

Supporting Information

A Free Radical Initiated Vinyl Helical Polymer Maintains Memory of Helical Sense Excess after Removal of the Inducing Chiral Pendant Group

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Supporting Information

Materials.

All solvents and reagents are used as obtained except tetrahydrofuran and benzene are refluxed over sodium and distilled out just before use.

Synthesis and purification of compound 3.

4-Alkoxybromobenzene is prepared by etherification of 4-bromophenol with alkyl p-toluenesulfonate using a literature method (Koide, N.; Uehara, K.; Timura, K. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 151). 4-Alkoxyphenylboronic acid is synthesized by a similar procedure used by Koide and co-workers (Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5239).

(+)-2,5-Bis[4'-((S)-2-methyl butyloxy)phenyl]toluene (3a): 0.048 mol (10 g) 4-[(S)-2-methyl butyloxy]phenylboronic acid dissolved in 20 ml of ethanol is added dropwise to the mixture of 0.02 mol (5 g) of 2,5-dibromotoluene, 0.8 mmol (0.924 g) tetrakis(triphenylphosphine)palladium Suzuki cross-coupling catalyst, 20 ml of benzene, 40 ml of ethanol, and 60 ml of 2M Na₂CO₃ aqueous solution under argon atmosphere. After adding, the mixture is refluxed for 24 hours with vigorous stirring. After the mixture is cooled to room temperature, 200 ml of dichloromethane is added to it. Then, the organic layer is separated and washed several times with DI water, followed by drying over sodium sulfate. The crude product, obtained by removing dichloromethane with rotator evaporator, is purified by silica gel column (dichloromethane/petroleum = 1/6), followed by recrystallization in petroleum ether (b.p. 60~90°C). Yield 82.0 %. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 0.943~0.985 (t, 6H, CH₃), 1.02~1.05 (d, 6H, CH₃), 1.25~1.35 (m, 2H, CH₂), 1.55~1.64 (m, 2H, CH₂), 1.86~1.94 (m, 2H, CH), 2.33 (s, 3H, Ar-CH₃), 3.74~3.79 (q, 2H, OCH₂), 3.84~3.88 (q, 2H, OCH₂), 6.92~6.99 (m, 4H, Ar), 7.22~7.28 (m, 3H, Ar), 7.39~7.46 (m, 2H, Ar), 7.52~7.56 (d, 2H, Ar). Anal. Calcd (%): C, 83.65; H, 8.65; O, 7.70. Found (%): C, 83.36; H, 8.90; O, 7.74. MS (EI, *m/e*): 416(parent), 346, 276(base), 186, 107. Optical specific rotation [α]_D²⁰ = + 13.8°, [α]₃₆₅²⁰ = +56.6° (c = 2.0 g/L in THF). Melting point: 88.7 °C.

2,5-Bis[4'-((RS)-2-methyl butyloxy)phenyl]toluene (3b): **3b** is synthesized using a similar method with **3a**. Yield 77.1 %.

2,5-Bis(4'-butyoxyphenyl)toluene (3c): **3c** is prepared with a similar procedure with **3a**. ¹H NMR (400MHz, CDCl₂, δ, ppm): 0.958~1.03 (t, 6H, CH₃), 1.51~1.55 (m, 4H, CH₂), 1.78~1.81 (m, 4H, CH₂), 2.33~2.24 (s, 3H, CH₃), 3.98~4.04 (t, 4H, CH₂O), 6.95~6.99 (m, 4H, aryl), 7.25~7.56 (m, 7H, aryl). Anal. Calcd. (%): C, 83.46; H, 8.302; O, 8.238. Found (%): C, 83.27; H, 8.492; O, 8.238. MS (EI, *m/e*): 388 (parent, base), 332, 276, 247, 202, 107, 70. Melting point: 106.4 °C.

Synthesis and purification of monomer **2**.

