Supporting Information for:

Effect of Intra- versus Intermolecular Cross-Linking on the Supramolecular Folding of a Polymer Chain

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1. Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded on a Varian 400MR 400 MHz or a Varian Mercury Vx 400 MHz (400 MHz for $^1$H NMR spectroscopy and 100 MHz for $^{13}$C NMR spectroscopy). The $^1$H NMR spectroscopy chemical shifts (δ) are reported in ppm downfield from tetramethysilane (TMS). $^{13}$C NMR spectroscopy chemical shifts are reported downfield from TMS using the resonance of the deuterated solvent as internal standard. Abbreviations used are d = doublet, dd = double doublet, m = multiplet, p = pentet, s = singlet, t = triplet and q = quartet.

Infrared spectroscopy was measured using a PerkinElmer FT-IR Spectrum Two equipped with a Perkin-Elmer UATR Two.

Matrix assisted laser desorption/ ionization time of flight mass spectra (MALDI-TOF-MS) was acquired using a Bruker Autoflex Speed MALDI-TOF using α-cyano-4-hydroxycinnamic acid (CHCA) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrices.

Size exclusion chromatography (SEC) measurements were performed on a Shimadzu Prominance-i LC-2030C 3D with a Shimadzu RID-20A refractive index detector. As elution, THF containing 10 mM LiBr (flow = 1 mL min$^{-1}$) was used operating at 40 °C with a mixed-C and mixed-D column combined in series (exclusion limit = 2.000.000 g mol$^{-1}$; 7.5 mm i.d. ⋅ 300 mm) calibrated with poly(styrene) (Polymer Laboratories).

A Luzchem LZC-4V photoreactor equipped with 14 UV-A lamps (Hitachi FL8BL-B) was used to irradiate the samples (11.5 mW cm$^{-2}$).

UV-Vis spectroscopy measurements were performed using a Jasco V-650 spectrophotometer.

The circular dichroism spectroscopy measurements were performed on a Jasco J-815 circular dichroism spectrometer equipped with a programmable temperature controller (Jasco PTC-348WI).

2. Materials

All commercial reagents were purchased from Aldrich and used as received unless stated otherwise. All solvents were purchased from Biosolve and the deuterated solvents were purchased from Cambridge Isotopes Laboratories. Dry solvents were obtained with an MBRAUN Solvent Purification System (MB-SPS).
3. Monomer synthesis and characterization

**Synthesis of coumarin-C₆-OH (3)**

DMF (20 mL) was added to a mixture of 6-bromohexanol-1-ol (2) (2.01 g, 11.10 mmol), 7-hydroxy-4-methylcoumarin (1) (2.55 g, 14.48 mmol) and potassium carbonate (2.06 g, 14.92 mmol). The suspension was stirred overnight at room temperature. Chloroform was added and the organic layer was washed with 1 M NaOH, H₂O, and brine, subsequently. After drying of the organic layer using MgSO₄, the solvent was evaporated in vacuo. The product (3) was further dried using the high vacuum line, but still contained traces of DMF (3.0 g, 10.88 mmol, 98%).

¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, J = 8.8 Hz, 1H), 6.85 (dd, J = 8.8, 2.5 Hz, 1H), 6.79 (d, J = 2.4 Hz, 1H), 6.12 (d, J = 1.3 Hz, 1H), 4.02 (t, J = 6.4 Hz, 2H), 3.67 (t, J = 6.7 Hz, 2H), 2.39 (d, J = 1.2 Hz, 3H), 1.93 – 1.72 (m, 2H), 1.70 – 1.57 (m, 2H), 1.58 – 1.32 (m, 2H), 1.57 – 1.32 (m, 5H).

¹³C NMR (100 MHz, CDCl₃): δ 162.15, 161.37, 155.24, 152.60, 125.45, 113.40, 112.62, 111.77, 101.30, 76.71, 68.43, 62.76, 32.60, 28.94, 25.79, 25.50, 18.65.

FT-IR (ATR): ν (cm⁻¹) = 3481, 3356, 3076, 2941, 2921, 2855, 1710, 1614, 1557, 1512, 1474, 1461, 1427, 1389, 1371, 1349, 1327, 1286, 1270, 1206, 1150, 1136, 1071, 1041, 1027, 1014, 995, 980, 878, 845, 801, 749, 724, 710, 639, 583, 557, 529, 518.

