

Electronic Supporting Information

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1. Materials

Grubbs catalyst second generation, norbornene-2-carboxylic acid (mixture of endo and exo, 98%), 4-phenylazophenol (98%), phenol (99%), sodium nitrite (99%), hydrochloric acid (assay 37%) and 4-dimethylaminopyridine (DMAP, 99%) are purchased from Sigma-Aldrich and used without further purification. Modified Grubbs catalyst second generation (H₂IMes)(pyr)₂(Cl)₂RuCHPh (mG2)¹ is synthesized. Dry methylene chloride (CH₂Cl₂, 99.8%), anhydrous tetrahydrofuran (THF, 99.9%), anhydrous dimethylformamide (DMF), oxalyl chloride (98%), ethyl vinyl ether (EVE, 99%), 4-methoxyphenol (99%), 4-cyanophenol (99%), 4-nitrophenol (99%) and pentane (99%) are obtained from Acros Organics while 12-bromo-1-dodecanol (98%) is obtained from TCI America.

2.Synthesis of Materials

2.1 Monomers Synthesis

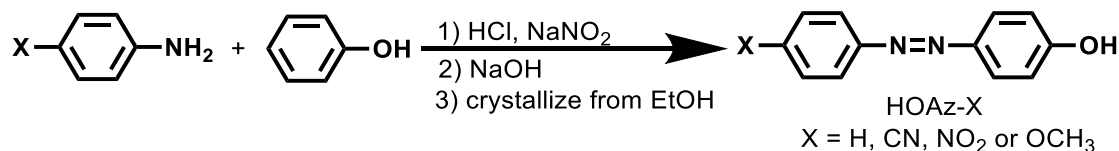
The monomers NBCh9², and NBMPEG³ are synthesized as per the previously reported procedures.

Synthesis of NBAz₁₂-X (X= H, CN, NO₂ or OCH₃)

NBAz₁₂-X (X =H, CN, NO₂, OCH₃) are synthesized using modified literature procedure^{4, 5} as shown in Schemes S1-3.

Step 1: Synthesis of HOAz-X

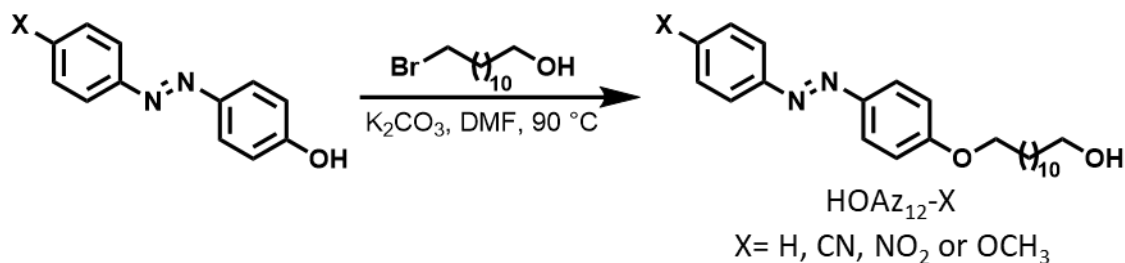
The following scheme was adapted for the synthesis of HOAz-X (X=H, CN, NO₂, OCH₃) Yield: 85-92%.



Scheme S1. Synthesis of hydroxyl azo biphenyl (HOAz-X)

Step 2: Synthesis of HOAz₁₂-X

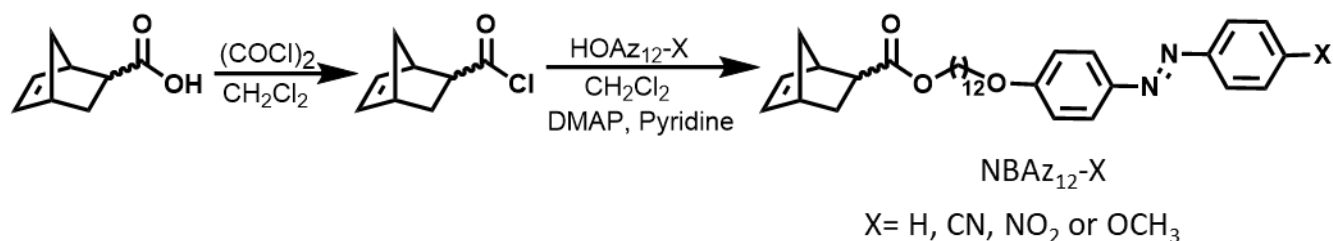
In a round bottom flask equipped with magnetic stir bar, 12-bromo-1-dodecanol (10 g, 37.7 mmol), HOAz-X (5.0 g, 25.1 mmol), K₂CO₃ (6.9 g, 50.2 mmol) and DMF (50mL) are charged and sealed with a rubber septum. The reaction mixture was purged with nitrogen for 10 min, and then stirred in oil bath for 48 h at 90 °C. The reaction mixture was then cooled down to room temperature and diluted with 50 mL of CH₂Cl₂. The mixture was washed with 300 mL of deionized water three times, and finally treated with 5% NaOH (aq, 200 mL). Organic layer was separated from the aqueous layer, collected and dried with MgSO₄. The crude product is further purified by recrystallization using 50 mL of ethanol (Yield: 88%).



Scheme S2. Synthesis of 12 spacer hydroxyl azo biphenyl (HOAz₁₂-X)

Step 3: Synthesis of NBAz₁₂-X

Flame dried air-free single neck flask equipped with a bubbler and a magnetic stir bar was charged with 5-norbornene-2-carboxylic acid (86/14 = *endo/exo*) (4.3 g, 31.4 mmol) and 30 mL of CH₂Cl₂, and purged with nitrogen for 10 min. To this solution, excess oxalyl chloride (6.7 mL, 78.4 mmol) was injected in a dropwise manner, followed by adding a drop of DMF. After 3 hours reaction at room temperature, unreacted oxalyl chloride was removed under reduced pressure, resulting in pale yellow liquid of norbornene carbonyl chloride, which was further diluted with 20 mL of CH₂Cl₂. To this solution, HOAz₁₂-X (6.0 g, 15.7 mmol) in dry CH₂Cl₂ (30 mL) was added, followed by catalytic amount of DMAP and pyridine mixture. The reaction mixture was then stirred overnight at room temperature under nitrogen. Afterward, the reaction mixture was filtered to remove organic salt, and then the filtrate was concentrated using rotary evaporator. The crude product was purified by column chromatography with ethyl acetate/hexane = 3/7 (v/v) as the mobile phase and silica gel as the stationary phase. The recovered product was further purified by recrystallization using ethanol (Yield: 80-86%)



Scheme S3. Synthesis of 12 spacer monomers, (NBAz₁₂-X)

2.3 General Procedure for Synthesis of Liquid Crystalline Random Copolymers (CP)

A random copolymer (CP) was synthesized as described as follows: In a 25mL round bottom flask, monomers NBCh9 (500 mg, 0.72 mmol) and NBAz₁₂-X (X =CN, 87.5 mg, 0.17 mmol) are

weighed. 12 ml of anhydrous CH_2Cl_2 was added to the flask then purged with nitrogen for 5 minutes. In a scintillation vial modified Grubs second generation (mG2) catalyst (3.55 mg, 0.0049 mmol) was dissolved in 3 ml of anhydrous CH_2Cl_2 and nitrogen was purged for 5 mins. Then, the catalyst solution was added to the solution in the flask containing monomers and the reaction allowed to proceed for 25 mins at room temperature. The reaction was terminated with the addition of excess ethyl vinyl ether (EVE). The resulting polymer was then precipitated in methanol, filtered, and dried overnight under vacuum at room temperature. All other copolymers were prepared with similar procedure.

^1H NMR was used to obtain monomer weights fractions in the final polymer by integrating characteristic peak corresponding to each monomer (4.6 and 7.0 ppm corresponding to NBCh9, and NBAz₁₂-X monomers, respectively.) For example, CP-85 (X= CN) refers to random copolymer comprising 85% of NBCh9 comonomer and 15% of NBAz₁₂-X (X= CN) comonomer.

2.2 General Procedure for Synthesis of Liquid Crystalline Random Terpolymers (TP)

A representative ring-opening metathesis polymerization (ROMP) of terpolymer is described as below. In a vial NBCh9 (500 mg, 0.72 mmol), NBAz₁₂-X (X=CN, 68 mg, 0.16 mmol) and NBMPEG (98 mg, 0.049 mmol) with modified Grubs second generation (mG2) (3.98 mg, 0.0055 mmol) in CH_2Cl_2 (12 mL). The monomer and catalyst stock solutions are prepared and purged with nitrogen for 5 min. Then, two solutions are combined together. Polymerization was allowed for 25- 30 min at room temperature and terminated by adding excess EVE. The resulting polymer was precipitated in methanol and then filtered, followed by drying overnight under vacuum at room temperature. All other terpolymers are prepared with similar procedure.

