ELECTRONIC SUPPLEMENTARY INFORMATION

Main-Chain Liquid Crystalline Polymers bearing Periodically Grafted Folding Elements

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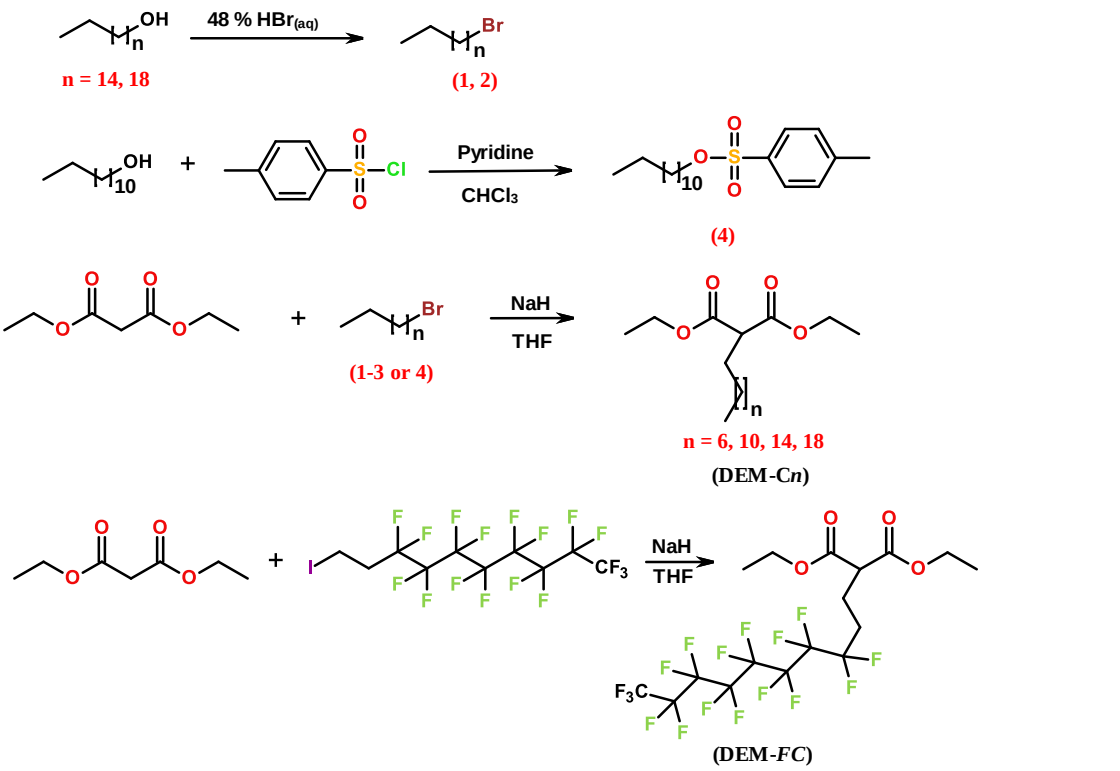
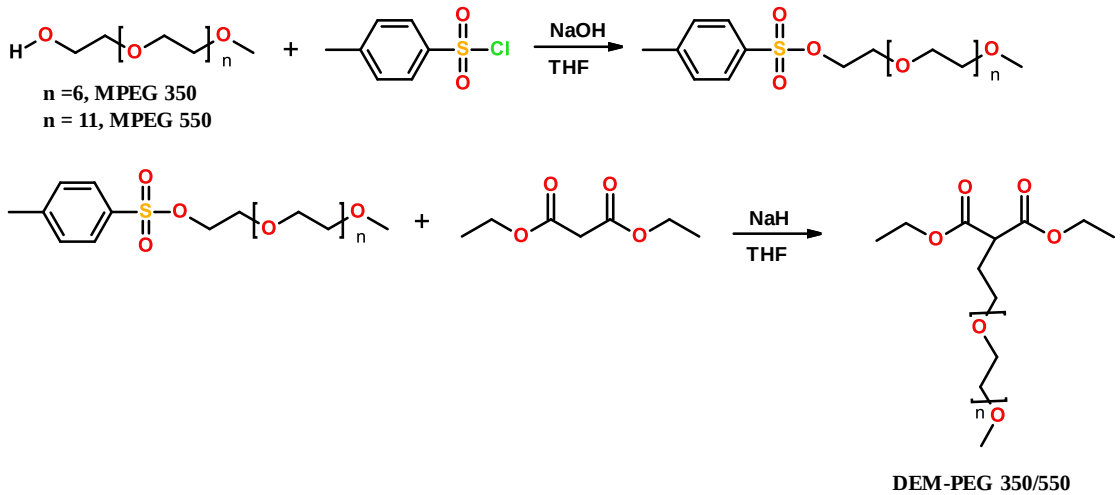
Table of contents

Synthesis of intermediates and monomers*



*1-Bromooctane (3) was used as received.



1-Bromoeicosane (2)

10.0 g of 1-Eicosanol was heated under reflux with 100 ml of 48 % $HBr_{(aq.)}$ for 24 h. After cooling to room temperature, the reaction mixture was extracted with $CHCl_3$ and the combined $CHCl_3$ layer was washed with aqueous $NaHCO_3$ solution followed by brine solution. This was then passed through anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. After drying in vacuo, the product was obtained as an off-white color solid in 99 % yield (12.01 g).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.39 (t, 2H, -C**H$_2$**Br), 1.82 (m, 2H, -C**H$_2$**CH_2Br), 1.25-1.42 (m, 34H, -(C**H$_2$**)$_{17}$$CH_3$), 0.86 (t, 3H, -$CH_2$C**H$_3$**)

1-Bromohexadecane (1)

This was prepared in a similar way as for **(2)** using cetyl alcohol. The crude product was distilled in Kugelrohr apparatus at 150 ^oC (< 1 Torr) to afford the product as oily liquid in 93 % yield.

Dodecyl-4-methylbenzenesulfonate or lauryl tosylate (4)

Dodecan-1-ol (10.0 g, 53.67 mmol) was dissolved in 50 ml of $CHCl_3$ and cooled in an ice-water bath. Pyridine (8.50 g, 107.34 mmol) was added followed by slow addition of tosyl chloride (20.46 g, 107.34 mmol) dissolved in 70 ml of $CHCl_3$. After 24 h of continuous stirring, the reaction was stopped, and excess amount of diethyl ether and water were added to the reaction mixture. The organic layer was washed successively with 2N HCl, 5% $NaHCO_{3(aq.)}$, and water. The organic extract was then passed through anhydrous Na_2SO_4, followed by solvent removal under reduced pressure. The crude tosylate was dissolved again in 60 ml of THF and treated with $NaOH_{(aq.)}$ solution to convert the unreacted tosyl chloride to tosylic acid. The solvent was then removed, and diethyl ether was added followed by filtration to remove the insoluble materials. After solvent removal, the product was obtained as deep orange color oil by distilling off the contaminant. The product was obtained in 79 % yield (14.47 g)