MALDI-TOF-MS: m/z calc.: 276.3; found: 277.1 (M + H⁺), 299.1 (M + Na⁺), 315.1 (M + K⁺).
Figure S1. $^1$H NMR spectrum of 3 in CDCl$_3$.

Figure S2. $^{13}$C NMR spectrum of 3 in CDCl$_3$.
Synthesis of coumarin-C6-methacrylate (5)\textsuperscript{S1}

Product 3 (1.0 g, 3.62 mmol) was dissolved in 15 mL dry DCM. Triethylamine (0.8 mL, 5.74 mmol) was added and the solution was placed under an argon atmosphere. The mixture was cooled using an ice bath before the dropwise addition of methacryloyl chloride (4) (0.6 mL, 6.14 mmol). After stirring the reaction for 3 hours, 10 mL of additional DCM was added. The organic layer was washed with a saturated NaHCO\textsubscript{3} solution, H\textsubscript{2}O, and brine, subsequently. After drying the organic layer over MgSO\textsubscript{4}, all volatiles were removed \textit{in vacuo}. Product 5 (1.0 g, 2.90 mmol, 80\%) was obtained after purification via column chromatography (silica, DCM) and evaporating all solvent using the vacuum line.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.49 (d, \(J = 8.8\) Hz, 1H), 6.85 (dd, \(J = 8.8, 2.5\) Hz, 1H), 6.80 (d, \(J = 2.4\) Hz, 1H), 6.13 (m, 1H), 6.10 (m, 1H), 5.55 (p, \(J = 1.6\) Hz, 1H), 4.17 (t, \(J = 6.6\) Hz, 2H), 4.02 (t, \(J = 6.4\) Hz, 2H), 2.40 (d, \(J = 1.2\) Hz, 3H), 1.94 (dd, \(J = 1.6, 1.0\) Hz, 3H), 1.89-1.79 (m, 2H), 1.77-1.69 (m, 2H), 1.56-1.41 (m, 4H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 167.51, 162.14, 161.35, 155.29, 152.58, 136.47, 125.48, 125.26, 113.45, 112.65, 111.84, 101.31, 68.38, 64.58, 28.89, 28.54, 25.78, 25.68, 18.67, 18.34.

FT-IR (ATR): \(\nu\) (cm\textsuperscript{-1}) = 3068, 2951, 2868, 1768, 1712, 1606, 1511, 1473, 1447, 1426, 1389, 1368, 1346, 1320, 1297, 1283, 1263, 1203, 1159, 1141, 1069, 1016, 984, 956, 941, 883, 873, 865, 842, 818, 806, 754, 739, 729, 708, 684, 641, 591, 550, 523, 495, 458.

MALDI-TOF-MS: m/z calc.: 344.2; found: 345.2 (M + H\textsuperscript{+}), 367.2 (M + Na\textsuperscript{+}), 383.2 (M + K\textsuperscript{+}).
Figure S3. The $^1$H NMR spectrum of 5 in CDCl$_3$.

Figure S4. $^{13}$C NMR spectrum of 5 in CDCl$_3$. 
Synthesis of (S,S)-BTA-C_{11}-OH (8)^{S2}

The (S,S)-BTA-COOH (6) (2.51 g, 5.13 mmol),^{S2} 11-amino-1-undecanol (7) (1.21 mL, 6.47 mmol),^{S2} and DMAP (0.19 g, 1.58 mmol) were dissolved in 30 mL of dry DCM. N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC) (1.30 g, 6.78 mmol) was dissolved in 20 mL of dry DCM and added to the reaction mixture. The mixture was stirred over the weekend at room temperature while under an argon atmosphere. Full conversion was never reached, so the crude reaction mixture was directly purified via column chromatography (silica, elution: 4% MeOH in DCM). Product 8 was obtained after evaporation of the solvents (3.0 g, 4.56 mmol, 89%).

{\textsuperscript{1}H} NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.36 (d, \(J = 1.6\) Hz, 2H), 8.34 (t, \(J = 1.6\) Hz, 1H), 6.65 (t, \(J = 5.6\) Hz, 1H), 6.58 (t, \(J = 5.6\) Hz, 2H), 3.63 (q, \(J = 6.3\) Hz, 2H), 3.47 (m, 6H), 1.69 – 1.05 (m, 40H), 0.94 (d, \(J = 6.5\) Hz, 6H), 0.86 (d, \(J = 6.6\) Hz, 12H).

