared by the following procedures. PMAA₅₁ macro-CTA (91.6 mg, 0.02 mmol), ACVA (2.9 mg, 0.01 mmol), Azo2MA*-8*R* (105.1 mg, 0.24 mmol), Azo6MA*-8*R* (474.2 mg, 0.96 mmol) and EtOH (7.68 mL) were added to a reaction tube in the glove box. The polymerization was carried out at 70 °C for 18 h. Then the polymerization was quenched by cooling the tube in an ice-water bath and exposing the solution to air. The resulting Azo copolymers were characterized by using ¹H NMR, TEM and CD instruments. The *M*_n and *D* were measured by GPC after chemical modification of the carboxylic acid groups by benzyl chloride.^{S2}

2.3. Synthesis of block PMAA₅₁-*b*-P(Azo2_n-*b*-Azo6_{1-n}) and PMAA₅₁-*b*-P(Azo6_{1-n}-*b*-Azo2_n) copolymer assemblies via seeded RAFT dispersion polymerization

Taking the block polymer PMAA₅₁-*b*-P(Azo2_n-*b*-Azo6_{1-n}) with DP = 60, and the ratio of Azo2 units *n* = 0.20 (DP = 60, *b*₂-0.20-*R*) as an example, PMAA₅₁ macro-CTA (91.6 mg, 0.02 mmol), ACVA

(1.45 mg, 0.005 mmol), Azo2MA*-8R (105.1 mg, 0.24 mmol) and EtOH (2.56 mL) were added to the reaction tube in the glove box, and the total solid content was 10%. After the polymerization was carried out at 70 °C for 10 h, the second monomer Azo6MA*-8R (474.2 mg, 0.96 mmol), ACVA (1.45 mg, 0.005 mmol), and EtOH (5.42 mL) were added to the reaction tube, and the polymerization was continued for 10 h at 70 °C. Then the polymerization was quenched by cooling the tube in an ice-water bath and exposing the solution to air. The resulting Azo copolymers were characterized by using ¹H NMR, TEM and CD instruments. The M_n and \bar{D} were measured by GPC after chemical modification of the carboxylic acid groups by benzyl chloride.^{S2} The procedures to prepare block polymer PMAA₅₁-*b*-P(Azo6_{1-n}-*b*-Azo2_n) assemblies is similar except the Azo6MA*-8R was treated as the first monomer and Azo2MA*-8R was used as the second monomer.

2.4. Chemical modification of carboxylic acid groups on PMAA₅₁ macro-CTA, PMAA₅₁-*b*-P(Azo2_n-*co*-Azo6_{1-n}) and PMAA₅₁-*b*-P(Azo6_{1-n}-*co*-Azo2_n) copolymers

For GPC studies, the carboxylic acid groups on the PMAA₅₁ macro-CTA, PMAA₅₁-*b*-P(Azo2_n-*b*-Azo6_{1-n}) and PMAA₅₁-*b*-P(Azo6_{1-n}-*co*-Azo2_n) copolymers were fully esterified using benzyl chloride with TMG as a promoter according to Bai and coworkers' study.^{S2} Taking the chemical modification of PMAA macro-CTA as an example, PMAA₅₁ macro-CTA (34.3 mg, 0.5 unit mmol) was dissolved in DMSO (1 mL). Then TMG (115.0 mg, 1 mmol) and benzyl chloride (95.0 mg, 0.75 mmol) were added. After that the mixture was stirred over night at room temperature. The polymer was then precipitated into a large amount of methanol and dried under vacuum at 40 °C to obtain a white powder polymer. The chemical modification of PMAA₅₁-*b*-P(Azo2_n-*b*-Azo6_{1-n}) and PMAA₅₁-*b*-P(Azo6_{1-n}-*co*-Azo2_n) copolymers were treated in a similar way except the 75/25% w/w CHCl₃/DMSO mixtures were used as the solvent.

3. Results and Discussion

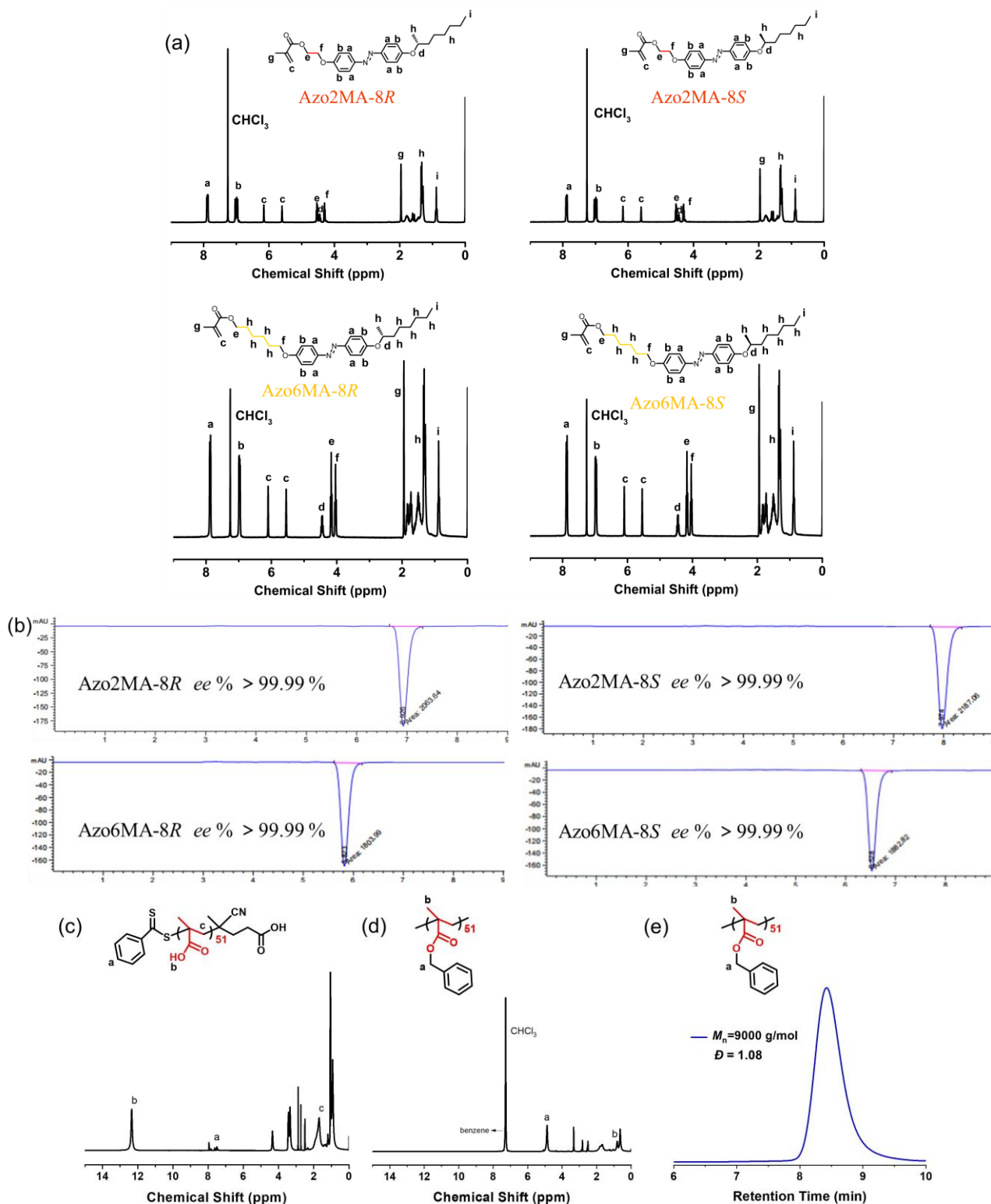


Figure S1. (a) ¹H NMR spectra of the chiral Azo-containing monomers. (b) The *ee* % values of the corresponding monomers. (c) ¹H NMR spectra of PMAA₅₁ macro-CTA and (d) PMAA₅₁ macro-CTA after chemical modification. (e) GPC curve of the PMAA₅₁ macro-CTA after chemical modification.

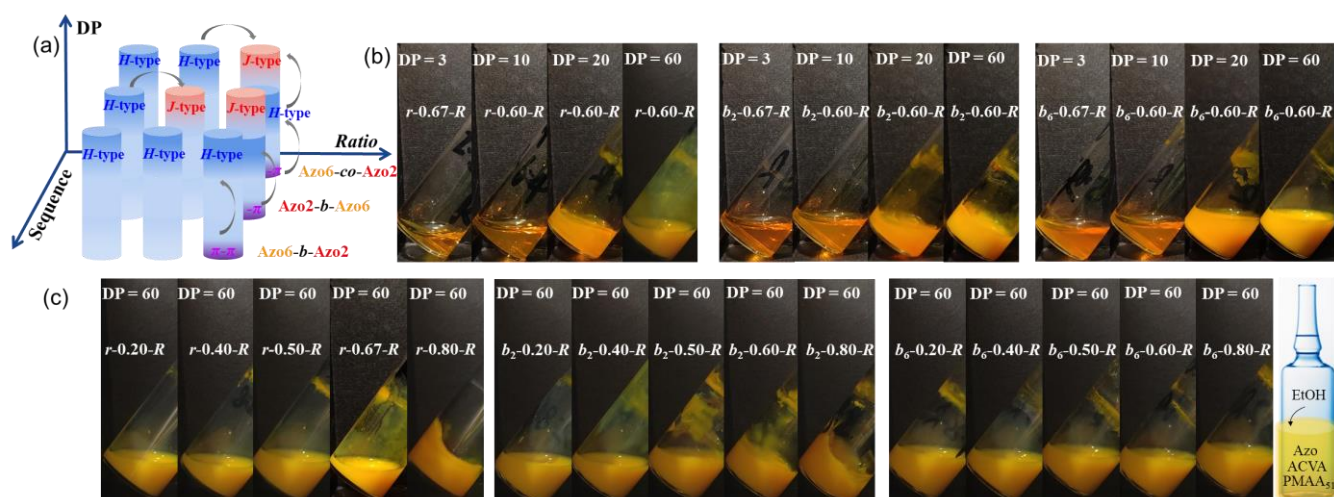


Figure S2. (a) Schematic presentation of the packing modes transition by adjusting the DP, Azo2 ratio, and sequence of the copolymers. (b) Digital images of Azo copolymer assemblies with the increase of DP of Azo blocks. (c) Digital images of Azo copolymer assemblies with the increase of Azo2 ratio. The abbreviation of ***r*-0.60-*R*** means **random** Azo6-*co*-Azo2 (*r*)-Azo2 ratio (**0.60**)-*R* polymer (***R***); ***b*₂-0.60-*R*** means **block** Azo2-*b*-Azo6 (*b*₂)-Azo2 ratio (**0.60**)-*R* polymer (***R***); ***b*₆-0.60-*R*** means block Azo6-*b*-Azo2 (*b*₆)-Azo2 ratio (**0.60**)-*R* polymer (***R***).

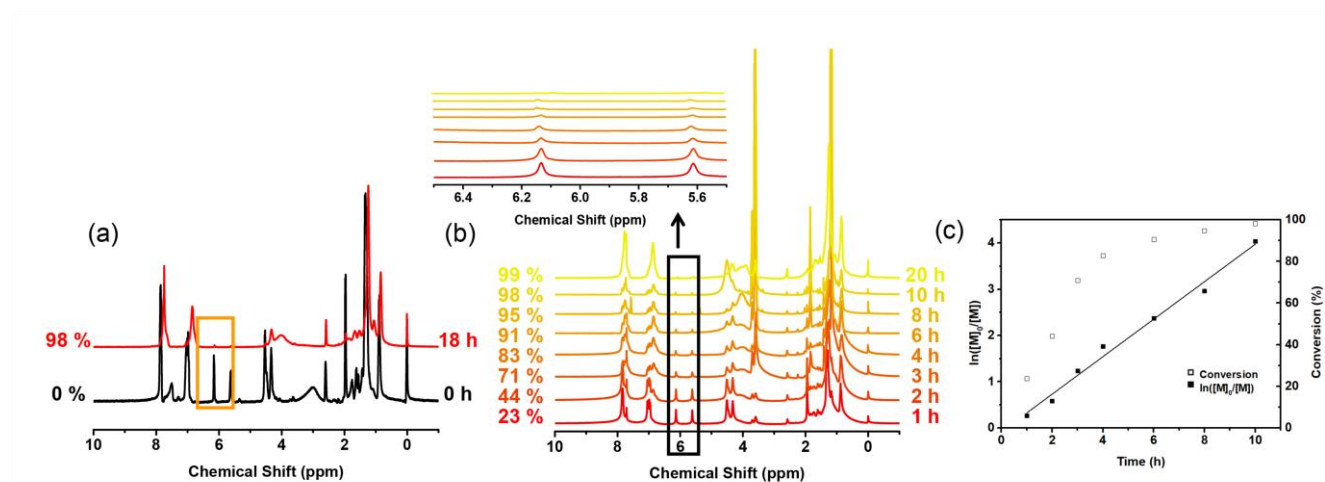


Figure S3. ¹H NMR spectra of the (a) *r*-0.50-*R* Azo copolymers, (b) *b*₂-0.50-*R* Azo copolymers with different polymerization time. The targeted DP of *b*₂-0.50-*R* is 60. After polymerization, the monomer conversion finally reached more than 98%. (c) The corresponding plots of polymerization kinetics.