^1H NMR was used to obtain monomer weight fractions in the final terpolymer by comparing the integration of the characteristic peak corresponding to each monomer (3.36, 4.58 and 6.99 ppm corresponding to NBMPEG, NBCh9, and NBAz₁₂-X monomers respectively).

2.4 Polymerization kinetics of individual monomers

The kinetics of the monomers was determined based on the previous reported procedure, where homopolymers of monomers NBCh9 and NBMPEG are shown to have similar rates of polymerizations.³ The polymerization kinetics of individual monomers was determined as follows: In 25 mL round bottom flask, 400 mg (0.79 mmol) of monomer NBAz₁₂-X (X=H) was dissolved in 8 mL of CDCl₃. This was followed by purging nitrogen for 5 minutes. Nitrogen was purged to a scintillation vial having weighed freshly prepared modified Grubs second generation (mG2) catalyst in 4 mL of CDCl₃ to obtain a stock solution. The catalyst was added to the monomer solution in the flask and polymerization allowed to proceed for 25 minutes at room temperature under nitrogen. To obtain monomer conversion, aliquots were taken out from reaction mixture at regular time interval and immediately quenched using ethyl vinyl ether (0.25 mL) in CDCl₃. The aliquots taken at different time intervals were used to monitor the disappearance of the olefinic protons (5.9- 6.1 ppm) in the norbornene monomers using ^1H NMR analysis.

3.0 Methods

^1H NMR spectra (Bruker DMX 500MHz NMR spectrometer) are recorded in CDCl₃ and 7.24 ppm peak s used as internal standard. Molecular weight and polydispersity indices (PDI) are determined by gel permeation chromatography (GPC) by using a Waters 1515 coupled with a PL-ELS1000 evaporative light scattering (ELS), refractive index (RI) and Waters 2487 dual wavelength

absorbance UV-Vis detectors with tetrahydrofuran (THF) or dimethylacetamide (DMAc) as the eluent. Polystyrene for THF and Poly(MethylMethacrylate) (PMMA) for DMAc are used as standard. Indium standard calibrated TA-2920 DSC (Q-100 series) instrument is used to analyze the thermal properties of the homopolymers and terpolymer. The amount of sample is 5-10 mg and scanning rate is 10 °C/min. Phase transition temperatures are determined by the first cooling or the second heating cycle using TA Universal Analysis software.

3.1 Small-angle X-ray scattering (SAXS) and Temperature controlled SAXS (T-SAXS)

Small-angle X-ray scattering (SAXS) is performed on a pin-hole collimated Rigaku SMAX3000 instrument configured with CuK α radiation (1.542 Å) produced by a micro-focus source. The beam diameter on the sample plane is 1 mm and the scattered intensity is recorded on a gas-wire electronic area (2D) detector. The area detector has a resolution of 1024 $\times$ 1024 pixels and is located at a distance of ~80 cm from the sample center permitting access of scattering vectors ranging from 0.015 to 0.22 Å⁻¹. Silver behenate (d-spacing=58.38 Å) is used to calibrate the SAXS diffraction patterns. All terpolymer and copolymer samples are compression molded between 90 °C to 105 °C depending on the phase transition temperatures to obtain free standing solid films which are characterized with SAXS. For T-SAXS, films of the samples sandwiched between the Kapton windows are subjected to a heating/cooling rate of 5 °C/min and held for 10 min at each temperature prior to 10 min data acquisition within temperature range of 25-110 °C.

3.2 Optical Properties analysis

Shimadzu UV-Vis Spectrometer (UV-2450) in reflectance mode with a wavelength range of 200 -1000 nm is used to obtain optical spectra of the polymer films. The free-standing films (~ 0.2 mm in thickness) are prepared by annealing the solid samples (150- 250 mg) in the temperature

range of 85- 110 °C between the polyimide Kapton films at the liquid crystalline transition phase for about 30 minutes. The liquid crystalline transition phase is preserved by rapidly cooling the sample to room temperature ($T < T_g$) using cold compressed air.

Olympus BX51P microscope equipped with Instec HCS410 hot stage was used to determine: optical texture of the films. The samples were placed between glass slides and annealed at temperature slightly above T_{LC1} and slightly below T_{LC2} transition temperatures for 24 h, and characteristic texture of mesophase was recorded.

Characterization Results:

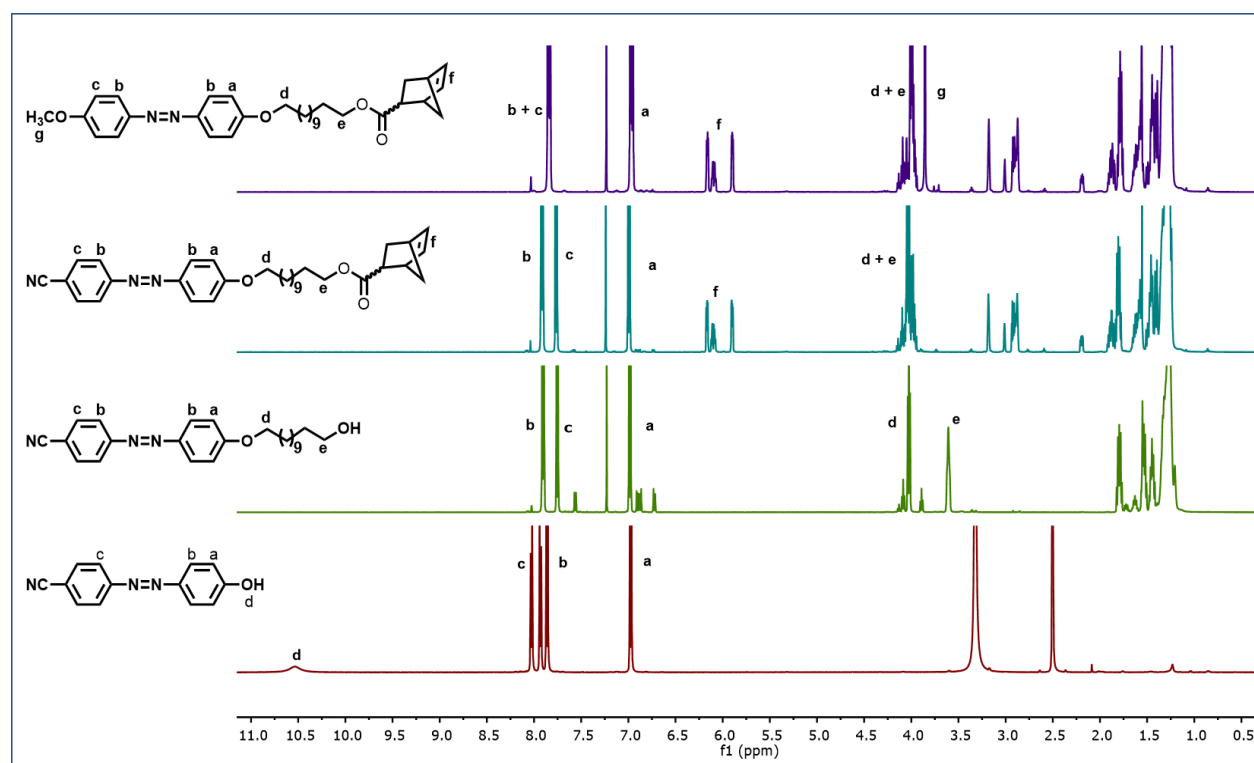


Figure S1: Representative ^1H NMR spectrum of HOAz-X (X=CN, in DMSO), HOAz₁₂-X (X=CN, in CDCl_3) and NBAz₁₂-X (X=CN or OCH_3 in CDCl_3) at room temperature.