(+)-2,5-Bis[4'-((S)-2-methyl butyoxy)phenyl]styrene (2a): The monomer *(+)-2,5-bis[4'-((S)-2-methyl butyoxy)phenyl]styrene* is prepared using aqueous Wittig reaction as the key step.

10 mmol (4.16 g) of *2,5-bis[4'-((S)-2-methyl butoxy)phenyl]toluene*, 10.2 mmol (1.86 g) of *N*-bromosuccinimide (NBS) and a small amount of benzoyl peroxide (BPO) are dissolved in carbon tetrachloride. The mixture is refluxed for 1 h. After cooling to room temperature, the floating solid is filtrated out. *2,5-Bis[4'-((S)-2-methyl butoxy)phenyl]benzyl bromide* is obtained by removing solvent.

The resulted bromide is reacted with triphenylphosphine in boiling acetone for 3 h. The quaternary phosphonium bromide obtained is obtained by evaporating out solvent and purified by column chromatography (silica gel, eluted first with dichloromethane, then methanol).

The monomer **2a** is obtained by aqueous Wittig reaction as following: add 20 ml 10% (w/v) NaOH aqueous solution dropwise to the mixture of 10 mmol (7.57 g) of the quaternary phosphonium bromide and 100 ml of 40% formaldehyde solution with vigorous stirring. After adding, the mixture is vigorously stirred for another 24 hours, then extracted with 100 ml dichloromethane for three times. The organic phase is washed several times with DI water, dried over sodium sulfate. The crude monomer was obtained by removing dichloromethane. The monomer is purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1/3), followed by recrystallization from petroleum ether (fraction b.p. 60~90°C). ¹H NMR (400MHz, CDCl₂, δ, ppm): 0.951~0.988 (t, 6H, CH₃), 1.03~1.05 (d, 6H, CH₃), 1.24~1.35 (m, 2H, CH₂), 1.54~1.65 (m, 2H, CH₂), 1.86~1.94 (m, 2H, CH), 3.78~3.81 (q, 2H, OCH₂), 3.86~3.89 (q, 2H, OCH₂), 5.20~5.23 (d, 1H, vinyl), 5.73~7.78 (d, 1H, vinyl), 6.75~6.83 (q, 1H, vinyl), 6.94~7.00 (m, 4H, Ar), 7.28~7.33 (q, 3H, Ar), 7.48~7.50 (q, 1H, Ar), 7.56~7.58 (d, 2H, Ar), 7.78~7.79 (d, 1H, Ar). Anal. Calcd. (%): C, 84.11; H, 8.41; O, 7.48. Found (%): C, 83.86; H, 8.71; O, 7.43. MS (EI, *m/e*): 428 (parent), 358, 288, 262 (base), 183, 152, 108, 57. Specific optical rotation [α]₃₆₅²⁰ = +60.4°, [α]_D²⁰ = +14.4° (c = 2.0 g/L, in THF). Melting point: 57.7 °C.

2,5-Bis[4'-((RS)-2-methyl butyoxy)phenyl]styrene (2b): **2b** is synthesized using a similar method with **2a** and has the same structure parameters with **2a** except it has no optical activity.

2,5-Bis(4'-butyoxyphenyl)styrene (2c): **2c** is prepared via a similar procedure with **2a**. ¹H NMR (400MHz, CDCl₃, δ, ppm): 0.958~1.03 (t, 6H, CH₃), 1.46~1.57 (m, 4H, CH₂), 1.73~1.84 (m, 4H, CH₂), 3.97~4.00 (t, 4H, CH₂O), 5.19~5.24 (d, 1H, vinyl), 5.71~5.79 (d, 1H, vinyl), 6.76~6.86 (q, 1H, vinyl), 6.93~7.00 (m, 4H, aryl), 7.24~7.34 (m, 3H, aryl), 7.47~7.59 (m, 3H, aryl), 7.78~7.79 (d, 1H, aryl). Anal. Calcd. (%): C, 83.79; H, 8.05; O, 8.16. Found (%): C, 83.52; H, 8.26; O, 8.21. MS (EI, *m/e*): 400 (parent, base), 344, 327, 287, 271, 194, 108. Melting point: 97.7 °C.