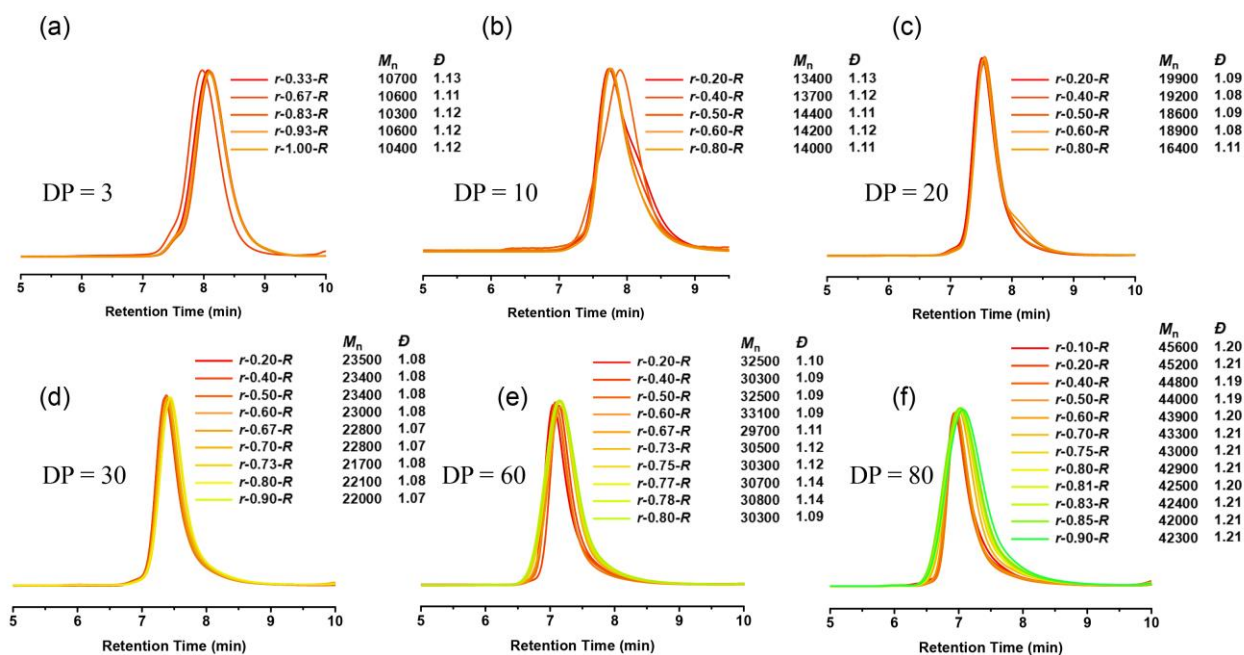


Figure S4. GPC curves of the random Azo6-co-Azo2 copolymers with (a) DP = 3, (b) DP = 10, (c) DP = 20, (d) DP = 30, (e) DP = 60, (f) DP = 80 (THF, PMMA standards). All the Azo copolymers were fully esterified using benzyl chloride with TMG as a promoter.

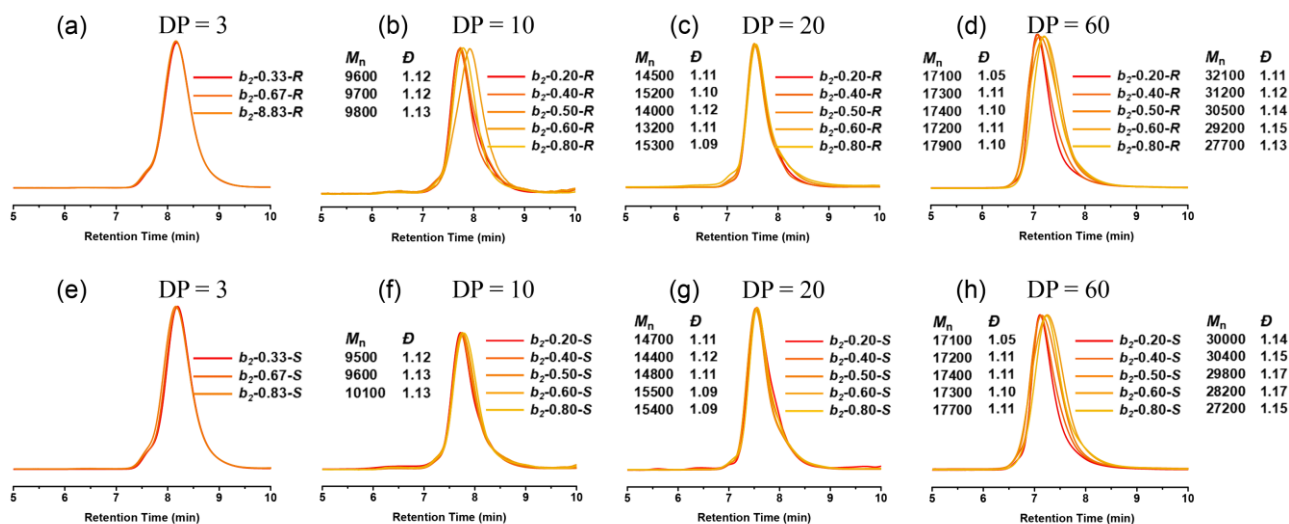


Figure S5. GPC curves of the block Azo2-b-Azo6 copolymers with (a) DP = 3, (b) DP = 10, (c) DP = 20, (d) DP = 60, and S-polymer with (e) DP = 3, (f) DP = 10, (g) DP = 20, (h) DP = 60 (THF, PMMA standards). All the Azo copolymers were fully esterified using benzyl chloride with TMG as a promoter.

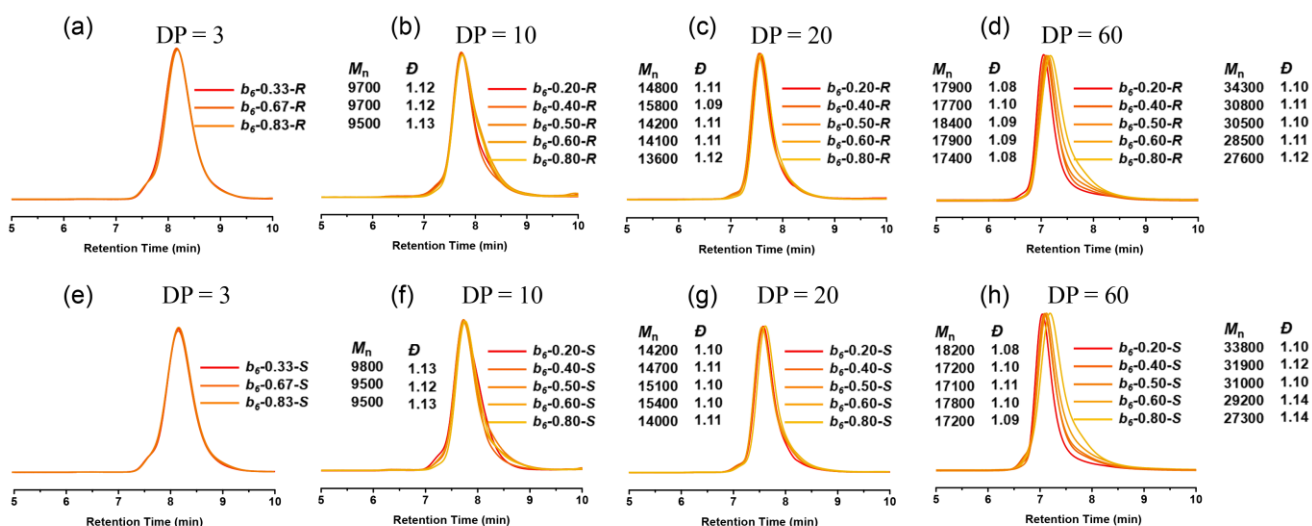


Figure S6. GPC curves of the block Azo6-*b*-Azo2 copolymers with (a) DP = 3, (b) DP = 10, (c) DP = 20, (d) DP = 60, and *S*-polymer with (e) DP = 3, (f) DP = 10, (g) DP = 20, (h) DP = 60 (THF, PMMA standards). All the Azo copolymers were fully esterified using benzyl chloride with TMG as a promoter.

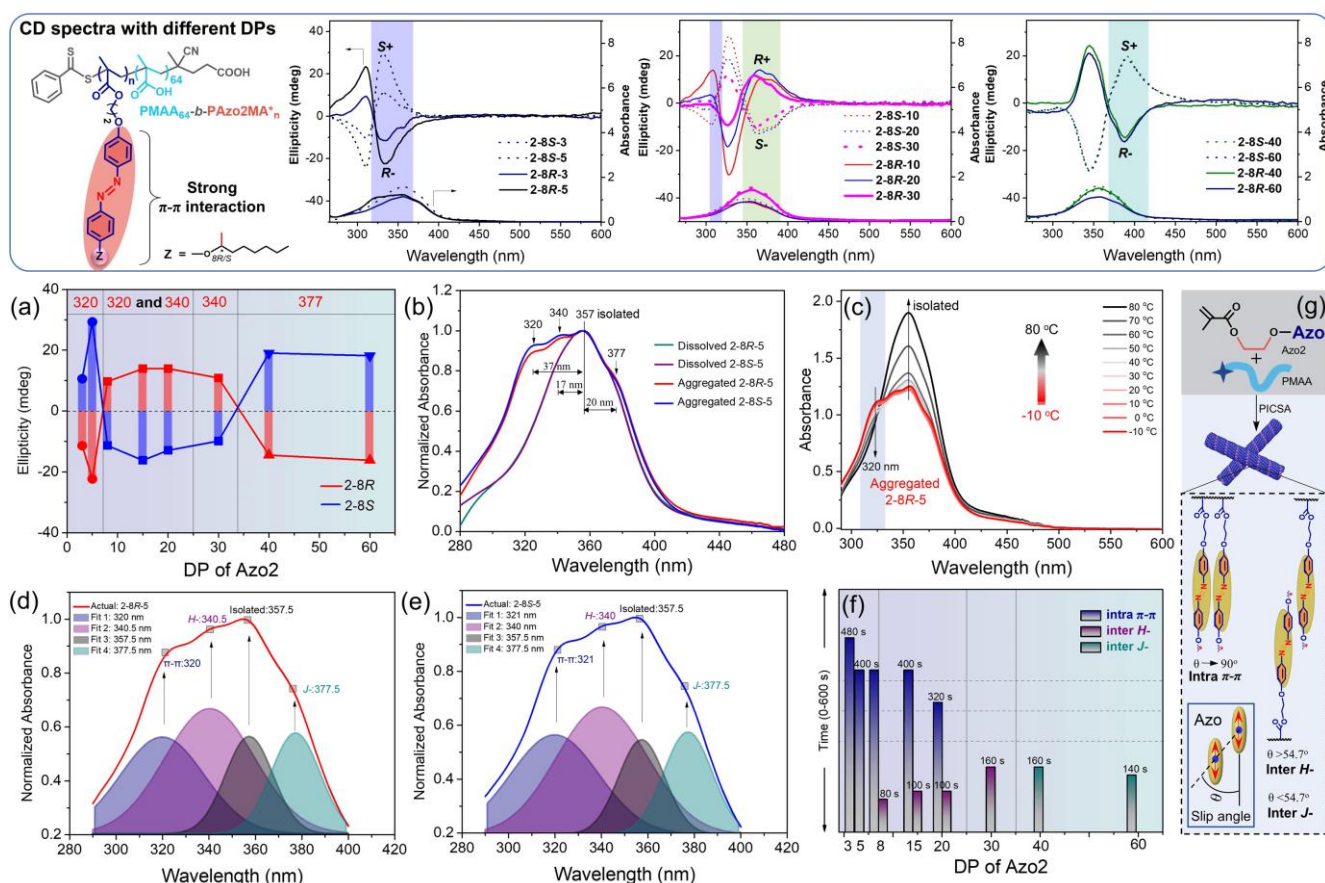


Figure S7. CD spectra of PMAA₆₄-*b*-PAzo2MA*_n diblock copolymer (2-8R or 2-8S) with different DPs. (a) The corresponding CD maximum values (first Cotton band) of 2-8R or 2-8S Azo-assemblies with different DP of Azo blocks. (b) The UV-vis spectra of aggregated and dissolved 2-8R or 2-8S with the DP of 5. (c) Temperature-dependent UV-vis spectra of 2-8S-5 Azo-assemblies. Gaussian-typed curve-fitting spectra of (d) 2-8R and (e) or 2-8S Azo-assemblies with the DP of 5. (f) Plots of relaxation time

versus DP by 365 nm UV-light irradiation. (g) Schematic representation of intra-chain π - π stacking, inter-chain *H*-aggregation and *J*-aggregation modes.