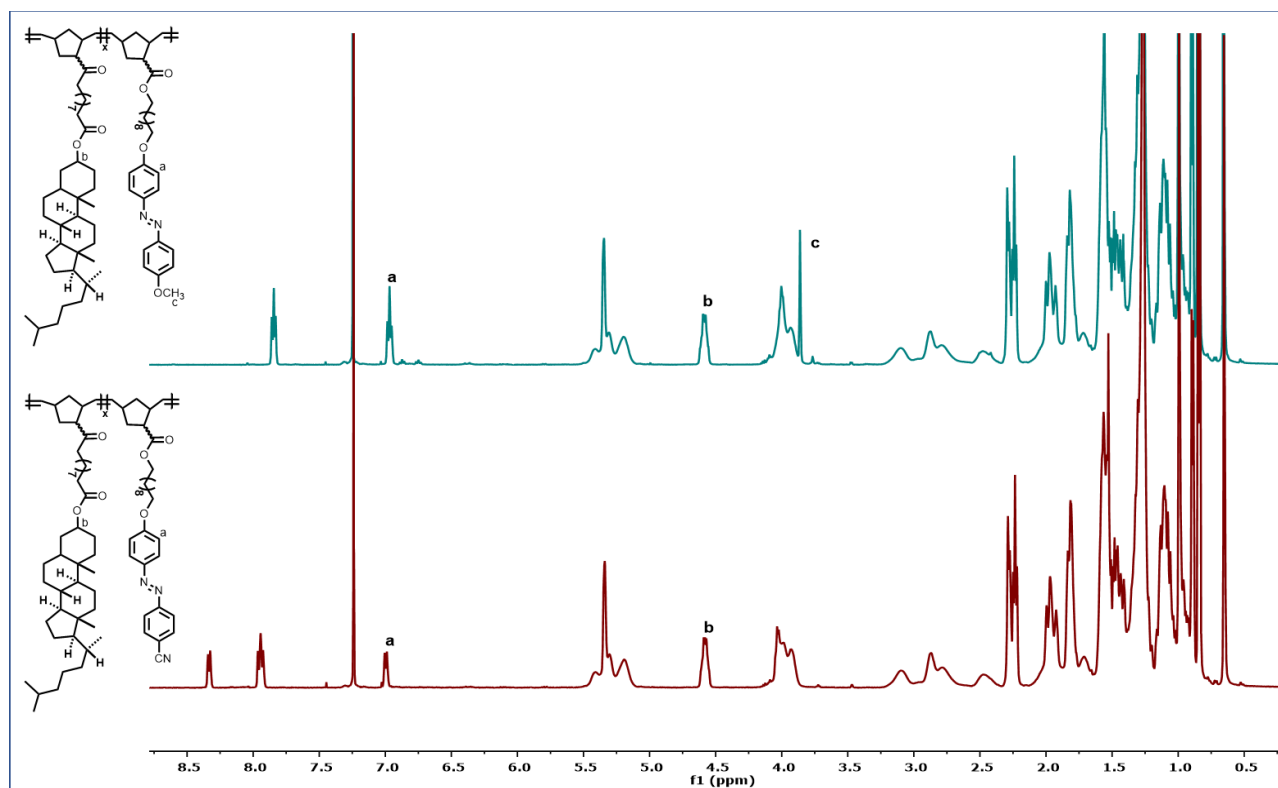


Figure S2: Representative ^1H NMR spectrum of copolymer (CP-85, $\text{X}=\text{CN}$ or OCH_3) in CDCl_3 at room temperature.

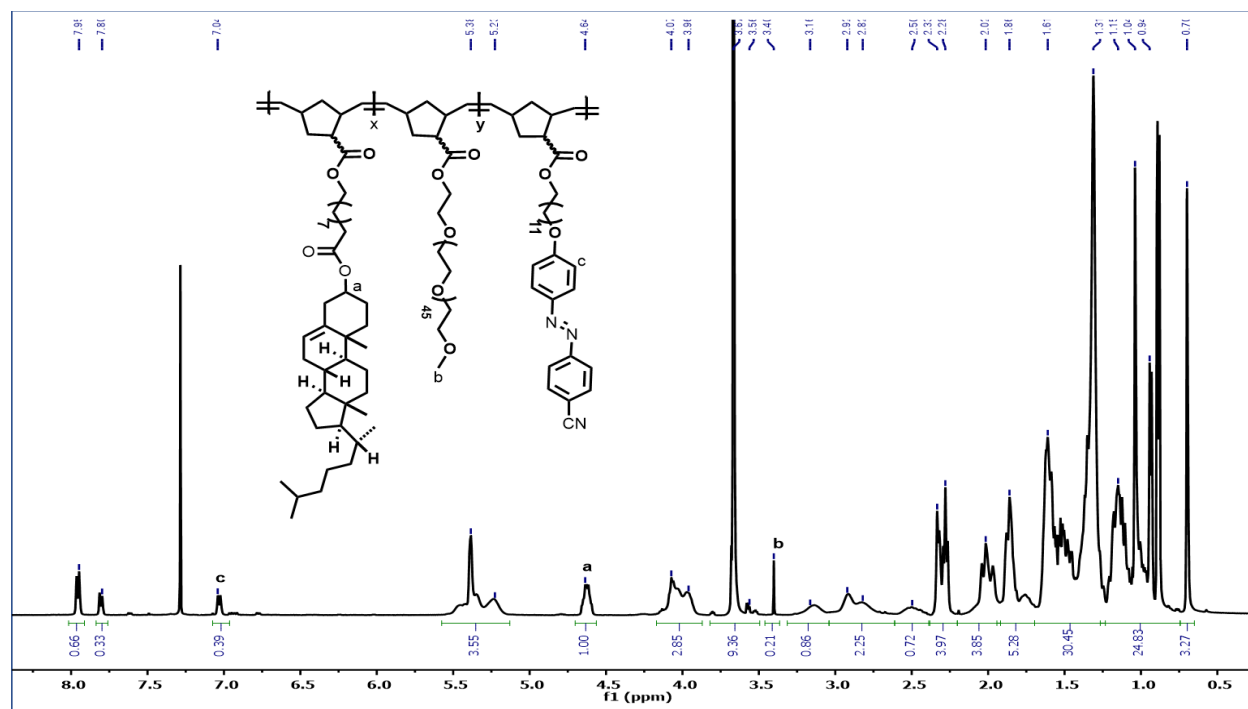


Figure S3: Representative ^1H NMR spectrum of TP-75 (X=CN) in CDCl_3 at room temperature.

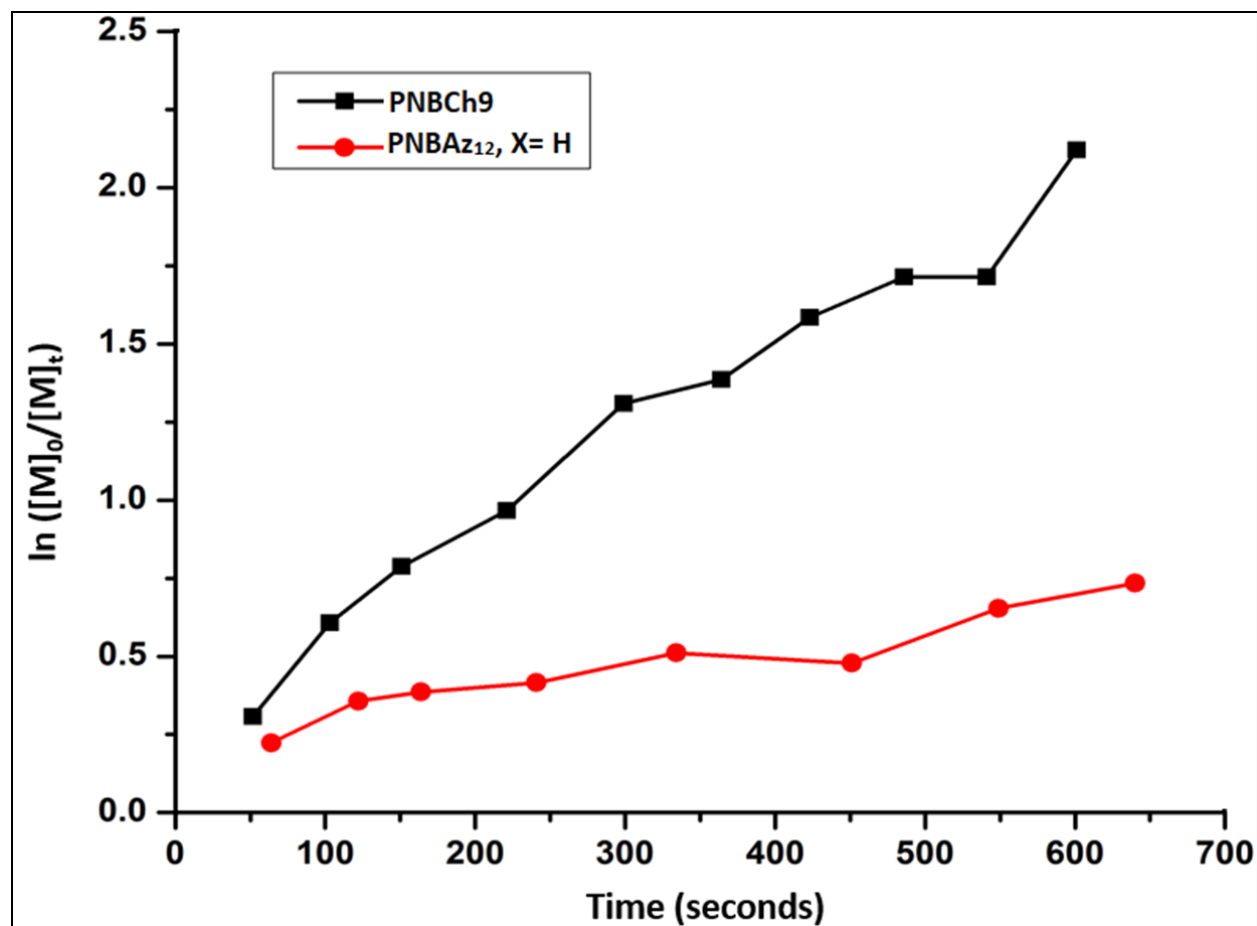


Figure S4: Ring Opening Metathesis Polymerization kinetics of NBCh9 and NBAz₁₂-X (X=H). The rate of polymerization of the monomers is determined by slope of the line in the plot of $\ln[(MM)_0/(MM)_t]$ vs time. From the plots, it is noted that NBCh9 and azo monomers (NBAz₁₂-H) exhibit different rates of under ring opening metathesis polymerization conditions. From our previous studies, we had shown that NBCh9 and NBMPEG monomers have similar rates of polymerization.³