Free radical polymerization of monomers.

The polymerization of the monomer was carried out in benzene solution at 60 °C for 24 hours using 3‰ mol equiv AIBN as initiator. The polymer was precipitated in and washed with methanol.

Chiral tails removal of polymer **1a**.

To a 50ml flask fitted with a septum and magnetic stirrer bar, 0.429 g of **1a** and 10 ml of dichloromethane are added under dry argon atmosphere. This mixture is cooled to about -65°C in a dry ice and acetone bath. 4 ml of 1 M tribromoboron in dichloromethane is added dropwise by syringe. After tribromoboron is added completely, the cooling bath is removed and the reaction mixture is allowed to stir at room temperature for 2 h. Then icy water is added and the mixture is

allowed to stir for another 1 h. The solid is obtained by filtration and washed with DI water three times. After drying under high vacuum at room temperature, 0.280 g of **1d**, poly(2,5-bis(4'-hydroxyphenyl)styrene), is obtained. Yield 98%. Polymer **1d** is purified further by repeated precipitation using THF as solvent and petroleum ether as precipitator. The final polymer is dried under vacuum at room temperature until no weight loss is detected.

Methylation of polymer 1d.

In a 250 ml flask, 1.00 g (3.47 mmol monomer unit) of polymer **1d** and 0.333 g of NaOH (8.32 mmol) was dissolved in 50 ml of methanol. The mixture was stirred and cooled in an ice water bath. 7.50ml of dimethyl sulfate (83.2 mmol) was added dropwise. The mixture was stirred overnight. The excess dimethyl sulfate was extinguished by ammonia.

After filtration, the obtained solid was washed with 50 ml of DI water for 3 times. The polymer **1e**, 0.987 g, was obtained by dissolving the crude product in 20 ml of THF, followed by precipitation in large amount of methanol, filtration, and drying under vacuum. Yield 90%.

Preparation of polymers 1a with different molecular weights.

The polymers **1a** with different molecular weights were synthesized by atom transfer free radical polymerization with the initiating system of BEB/PMDETA/CuBr = 1:1:1. (1-Bromoethyl)benzene (BEB, ACROS, 97%), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich 99%), and CuBr were used as obtained. The molecular weight was adjusted by changing the molar ratio of the monomer **2a** to the initiator BEB. Polymerization temperature: 90 °C; solvent: anisole; reaction time: 24 hours.

Measurements.

All ¹H NMR spectra are measured on a Bruker ARX 400 spectrometer at room temperature. Mass spectra are obtained on Finnigan-MAT ZAB-HS spectrometer. Thermal diagrams are obtained on a PE DSC 7 differential scanning calorimeter under nitrogen atmosphere. Thermal stability of polymers are measured on a TA SDT2960 equipment under nitrogen atmosphere at a heating rate 20 °C/min. Circular dichroism spectra are recorded on JOBINYVON-SPEX CD6 using 1cm quartz cell. Optical rotations are measured at 589 nm and 365 nm wavelength, respectively, using 1dm quartz cell with PE polarimeter MODEL-341. The number-average molecular weight and polydispersity of the polymers are measured using a set of Waters Styragel columns HT2+HT3+HT4, and Waters 2410 RI detector, polystyrene as standard, THF as eluant at flow rate 1.0 ml/min. The texture of polymers are observed on a Leitz Laborlux 12 polarized microscope with Leitz 350 heating stage. WAXD powder experiment was performed on Philips X'pert using maximum 2.2 KW Ceramic Diffraction X-ray tube (Cu K_α radiation) and Anton Paar TTK 450 heating stage with Anton Paar thermal control TCU 100 under nitrogen. The powder polymer samples are mounted on iron sheets and scanned in a 2 θ from 2° to 30°. Background scattering is recorded and subtracted from WAXD pattern.