Reproducible results were obtained by fitting the absorption spectrum using four peaks with local absorption maxima at 320 nm for intra-chain π - π stacking, 340 nm for inter-chain *H*-aggregation, 357 nm for non-associated chromophores, and 377 nm for inter-chain *J*-aggregation. In Figure S7f, since the distance and interactions of intra-chain stacking are closer and stronger, the supramolecular chirality constructed by intra-chain π - π stacking also displayed improved UV-resistance (PSS > 320 s) compared with the inter-chain *H*- and *J*-type counterparts (PSS < 160 s) (reference 30 in the manuscript).

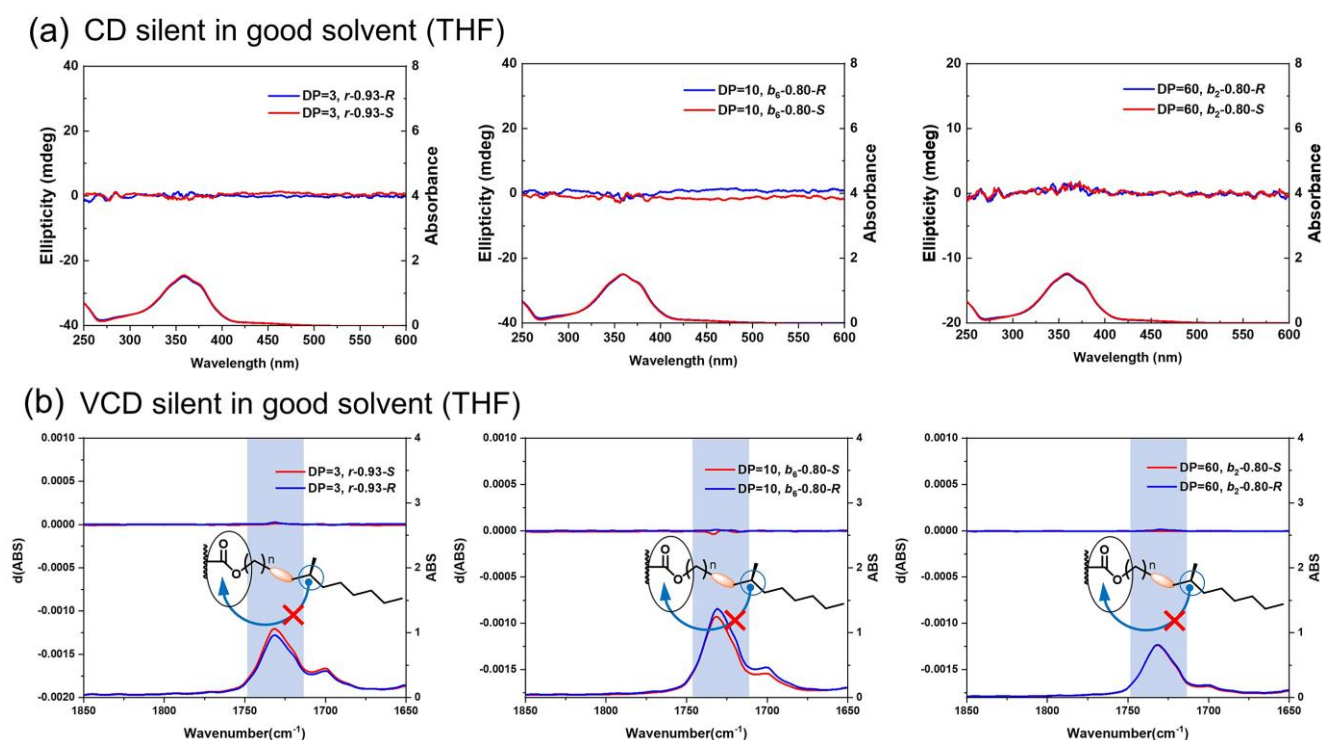
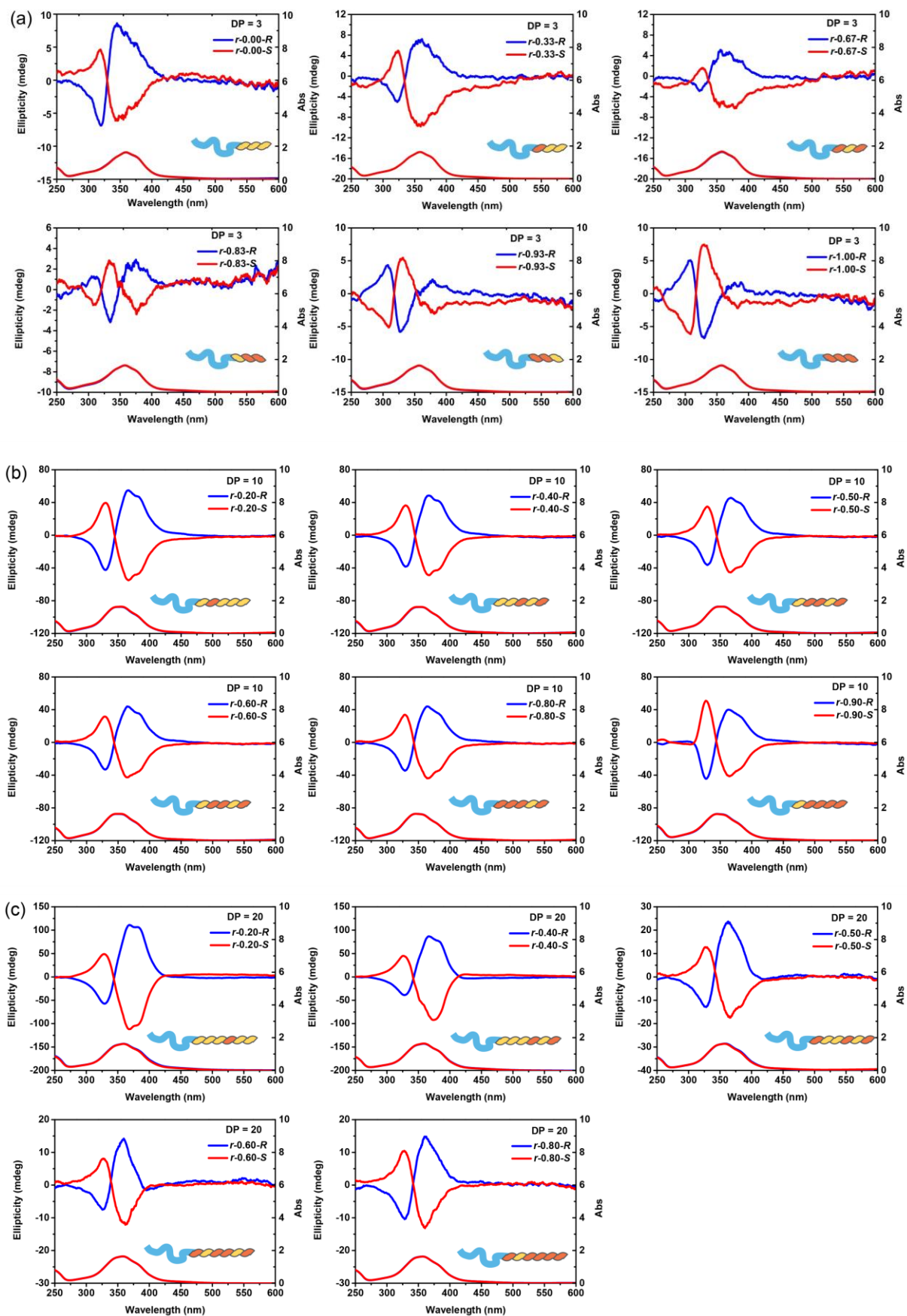


Figure S8. (a) CD and (b) VCD spectra of random Azo6-*co*-Azo2 copolymer with DP = 3 and $n = 0.93$ (r -0.93-*R* and r -0.93-*S*), block Azo6-*b*-Azo2 copolymer with DP = 10 and $n = 0.80$ (b_6 -0.80-*R* and b_6 -0.80-*S*), block Azo2-*b*-Azo6 copolymer with DP = 60 and $n = 0.80$ (b_2 -0.80-*R* and b_2 -0.80-*S*) in good solvent THF.