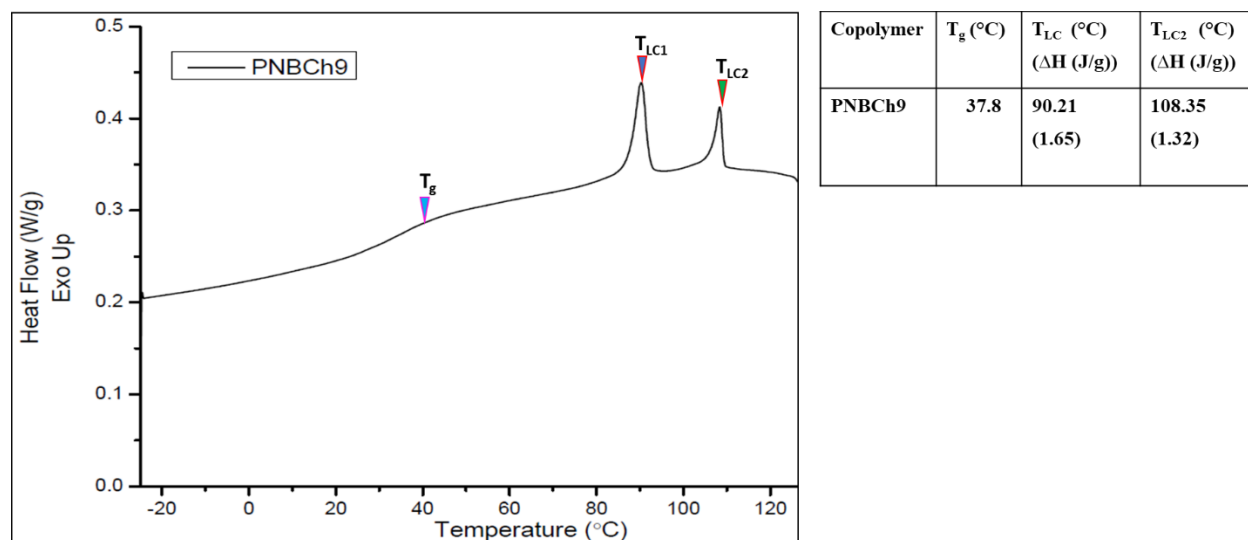


Figure S5: The first cooling cycle DSC thermogram of homopolymer PNBCh9. The table alongside shows that homopolymer exhibits T_g and two liquid crystalline transition temperatures (T_{LC1} and T_{LC2}) as reported previously.⁶

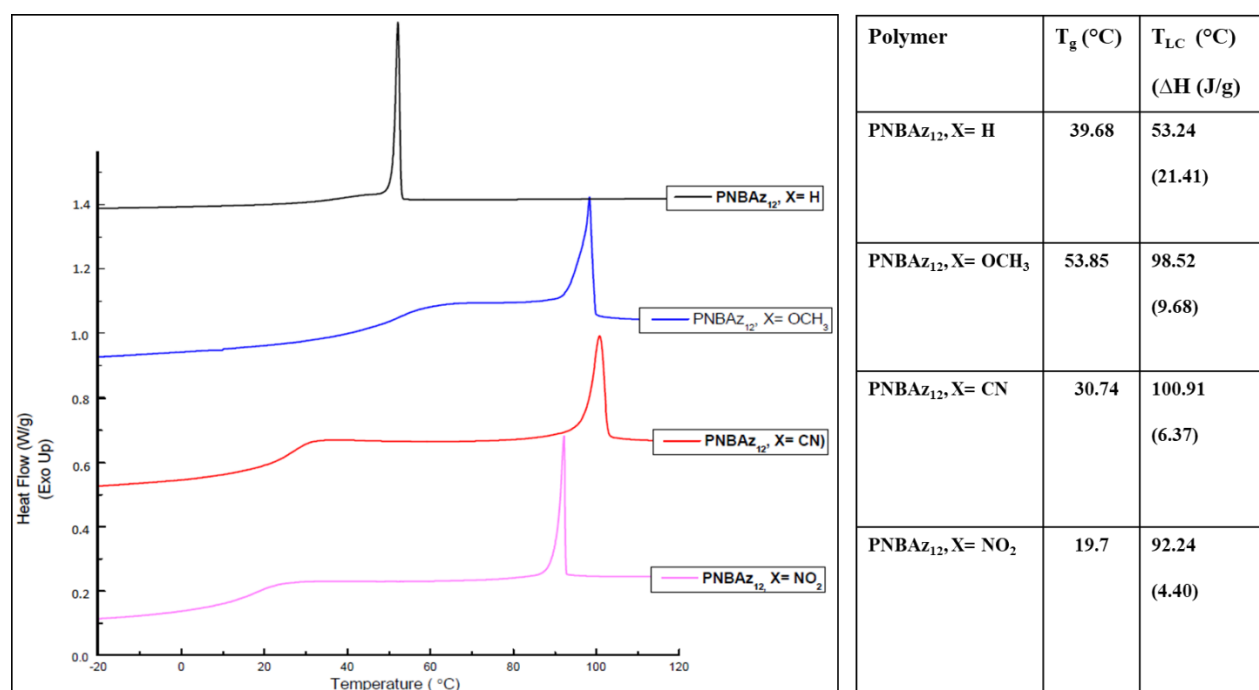


Figure S6: The first cooling cycle DSC thermogram of azobenzene homopolymers PNBxAz12 (X=NO₂, CN, OCH₃ and H). The table alongside shows the homopolymers exhibit T_g and one liquid crystalline transition temperatures (T_{LC}).

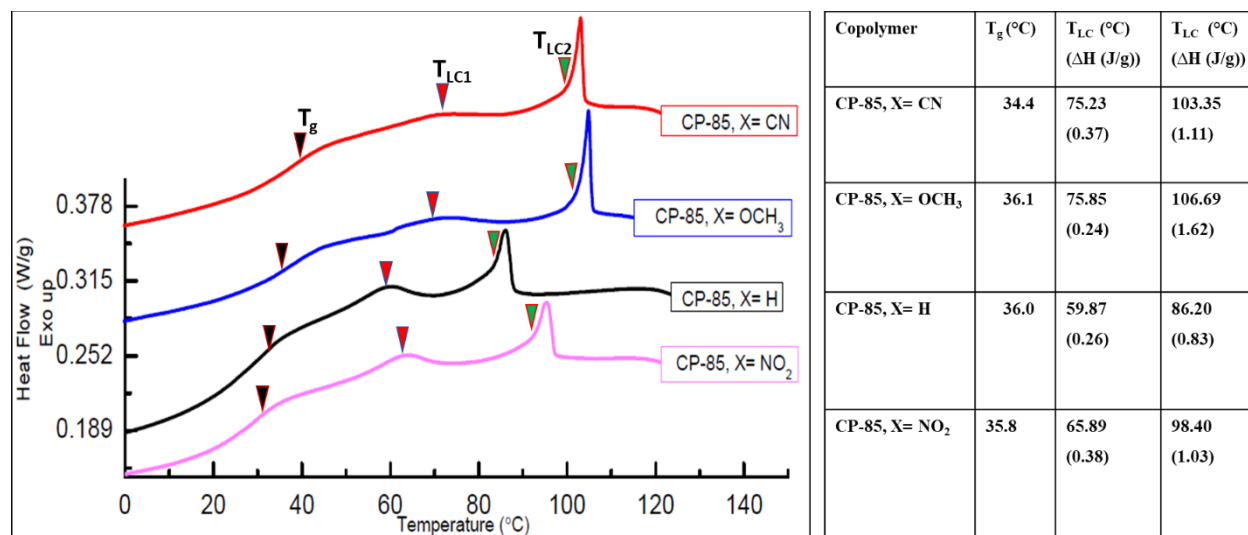


Figure S7: The first cooling cycle DSC thermogram of azobenzene copolymers CP (X=CN, NO₂, OCH₃ and H). The table alongside shows CP-85 copolymers exhibit T_g and two liquid crystalline transitions (T_{LC1} and T_{LC2}).

