Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPLEMENTARY INFORMATION

De-symmetrizing periodically grafted amphiphilic copolymers: Design, synthesis and generation of *Janus* folded chains

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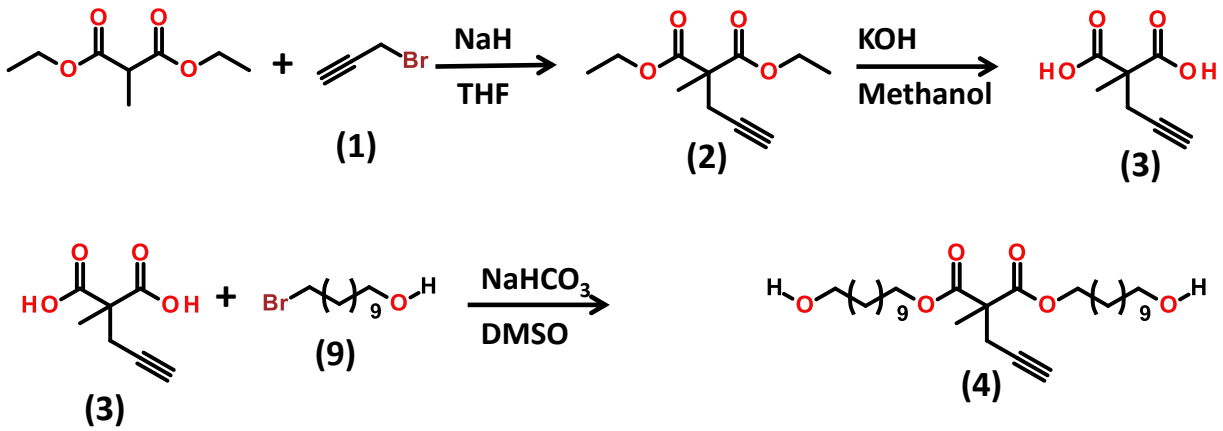


Scheme 1: Synthesis scheme of propargyl bearing diol monomer (**I**)

Propargyl bromide (1)

50 mL propargyl alcohol (866.9 mmol) and 10 mL pyridine (124.1 mmol) were taken in 250 mL round bottom flask. The mixture was placed on an ice-bath. 30 mL (315.8 mmol) phosphorous tribromide was added dropwise to the mixture while maintaining the temperature at 0 °C. The mixture was stirred overnight at room temperature. Finally, propargyl bromide was selectively distilled under reduced pressure at 80 °C with 64 % (66.5 g) yield. Product was stored in freezer.

^{1}H NMR (δ, $CDCl_3$): 3.88 (d, 2H, Br**CH_2**CCH); 2.52 (t, 1H, $BrCH_2C$**CH**)

Diethyl-2-methyl-2propargylmalonate (2)

5.17 g sodium hydride (60 wt. % in mineral oil, 129.3 mmol) was taken in a 250 mL round bottom flask fitted with calcium chloride guard tube and 150 mL freshly dried THF was added to it. 15 g (86.1 mmol) diethyl methylmalonate was added dropwise to the mixture. The contents were stirred continuously at 0 ˚C for 2 h. 15.4 g freshly prepared propargyl bromide (129.3 mmol) was added dropwise, while maintaining the temperature at 0 ˚C. The reaction was continued at room temperature for 24 h. Subsequently, THF was removed by rotary evaporator and 150 mL ethyl acetate was added to it. The organic layer was washed twice (2 x 100 mL) with water. Removal of organic solvent resulted crude product, which was further purified to a colorless liquid by Kugelrohr distillation at 80 ˚C under reduced pressure with a yield of 13.2 g product (72 % yield).

^{1}H NMR (δ, $CDCl_3$): 4.21 (m, 4H, -**CH_2**CH_3); 2.78 (d, 2H, -**CH_2**CCH); 2.01 (t, 1H, -CH_2C**CH**); 1.54 (s, 3H, -**CH_3**); 1.25 (t, 6H, -CH_2**CH_3**)

2-Methyl-2-propargylmalonic acid (3)