{\textsuperscript{13}C} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 165.69, 135.25, 127.97, 63.00, 40.34, 39.24, 38.54, 37.13, 36.62, 32.77, 30.76, 29.44, 29.39, 29.28, 29.25, 29.11, 27.95, 26.85, 25.66, 24.63, 22.70, 22.60, 19.48.

FT-IR (ATR): \(\nu\) (cm\textsuperscript{-1}) = 3462, 3242, 3074, 2953, 2924, 2854, 1687, 1556, 1463, 1382, 1366, 1296, 1146, 1057, 907, 796, 722, 691.

MALDI-TOF-MS: m/z calc.: 658.0; found: 658.6 (M + H\textsuperscript{+}), 680.5 (M + Na\textsuperscript{+}), 696.5 (M + K\textsuperscript{+}).

Figure S5. \textsuperscript{1}H NMR spectrum of 8 in CDCl\textsubscript{3}.
Figure S6. $^{13}$C NMR spectrum of 8 in CDCl$_3$.

**Synthesis of (S,S)-BTA-C$_{11}$-methacrylate (9)$^{S3}$**

The (S,S)-BTA-C$_{11}$-OH (2.86 g, 4.35 mmol) and triethylamine (0.75 mL, 5.38 mmol) were dissolved in 25 mL of dry DCM and the solution was placed under an argon atmosphere. The mixture was cooled using an ice bath before a mixture of methacryloyl chloride (4) (0.55 mL, 5.63 mmol) and 20 mL dry DCM was added in a dropwise fashion.$^{S3}$ The reaction was stirred overnight and washed with 1 M HCl (2×), saturated NaHCO$_3$ (2×), and brine, subsequently. After drying the organic layer over MgSO$_4$, the product was purified via column chromatography (silica, elution: 15% EtOAc in CHCl$_3$). After evaporation of all volatiles, product 9 was obtained as a white wax (2.6 g, 3.58 mmol, 82%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.31 (s, 3H), 6.74 (t, $J = 5.6$ Hz, 1H), 6.70 (t, $J = 5.6$ Hz, 2H), 6.09 (m, 1H), 5.54 (m, 1H), 4.13 (t, $J = 6.7$ Hz, 2H), 3.54 – 3.37 (m, 6H), 1.94 (m, 3H), 1.73 – 1.06 (m, 40H), 0.93 (d, $J = 6.5$ Hz, 6H), 0.86 (d, $J = 6.6$ Hz, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.57, 165.83, 165.80, 136.53, 135.30, 127.93, 125.14, 77.35, 77.03, 76.71, 64.83, 40.38, 39.24, 38.53, 37.13, 36.62, 30.78, 29.53, 29.47, 29.29, 29.22, 28.60, 27.94, 27.00, 25.96, 24.62, 22.69, 22.59, 19.47, 18.33.
FT-IR (ATR): \( \nu (\text{cm}^{-1}) = 3237, 3072, 2953, 2925, 2855, 1721, 1636, 1558, 1456, 1381, 1366, 1295, 1161, 1011, 937, 905, 814, 729, 691, 594. \)

Figure S7. \(^1\)H NMR spectrum of \( 9 \) in CDCl\(_3\).

Figure S8. \(^{13}\)C NMR spectrum of \( 9 \) in CDCl\(_3\).
4. Polymer synthesis and characterization

Polymerization of \( n \)-butyl methacrylate (P1)

The chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (10) (10.0 mg, 36.0 \( \mu \)mol) was dissolved in \( n \)-butyl methacrylate (11) (2.14 g, 15.0 mmol). This mixture was used to dissolve the 2,2′-azobis(2-methylpropionitrile) (AIBN) (0.58 mg, 3.53 \( \mu \)mol). The vials were washed with 1,4-dioxane (1.0 mL) and added to the reaction mixture. The reaction mixture was sparged with argon for one hour and placed in a pre-heated oil bath (75 °C), while being kept under an argon atmosphere. Overnight the polymerization gelated, after freezing the reaction mixture in liquid nitrogen the conversion was determined to be 88\% (determined via \( ^1 \)H NMR spectroscopy). The polymers were purified via precipitation in cold MeOH (3x, after each step the polymer was redissolved in THF) and subsequently dried using the high vacuum line.

\( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 4.10 – 3.82, 2.07 – 1.70, 1.70 – 1.53, 1.53 – 1.31, 1.16 – 0.56. SEC (THF): \( M_n = 52.5 \) kg mol\(^{-1}\), \( D_M = 1.05 \).

