

Electronic Supplementary Information (ESI)

Liquid crystalline side-chain triblock copolymers consisting of a nematic central subblock edged by photochromic azobenzene-containing fragments: synthesis, structure and photooptical behaviour

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Synthesis of macromolecular chain transfer agent (homopolymer pA_n). The synthesis of pA₂₀ is given here as a typical example (hereinafter, subscripts indicate the polymerization degrees of subblocks). Monomer A (3.8 mol/L), BMITC (0.078 mol/L) were loaded in an ampoule, and a solution of AIBN (10⁻³ mol/L) in anisole was added. The resulting solutions were purged with argon for 15 min, and the ampoule was sealed. The flask was then placed in an oil bath of 80°C for 1 hour. Polymers were purified from non-reacted monomer by boiling in ethanol and then they were filtered, and dried in vacuum oven for 24 h. Yield: 54%. ¹H NMR (CDCl₃, TMS, 500 MHz): δ 1.5–2.0 (4H, m, –CH₂–CH₂–CH₂–, –CH₂–CH–COO–), 2.2–2.5 (1H, s, –CH₂–CH–COO–), 2.7–2.9 (3H, s, N–CH₃), 3.2–3.4 (2H, s, N–CH₂–), 3.9–4.1 (s, 2H, –CH₂–OOC–), 6.5–6.8 (m, 3H, Ar), 7.1–7.3 (m, 2ArH, meta κ N(CH₃) –).

Synthesis of triblock copolymer pA₁₀-b-pPhM₈₀-b-pA₁₀. The macromolecular chain transfer agent pA₂₀ (153 mg, 0.032 mmol), monomer PhM (700 mg, 1.70 mmol) and anisole (0.7 ml) were added into an ampoule and solution (0.16 mL) of AIBN (0.32 mg, 1.95 μmol) dissolved in anisole. The resulting solutions were purged with argon for 15 min, and the ampoule was sealed. After heating at 80°C overnight, the ampoules were cooled with ice water and opened, the solvent was removed under reduced pressure, and the polymers were purified as described above. Yield: 89%. ¹H NMR (CDCl₃, TMS, 500

MHz), δ (ppm): 1.3–1.8 (m, 4H, $-\text{CH}_2-\underline{\text{CH}}_2-\text{CH}_2-$ and $-\underline{\text{CH}}_2-\text{CH}-$, 6H, $\text{CH}_2=\text{CHCOOCH}_2(\underline{\text{CH}}_2)_3\text{CH}_2\text{COO}-$), 1.9–2.0 (s, 1H, $-\text{CH}_2-\underline{\text{CH}}-$), 2.5 (s, 2H, $-\text{CH}_2\underline{\text{CH}}_2\text{COOAr}$), 2.8–3.0 (s, 3H, N-CH₃), 3.2–3.5 (s, 2H, N-CH₂), 3.7–3.9 (s, 3H, -PhOCH₃) 3.9–4.2 (s, 2H, $-\underline{\text{CH}}_2-\text{OOC}-$), 6.4–6.7 (s, 2ArH, *ortho* to N(CH₃)-), 6.8–7.0 (s, 2ArH, *ortho* to -OCH₃), 7.0–7.2 (m, 4H, ArH), 7.5–7.8 (m, 3H, ArH), 8.0–8.15 (s, 2ArH, *ortho* to -COO-).

The other triblock copolymer pA₄-*b*-pPhM₈₀-*b*-pA₄ and random copolymer pA₇-*ran*-pPhM₃₀ were synthesized via a similar procedure by changing the monomer feed ratios and reaction time.

Synthesis of triblock copolymer pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀. The chemical modification of triblock copolymer pA₁₀-*b*-pPhM₈₀-*b*-pA₁₀ via azocoupling reaction was conducted as follows.⁶¹ The *p*-aminobenzonitrile (48 mg, 0.41 mmol) was dissolved in a mixture of glacial acetic acid (1.2 mL) and concentrated sulfuric acid (0.08 mL). The mixture was cooled to 0°C, and sodium nitrite (33 mg, 0.47 mmol) dissolved in water (0.24 mL) was added dropwise under stirring. The mixture was stirred at 0 °C for 5 min and urea was added to decompose the excess amount of nitrous acid. The diazonium salt solution was then added dropwise into a solution of pA₁₀-*b*-pPhM₈₀-*b*-pA₁₀ (619 mg, 0.27 mmol per A monomer unit) in DMF (55 mL) at 0°C. After the reaction was carried out at 0 °C for 12 h, the solution was poured into an excess amount of water and the precipitate was filtered off, washed with water, and dried in vacuum. After drying, the product was dissolved in THF (20 mL) and the solution was then added into a 5-fold excess amount of petroleum ether under stirring. The precipitate was filtered off, washed with petroleum ether, and dried in a vacuum at 70°C. The yield of target polymer was 610 mg (93 %). ¹H NMR (CDCl₃, TMS, 500 MHz), δ (ppm): 1.4–1.9 (m, 4H, $-\text{CH}_2-\underline{\text{CH}}_2-\text{CH}_2-$ and $-\underline{\text{CH}}_2-\text{CH}-$, 6H, $\text{CH}_2=\text{CHCOOCH}_2(\underline{\text{CH}}_2)_3\text{CH}_2\text{COO}-$), 2.0–2.1 (s, 1H, $-\text{CH}_2-\underline{\text{CH}}-$), 2.2–2.4 (2H, $-\text{CH}_2\underline{\text{CH}}_2\text{COOAr}$), 2.7 (s, 3H, -PhOCH₃) 2.8–3.0 (s, 3H, N-CH₃), 3.2–3.5 (s, 2H, N-CH₂), 3.8–4.2 (s, 2H, $-\underline{\text{CH}}_2-\text{OOC}-$), 6.5–6.8 (s, 2ArH, *ortho* to N(CH₃)-), 6.9 (s, 2ArH, *ortho* to -OCH₃), 7.0–7.3 (m, 4H, ArH), 7.6–8.0 (m, 6H, ArH), 8.1 (d, 2ArH, *ortho* to -COO-).