Thermal behavior of polymer 1a

Polymer **1a** is amorphous at room temperature determined by POM and WAXD studies. It is thermally quite stable, since the onset temperature for 5% weight loss under nitrogen atmosphere is as high as 386 °C. It undergoes glass transition at 186 °C and then enters an isotropic melt. At about 240 °C, the isotropic melt becomes birefringent observed under POM. Upon further heating, no visual disappearance of birefringence can be observed before the polymer decomposes. When cooled to room temperature from 300 °C, the birefringence of the sample remains unchanged. It implies that the ordered structure formed at high temperature is kept upon cooling.

The wide-angle X-ray diffraction powder patterns of **1a** at room temperature or temperature lower than 240 °C have only two diffuse halos centered at 2 θ = 5.06° (d-spacing of 1.74 nm) and 2 θ = 21.6° (d-spacing of 0.41 nm), respectively, which means that no long-range orders on the scale of supramolecular length and crystal structure formation via molecular packing on the scale of 0.4 nm exists. At temperature higher than 240 °C, the diffuse peak at small angle becomes intense and sharp. When the intensity of low-angle diffraction is plotted against temperature, a sudden increase in intensity is observed at 240 °C during heating. This discontinuous change of intensity represents a

characteristic feature of a first-order transition. When the polymer is cooled from 280 °C to room temperature, no such discontinuous change is observed, suggesting the ordered structure formed at high temperature keeps unchanged during cooling. It is consistent with the results from DSC studies.

Table 1. Specific optical rotation of model compound **3a**, monomer **2a**, and polymers **1a**, **1d** and **1e** in THF (c = 2.0 g/L).

Sample	3a	2a	1a	1d	1e
$[\alpha]_D^{20}$ (°)	+13.8	+13.8	-5.2	-14.4	-10.6
$[\alpha]_{365}^{20}$ (°)	+56.6	+60.4	-71.9	-113.6	-93.6

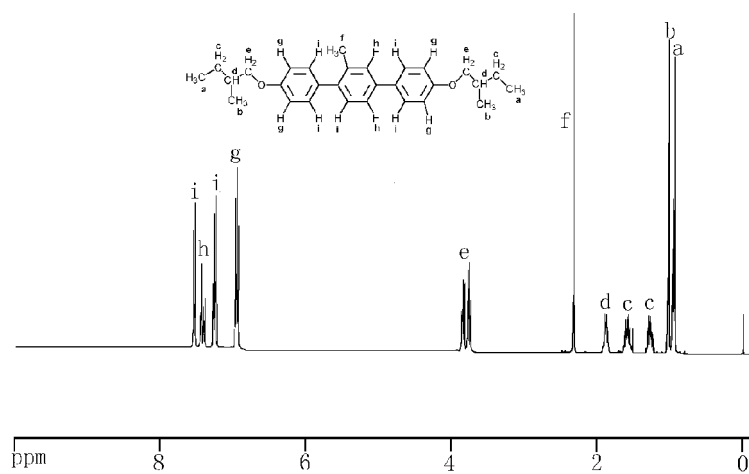


Figure 1. ^1H NMR spectrum of model compound **3a** recorded in CDCl_3 using TMS as standard.

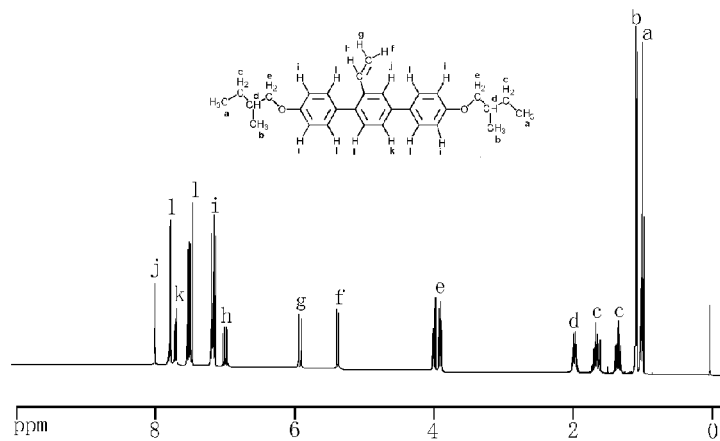


Figure 2. ^1H NMR spectrum of monomer 2a recorded in CDCl_3 using TMS as standard.