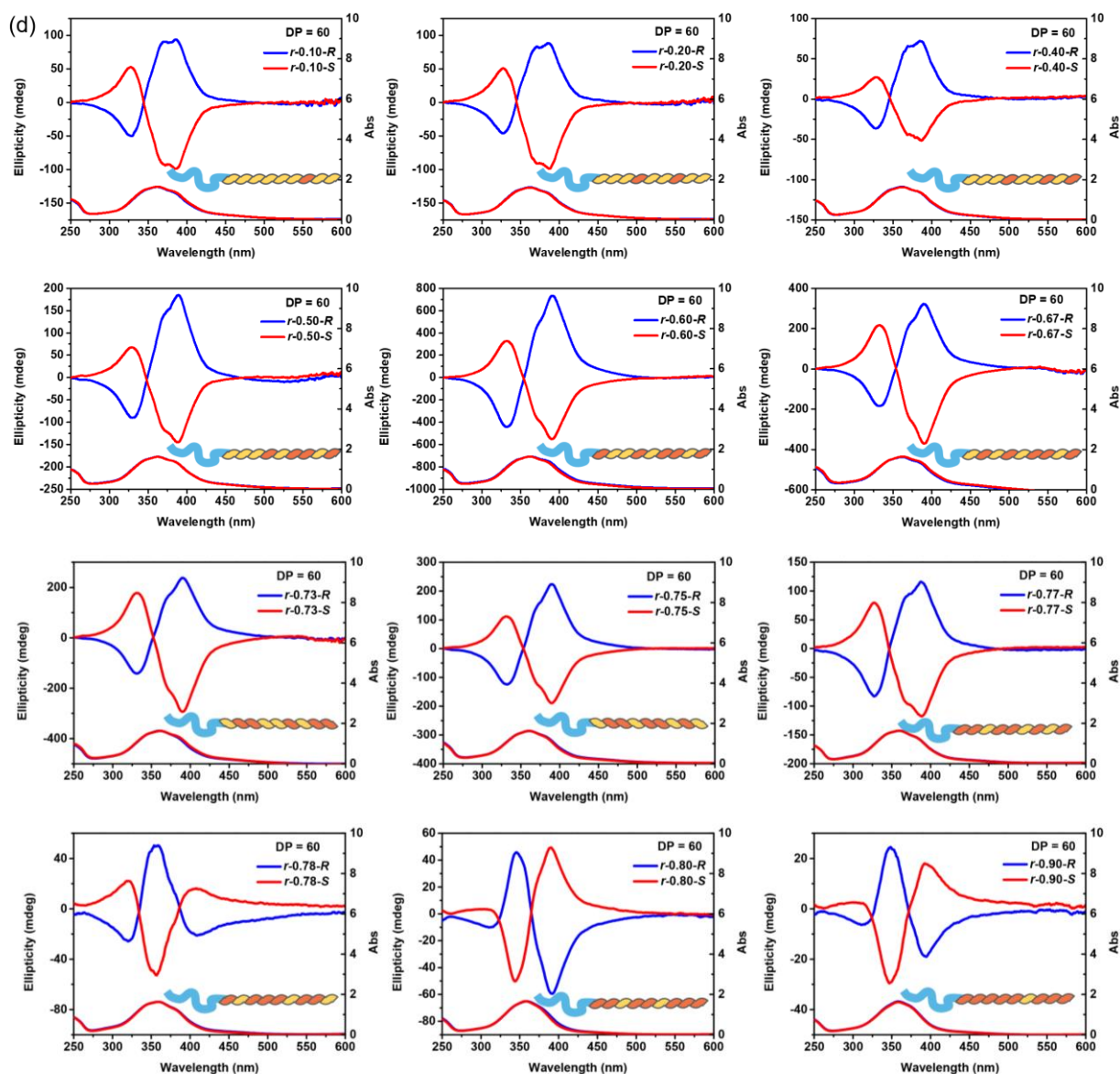
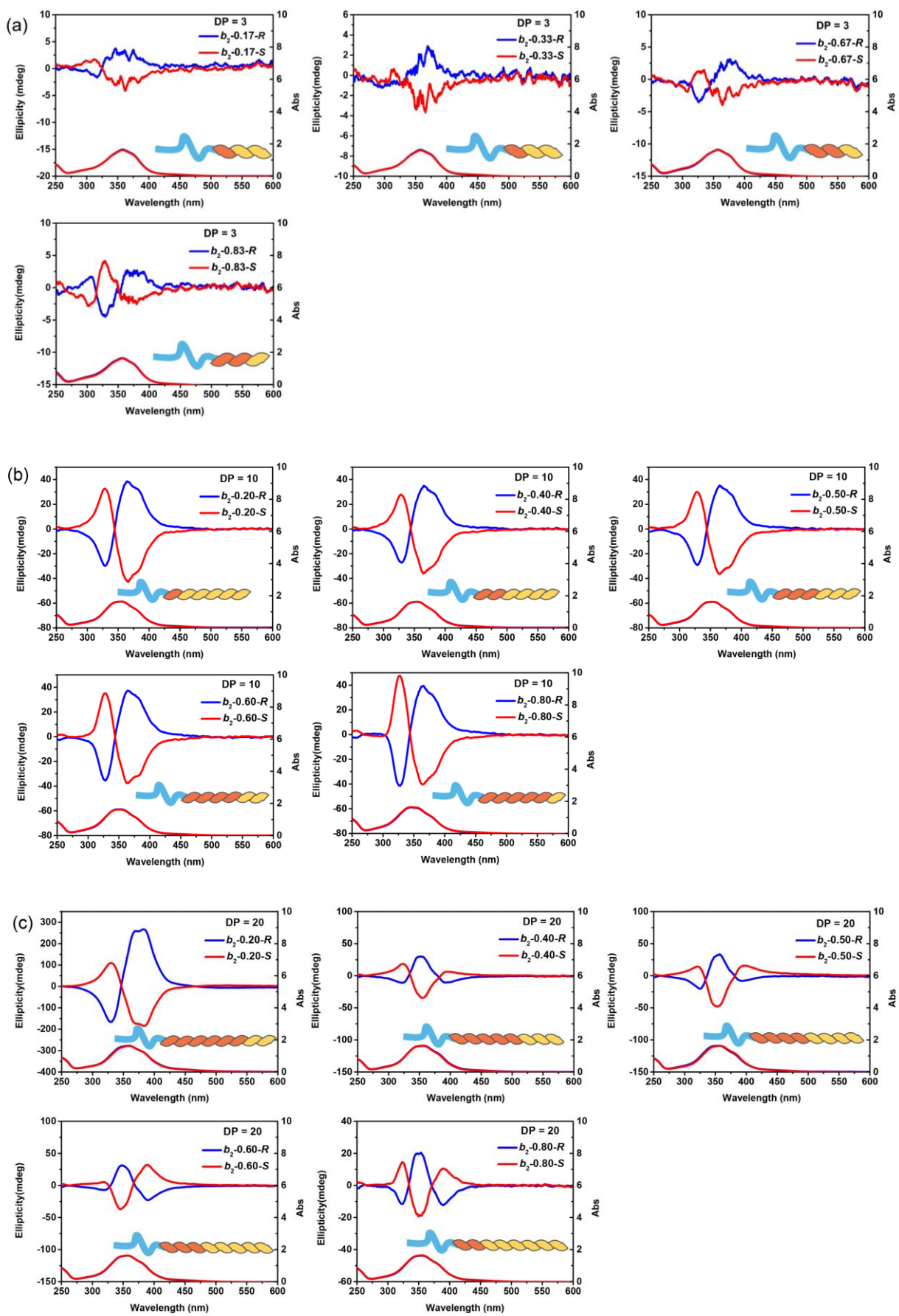


Figure S9. CD spectra of the random copolymers Azo6-*co*-Azo2 with the increase of DP and Azo2 ratios.

(a) DP = 3, (b) DP = 10, (c) DP = 20 and (d) DP = 60.



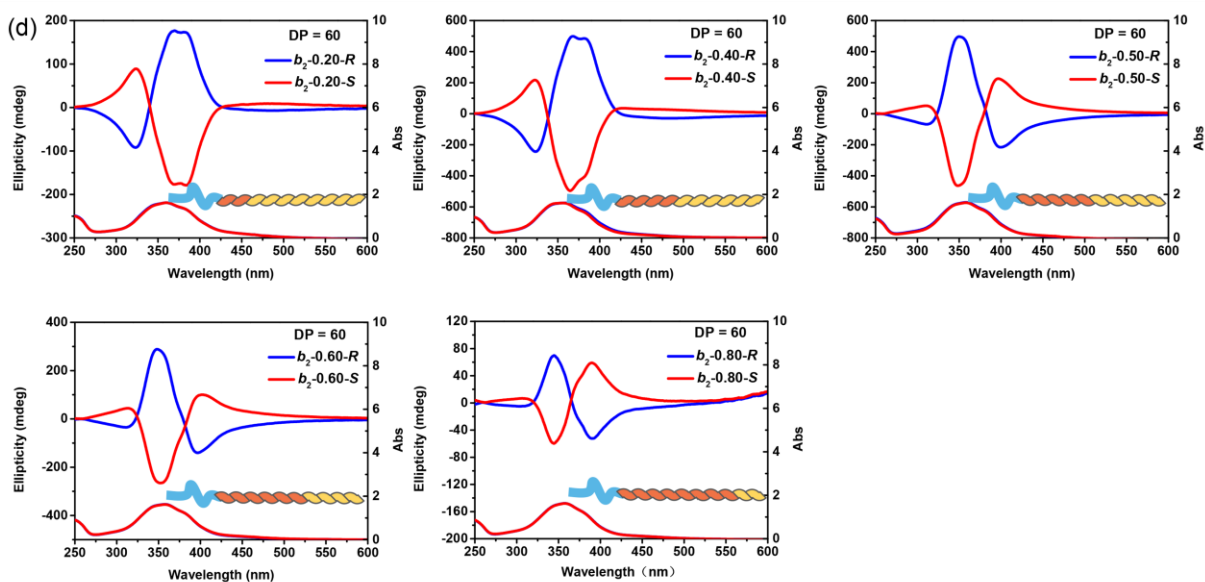
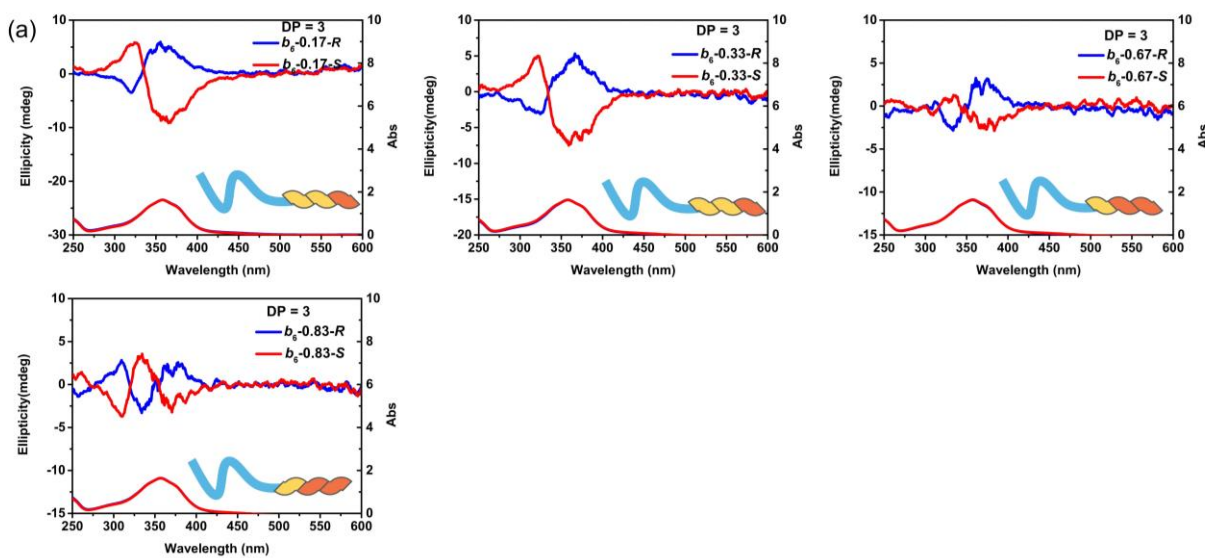


Figure S10. CD spectra of the block copolymers Azo2-*b*-Azo6 with the increase of DP and Azo2 ratios.

(a) DP = 3, (b) DP = 10, (c) DP = 20 and (d) DP = 60.



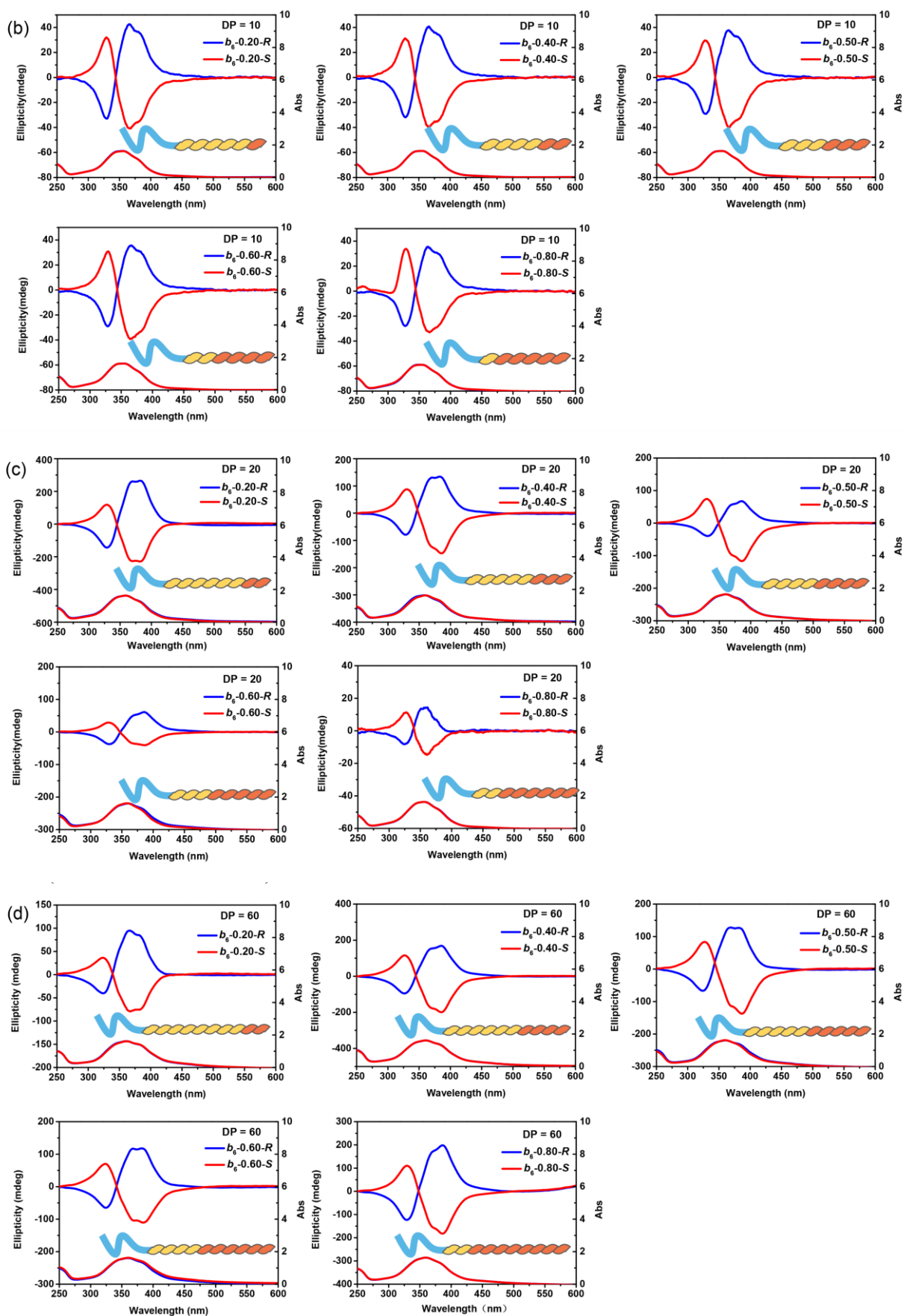


Figure S11. CD spectra of the block copolymers Azo6-*b*-Azo2 with the increase of DP and Azo2 ratios. (a) DP = 3, (b) DP = 10, (c) DP = 20 and (d) DP = 60.