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.78 (d, 2H,- Ar**H**), 7.33 (d, 2H, -Ar**H**), 3.99 (t, 3H, -$ArSO_3C$**H$_2$**-), 2.44 (s, 1H, -ArC**H$_3$**), 1.60 (m, 2H, - $ArSO_3CH_2C$**H$_2$-**), 1.21-1.29 (m, 18, -C**H$_2$**-), 0.86 (t, 3H, - CH_2C**H$_3$**)

Diethyl 2-dodecylmalonate (DEM-C_{12})

1.77 g of Sodium hydride (60 wt. % in mineral oil, 44.06 mmol) was added to 50 ml of freshly dried THF, 14.11 g (88.11 mmol) of diethylmalonate was added dropwise to the reaction mixture kept in ice-bath. The mixture was stirred for 2 h in ice-cold condition, after which 10.00 g (29.37 mmol) of dodecyl-4-methylbenzenesulfonate (or lauryl tosylate) along with catalytic amount of KI was added dropwise to the reaction mixture maintained in ice-cold condition. The reaction mixture was heated under reflux for 36 h. After cooling to room temperature, THF was removed using rotary evaporator and the product was extracted with water and ethyl acetate. The combined organic extract was washed with brine solution, passed through anhydrous Na_2SO_4, concentrated under reduced pressure and dried in vacuo. The excess DEM was distilled out of the crude product using Kugelrohr apparatus to afford the product in 52 % yield (4.99 g).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 4.16 (q, 4H, -OC**H$_2$**CH_3), 3.29 (t, 1H, -OCOC**H**COO-), 1.87 (q, 2H, - OCOCH(C**H$_2$**)COO-), 1.24-1.30 (m, 26H, C**H$_3$**OCOCH(C**H$_2$**)$_{10}$-), 0.86 (t, 3H, -CH_2C**H$_3$**)

Synthesis of MPEG-550 Derivatized DEM (DEM-*PEG 550*)

To obtain this, MPEG 550 tosylate was first prepared as follow. 10.10 g (18.36 mmol) of PEG 550 monomethyl ether (MPEG 550) was dissolved in 50 ml of THF, to this solution was added 2.20 g (55.08 mmol) of NaOH taken in 10 ml of water. The reaction mixture was placed in an ice-bath and 5.25 g (27.54 mmol) of tosyl chloride dissolved in 20 ml of THF was added dropwise to it. The reaction mixture was left to warm up to ambient temperature and stirred overnight. The organic layer was separated, passed through anhydrous Na_2SO_4, followed by solvent removal under reduced pressure. The product was then extracted into diethyl ether and after solvent removal, the product was obtained as light-yellow oil in 97 % yield (12.75 g)

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.78 (d, 2H, -OSO_2Ar**H**CH_3), 7.32 (d, 2H, -OSO_2Ar**H**CH_3), 4.14 (t, 2H,-CH_2C**H$_2$**OSO_2ArCH_3), 3.57-3.65 (m, 44H,- OC**H$_2$**C**H$_2$**O-), 3.37 (s, 3H, -OC**H$_3$**), 2.44 (s, 3H, -OSO_2ArC**H$_3$**)

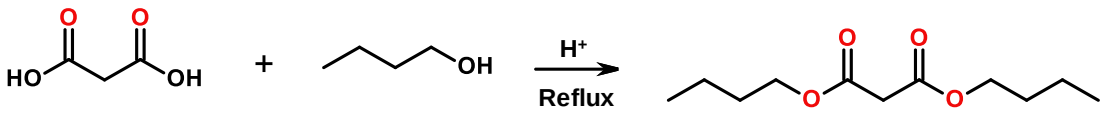
0.50 g of Sodium hydride (60 wt. % in mineral oil, 12.06 mmol) was added to 40 ml of freshly dried THF, 4.10 g (25.60 mmol) of diethylmalonate was added dropwise to the reaction mixture kept in ice-bath. The mixture was stirred for 2 h in ice-cold condition, after which 6.00 g (8.40 mmol) of MPEG 550 tosylate along with catalytic amount of KI was added dropwise to the reaction

mixture maintained in ice-cold condition. The reaction mixture was heated under reflux for 36 h and the progress of the reaction was monitored by TLC. After cooling to room temperature, THF was removed using rotary evaporator and the product was extracted with water and ethyl acetate. The combined organic extract was washed with brine solution, passed through anhydrous Na_2SO_4, concentrated under reduced pressure and dried in vacuo. The excess DEM was distilled out of the crude product using Kugelrohr apparatus at 210 ^oC under vacuum to afford the product as brown color oil in 73 % yield (4.29 g). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 4.14 (q, 4H, -CH(COOC**H**$_2$CH$_3$)$_2$), 3.49-3.64 (m, 49H, -OCOC**H**COO-,(OC**H**$_2$C**H**$_2$)$_{12}$), 3.36 (s, 3H, -(OCH$_2$CH$_2$)$_{12}$C**H**$_3$), 1.23 (t, 6H, -CH(COOCH$_2$C**H**$_3$)$_2$)

MPEG 350 Tosylate and DEM-*PEG 350* monomer were prepared using the same procedure as for MPEG 550 Tosylate and DEM-*PEG 550* monomer, and obtained in 90 % and 97 % yield, respectively.

Diethyl 2-octyl malonate (DEM-C$_8$), diethyl 2-hexadecyl malonate (DEM-C$_{16}$), diethyl 2-eicosyl malonate (DEM-C$_{20}$), and **diethyl 2-1H, 1H, 2H, 2H-perfluorodecyl malonate (DEM-*FC*)** were synthesized in the same way as for **(DEM-C$_{12}$)** . The monomers were obtained in the following yield 71 %, 88 %, 91 %, and 48 %, respectively.

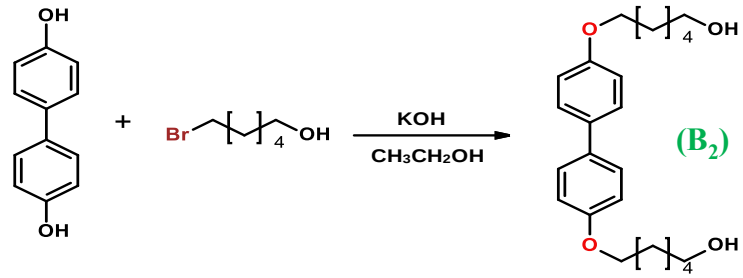
Dibutyl malonate for model polymer



Mixture of 5 g (48.05 mmol) of malonic acid, 60.12 g (811.08 mmol) of butan-1-ol and 2 ml of sulphuric acid was heated under reflux for 12 h. After cooling to room temperature, the reaction mixture was concentrated to half of its volume and then poured into ice-water. The aqueous solution was extracted with $CHCl_3$, the combined $CHCl_3$ layer was washed with sodium bicarbonate solution, passed through anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was distilled in Kugelrohr apparatus at 100 ^oC (< 1 Torr) to afford the pure product as colorless oily liquid in 69 % yield (7.16 g)