Figure S9. \( ^1 \)H NMR spectrum of P1 in CDCl\(_3\).
Copolymerization of \( n \)-butyl methacrylate and coumarin-C\(_6\)-methacrylate (P2)

The chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (10) (5.0 mg, 18.0 \( \mu \)mol) was dissolved in \( n \)-butyl methacrylate (11) (488.8 mg, 3.44 mmol). This mixture was used to dissolve the 2,2’-azobis(2-methylpropionitrile) (AIBN) (0.31 mg, 1.86 \( \mu \)mol), and added to the coumarin-C\(_6\)-methacrylate (5) (203.9 mg, 0.59 mmol). After the addition of dry 1,4-dioxane (0.7 mL) a homogeneous mixture was obtained, that was sparged with argon for one hour. The reaction mixture was placed in a pre-heated oil bath (75 °C), while being kept under an argon atmosphere. After approximately 3.5 hours the reaction was quenched at a 68% conversion (determined via \( ^1 \)H NMR spectroscopy) by opening the reaction flask to air and freezing it in liquid nitrogen. The polymers were purified via precipitation in cold MeOH (3\( \times \), after each step the polymer was redissolved in THF) and subsequently dried using the high vacuum line. The final polymer composition was determined using \( ^1 \)H NMR spectroscopy and matched the feed ratio.

\[ ^1 \text{H NMR (400 MHz, CDCl}_3\text{):} \delta 7.54 – 7.44, 6.90 – 6.72, 6.17 – 6.06, 4.18 – 3.53, 2.39, 2.10 – 1.13, 1.13 – 0.62. \]

SEC (THF): \( M_n = 24.7 \text{ kg mol}^{-1}, D_M = 1.13. \)

![Figure S10. \( ^1 \)H NMR spectrum of P2 in CDCl3.](image)
Copolymerization of $n$-butyl, coumarin-C$_6$- and (S,S)-BTA-C$_{11}$-methacrylate (P3)

The chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (10) (2.00 mg, 7.16 μmol) was dissolved in $n$-butyl methacrylate (256.5 mg, 1.8 mmol) (11). This mixture was used to dissolve the 2,2’-azobis(2-methylpropionitrile) (AIBN) (0.12 mg, 0.73 μmol), and added to the coumarin-C$_6$-methacrylate (5) (61.8 mg, 0.18 mmol) and BTA-C$_{11}$-methacrylate (9) (65.1 mg, 0.09 mmol). After the addition of dry 1,4-dioxane (0.6 mL) a homogeneous mixture was obtained, that was sparged with argon for one hour. The reaction mixture was placed in a pre-heated oil bath (75 °C), while being kept under an argon atmosphere. After approximately 5 hours the reaction was quenched at an 85% conversion (determined via $^1$H NMR spectroscopy) by opening the reaction flask to air and freezing it in liquid nitrogen. The polymers were purified via precipitation in cold MeOH ($3\times$, after each step the polymer was redissolved in THF) and subsequently dried using the high vacuum line. The final polymer composition was determined using $^1$H NMR spectroscopy and matched the feed ratio.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.35, 7.58 – 7.44, 6.94 – 6.45, 6.12, 4.17 – 3.66, 3.57 – 3.31, 2.40, 2.16 – 0.62.
SEC (THF): $M_n = 30.2$ kg mol$^{-1}$, $D_M = 1.12$.

Figure S11. $^1$H NMR spectrum of P3 in CDCl$_3$. 
Copolymerization of \(n\)-butyl-, coumarin-C\(_6\)- and (S,S)-BTA-C\(_{11}\)-methacrylate (P4)

The chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (10) (2.00 mg, 7.16 \(\mu\)mol) was dissolved in \(n\)-butyl methacrylate (11) (257.9 mg, 1.8 mmol). This mixture was used to dissolve the 2,2’-azobis(2-methylpropionitrile) (AIBN) (0.12 mg, 0.73 \(\mu\)mol), and added to the coumarin-C\(_6\)-methacrylate (5) (30.8 mg, 0.09 mmol) and BTA-C\(_{11}\)-methacrylate (9) (130.0 mg, 0.18 mmol). After the addition of dry 1,4-dioxane (0.6 mL) a homogeneous mixture was obtained, that was sparged with argon for one hour. The reaction mixture was placed in a pre-heated oil bath (75 °C), while being kept under an argon atmosphere. After approximately 5 hours the reaction was quenched at an 80% conversion (determined via \(^1\)H NMR spectroscopy) by opening the reaction flask to air and freezing it in liquid nitrogen. The polymers were purified via precipitation in cold MeOH (3x, after each step the polymer was redissolved in THF) and subsequently dried using the high vacuum line. The final polymer composition was determined using \(^1\)H NMR spectroscopy and matched the feed ratio.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.41 – 8.11, 7.58 – 7.44, 6.94 – 6.72, 6.12, 4.12 – 3.83, 3.57 – 3.18, 2.40, 2.13 – 0.61.