The other triblock copolymer pAzo₄-*b*-pPhM₈₀-*b*-pAzo₄, random copolymer pAzo₇-*ran*-PhM₃₀, homopolymers pAzo₂₀ and pAzo₈ with Azo containing groups were synthesized via similar procedures. All synthesized polymers were characterized by GPC and spectroscopic methods.

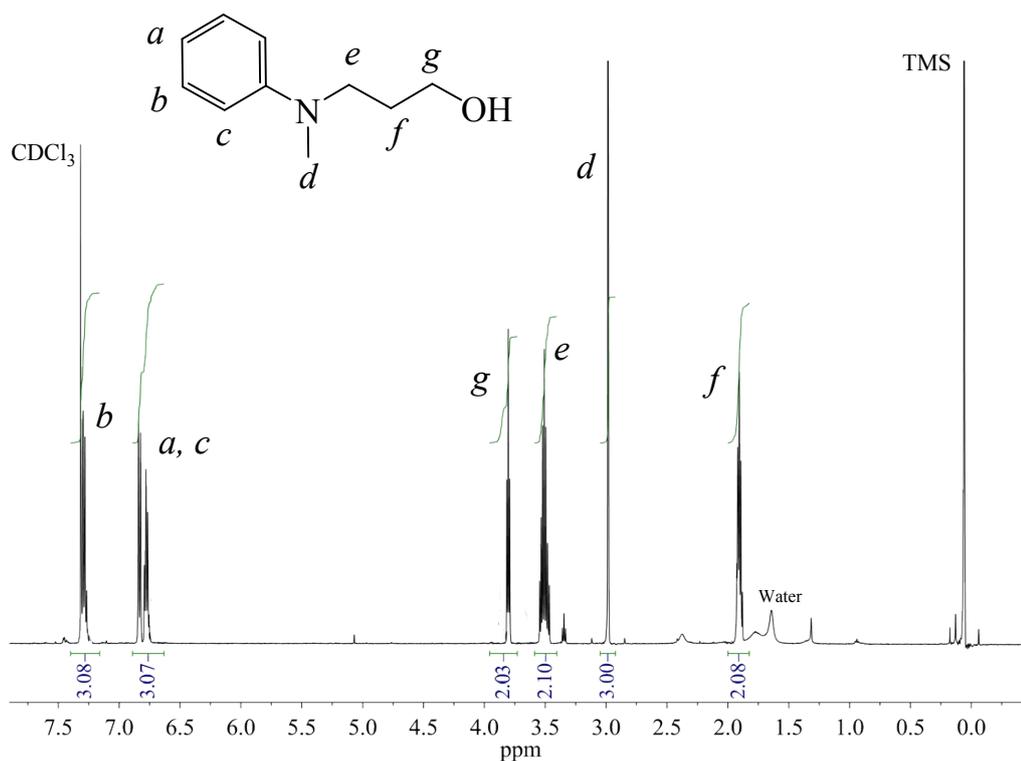


Fig. S1 ¹H NMR spectrum of 3-[methyl(phenyl)amino]propanol.

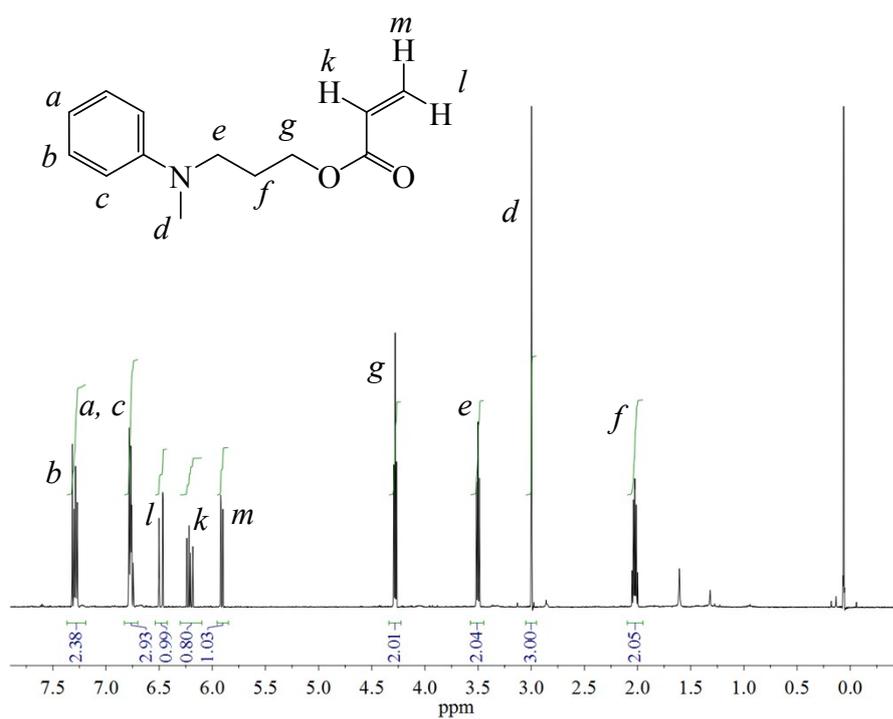


Fig. S2 ¹H NMR spectrum of 3-[methyl(phenyl)amino]propyl acrylate (monomer A).