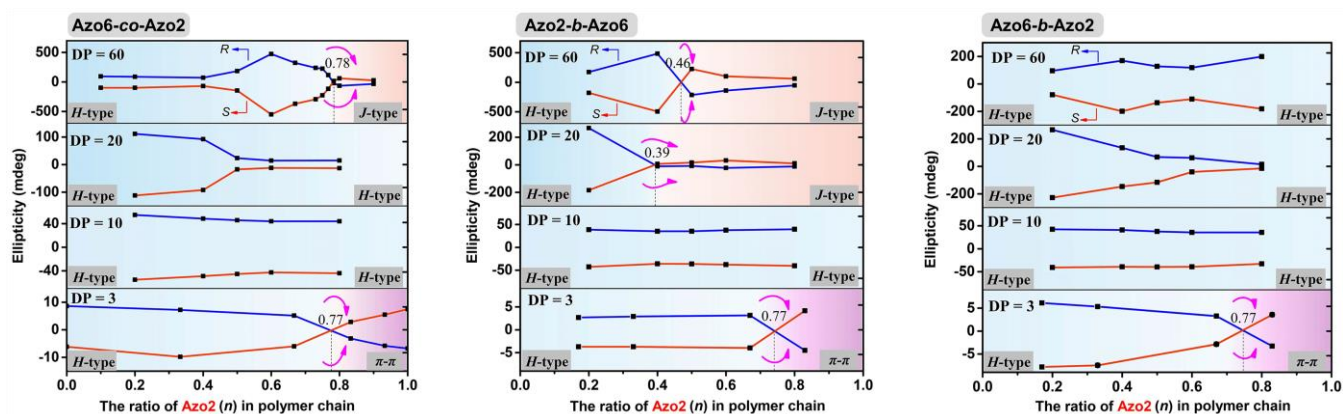
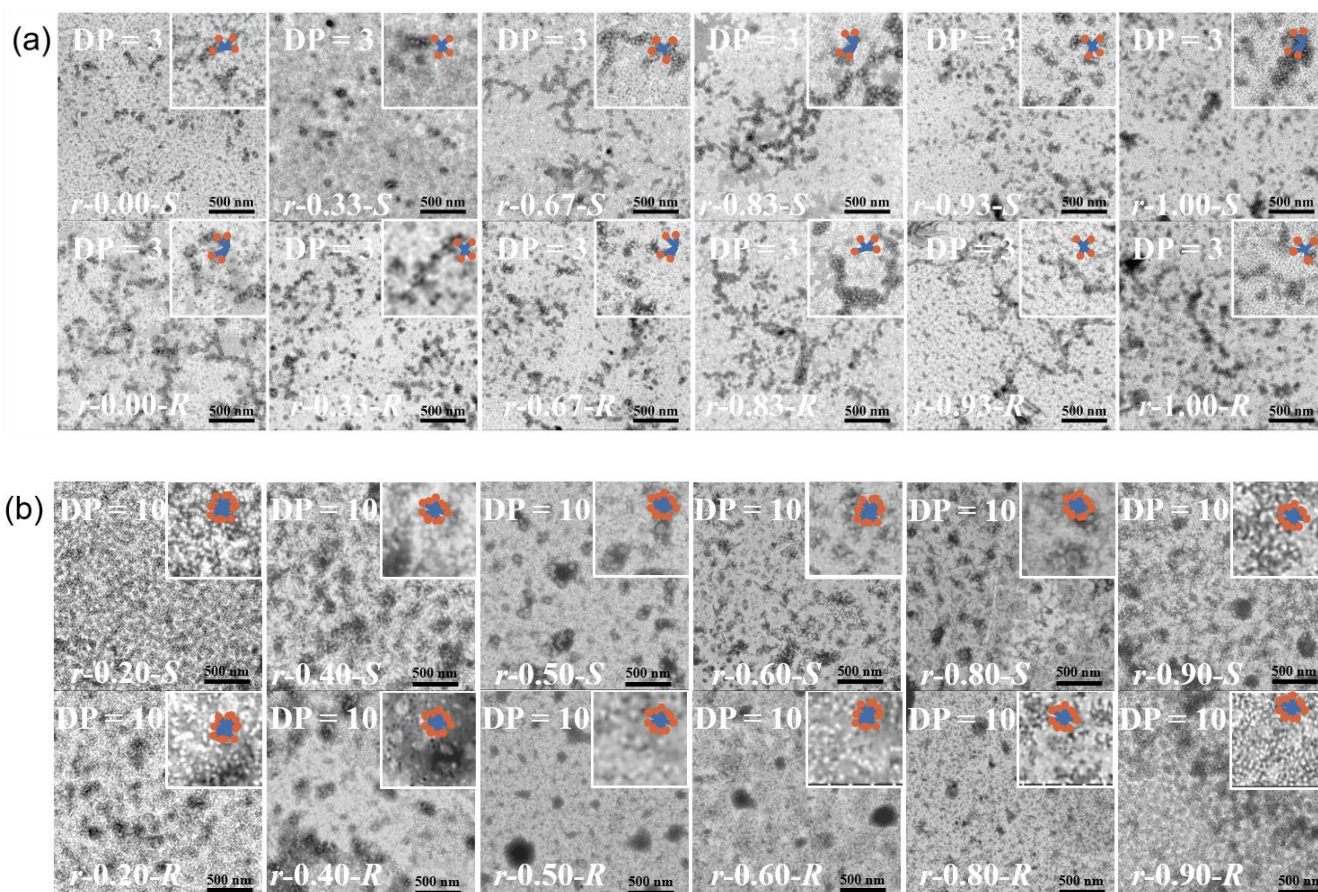
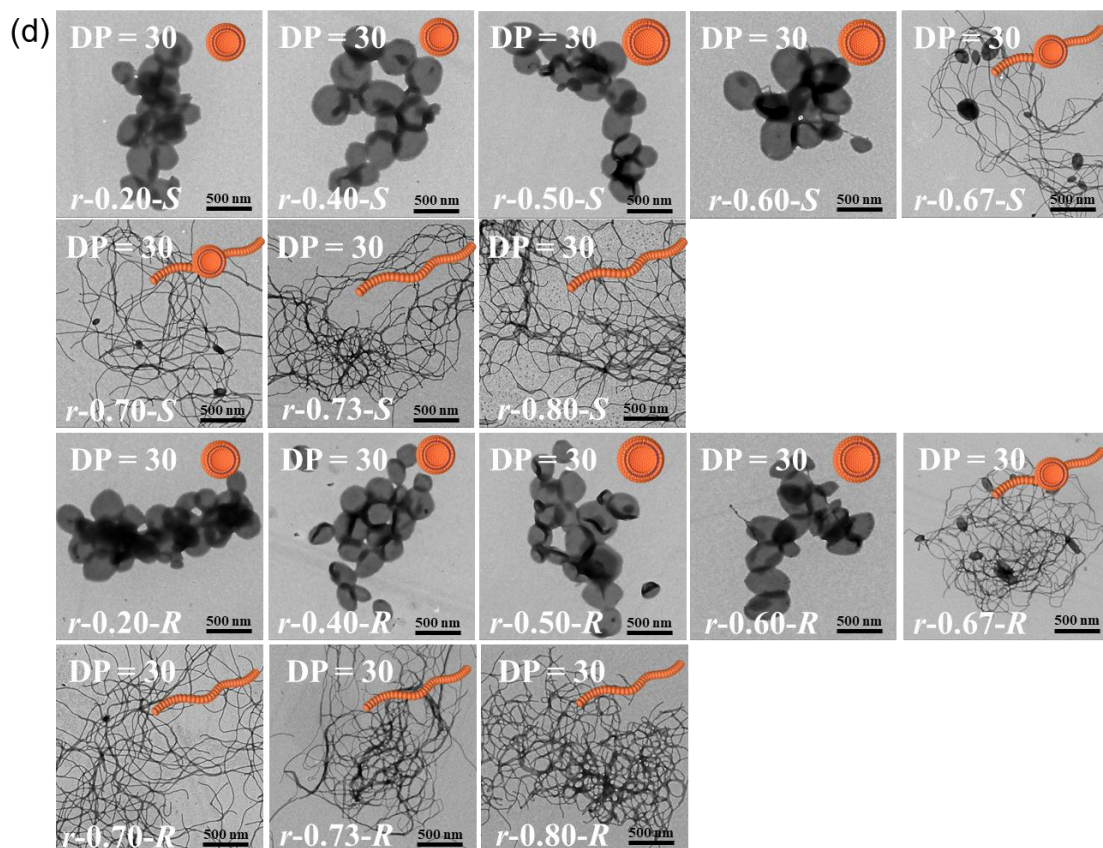
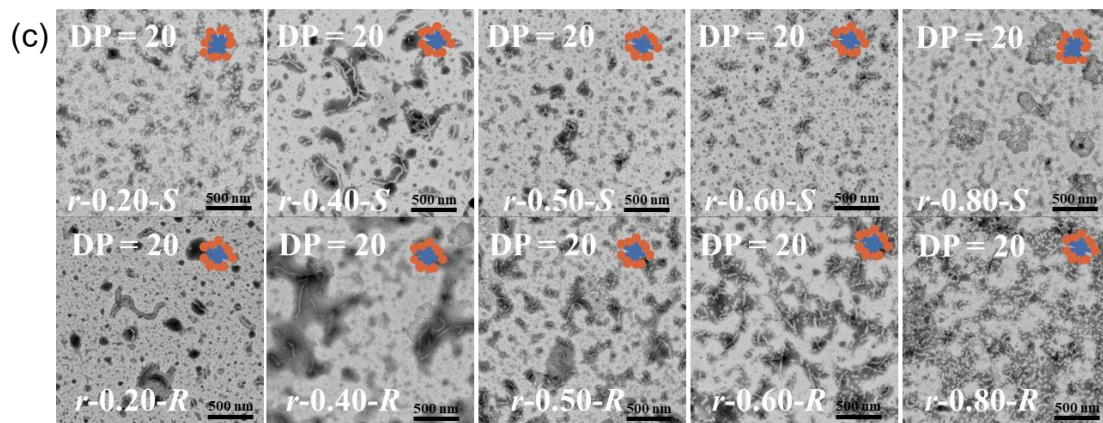


Figure S12. The CD maximum values of (a) random Azo6-co-Azo2, (b) block Azo2-b-Azo6 and (c) block Azo6-b-Azo2 copolymer assemblies with the increase of DP and Azo2 ratios.