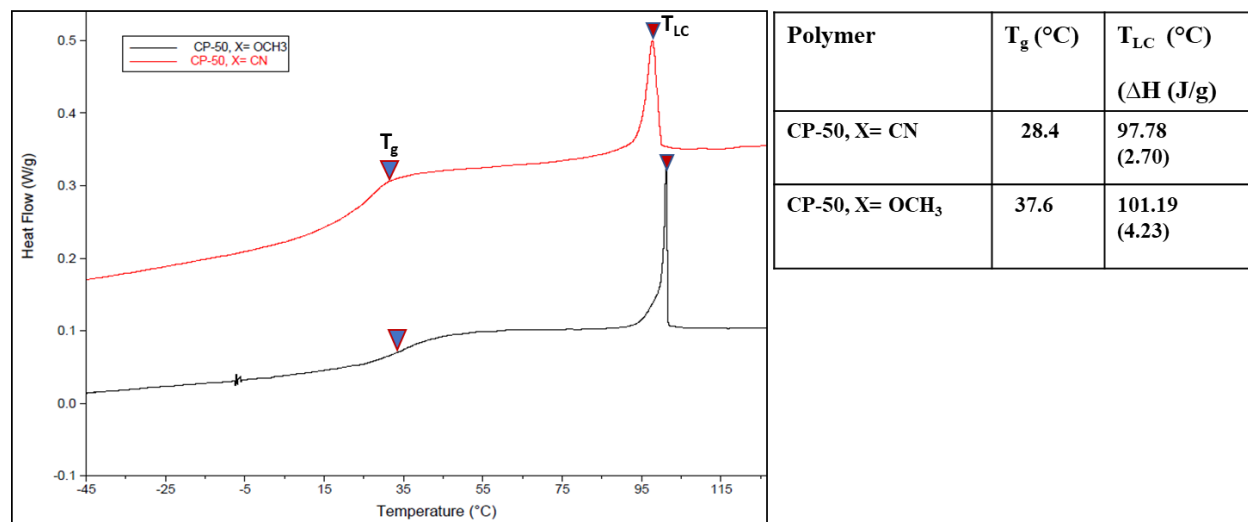


Figure S8: The first cooling cycle DSC thermogram of azobenzene copolymers CP (X= CN, OCH₃). The table alongside shows CP-50 copolymers exhibit T_g and one liquid crystalline transition T_{LC} ,

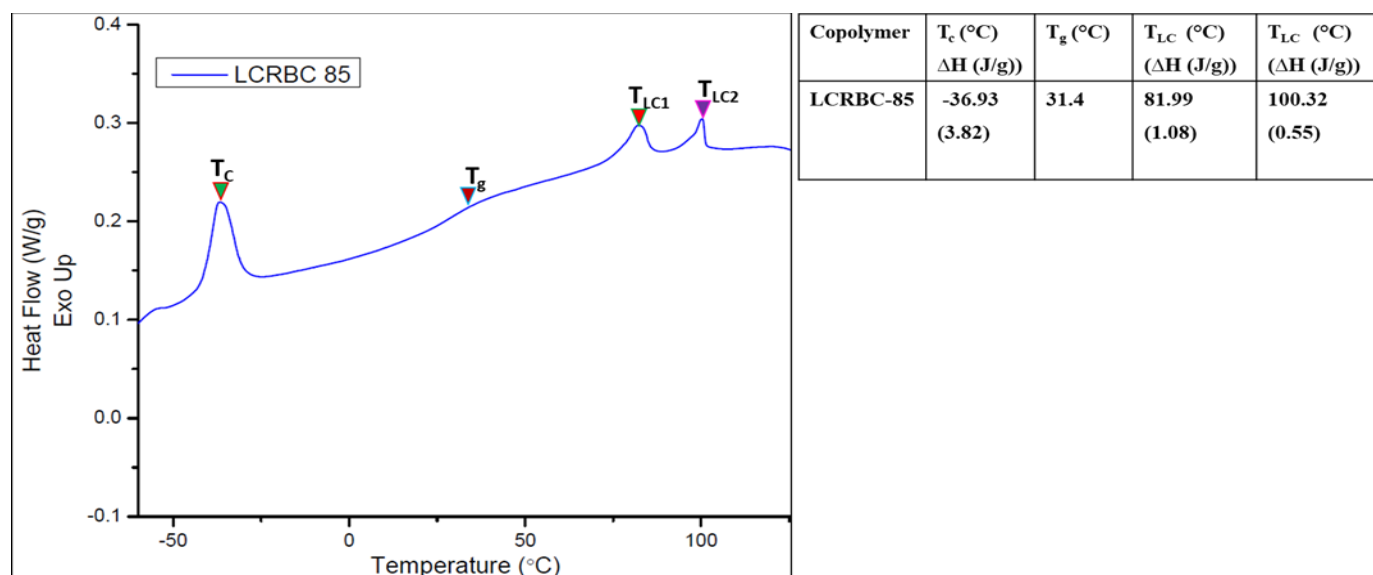


Figure S9: The first cooling cycle DSC thermogram of LCRBC85 comprising of 85 wt % of NBCh9 and 15 wt% of NBMPEG. The table alongside shows the copolymer exhibit PEG crystallization transition (T_c), glass transition temperature (T_g) and two liquid crystalline transition temperatures (T_{LC1} and T_{LC2}) as reported in the literature.³

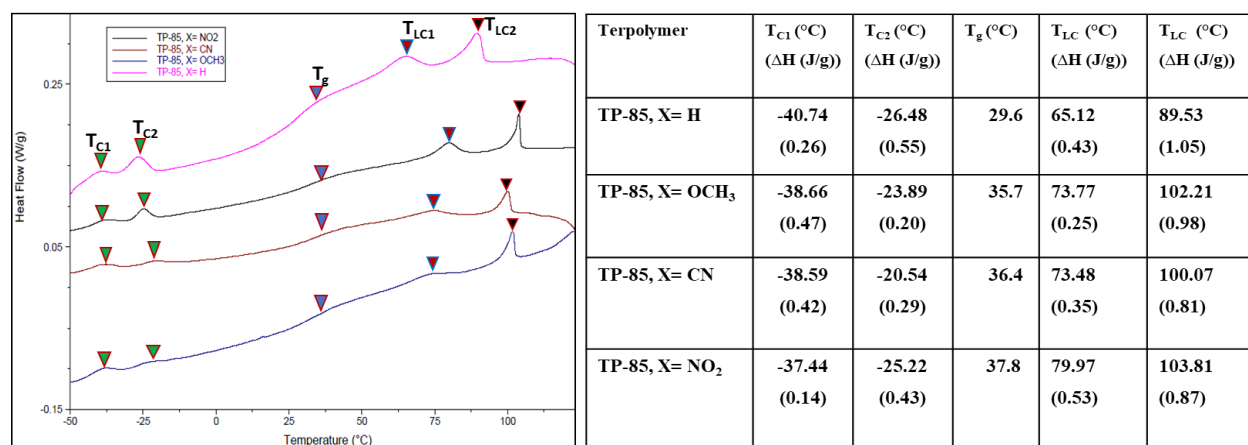


Figure S10: The first cooling cycle DSC thermogram of azobenzene terpolymers TP-85 ($X=H, OCH_3, CN$ and NO_2). The table alongside shows the TP-85 terpolymers exhibit two liquid crystalline transitions (T_{LC1} and T_{LC2}), T_g and suppressed PEG crystallization (T_c) transition. a) Two different population regions (T_{C1} and T_{C2}) which correspond to homogeneous and heterogeneous nucleated PEG crystals respectively, indicating the amorphous nature of PEG domains at room temperature hence functions as a plasticizer during processing of polymers b) Azobenzene mesogens along with cholesteric mesogen induce slightly different levels of side chain interdigitation as suggested by the width of T_{LC1} - T_{LC2} .