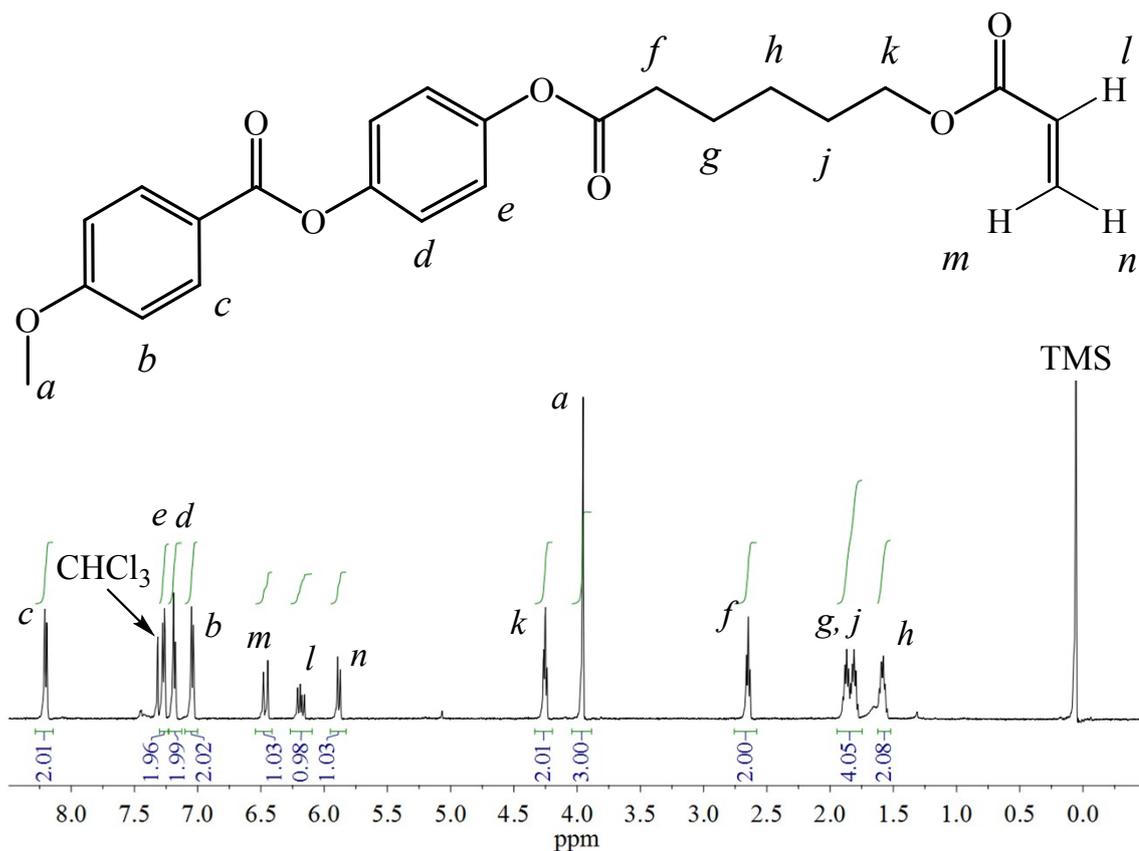


Fig. S3 ¹H NMR spectrum of *p*-(6-acryloyloxycapryloyloxyphenyl)-*p*-methoxybenzoate (monomer PhM).

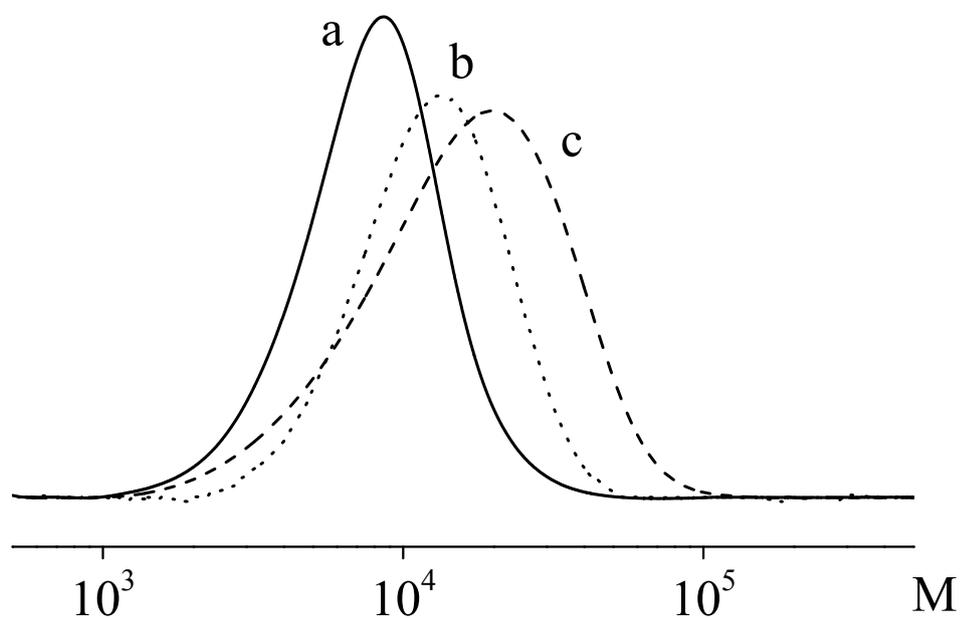


Fig. S4 GPC curves of homopolymers pAzo₂₀ (a, solid line), random copolymer pAzo₇-ran-pPhM₃₀ (b, dotted line), triblock copolymer pAzo₄-b-pPhM₈₀-b-pAzo₄ (c, dashed line).