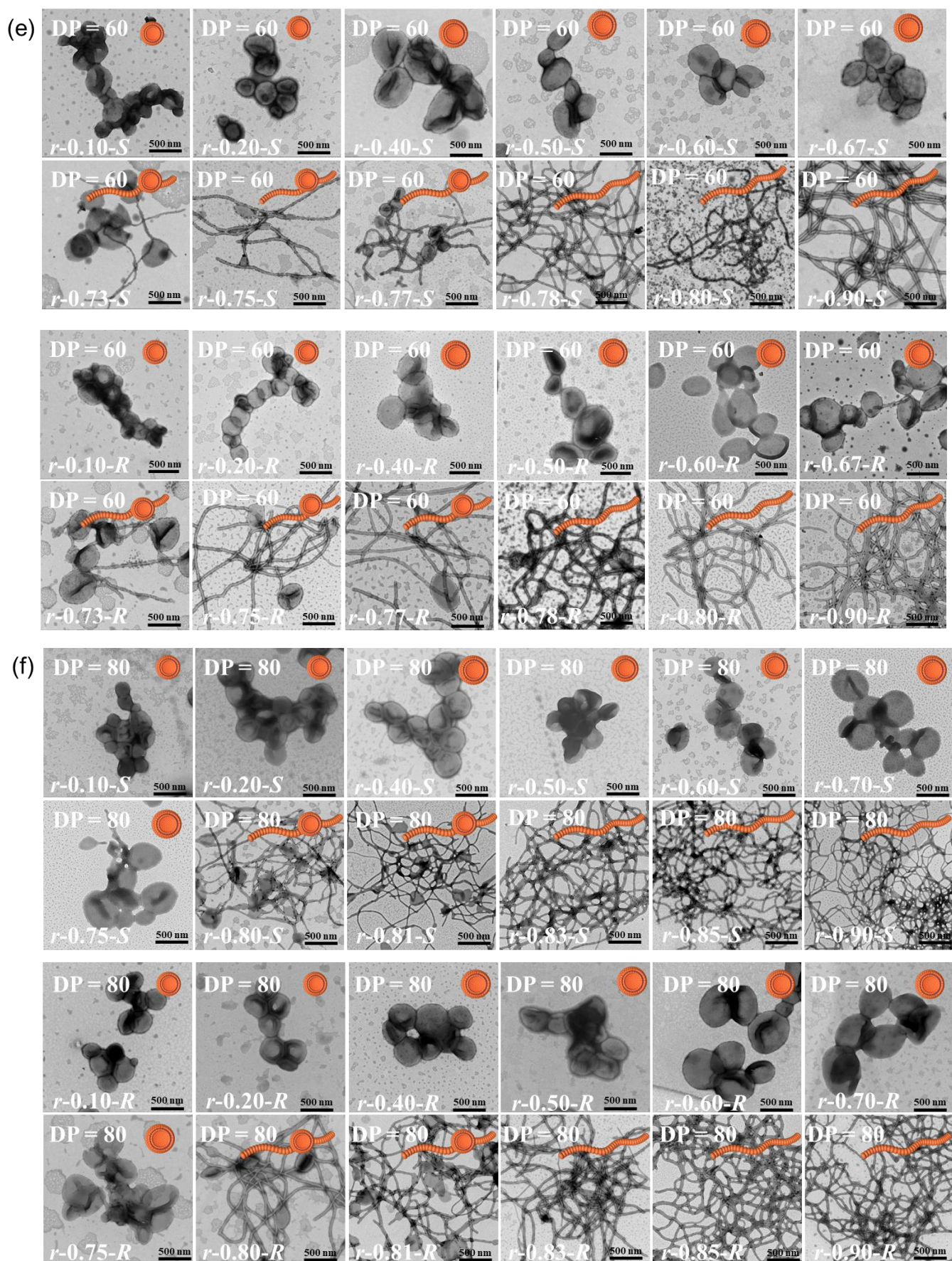


Figure S13. TEM images of the random Azo6-co-Azo2 assemblies with the increase of DP and Azo2 ratio. (a) DP = 3, (b) DP = 10, (c) DP = 20, (d) DP = 30, (e) DP = 60, (f) DP = 80.

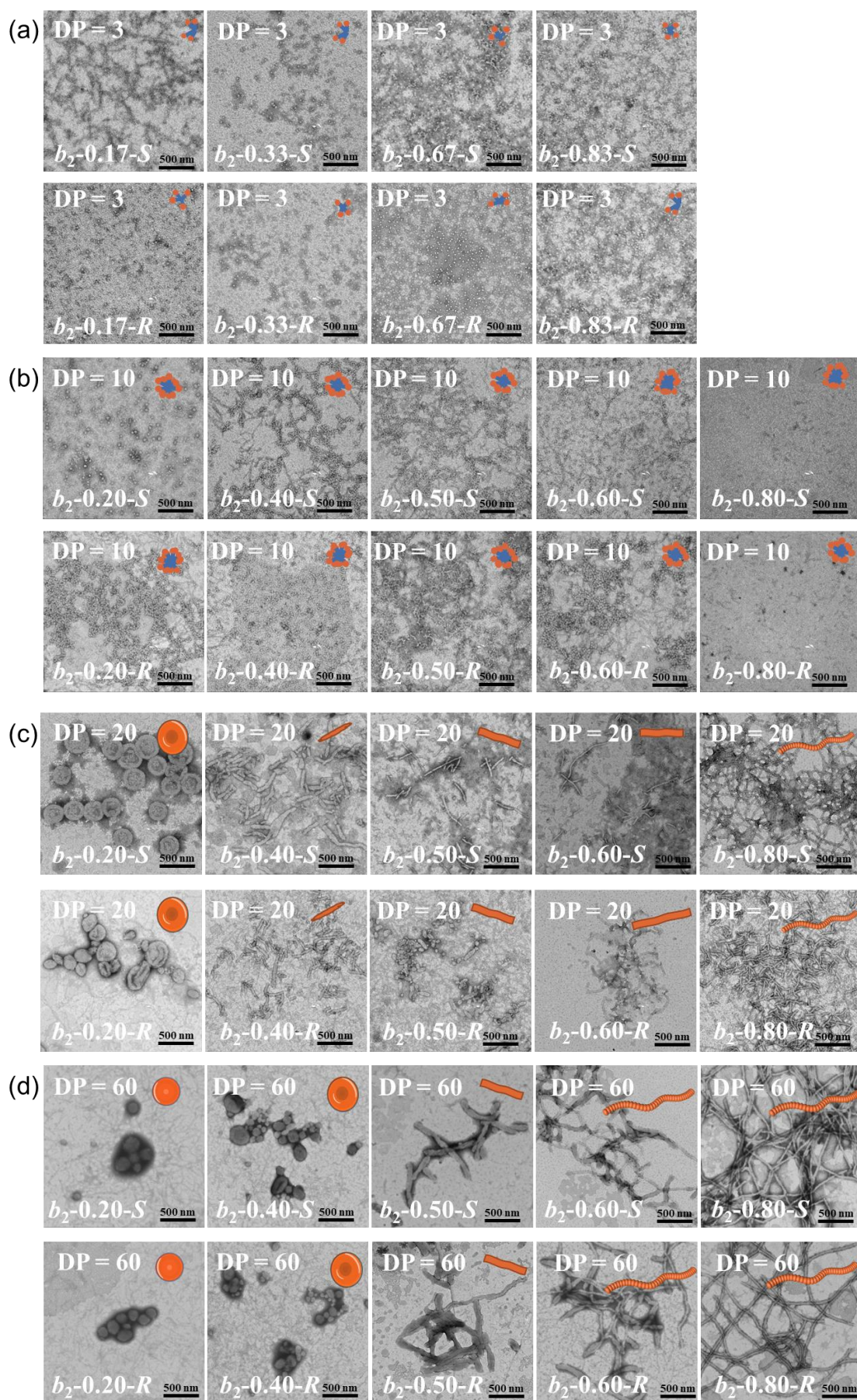


Figure S14. TEM images of the block Azo2-*b*-Azo6 assemblies with the increase of DP and Azo2 ratios.
(a) DP = 3, (b) DP = 10, (c) DP = 30, (d) DP = 60.

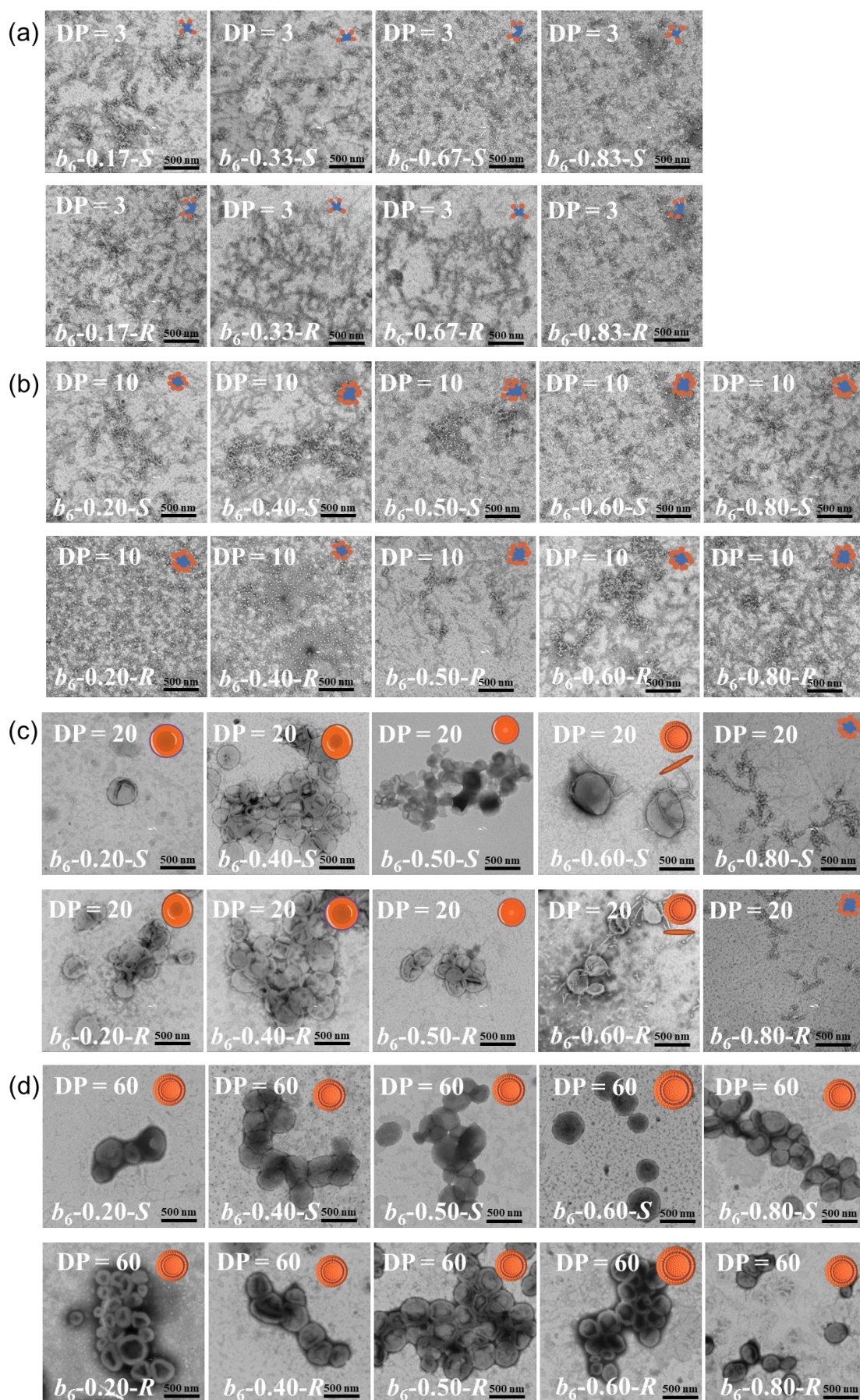


Figure S15. TEM images of the block Azo6-*b*-Azo2 assemblies with the increase of DP and Azo2 ratios.

(a) DP = 3, (b) DP = 10, (c) DP = 30, (d) DP = 60.

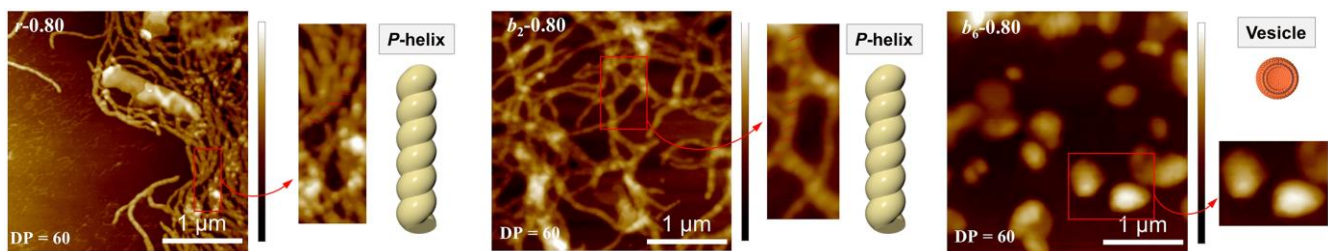


Figure S16. AFM images of S -type random Azo6-co-Azo2 (r -0.80), block Azo2-b-Azo6 (b_2 -0.80) and block Azo6-b-Azo2 (b_6 -0.80) assemblies ($n = 0.8$, DP = 60).