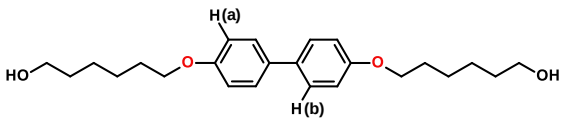
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 4.12 (m, 4H, -COOC**H$_2$**$CH_2CH_2CH_3$), 3.35 (s, 2H, -OCOC**H$_2$**COO-), 1.58 (m, 4H, - $COOCH_2C$**H$_2$**CH_2CH_3), 1.32 (m, 4H, - $COOCH_2CH_2C$**H$_2$**CH_3), 0.90 (t, 6H, - $COOCH_2CH_2CH_2C$**H$_3$**)

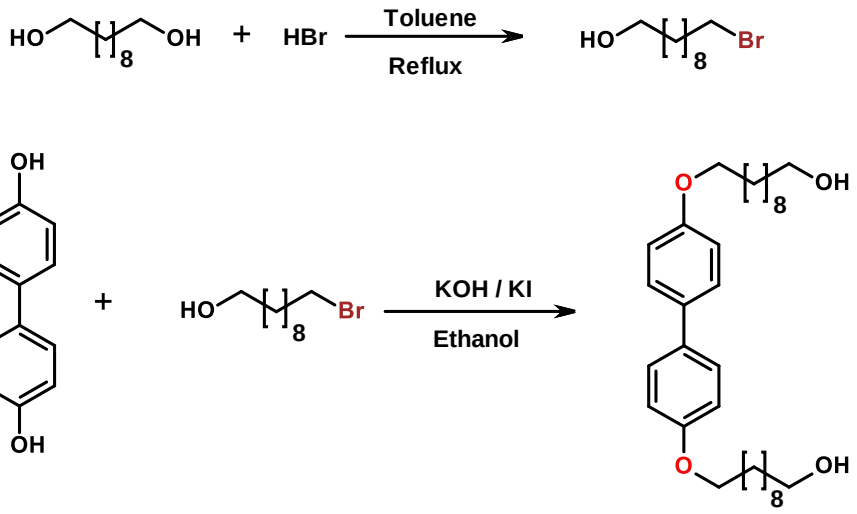
4,4′-Bis(6-hydroxyhexyloxy) biphenyl



5.0 g (26.85 mmol) of 4,4′-Dihydroxybiphenyl taken in 70 ml of degassed absolute ethanol was treated with 14.59 g (80.55 mmol) of 6-Bromohexan-1-ol, 4.52 g (80.55 mmol) of KOH and catalytic amount of KI. The mixture was heated under reflux for 48 h and the completion of reaction was confirmed by TLC. After cooling the reaction mixture to room temperature, the colorless solid obtained was suction filtered and washed with absolute ethanol. The crude product obtained was stirred with water at room temperature overnight to remove the salt formed during the reaction, the mixture was then suction filtered, rinsed with absolute ethanol and dried in the oven to a constant weight. The pure product was obtained as colorless solid in 68 % yield (7.10 g). Melting point: 173 ^{o}C (Reported: 167-170 ^{o}C).[1] The same approach was used to synthesize 4,4′-Bis(10-hydroxydecyloxy) biphenyl and obtained in 62 % yield (as shown in the scheme below).

^{1}H NMR (400 MHz, DMSO-d6, δ ppm): 7.50 (d, 4H, -Ar**H**(b)), 6.96 (d, 4H, - Ar**H**(a)), 4.37 (t, 2H, -CH_2**OH**), 3.96 (t, 4H, -C**H$_2$**OAr-ArOC**H$_2$**-), 3.38 (t, 4H, HOC**H$_2$**$(CH_2)_5$OAr-ArO$(CH_2)_5$C**H$_2$**OH), 1.70 (m, 4H, -C**H$_2$**CH_2OAr-ArOCH_2C**H$_2$**-), 1.34-1.44 (m, 12H, $HOCH_2(CH_2)_3CH_2CH_2$OAr-ArO$CH_2CH_2(CH_2)_3CH_2$OH)





10-Bromo-1-decanol

This was synthesized following the procedure reported by Chong and co-workers[2] with modification as follows: The mixture of 1,10-decane diol (10.0 g, 57.38 mmol), 48 % $HBr_{(aq.)}$ (18.0 ml, 106.73 mmol) and 200 ml of toluene was heated under reflux for 48 hour. After cooling the reaction mixture to room temperature, the two layers were separated. The organic layer was washed with water (3 x100 ml) followed by brine solution and then passed through anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and dried *in vacuo* to afford a crude product as light-yellow liquid, which after distillation using Kugelrohr apparatus at 150 ^oC (< 1 Torr) afforded the pure product as colorless liquid in 91 % yield (12.33 g).

^1H NMR (400 MHz, $CDCl_3$, δ ppm): 3.65 (t, 2H, -**C**$\mathbf{H_2}$OH), 3.42 (t, 2H, -**C**$\mathbf{H_2}$Br), 1.89 (m, 2H, -**C**$\mathbf{H_2}$$CH_2$Br), 1.60-1.30 (m, 14H, -$\mathbf{(CH_2)_7}$-)