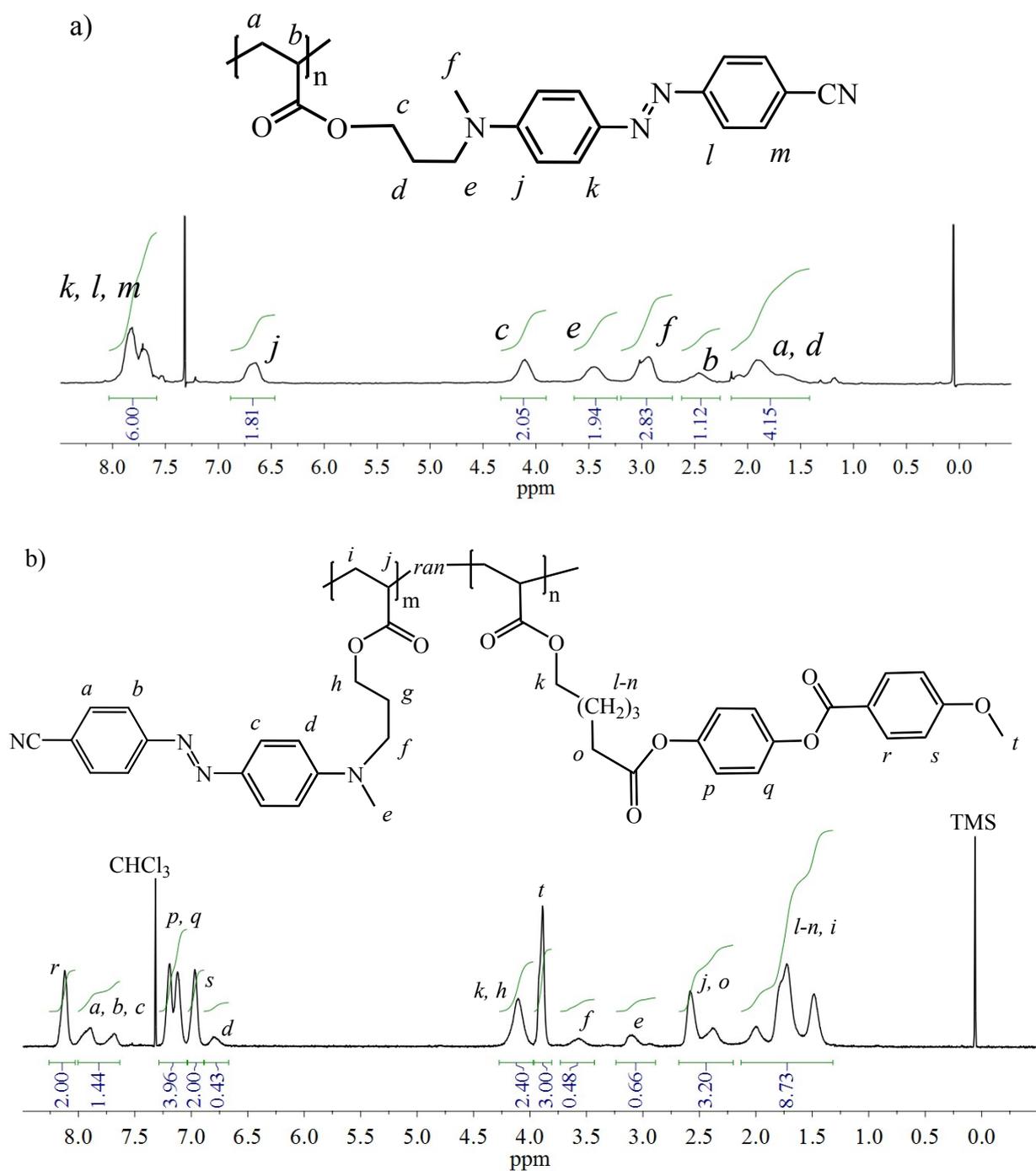


Fig. S5 ^1H NMR spectra of homopolymer pAzo₂₀ (a) and statistical copolymer pAzo₇-ran-pPhM₃₀ (b).