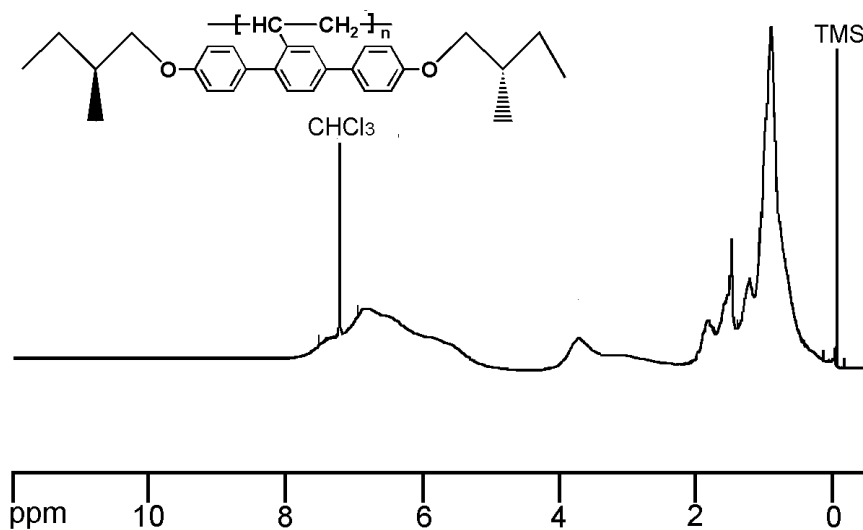


Figure 3. ^1H NMR spectrum of polymer 1a recorded in CDCl_3 using TMS as standard.

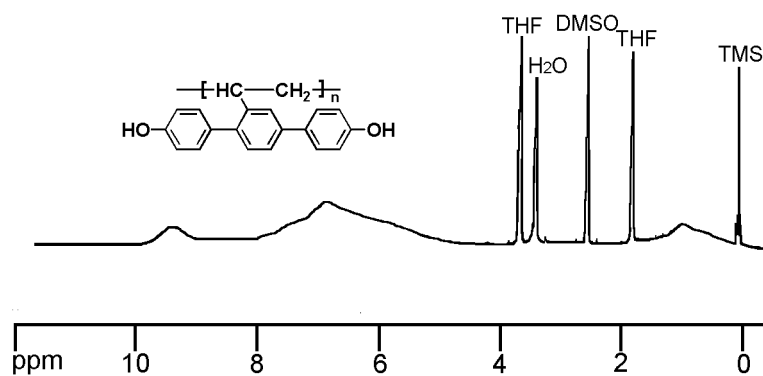


Figure 4. ^1H NMR spectrum of polymer 1d recorded in d-DMSO using TMS as standard.

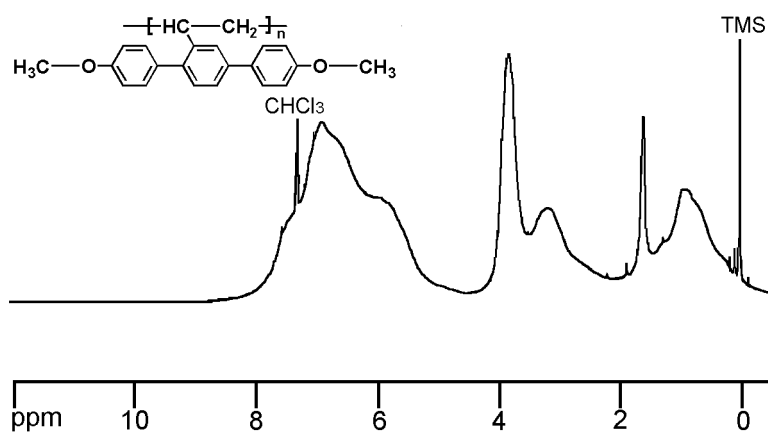


Figure 5. ^1H NMR spectrum of polymer 1e recorded in CDCl_3 using TMS as standard.