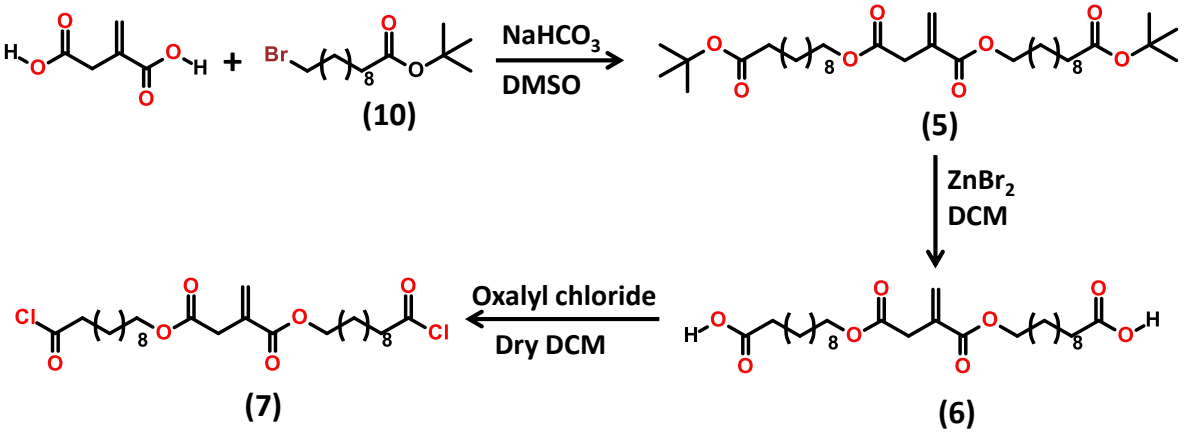
16.4 g (292.3 mmol) potassium hydroxide was taken in 250 mL round bottom flask and dissolved in minimum amount of water. 10 g (47.1 mmol) diethyl-2-methyl-2-propargylmalonate (2) was added to solution along with 200 mL of methanol. The contents were stirred at 50 ^{o}C for 24 h. Subsequently, 100 mL water was added to it and methanol was removed by rotary evaporation. pH of the solution was brought down to 3-4 by HCl and product was extracted in 150 mL (3 x 50 mL) ethyl acetate. The organic solvent was dried over sodium sulfate. Finally, removal of organic solvent under reduced pressure resulted 6.7 g solid product with 91 % yield.

^{1}H NMR (δ, DMSO-d6): 12.95 (s, 2H, -CO_2**H**); 2.87 (t, 1H, -CH_2C**CH**); 2.62 (d, 2H, -**CH_2**CCH); 1.37 (s, 3H, -**CH_3**)

Di (ω-hydroxyundecanyl) 2- methyl-2- propargylmalonate (4)

3.4 g (21.7 mmol) 2-methyl-2propargylmalonic acid (3) and 9.12 g (108.6 mmol) sodium bicarbonate were taken in 100 mL DMSO. 12 g (47.8 mmol) 11-bromoundecanol along with catalytic amount potassium iodide were added to it. The resulted reaction mixture was stirred at 40 ˚C for 4 days. 150 mL ethyl acetate was added to it and DSMO was extracted in 450 mL (3 x 150 mL) 1 wt. % aqueous solution of lithium chloride. Organic layer was dried over sodium sulfate and concentrated to yield final product. The crude product was first recrystallized from cold methanol and subsequently, purified by column chromatography. Product was obtained at 25 % eluent composition of ethylacetate/light petroleum ether with 36 % yield (3.88 g)

^{1}H NMR (δ, $CDCl_3$): 4.13 {(m, 4H, -CO_2**CH_2**(CH_2)$_9$$CH_2$OH)}; 3.63 {(t, 4H, HO**$CH_2$**($CH_2$)$_9$$CH_2$-)}; 2.78 (d, 2H, -**$CH_2$**CCH); 2.01 (t, 1H, -$CH_2$C**CH**); 1.54 (s, 3H, -**CH_3**)



Scheme 2: Synthesis scheme of itaconate bearing diacid monomer (**II**)

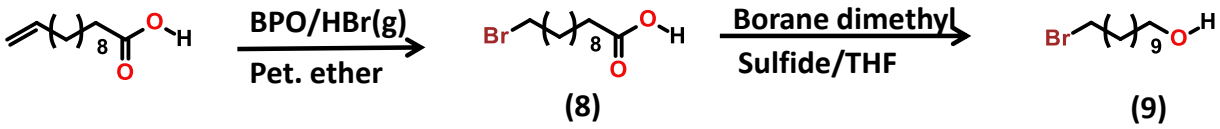
Di (ω-t-butylundecanoate) itaconate (5)

2.4 g (18.4 mmol) itaconic acid and 7.75 g (92.3 mmol) sodium bicarbonate were taken in 100 mL DMSO. To the contents, 13 g (40.4 mmol) 11-bromo-t-butylundecanoate and catalytic amount potassium iodide were added and stirred at 40 ˚C for 4 days. 150 mL ethyl acetate was added to it and DSMO was removed by extraction with 450 mL (3 x 150mL) 1 wt. % aqueous solution of lithium chloride. Ethyl acetate layer was dried over sodium sulfate and concentrated to yield 7 g liquid product 5 with 62 % yield. Compound 5 was used for next step of conversion without further purification.