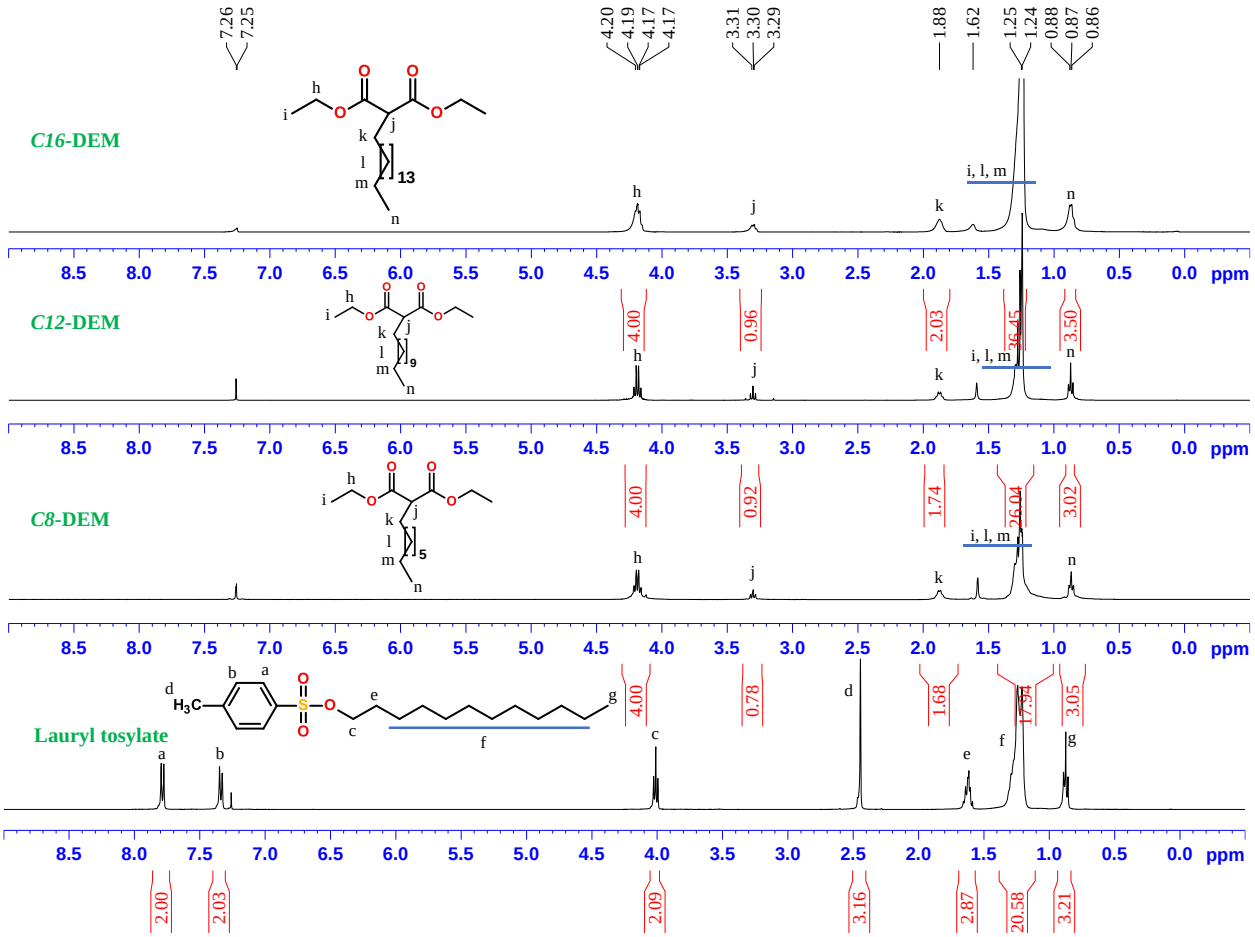


Figure S1. *Stack plot of ^{1}H NMR spectra (in $CDCl_3$) of hydrocarbon-derivatized DEM monomers and intermediate*

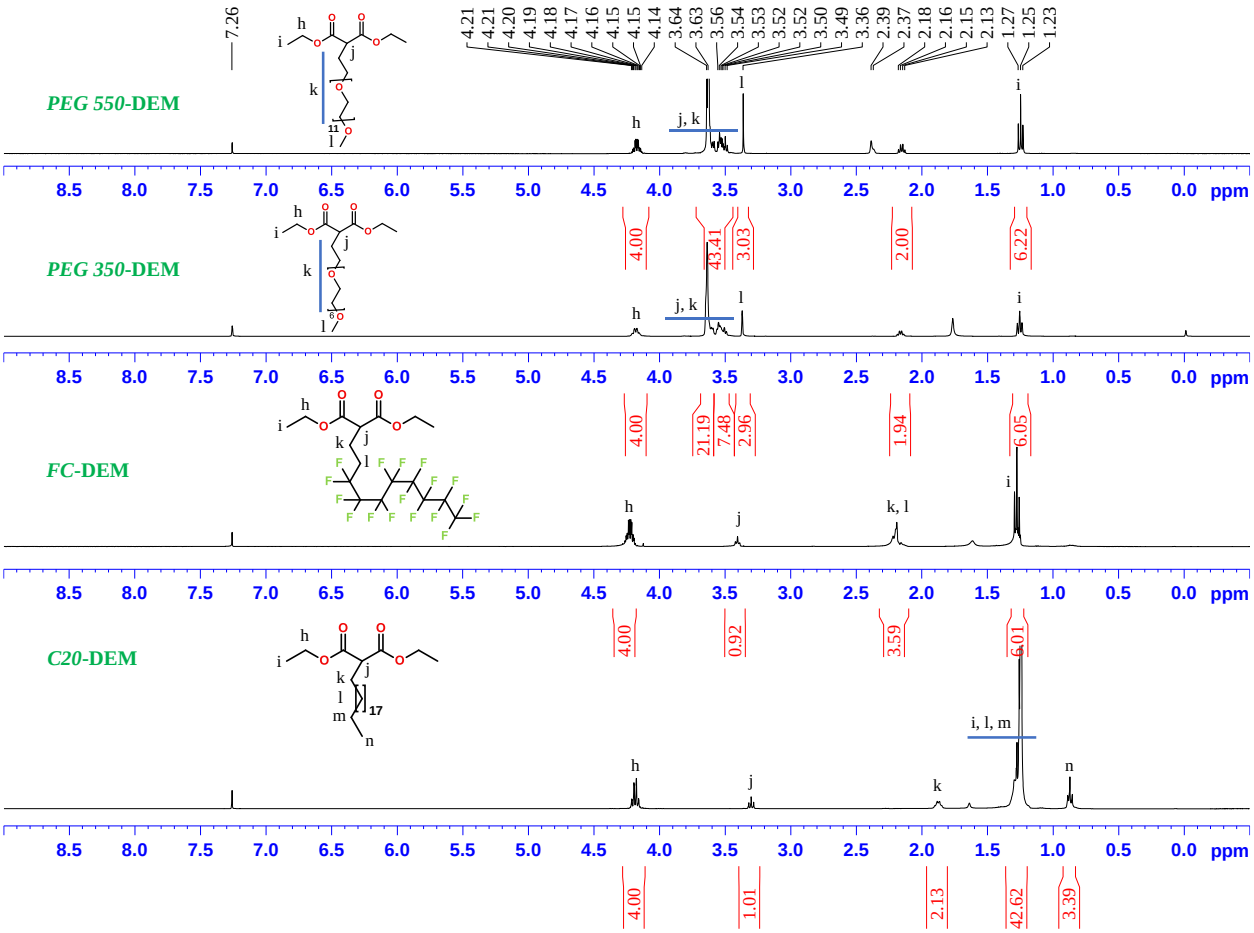


Figure S2. *Stack plot of ^{1}H NMR spectra (in $CDCl_3$) of C20, PEG, and fluorocarbon-derivatized DEM monomers*