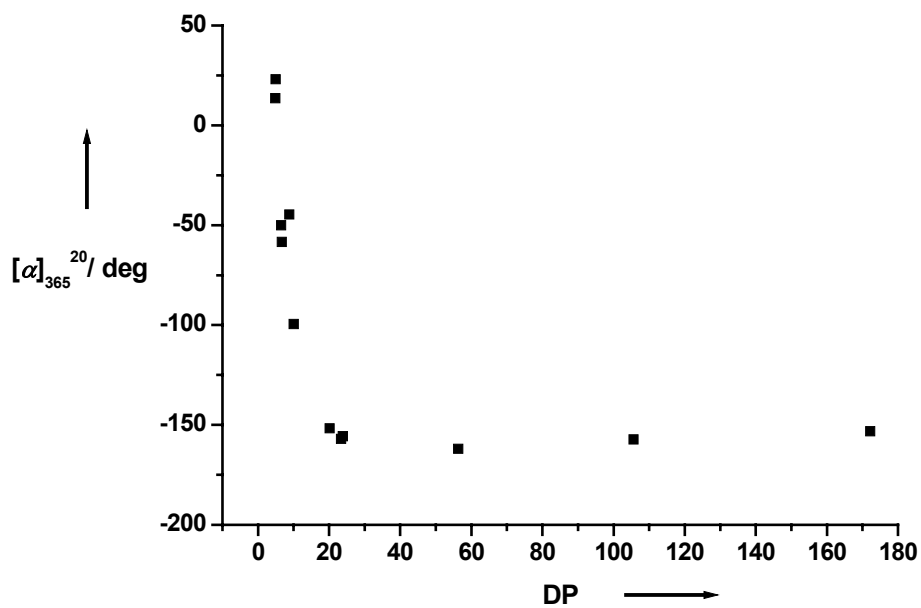


Figure 6. Dependence of optical activity of 1a on degree of polymerization. $[\alpha]_{365}^{20}$ was measured in THF ($c = 2.0 \text{ g L}^{-1}$).

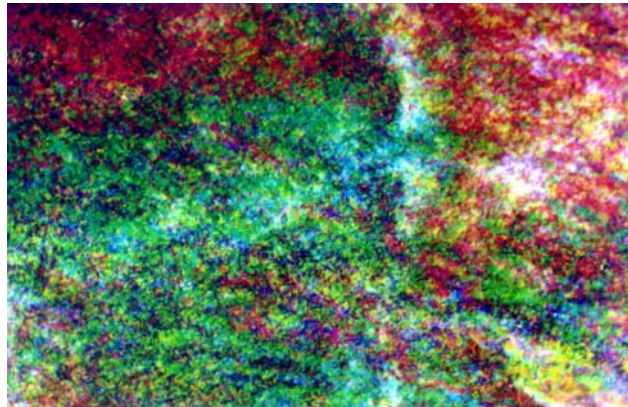
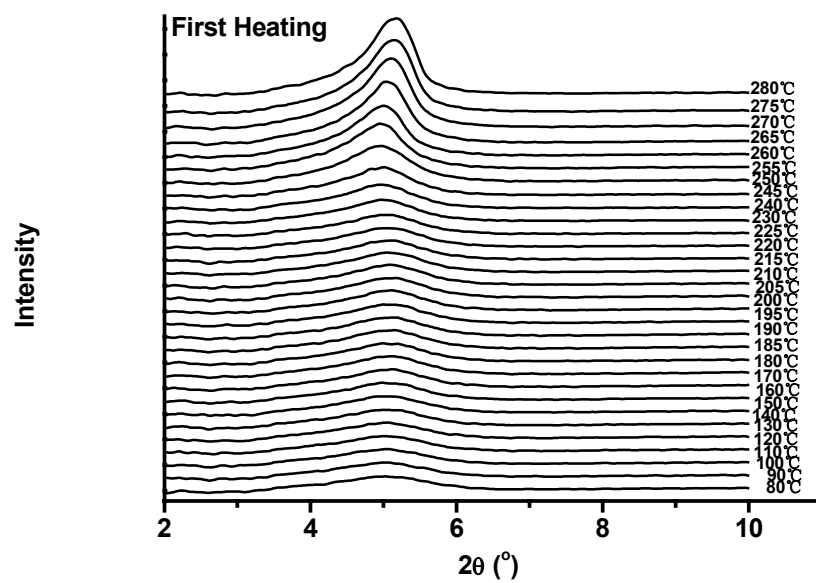