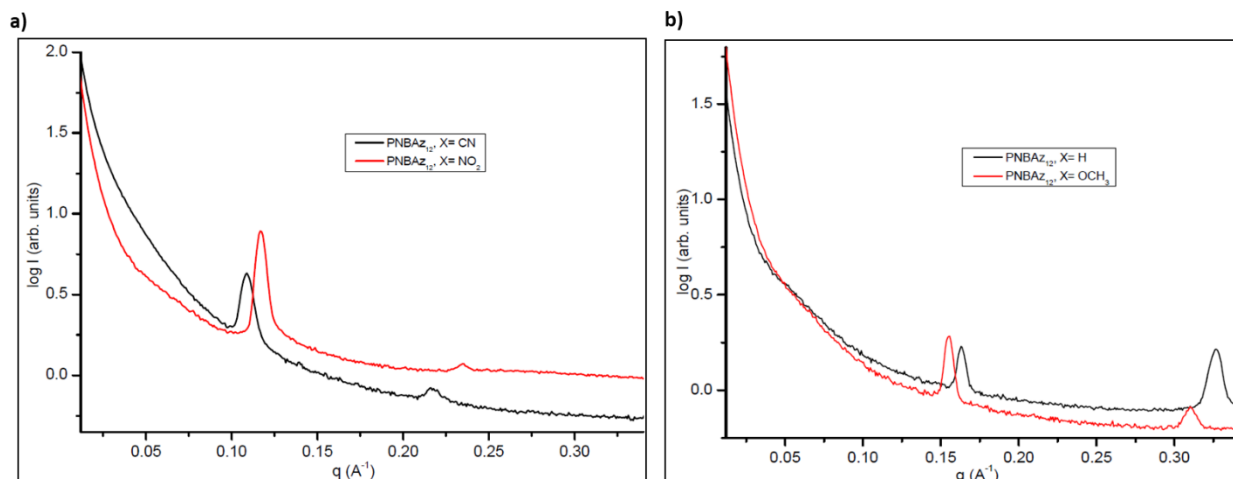


Figure S11. Room temperature 1D-SAXS for PNBAz₁₂, X=CN and NO₂ (a) and PNBAz₁₂, X=H and OCH₃ (b) compression molded at distinctive temperature depending on T_{LC} and quenched to room temperature. These homopolymers mostly show smectic mesophases at room temperature.

Polymer	d ₁ (nm)	d ₂ (nm)	Side-chain length ¹ (nm)
PNBAz ₁₂ , X= CN	5.8	2.9	2.91
PNBAz ₁₂ , X= NO ₂	5.4	2.7	2.90
PNBAz ₁₂ , X= H	3.9	1.9	2.93
PNBAz ₁₂ , X= OCH ₃	4.1	2.0	2.78

Table S1: Domain (d) spacing values for PNBAz₁₂, X=H, CN, NO₂ or OCH₃ Homopolymers determined by SAXS. ¹Calculated value of the NBAz₁₂, (X=H, CN, NO₂ or OCH₃) side-chains using ChemDraw 3D software.

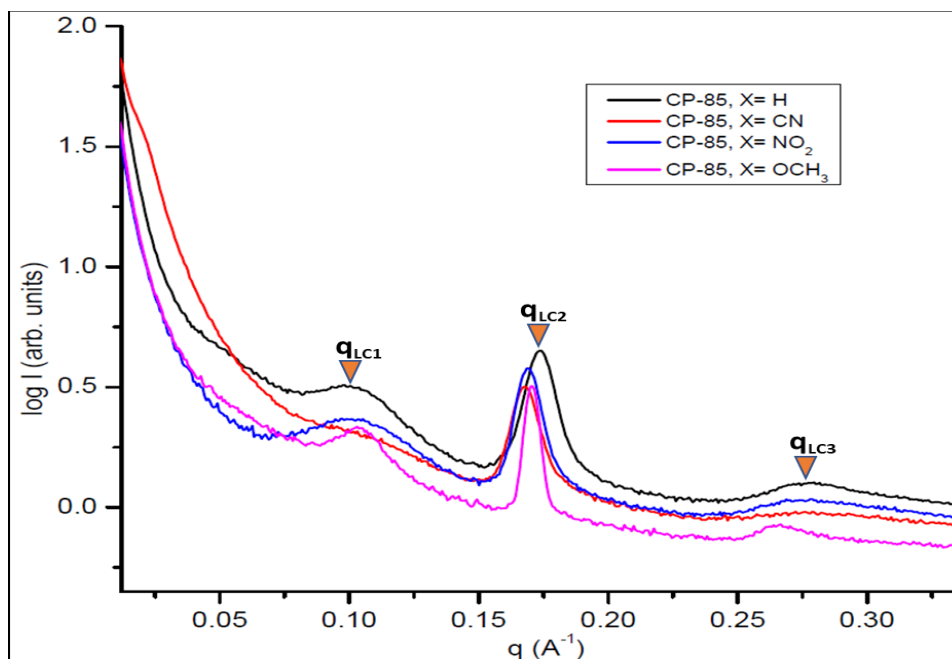


Figure S12. Room temperature 1D-SAXS for CP-85, X=H, CN NO₂ and OCH₃ compression molded at distinctive temperature depending on T_{LC} and quenched to room temperature.

Polymer	d ₁ (nm)	d ₂ (nm)	d ₃ (nm)
CP-85, X= H	6.2	3.6	2.3
CP-85, X= CN	6.3	3.8	2.3
CP-85, X= NO ₂	6.0	3.7	2.3
CP-85, X= OCH ₃	6.0	3.7	2.4

Table S2: Domain (d) spacing values for CP-85, X=H, CN, NO₂ or OCH₃ copolymers determined by SAXS at room temperature.

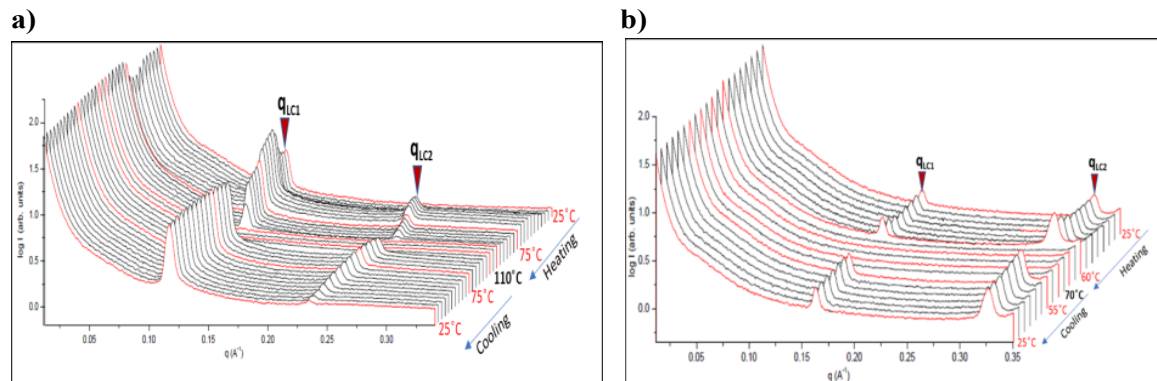


Figure S13. Temperature dependent 1D-SAXS of PNBAz12, X= NO₂ (a) and PNBAz12, X= H compression molded at different temperatures in reference to T_{LC} and quenched to room temperature

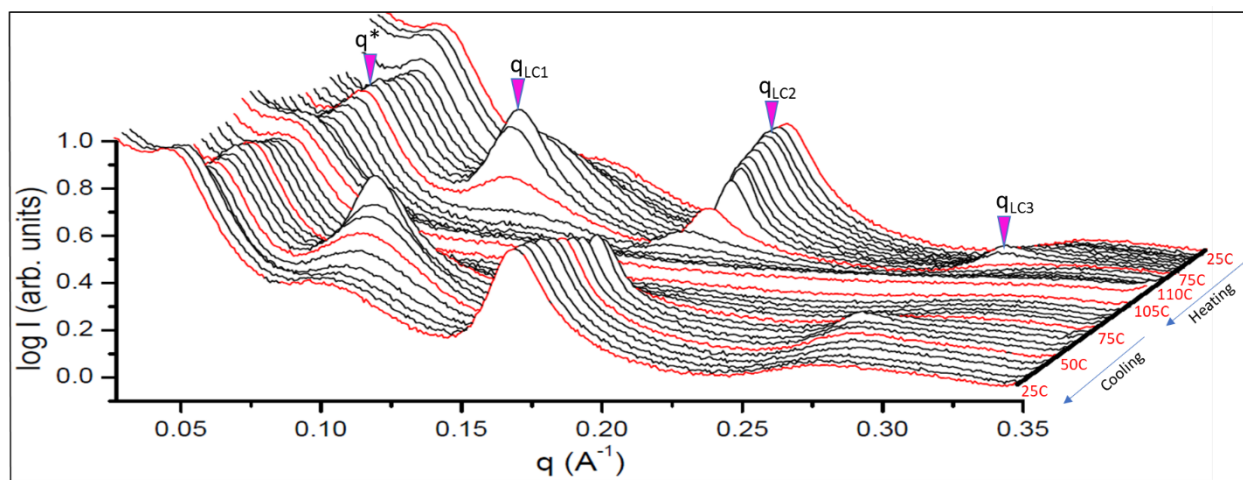


Figure S14. Temperature dependent 1D-SAXS of TP-75 (X=NO₂) compression molded at 90 °C and quenched to room temperature.