Di (ω-carboxyundecanyl) itaconate (6)

8 g (13.1 mmol) of compound 5 and 14.5 g (64.4 mmol) zinc bromide were taken in 250 mL round bottom flask fitted with calcium chloride guard tube. 100 mL dry DCM was added to the mixture and stirred at room temperature for 24 h. Organic solvent containing product was washed twice (2 x 100 mL) with water and dried over sodium sulfate. Removal of DCM under reduced pressure yielded solid product which was purified further by reprecipitation form light petroleum ether with 42 % (2.77 g) yield.

^{1}H NMR (δ, $CDCl_3$): 6.31 (s, 1H, **H_2**C=C-); 5.68 (s, 1H, **H_2**C=C-); 4.13 {(t, 2H, -OCO**CH_2** $(CH_2)_8$ CH_2CO_2H)}; 4.07 {(t, 2H, -OCO**CH_2**$(CH_2)_8CH_2CO_2H$)}; 3.31 (s, 2H, -OCO**CH_2**C(=CH_2)CO_2-); 2.33{(t, 4H,-OCO$CH_2(CH_2)_8$**CH_2**CO_2H)}



(8) **(9)**

Scheme 3: Synthesis scheme of 11-bromo undecanol (**9**)

11-Bromonundecanoic acid (8)

20 g (108.5 mmol) 10-undecenoic acid and 6 g (75 wt. % in water, 18.5 mmol) benzoyl peroxide were taken in 500 mL RB. containing 250 mL light petroleum ether. HBr gas, instantly generated by adding sulfuric acid dropwise to sodium bromide, was purged thorough the solution for 1 h at room temperature. The contents were continued stirring at room temperature for 24h. The

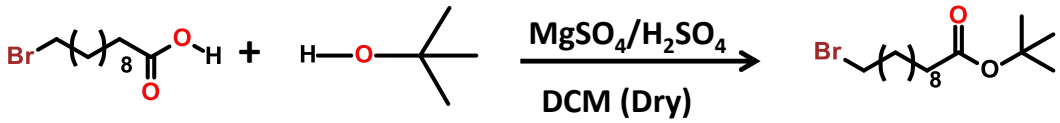
solution was decanted to get rid of solid residue. Product was obtained by concentrating the solution, which was reprecipitated thrice from light petroleum ether at 0 ˚C to afford white solid product with 36 % (10.5 g) yield.

^{1}H NMR (δ, $CDCl_3$): 6.36 {(s, 1H, $BrCH_2(CH_2)_8CH_2CO_2\mathbf{H}$)}; 3.40 {(t, 2H, $Br\mathbf{CH_2}(CH_2)_8CH_2CO_2H$)}; 2.35 {(t, 2H, $BrCH_2(CH_2)_8\mathbf{CH_2}CO_2H$)}; 1.85 {(m, 2H, $BrCH_2\mathbf{CH_2}(CH_2)_7CH_2CO_2H$)}; 1.63 {(m, 2H, $BrCH_2(CH_2)_8\mathbf{CH_2}CH_2CO_2H$)}

11-Bromo-1-undecanol (9)

18 g (67.8 mmol) 11-bromoundecanoic acid (8) was taken in 500 mL double neck round bottom flask along with 200 mL THF. The solution was purged with nitrogen gas for 10 min. 5.62 g (74 mmol) borane dimethylsulfide was added dropwise to the solution at room temperature with continuous nitrogen purging. The reaction mixture was stirred at room temperature for overnight. 50 mL 4 (N) HCl was added to the mixture slowly and stirred for 2 h. Subsequently, THF was removed by rotary evaporation. 200 mL chloroform was added to it and the organic solvent containing product was washed twice (2 x 100 mL) with water. Finally, organic layer was passed through Na_2SO_4 and concentrated to yield 14.3 g (84 % yield) product.