Figure 7. POM Photograph of the polymer 1a taken at 290 °C.



Figur 8. WAXD powder patterns of polymer 1a at different temperature (°C) during first heating scan.

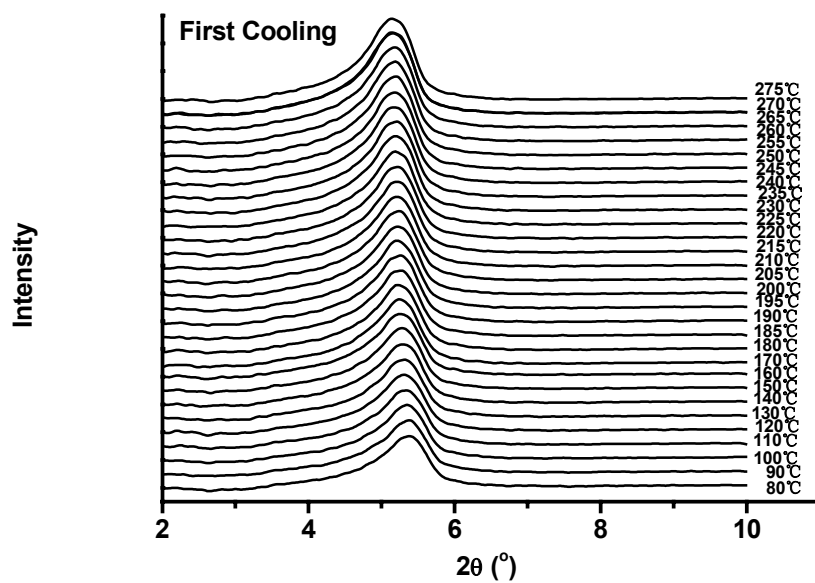


Figure 9. WAXD powder patterns of polymer 1a at different temperature (°C) during first cooling scan.