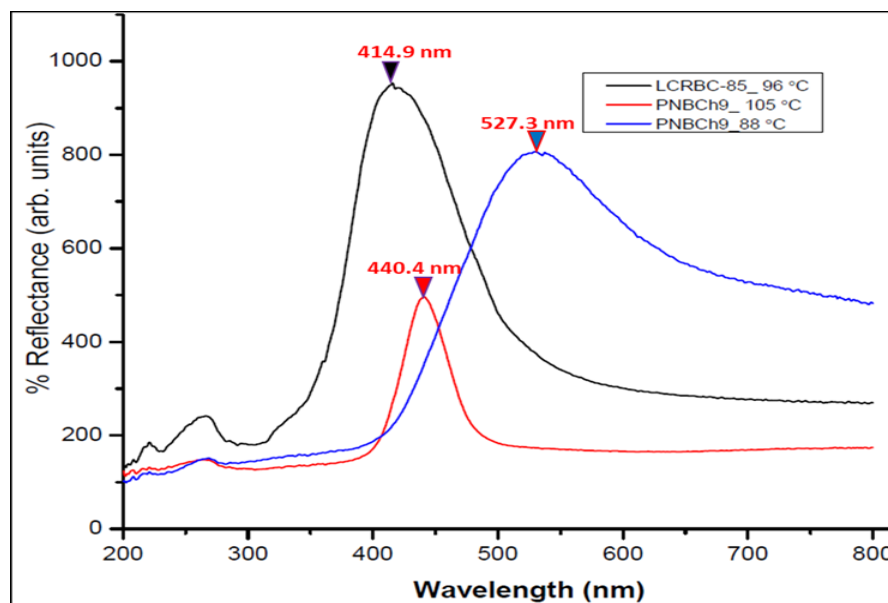


Figure S15: Light reflection of PNBCh9 and copolymer of Ch9-PEG 85 (LCRBC85) film samples prepared by compression molding at distinctive temperatures depending on the liquid crystalline transition temperatures (T_{LC1} and T_{LC2}).^{3, 6}

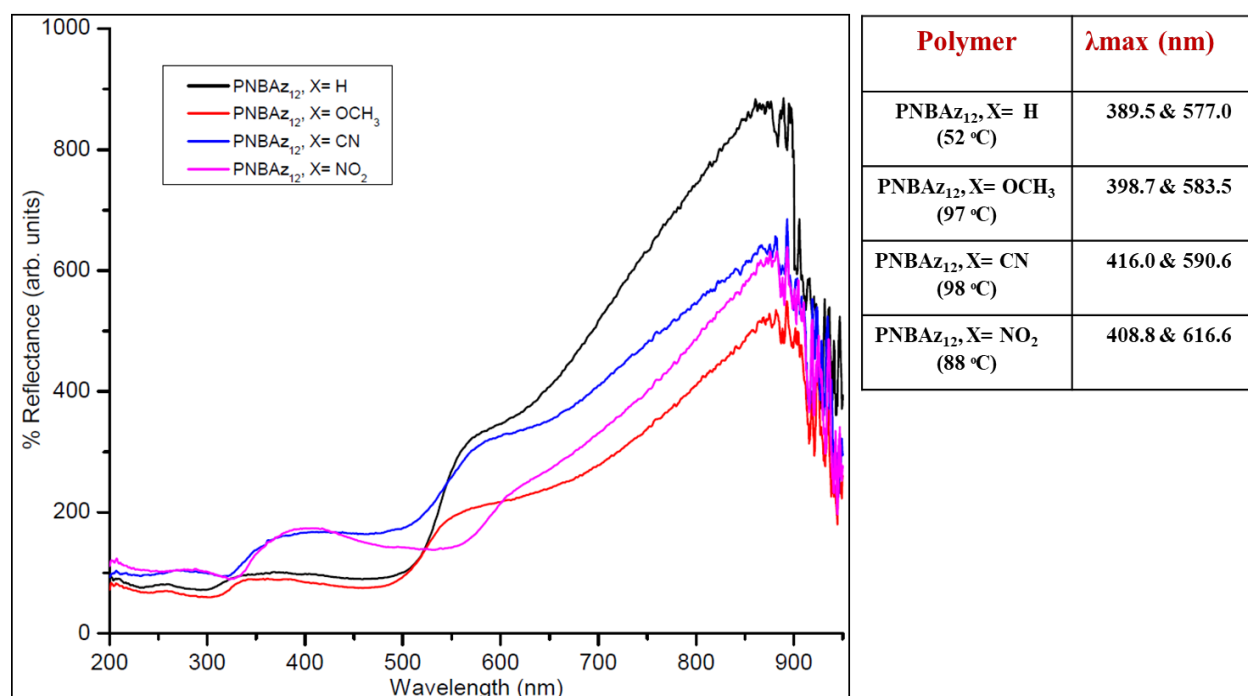


Figure S16: Light reflection of azo homopolymers (PNBAz₁₂, X=H, OCH₃, CN and NO₂) film samples prepared by compression molding at distinctive temperatures (table alongside) depending on the liquid crystalline transition temperature (T_{LC}).

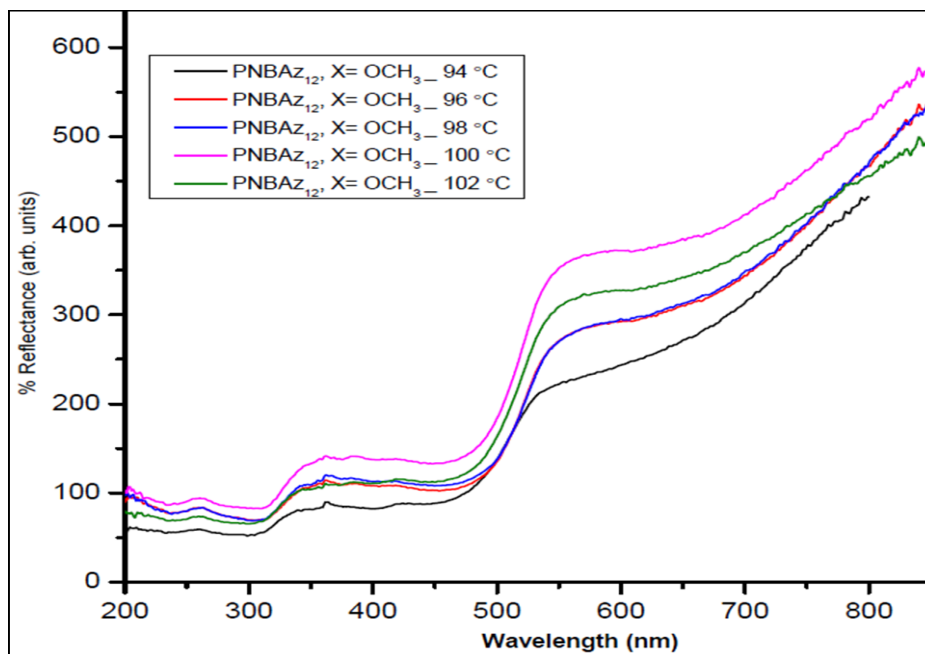


Figure S17: Light reflection of azo homopolymers (PNBAz₁₂, X=OCH₃) film samples prepared by compression molding at distinctive temperatures depending on the T_{LC}.