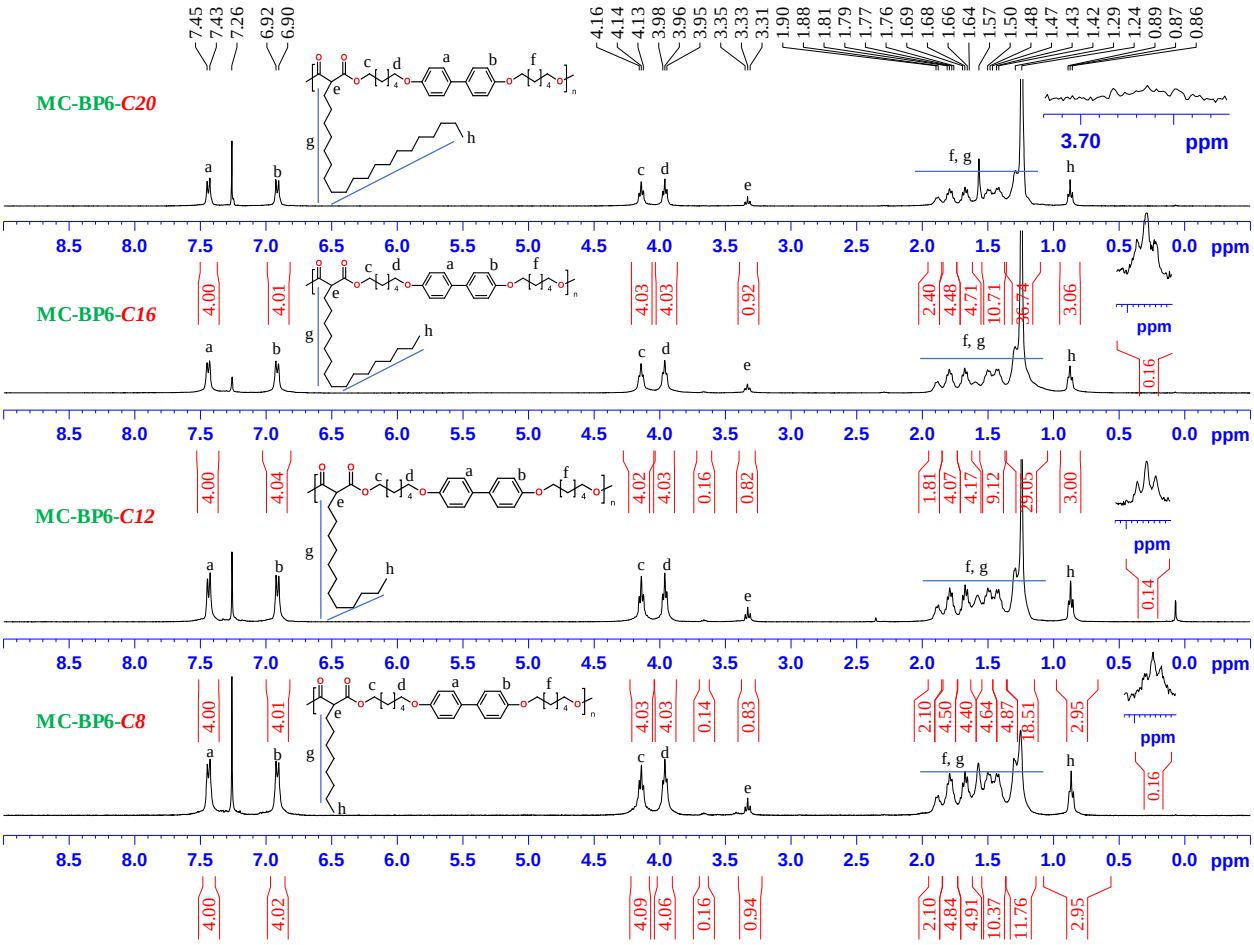


Figure S3. *Stack plot of ^{1}H NMR spectra (in $CDCl_3$) of biphenyl-based PS-MCLCPs with pendant HC (C8, C12, C16, C20) segments*

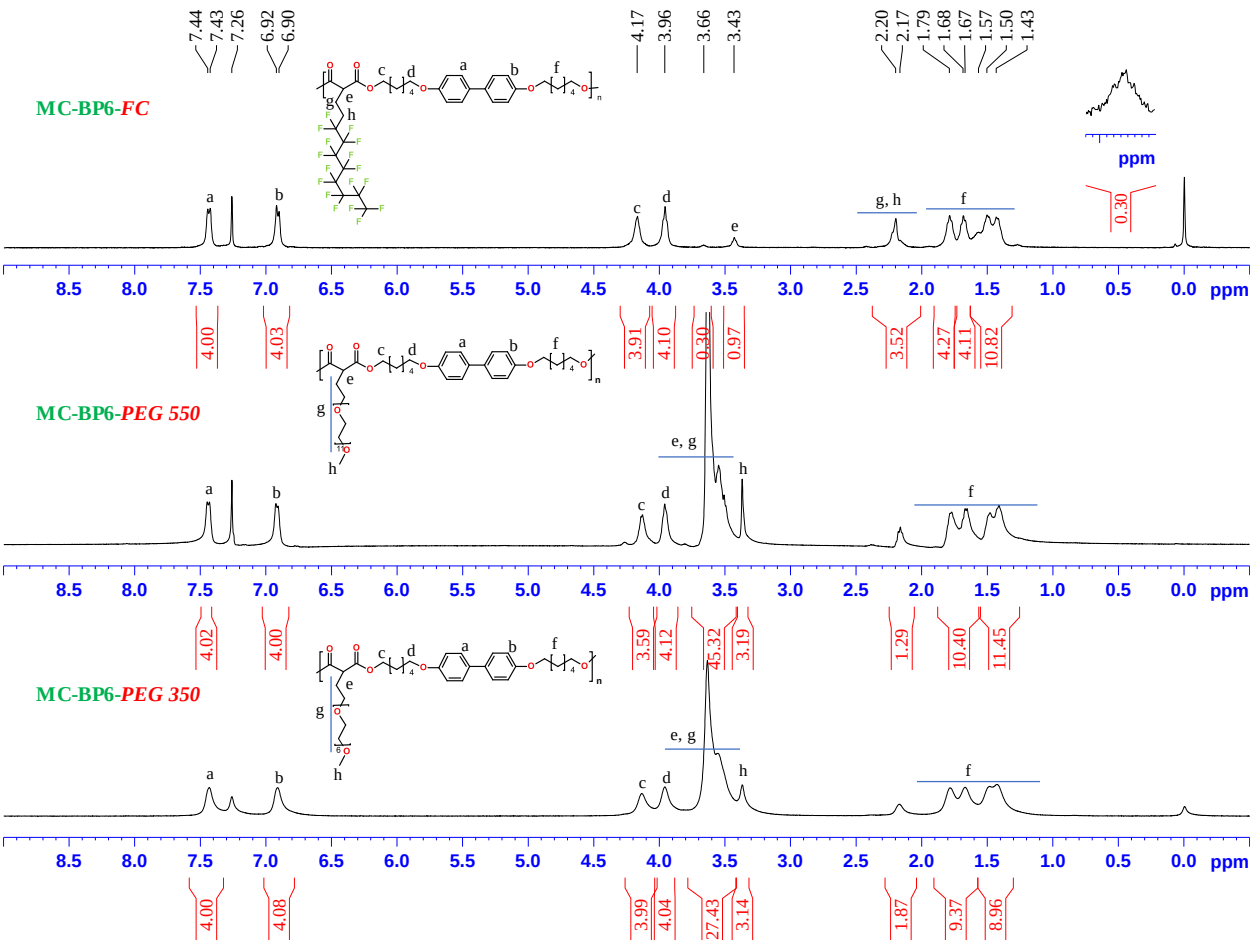


Figure S4. *Stack plot of ^{1}H NMR spectra (in $CDCl_3$) of biphenyl-based PS-MCLCPs bearing pendant PEG (350, 550) and fluorocarbon segments*