SEC (THF): \(M_n = 40.8\) kg mol\(^{-1}\), \(D_M = 1.29\).

Figure S12. \(^1\)H NMR spectrum of P4 in CDCl\(_3\).
Copolymerization of \( n \)-butyl-, coumarin-C\(_6\)- and (S,S)-BTA-C\(_{11}\)-methacrylate (P5)

The chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (10) (2.00 mg, 7.16 \( \mu \)mol) was dissolved in \( n \)-butyl methacrylate (11) (326.2 mg, 2.3 mmol). This mixture was used to dissolve the 2,2’-azobis(2-methylpropionitrile) (AIBN) (0.12 mg, 0.71 \( \mu \)mol), and added to the coumarin-C\(_6\)-methacrylate (5) (98.80 mg, 0.29 mmol) and BTA-C\(_{11}\)-methacrylate (9) (207.90 mg, 0.29 mmol). After the addition of dry 1,4-dioxane (1 mL) a homogeneous mixture was obtained, that was sparged with argon for one hour. The reaction mixture was placed in a pre-heated oil bath (75 \( ^\circ \)C), while being kept under an argon atmosphere. After approximately 6 hours the reaction was quenched at an 85\% conversion (determined via \(^1\)H NMR spectroscopy) by opening the reaction flask to air and freezing it in liquid nitrogen. The polymers were purified via precipitation in cold MeOH (3\times, after each step the polymer was redissolved in THF) and subsequently dried using the high vacuum line. The final polymer composition was determined using \(^1\)H NMR spectroscopy and matched the feed ratio.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.40 – 8.16, 7.56 – 7.44, 7.10 – 6.49, 6.11, 4.11 – 3.80, 3.54 – 3.28, 2.40, 2.14 – 0.54.

SEC (THF): \( M_n = 75.1 \text{ kg mol}^{-1}, D_M = 1.17. \)

**Figure S13.** \(^1\)H NMR spectrum of P5 in CDCl\(_3\).
5. Dynamic light scattering
Dynamic light scattering (DLS) measurements were performed using a Malvern µV Zetasizer equipped with an 830 nm laser and a scattering angle of 90°. A fluorescence cell with a 1 cm path length was used for the measurements. The determined hydrodynamic radius is an apparent radius, therefore \( R_H \) in the main text equals \( R_{H, \ 90° \ \text{app}} \). The temperature-dependent viscosity of 1,2-dichloroethane was obtained from literature.\(^{S4}\)

The DLS samples were prepared according to the following protocol:

- The polymers were sonicated for 30 minutes using a sonication bath.
- The sonicated samples were transferred to a preheated oven at 60 °C and heated for one hour.
- The samples were filtered at 60 °C using a 100 nm PVDF filter.

Figure S14. Hydrodynamic radius of P2 in THF (\( c_{\text{polymer}} = 10 \text{ mg mL}^{-1}, 200 \text{ nm PVDF filter} \)).

Figure S15. Correlation function of P4 in THF (\( c_{\text{polymer}} = 1 \text{ mg mL}^{-1}, 100 \text{ nm PVDF filter} \)).
Figure S16. A) Correlation functions of \( P5 \) in THF as a function of temperature, before irradiation with UV-A light; B) Correlation functions of \( P5 \) in THF before and after two hours of irradiation with UV-A light (\( c_{\text{polymer}} = 1 \text{ mg mL}^{-1} \), 100 nm PVDF filter).

Figure S17. Viscosity of 1,2-dichloroethane as function of temperature.\(^{S4}\)

Figure S18. Hydrodynamic diameters of \( P1 \) in DCE as a function of temperature (\( c_{\text{polymer}} = 1 \text{ mg mL}^{-1} \)).
6. UV-Vis spectroscopy

UV-Vis spectroscopy measurements were performed using a Jasco V-650 spectrophotometer. A quartz cuvette with an optical path length of 2 mm was used, filled with a 1 mg mL$^{-1}$ polymer solution. The sample was transferred between the spectrophotometer and a Luzchem LZC-4V photoreactor, equipped with 14 UV-A lamps (Hitachi FL8BL-B), in which it was irradiated with UV-A light.