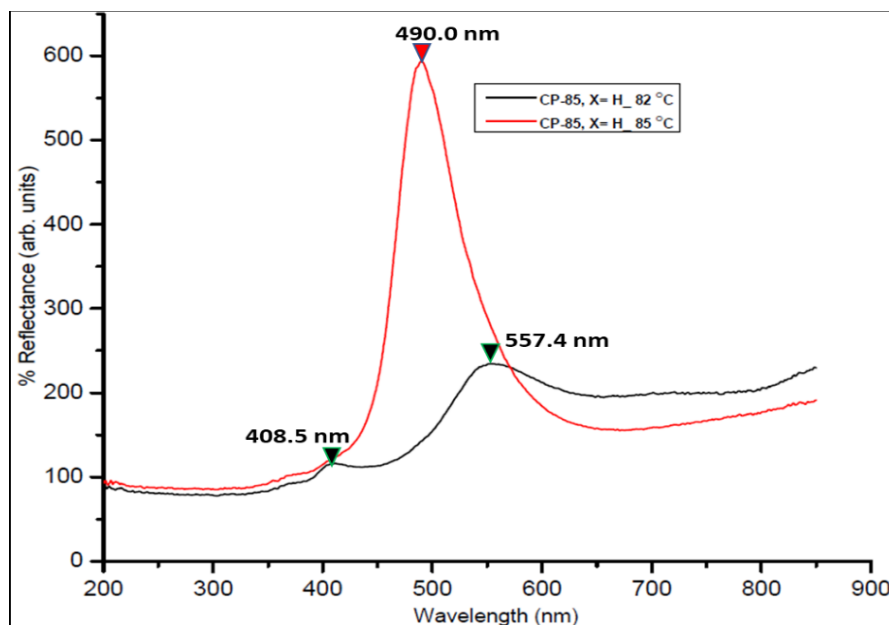


Figure S18: Light reflection of CP-85, X=H film samples prepared by compression molding at distinctive temperatures depending on the liquid crystalline transition temperatures (T_{LC1} and T_{LC2}).

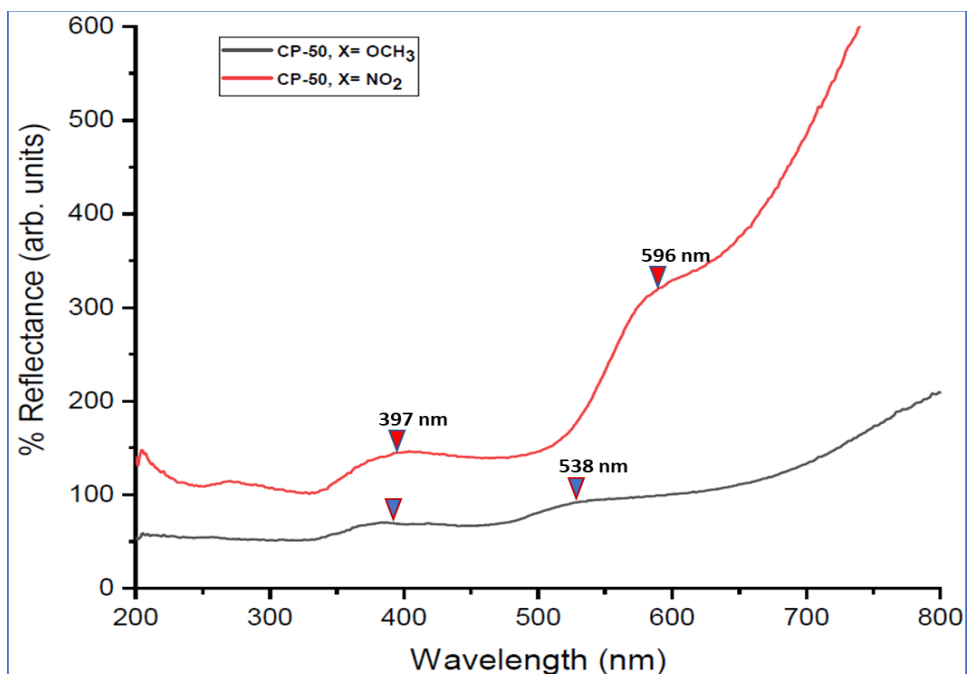


Figure S19: Light reflection of CP-50, X= OCH₃ and NO₂ film samples prepared by compression molding at distinctive temperatures depending on the liquid crystalline transition temperatures (T_{LC}).

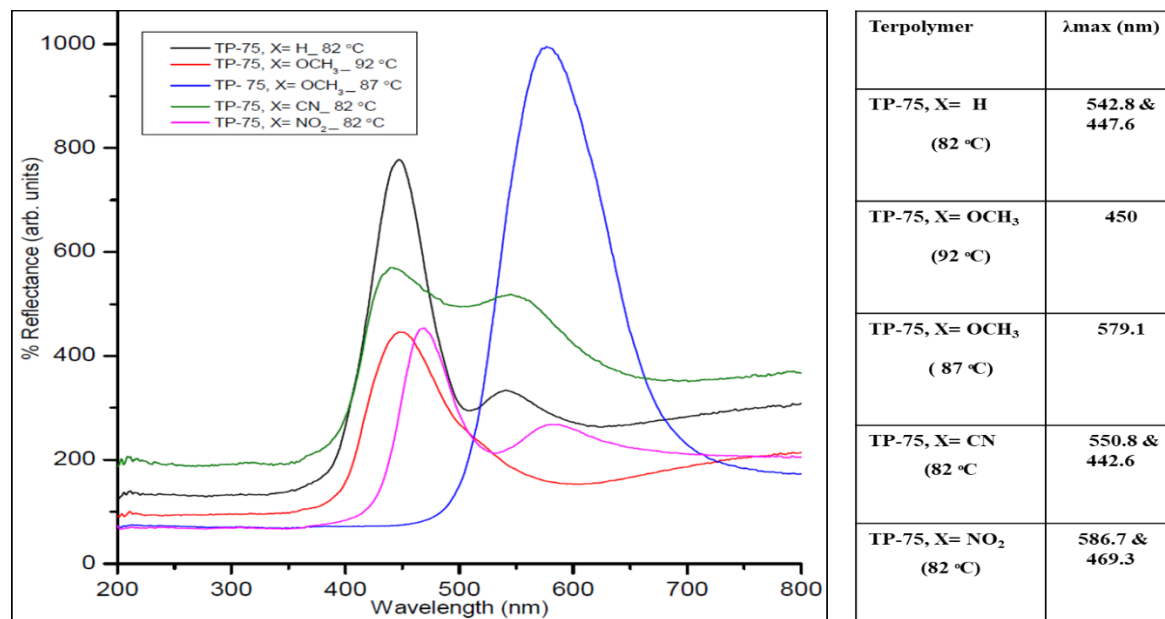


Figure S20: Light reflection of TP-75 (X=H, NO₂, CN and OCH₃) film samples prepared by compression molding at distinctive temperatures depending on the liquid crystalline transition temperature (T_{LC2}).

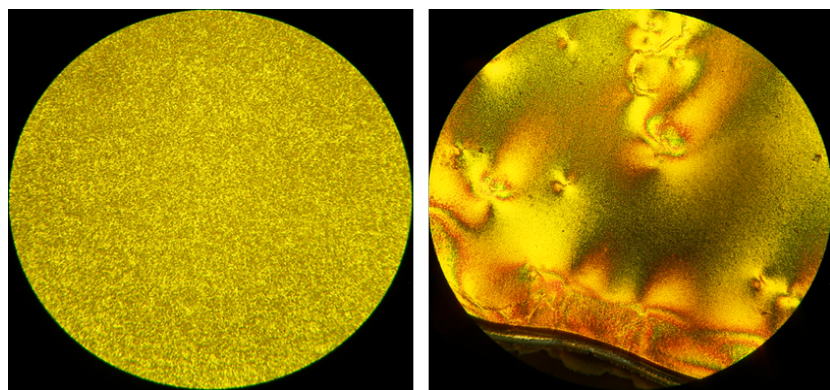


Figure S21. Cholesteric oily streak texture and smectic phase observed under POM at 85 °C and 102 °C respectively after 24 h of annealing inside hot stage for CP-85, X= OCH₃ sample.

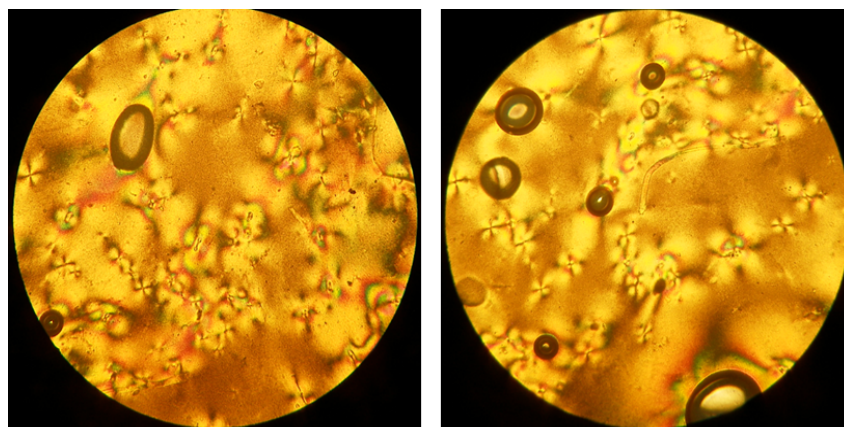


Figure S22. Smectic phase and cholesteric oily streak observed under POM at 85 °C and 96 °C respectively after 24 h of annealing inside hot stage for TP-75, X= CN sample.

References

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