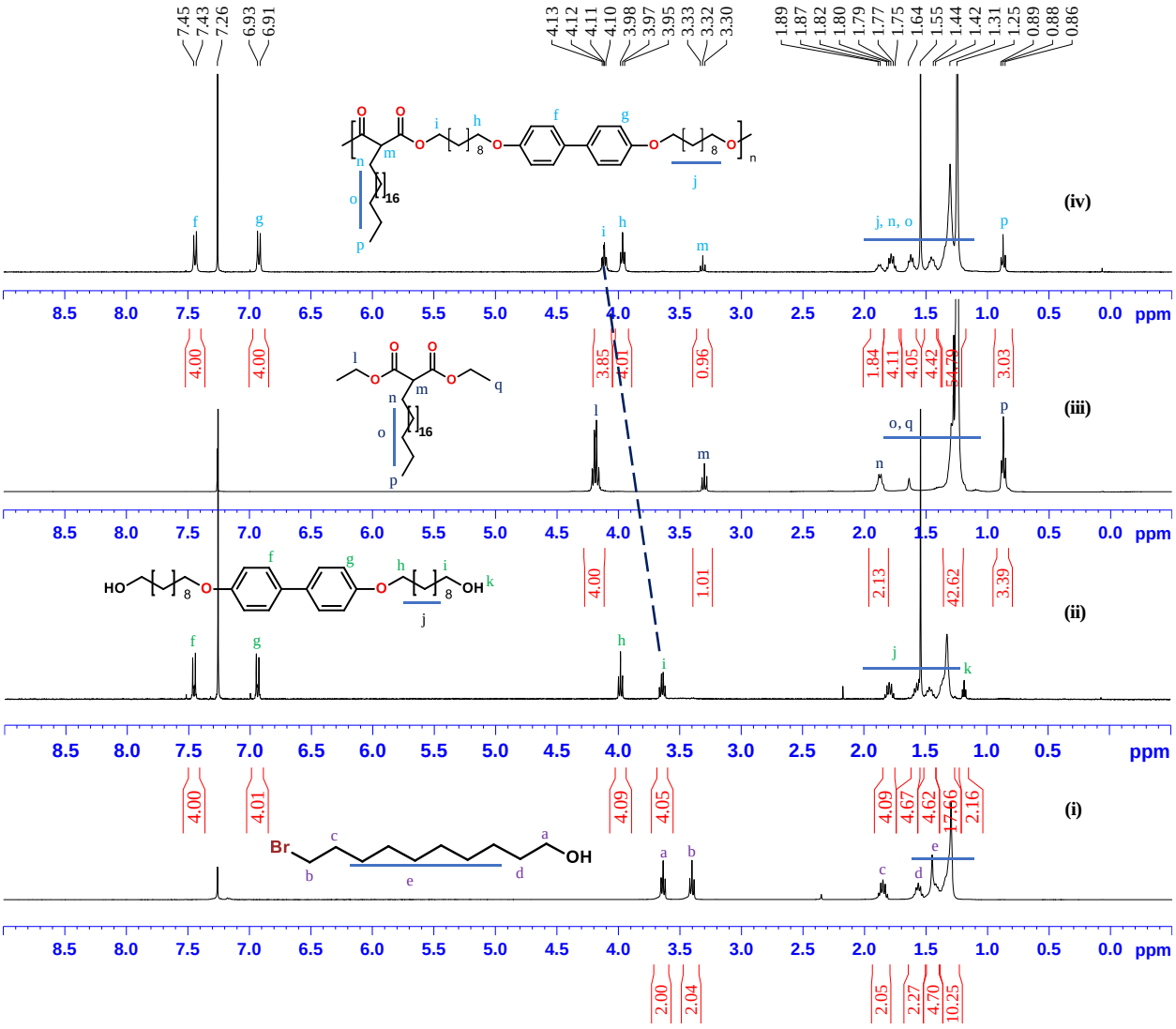


Figure S5. *Stack plot of ^{1}H NMR spectra (in $CDCl_3$) of (i)10-Bromo-1-decanol, (ii) C10-based mesogenic diol, (iii) C20-functionalized DEM and, (iv) the corresponding BP10-C20 polymer*

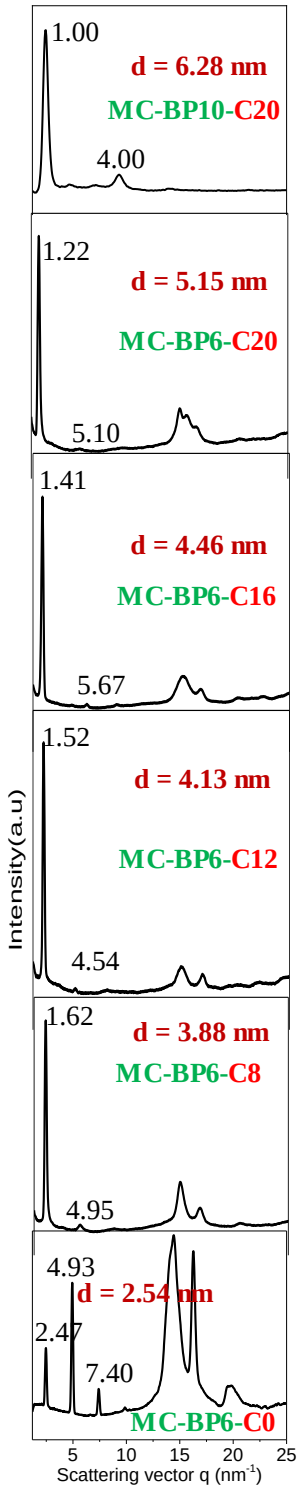


Figure S6. *X-ray scattering profiles showing the variation of d-spacing with increasing pendant alkyl chain length in biphenyl-based MCLCPs.*