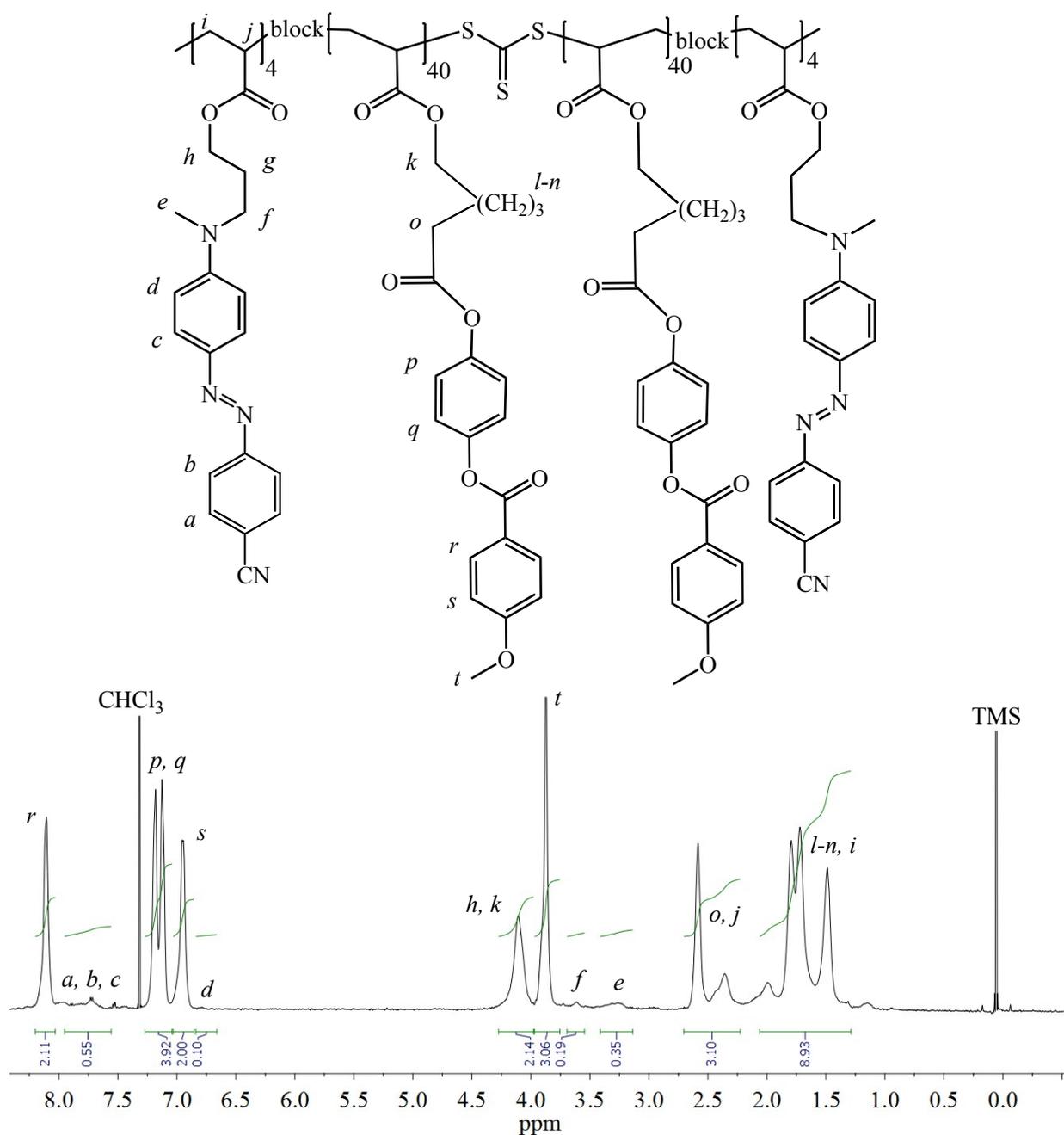


Fig. S6 1H NMR spectrum of triblock copolymer $pAzo_4-b-pPhM_{80}-b-pAzo_4$.