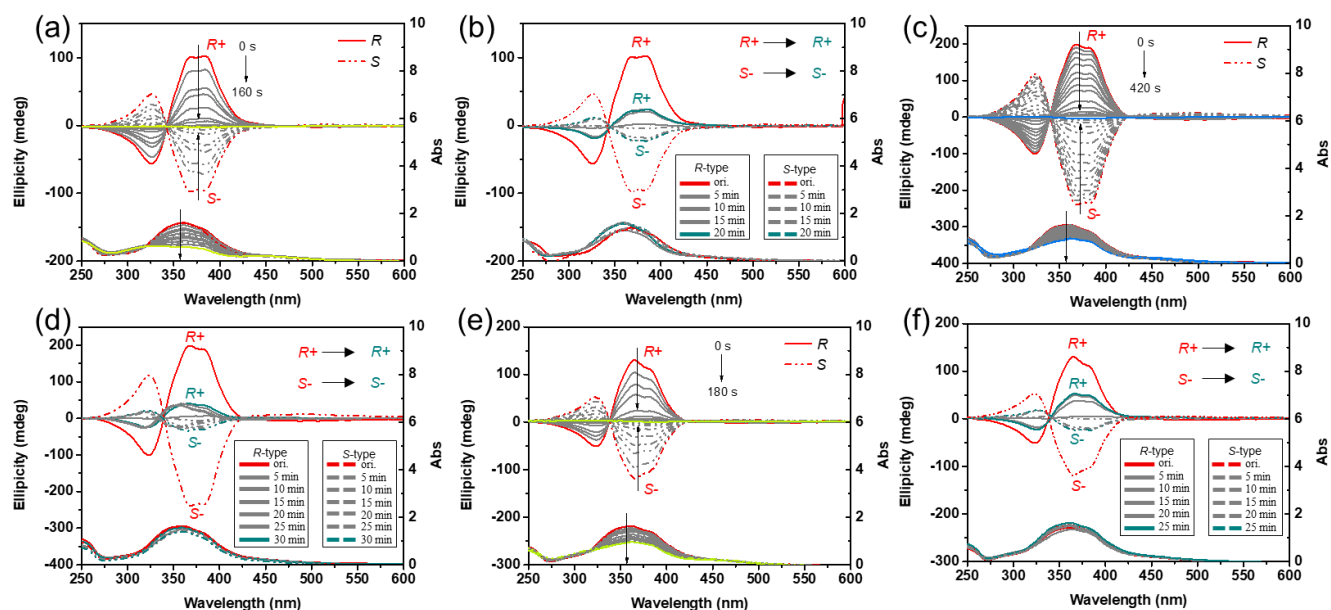


Figure S17. CD and UV-vis spectra of (a), (b) r -0.20-R and r -0.20-S, (c), (d) b_2 -0.20-R and b_2 -0.20-S, (e), (f) b_6 -0.20-R and b_6 -0.20-S Azo assemblies upon (a), (c), (e) 365 nm UV light irradiation and (b), (d), (f) heating-cooling treatment. The targeted DP of the copolymers is 60.

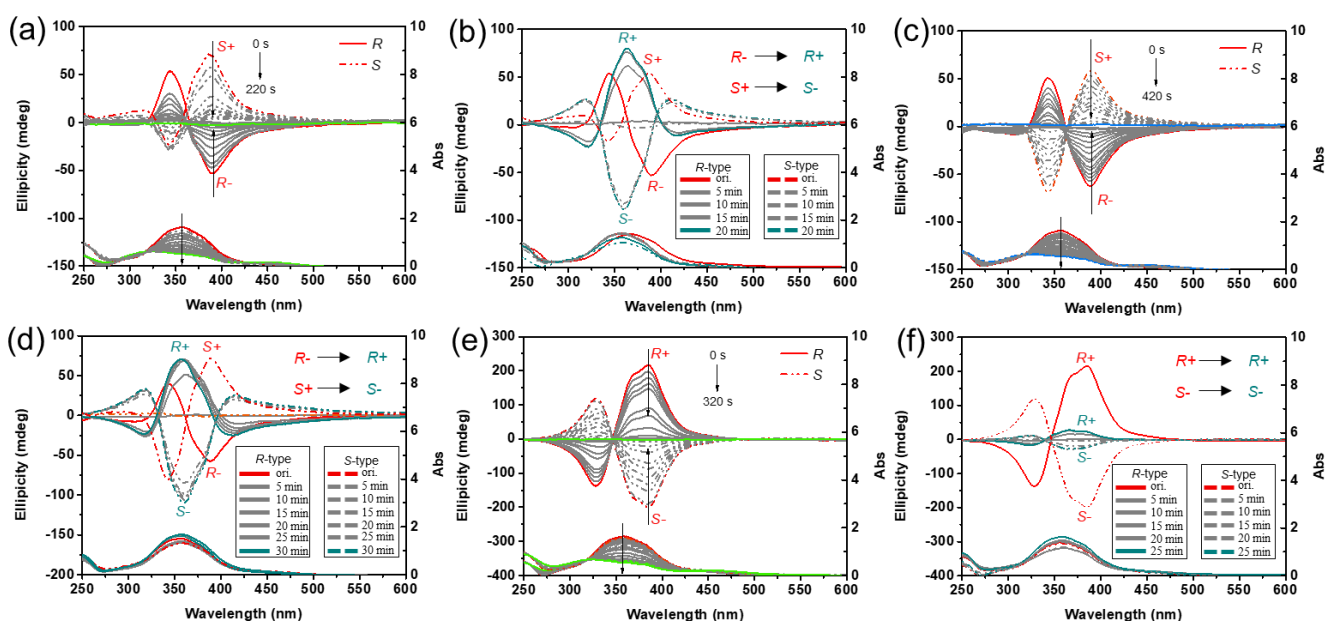


Figure S18. CD and UV-vis spectra of (a), (b) r -0.80- R and r -0.80- S , (c), (d) b_2 -0.80- R and b_2 -0.80- S , (e), (f) b_6 -0.80- R and b_6 -0.80- S Azo assemblies upon (a), (c), (e) 365 nm UV light irradiation and (b), (d), (f) heating-cooling treatment. The targeted DP of the copolymers is 60.

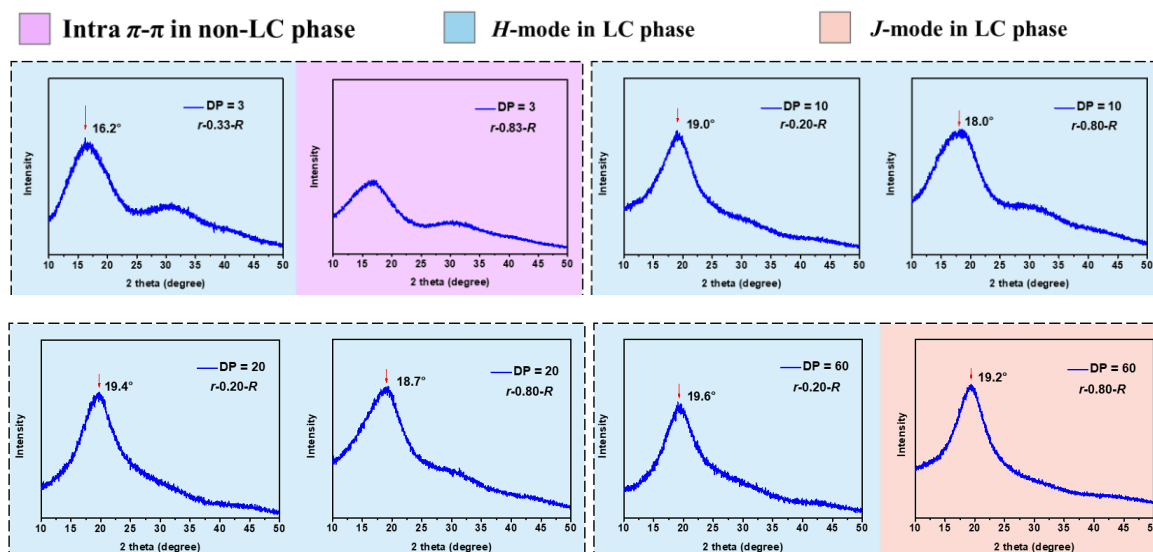


Figure S19. WAXD patterns of the random Azo6-*co*-Azo2 copolymers with the increase of DP and Azo2 ratios.

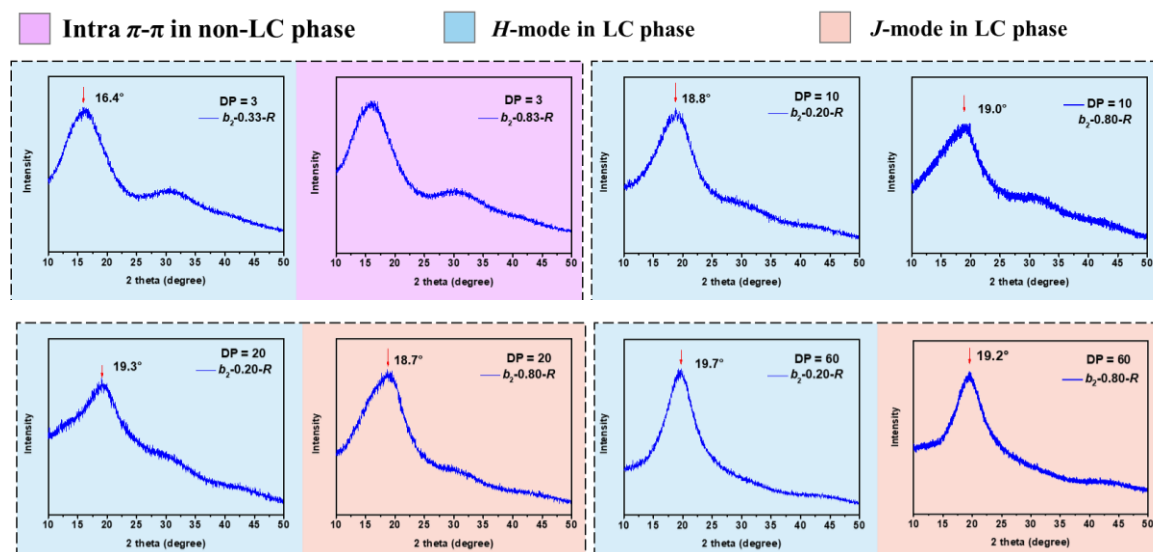
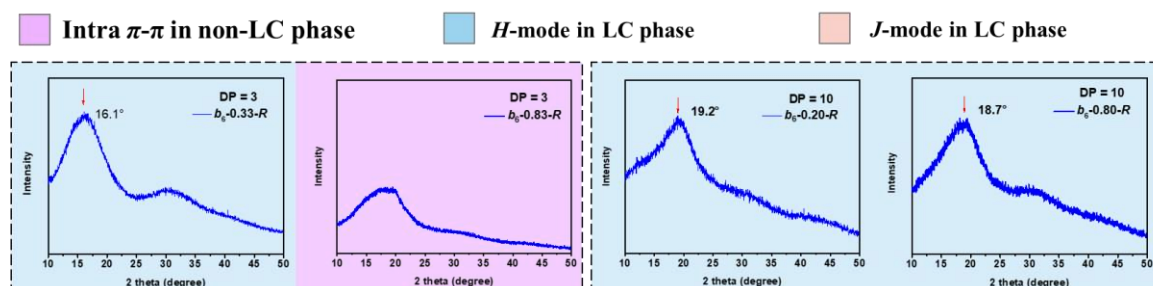


Figure S20. WAXD patterns of the block Azo2-*b*-Azo6 copolymers with the increase of DP and Azo2 ratios.



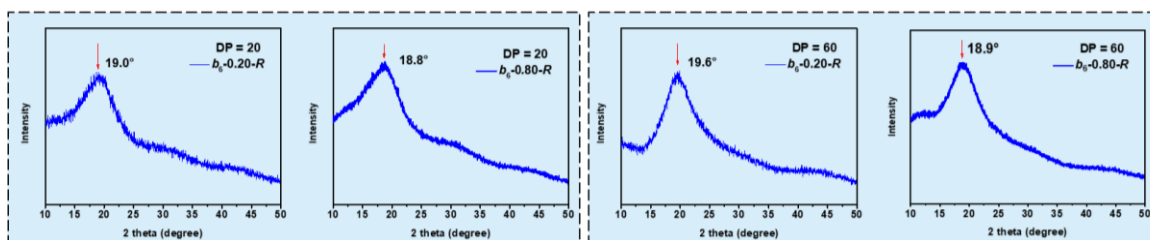


Figure S21. WAXD patterns of the block Azo6-*b*-Azo2 copolymers with the increase of DP and Azo2 ratios.