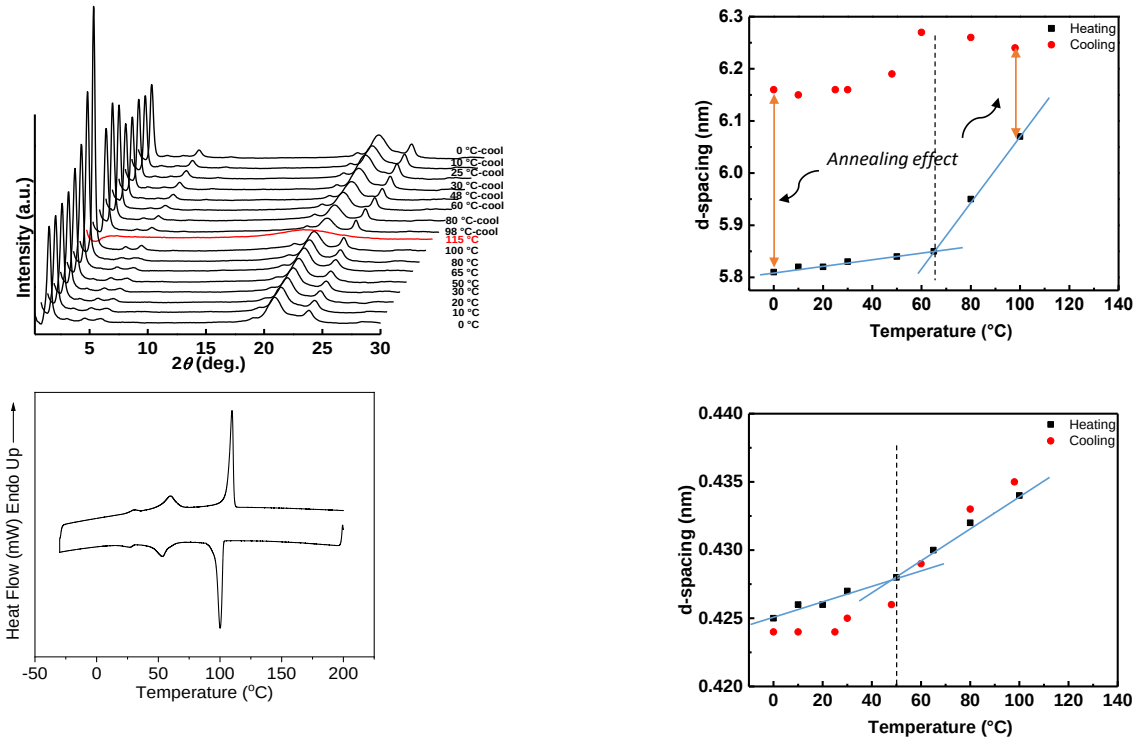


Figure S7. Plots of *d*-spacing in the small-angle and wide-angle region as a function of temperature for sample, MC-BP10-C20, revealing the nature of the crystal-crystal transition. Evidently, there is an increase in the ordering during the transition between ~ 50-60 °C, as reflected in the change the slope of the variation of *d*-spacing.

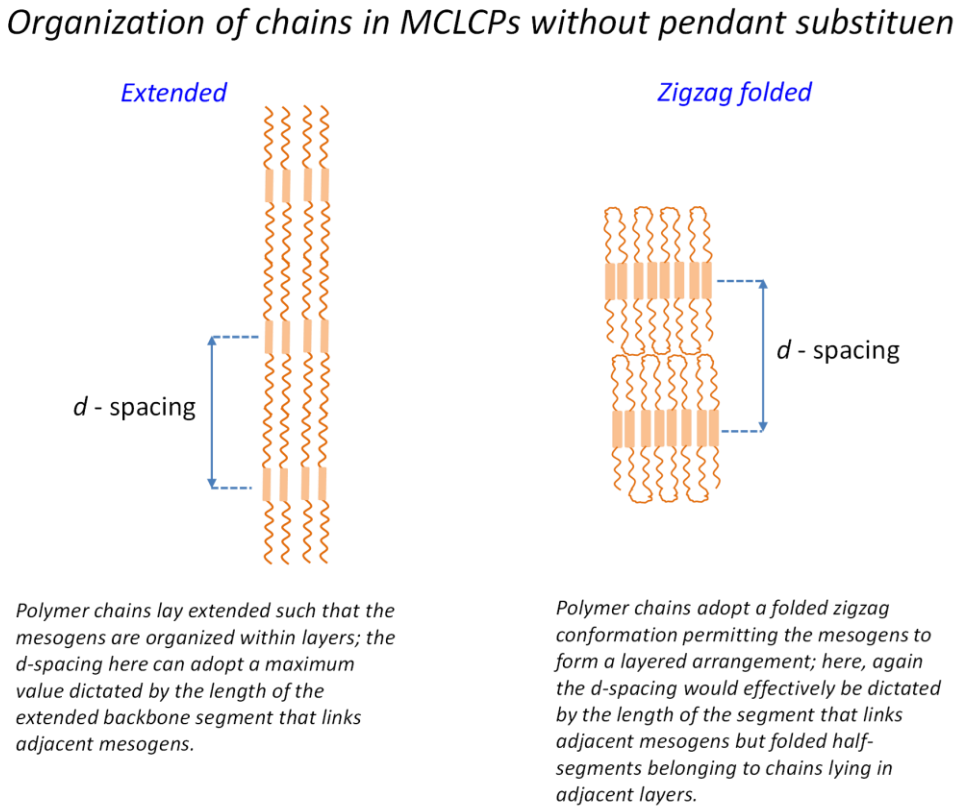


Figure S8. Schematic depiction of the two possible organization of the polymer chains in the absence of a pendant substituent, namely in the case of MC-BP6-C0.