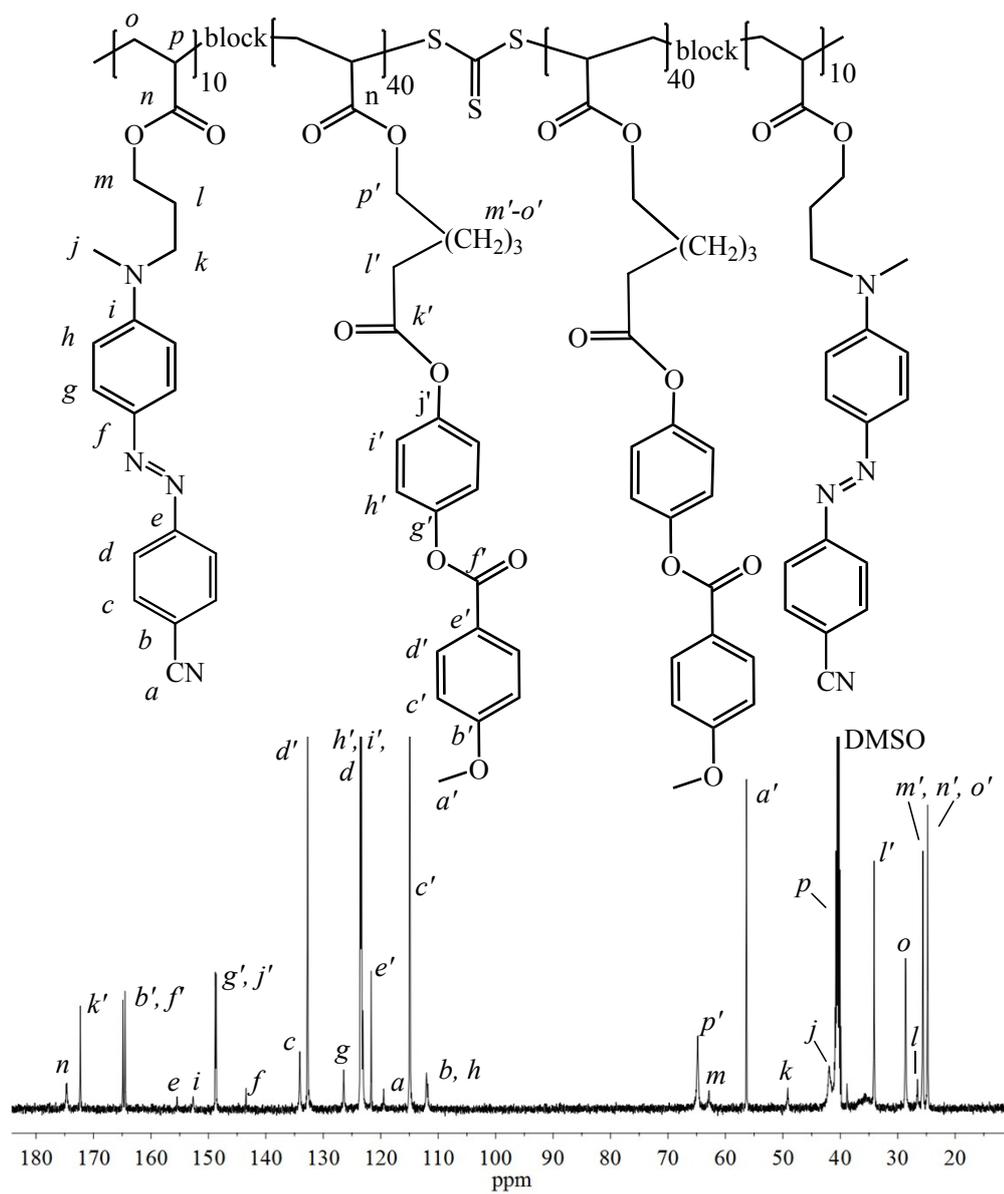


Fig. S7 ^{13}C NMR spectrum of triblock copolymer $pAzo_{10}-b-pPhM_{80}-b-pAzo_{10}$.