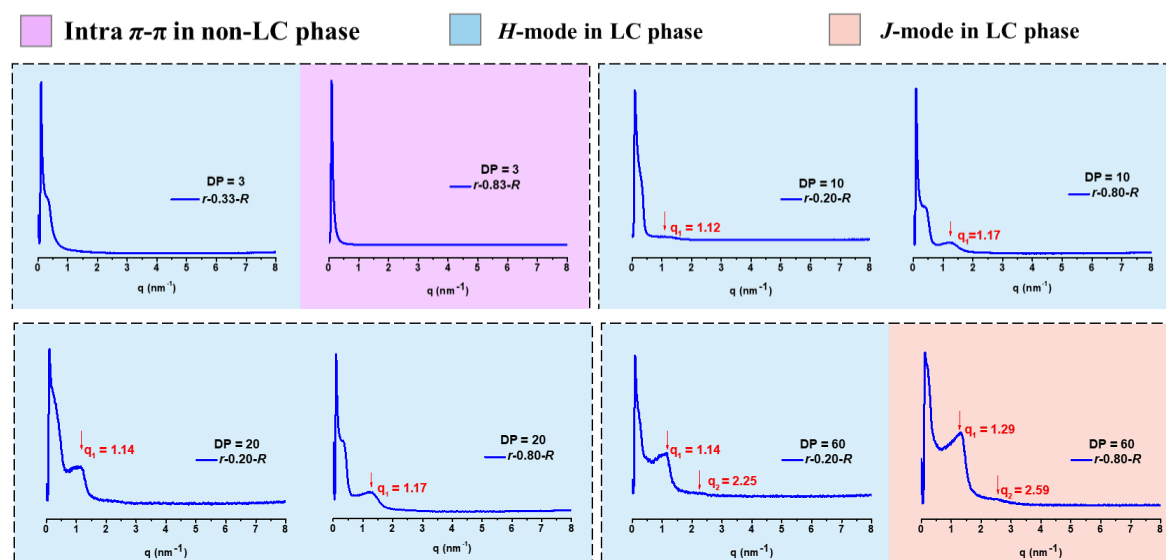


Figure S22. SAXS patterns of the random Azo6-*co*-Azo2 copolymers with the increase of DP and Azo2 ratios.

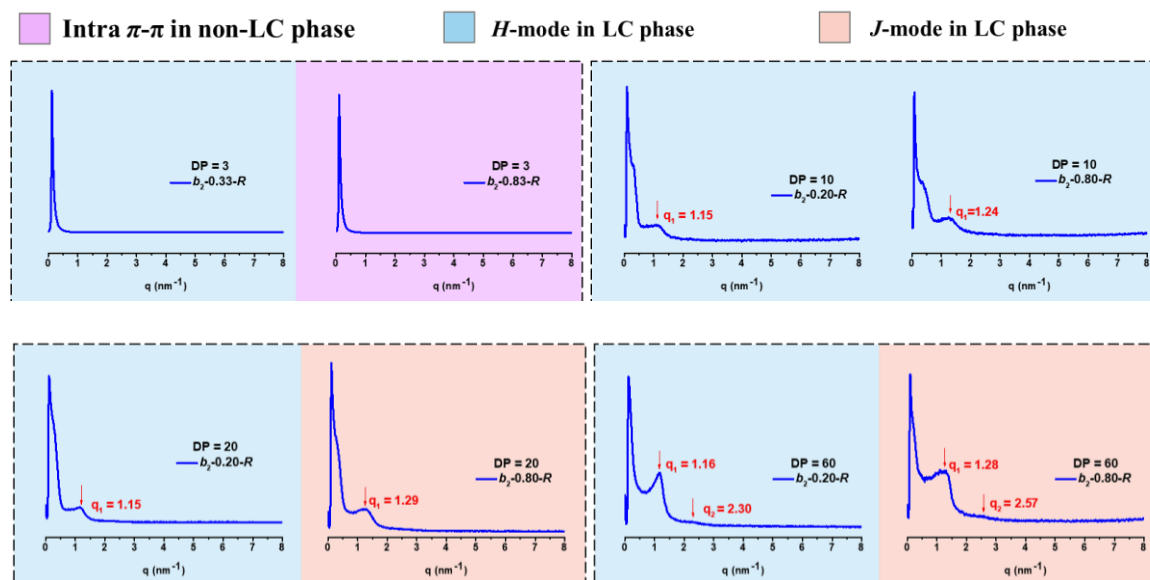


Figure S23. SAXS patterns of the block Azo2-*b*-Azo6 copolymers with the increase of DP and Azo2 ratios.

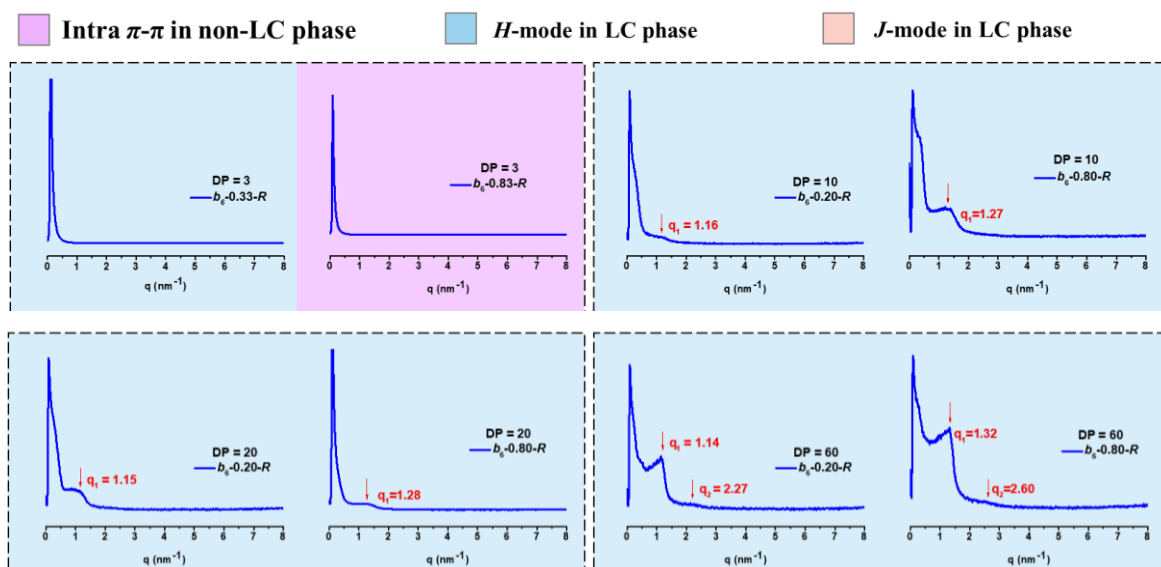


Figure S24. SASX patterns of the block Azo6-*b*-Azo2 copolymers with the increase of DP and Azo2 ratios.

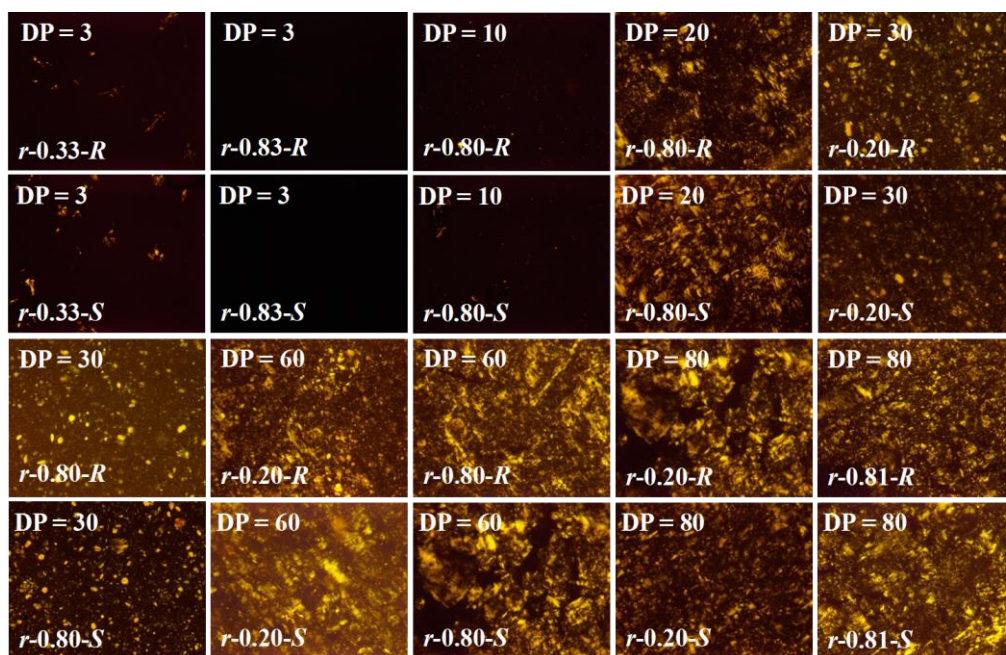


Figure S25. POM images of random Azo6-*co*-Azo2 copolymers with the increase of DP and Azo2 ratios.

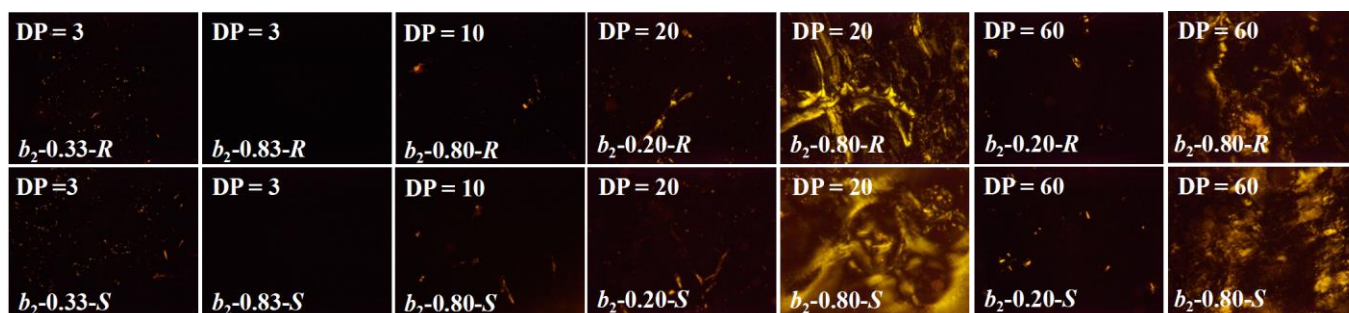


Figure S26. POM images of block Azo2-*b*-Azo6 copolymers with the increase of DP and Azo2 ratios.

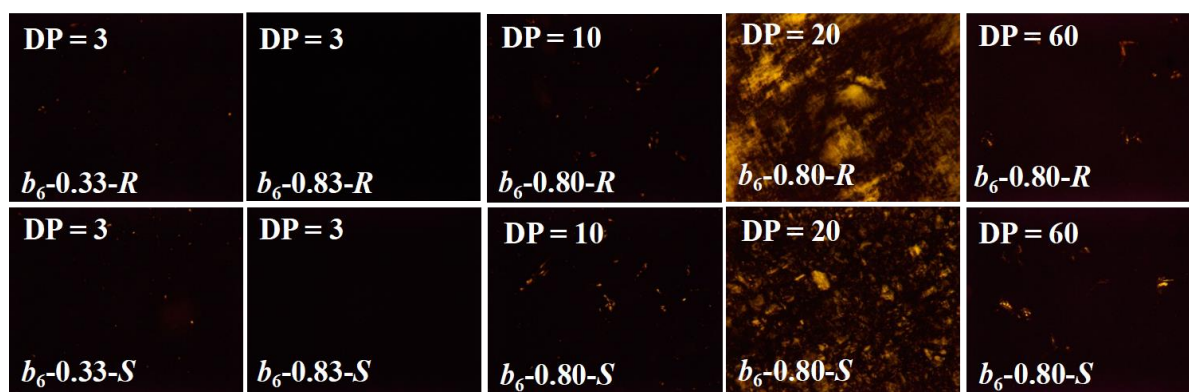


Figure S27. POM images of block Azo6-*b*-Azo2 copolymers with the increase of DP and Azo2 ratios.

References

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