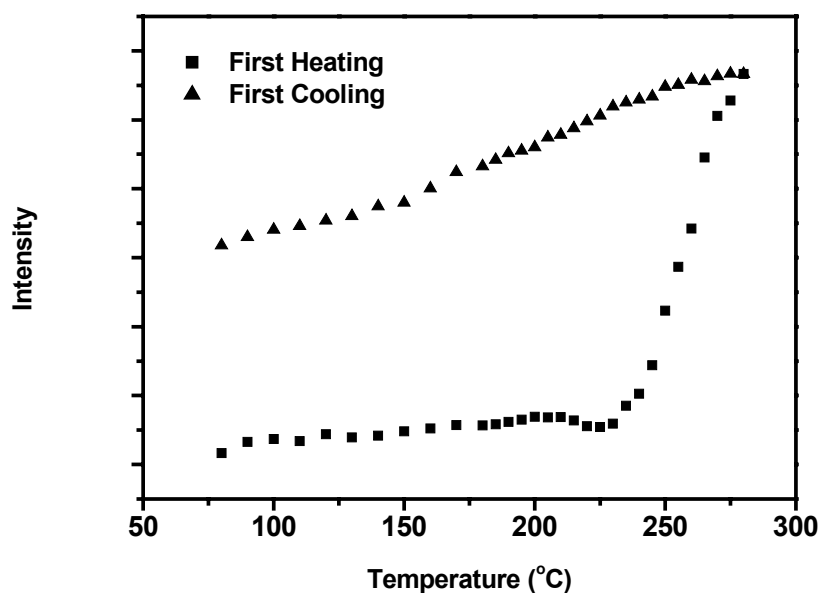


Figure 10. The relationship between the intensity of the low-angle diffraction and temperature for polymer 1a during heating and cooling at a rate of 2.5 °C/min under N₂ atmosphere.

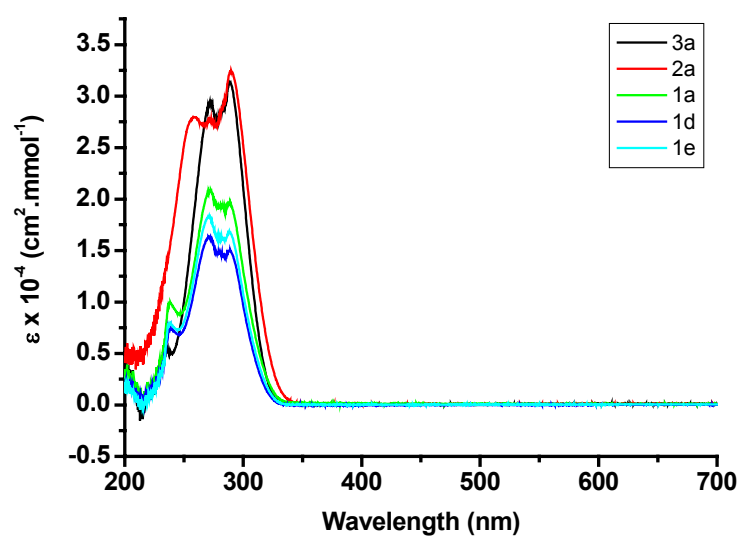


Figure 11 UV-vis absorption spectra of model compound 3a, monomer 2a, and polymers 1a, 1d, 1e (recorded at 20 °C in THF).

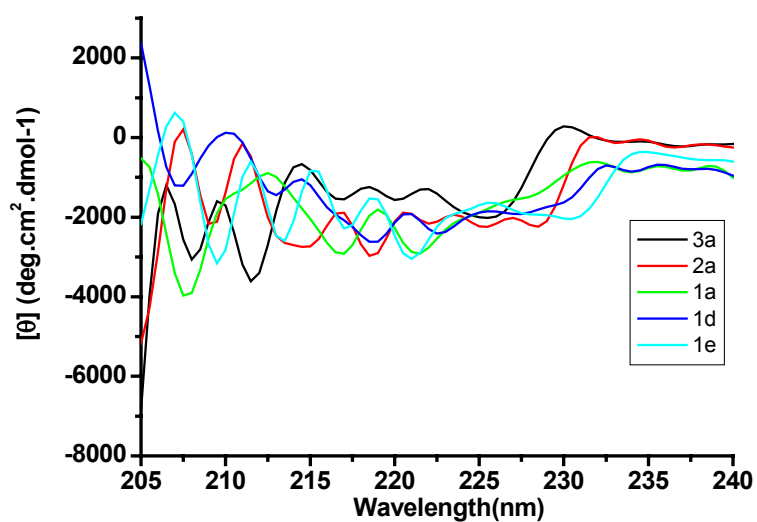


Figure 12 Comparison of the CD spectra of model compound 3a, monomer 2a, and polymers 1a, 1d, 1e (recorded at 20 °C in THF). $[\theta]$ = molar ellipticity with repeating unit: $\text{deg cm}^2 \text{ dmol}^{-1}$.