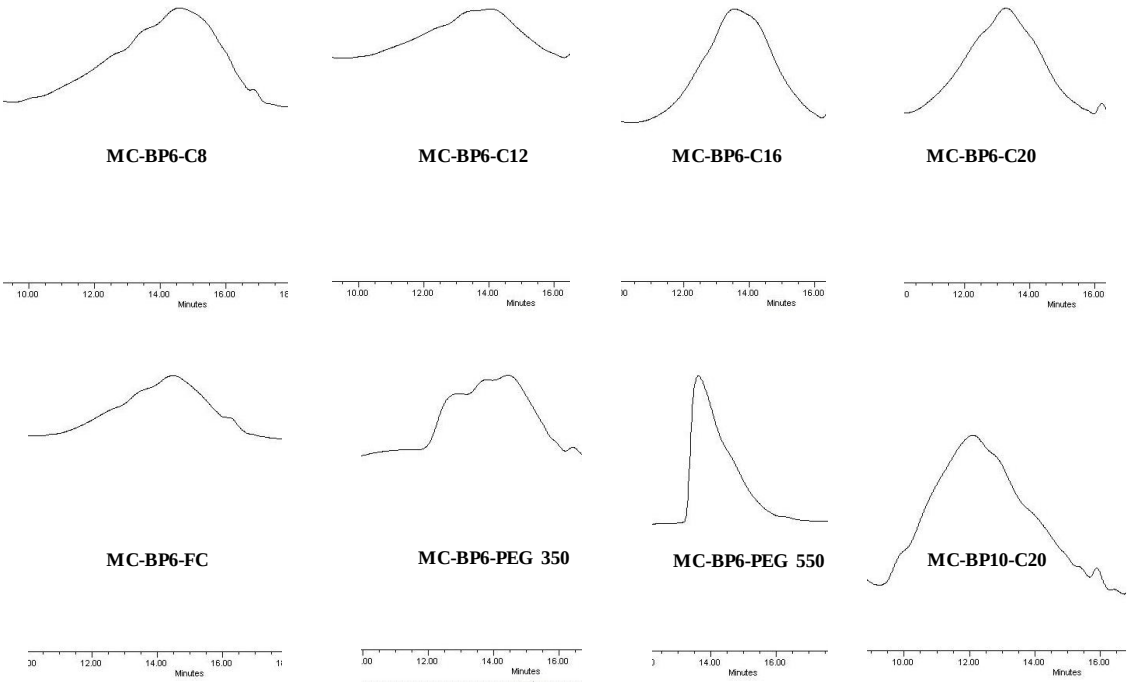


Figure S9. *GPC traces of biphenyl-based periodically grafted MCLCPs*

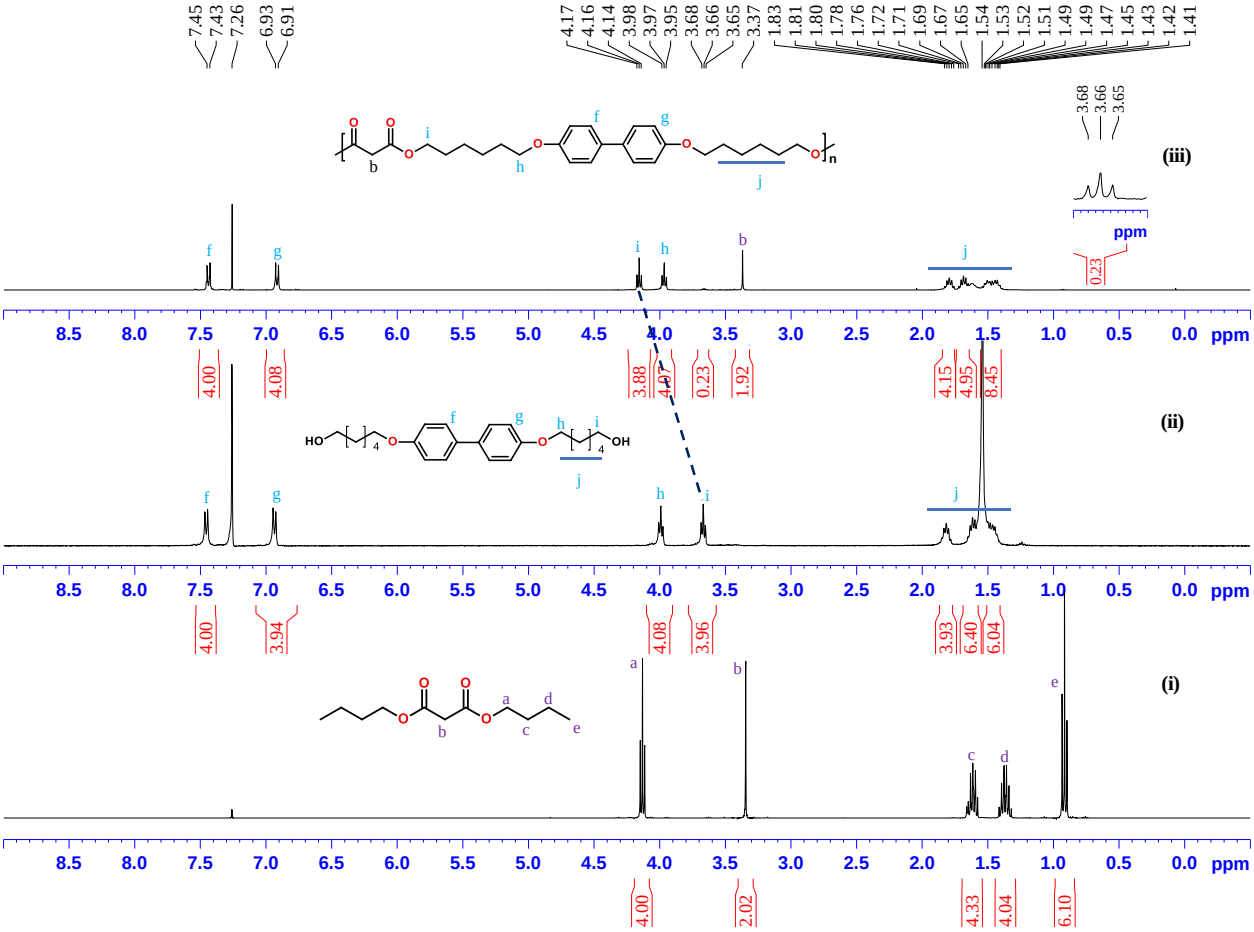


Figure S10. *Stack plot of ^{1}H NMR spectra (in $CDCl_3$) of (i)Dibutyl malonate, (ii) BP6-based mesogenic diol, (iii) corresponding BP6-based model polymer*

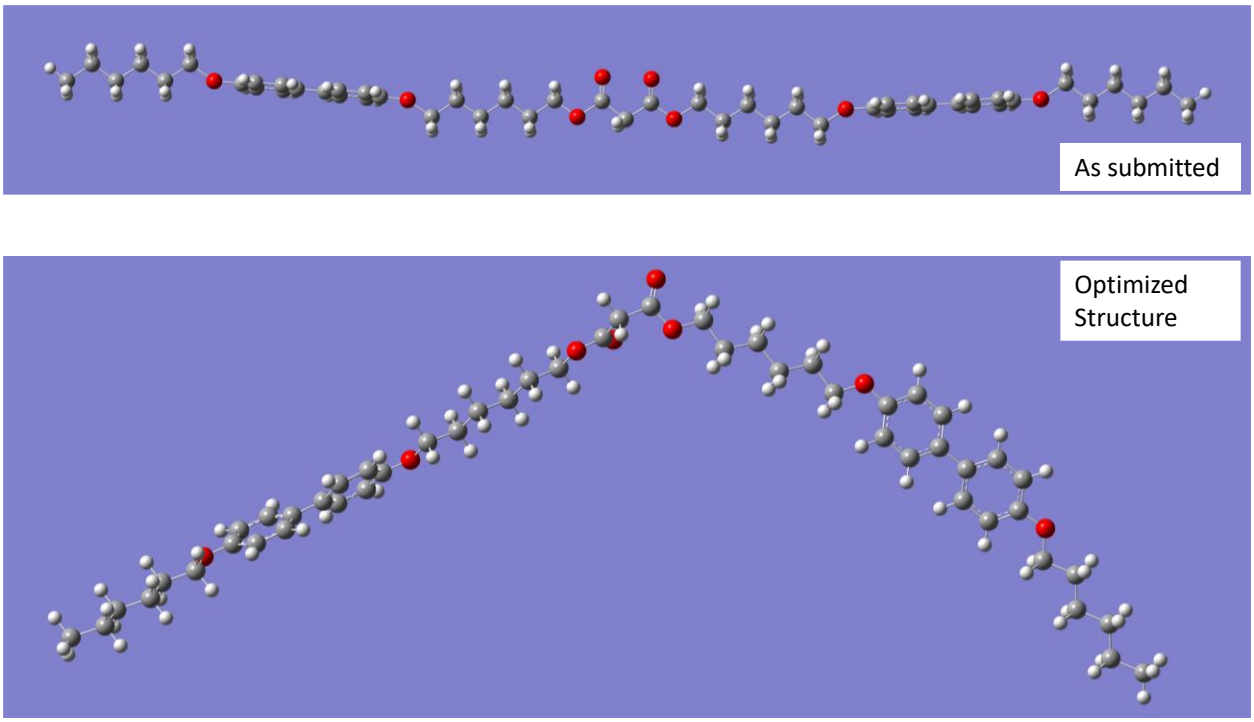


Figure S11. *Energy minimized structure of a model dimer containing two biphenyl bearing mesogenic segments linked to a central malonate unit. The top structure was submitted, and the structure below is the energy-minimized structure using Gaussian 09.*