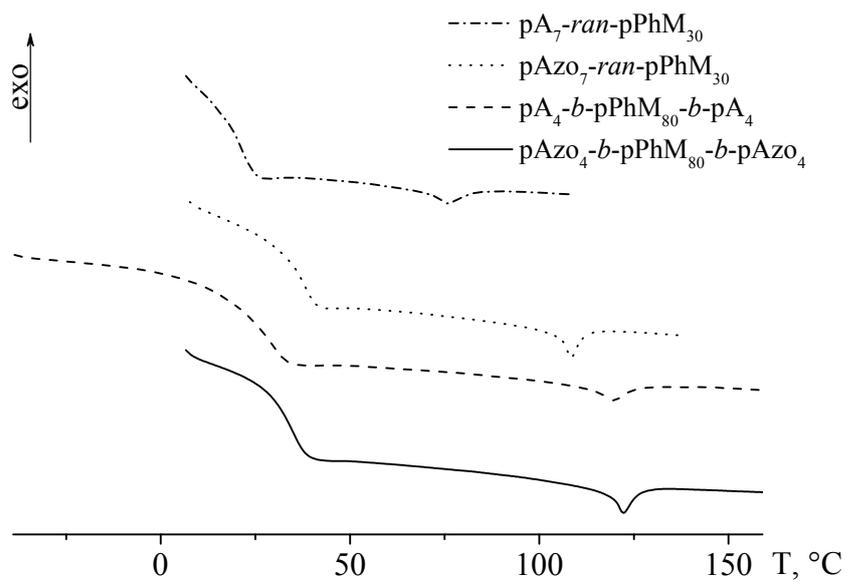
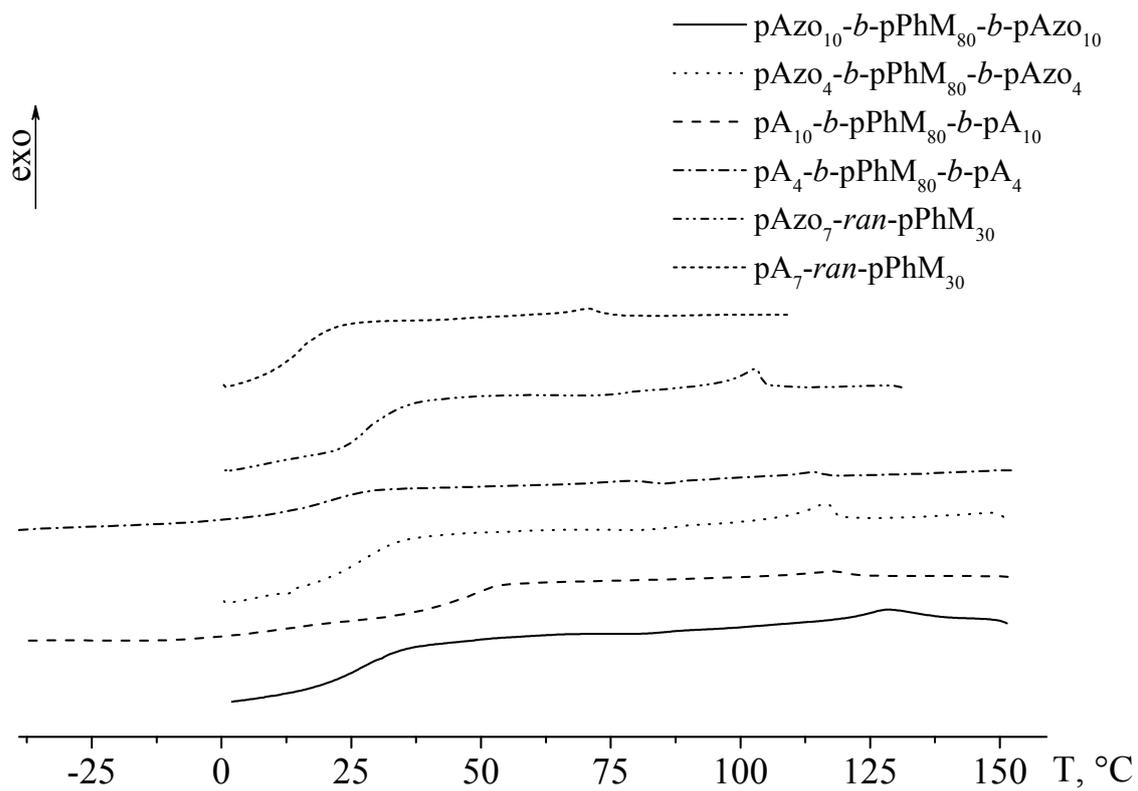
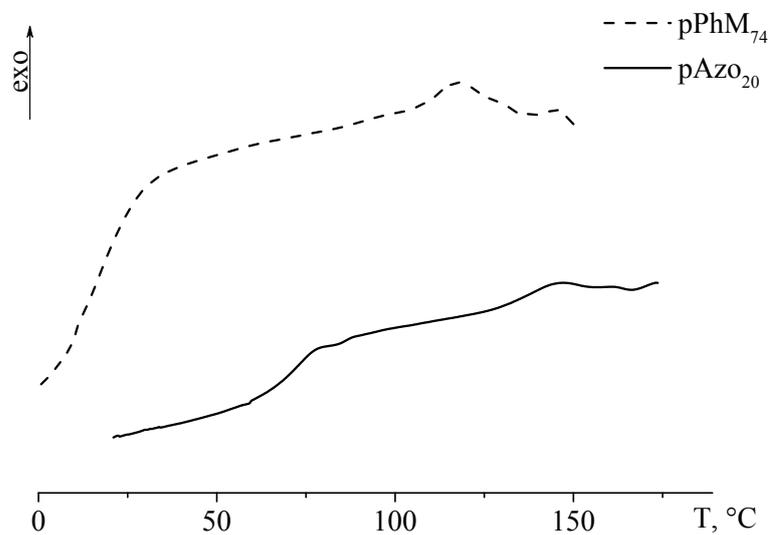