Figure S19. A) UV-Vis spectra of P4 in THF as a function of the time the sample has been exposed to UV-A irradiation ($c_{\text{polymer}} = 1.0 \text{ mg mL}^{-1}$, $l = 0.2 \text{ cm}$). B) Absorbance at 320 nm as a function of the UV-A exposure time.
7. Size-exclusion chromatography

**Figure S20.** SEC trace before and after two hours of irradiation with UV-A light in THF for polymer; A) P1; B) P2; C) P3; D) P4.
8. Circular dichroism spectroscopy
Measurements were performed on a Jasco J-815 circular dichroism (CD) spectropolarimeter equipped with a PFD-425S/15 Peltier-type temperature controller. A quartz cuvette with an optical path length of 5 mm was used. The temperature-dependent CD measurements were performed by monitoring the magnitude of the CD effect at a single wavelength ($\lambda = 225$ nm) during heating and cooling.

**Figure S21.** A) CD spectrum of P4 in DCE after being irradiated with UV-A in THF for two hours ($c_{\text{polymer}} = 0.18$ mg mL$^{-1}$, $t_{\text{UV-A}} = 2$ h); B) CD cooling curve of P4 in DCE after being irradiated with UV-A in THF for two hours ($c_{\text{polymer}} = 0.18$ mg mL$^{-1}$, $\lambda = 225$ nm).

**Figure S22.** A) Comparison of the CD spectra of P4 in THF and DCE, as well as the CD spectrum after one hour of UV-A irradiation in DCE ($c_{\text{polymer}} = 0.18$ mg mL$^{-1}$); B) CD cooling curves as a function of the time exposed to UV-A irradiation ($c_{\text{polymer}} = 0.18$ mg mL$^{-1}$, $\lambda = 225$ nm).
Figure S23. A) CD cooling curve of P4 after two hours of UV-A irradiation in DCE ($c_{\text{polymer}} = 0.18 \text{ mg mL}^{-1}, \lambda = 225 \text{ nm}$); B) Time-dependent measurement at the maximum of the non-monotonic feature ($c_{\text{polymer}} = 0.18 \text{ mg mL}^{-1}, \lambda = 225 \text{ nm, } 7 \degree \text{C}$).

Figure S24. A) CD cooling curve of P4 after two hours of UV-A irradiation in DCE ($c_{\text{polymer}} = 0.18 \text{ mg mL}^{-1}, \lambda = 225 \text{ nm}$); B) Full CD spectra acquired at various temperatures along the cooling curve ($c_{\text{polymer}} = 0.18 \text{ mg mL}^{-1}, \lambda = 225 \text{ nm}$).
Figure S25. A) CD cooling curves of P5 as function of the time exposed to UV-A light in DCE ($c_{\text{polymer}} = 0.11 \, \text{mg mL}^{-1}, \lambda = 225 \, \text{nm}$). B) CD cooling curves of P5 as a function of the cooling rate ($c_{\text{polymer}} = 0.11 \, \text{mg mL}^{-1}, \lambda = 225 \, \text{nm}, t_{\text{UV-A}} = 2 \, \text{h}$).

Figure S26. A) Structure of a BTA containing reference polymer; B) Its CD cooling curves as a function of the time exposed to UV-A light in DCE ($c_{\text{polymer}} = 0.18 \, \text{mg mL}^{-1}, \lambda = 225 \, \text{nm}$).
9. Images
When irradiating a polymer solution in DCE at a higher concentration \((c_{\text{polymer}} = 1.0 \text{ mg mL}^{-1})\), aggregates were visible to the naked eye (Figure S27B). These aggregates remained visible up to 70 °C. By contrast, when crosslinked in THF and subsequently transferred to DCE, no such aggregates were observed at elevated temperatures (Figure S27A).

Figure S27. A) Image of P5 in DCE after crosslinking in THF \((c_{\text{polymer}} = 1 \text{ mg mL}^{-1})\); B) Image of P5 in DCE after being crosslinked in DCE \((c_{\text{polymer}} = 1 \text{ mg mL}^{-1})\).

10. References
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