Fig. S8 DSC curves for block copolymers and random copolymers obtained from the second heating scans.



a



b

Fig. S9 DSC curves for block copolymers and random copolymers obtained from the first cooling scans.

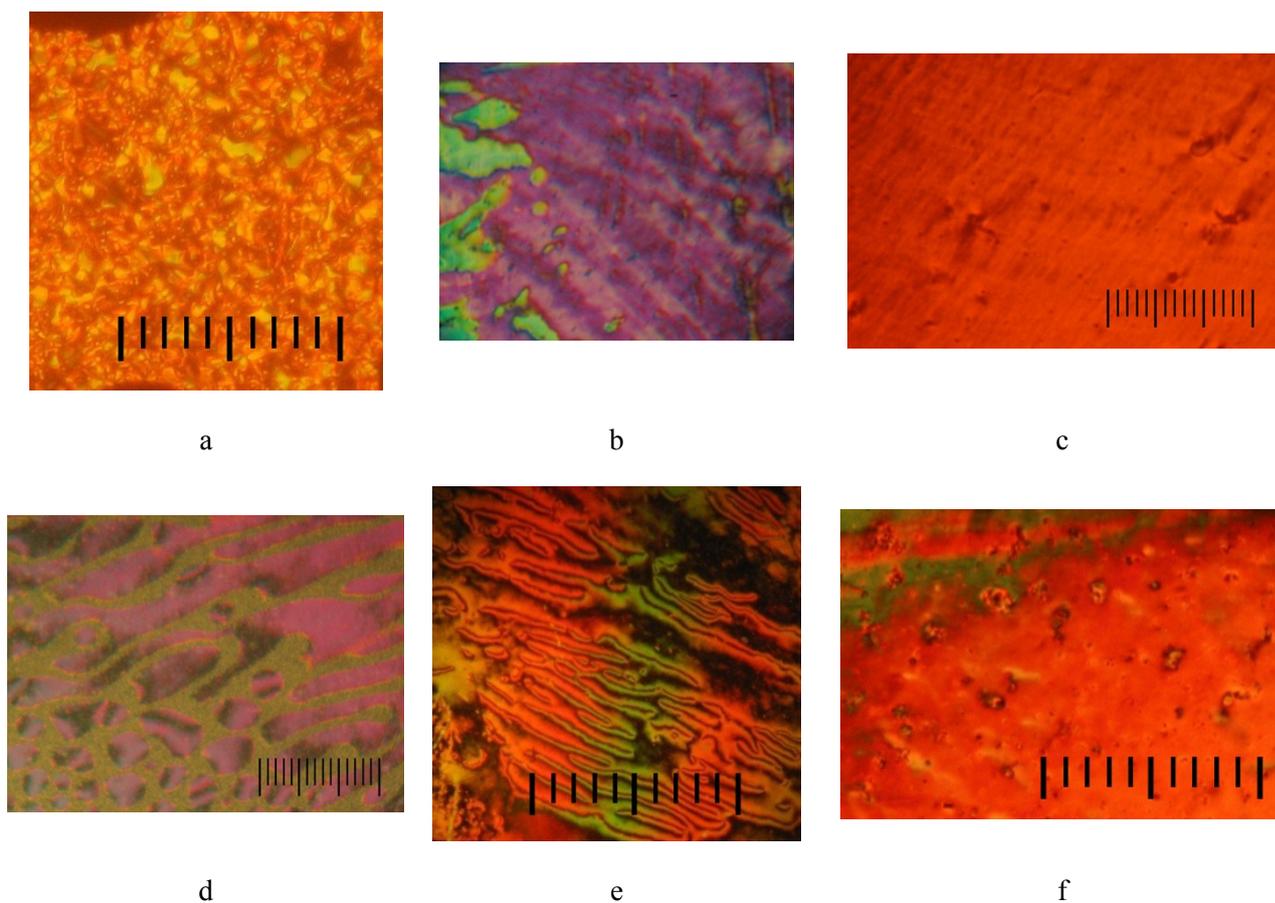


Fig. S10 Polarizing optical micrographs (scale-division value is equal 10 μm) of Azo₂₀ (a), pPhM₈₀ (b), pAzo₄-*b*-pPhM₈₀-*b*-pAzo₄ (c), pA₁₀-*b*-pPhM₈₀-*b*-pA₁₀ (d), pAzo₁₀-*b*-pPhM₈₀-*b*-pAzo₁₀ (e), pAzo₇-*ran*-PPhM₃₀ (f) at room temperature.

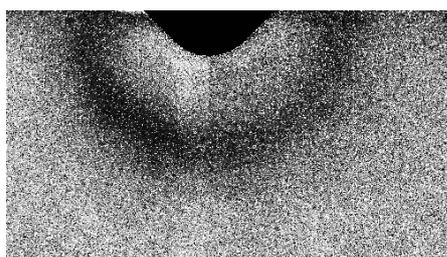


Fig. S11 2D WAXS pattern for the film sample of the pAzo₇-*ran*-pPhM₃₀.

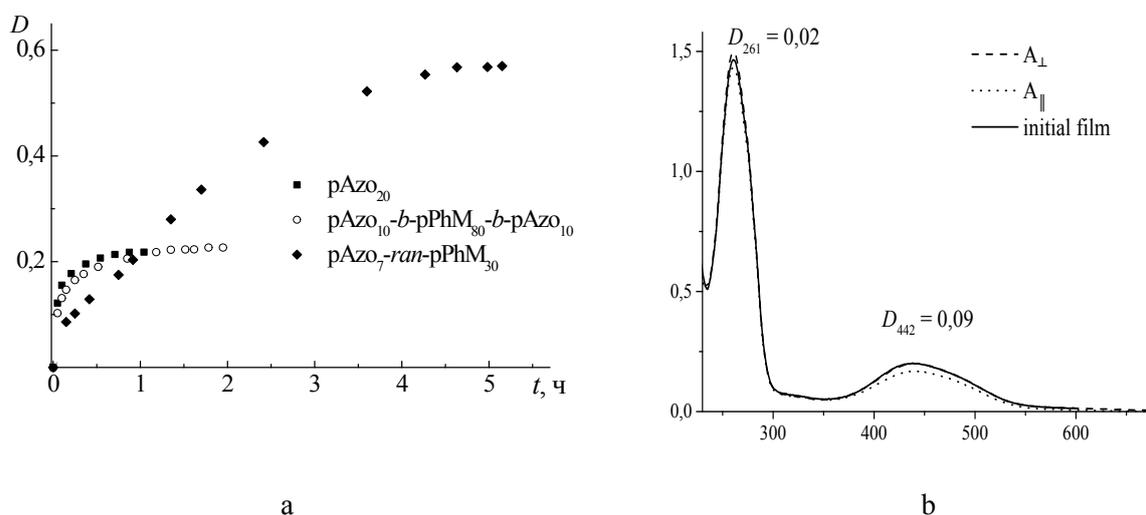


Fig. S12 Kinetic curves of dichroism growth (a) during polarized light irradiation of amorphousized polymer films (546 nm, 2 mW/cm², 22 °C); Polarized absorbance spectra of as-casted films pAzo₄-*b*-pPhM₈₀-*b*-pAzo₄ before (solid line) and after h polarized light action (dash and dot line). Irradiation conditions: 546 nm, 2 mW/cm², 22 °C. Film thickness is about 1 μm. Irradiation time is equal to 1 hour (b).

Table S1. Molecular mass characteristic of poly(3-[methyl(phenyl)amino]propyl acrylate) formed in RAFT mediated polymerization. $[M]_0 = 3.8$, $[BMITC]_0 = 0.1$, and $[AIBN]_0 = 10^{-3}$ mol/L

Time, min	Conversion	M_n	M_n^{theory}	PDI
15	0.24	1900	2300	1.11
30	0.43	2900	3900	1.24
45	0.51	3500	4500	1.26
60	0.61	4500	5400	1.33
120	0.7	4800	6100	1.40