^{1}H NMR (δ, $CDCl_3$): 3.63 {t, 2H, $HO\mathbf{CH_2}CH_2(CH_2)_7CH_2CH_2Br$}; 3.40 {t, 2H, $HOCH_2CH_2(CH_2)_7CH_2$ - $\mathbf{CH_2}Br$}; 1.85 {m, 2H, $HOCH_2CH_2(CH_2)_7\mathbf{CH_2}CH_2Br$}; 1.56 {m, 2H, $HOCH_2\mathbf{CH_2}(CH_2)_7CH_2CH_2Br$}



(8) **(10)**

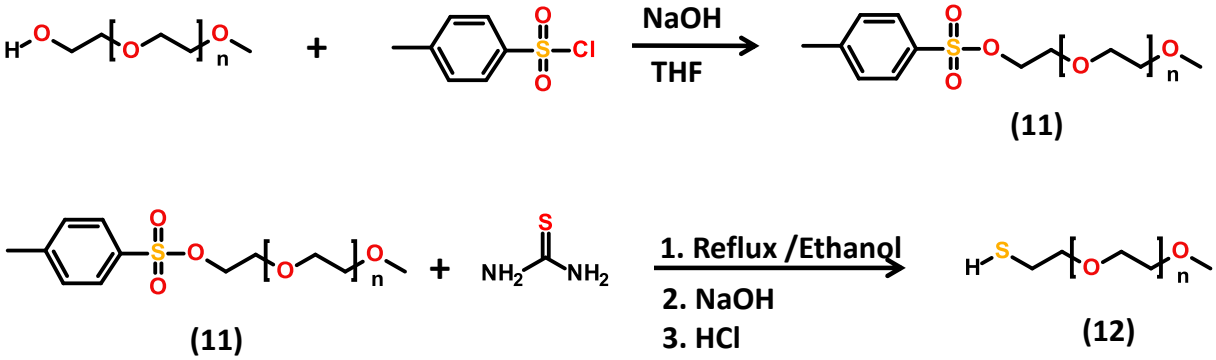
Scheme 4: Synthetic scheme of preparation of 11-bromo-t-butylundecanoate (10)

11-Bromo-t-butylundecanoate (10)

11-Bromo-t-butylundecanoate was prepared following the synthetic procedure reported by Wright et. all.[1] A 500 mL round bottom flask containing 250 mL dry DCM was charged with 29 g (240.9 mmol) anhydrous magnesium sulfate and 3.4 mL (63.8 mmol) sulfuric acid was added to it. The contents were stirred rigorously for 15 min, subsequently 16 g (60.3 mmol) 11-bromo-undecanoic acid (8) was added to it. 22.5 mL (237.1 momol) t-butanol was added at the end. Resulting mixture was air tighten and stirred at room temperature for 48 h. Saturated aqueous solution of sodium bicarbonate was added and stirred until no solid residue was left. Organic and aqueous parts were separated, and organic portion was washed twice (2 x 150 mL) with water. The crude product was purified by column chromatography where product obtained at 1.5 %

ethyl acetate /petroleum ether eluent. The final product obtained in the form of colorless liquid with 66 % (12.8 g) yield.

^{1}H NMR (δ, $CDCl_3$): 3.40 {(t, 2H, $(CH_3)_3COC(O)CH_2CH_2(CH_2)_6CH_2$**$CH_2$**Br)}; 2.19 {(t, 2H, $(CH_3)_3COC(O)$-**CH_2**$CH_2(CH_2)_6CH_2CH_2Br$)}; 1.84 {(t, 2H, $(CH_3)_3COC(O)CH_2CH_2(CH_2)_6$**$CH_2$**$CH_2Br$)}; 1.58 {(t,2H, $(CH_3)_3COC(O)CH_2$**CH_2**$(CH_2)_6CH_2CH_2Br$)}; 1.43 {(s, 9H, **$(CH_3)_3$**$COC(O)CH_2CH_2(CH_2)_6CH_2CH_2Br$)}



Scheme 5: Synthesis scheme of PEG750 thiol preparation

PEG750-tosylate monomethyl ether (11)

2.4 g (60 mmol) sodium hydroxide was taken in 250 mL round bottom flask and dissolved in minimum amount of water. 15 g (20 mmol) PEG750 monomethyl ether and 150 mL THF was then added to it. The contents were placed on an ice bath and subsequently, 5.72 g (30 mmol) tosyl chloride was added to it. The mixtures were stirred for 36 h at room temperature. THF was removed by rotary evaporator and 150 mL DCM was added to it. DCM containing PEG tosylate was washed twice (2 x 50 mL) with water. Finally, organic layer was passed through sodium sulfate and concentrated under vacuum to yield product with 58 % (10.5 g) yield.

^{1}H NMR (δ, $CDCl_3$): 7.76 (d, 2H, Ar); 7.31 (d, 2H, Ar); 4.13 (d, 2H, CH_3O-$[CH_2CH_2O]_n$-CH_2**CH_2**O-Ar-CH_3); 3.62 (m, CH_3O-[**CH_2CH_2**$O]_n$-CH_2CH_2O-Ar-CH_3); 3.35 (s, 3H, **CH_3**O-$[CH_2CH_2O]_n$-CH_2CH_2O-Ar-CH_3); 2.42 (s, 3H, CH_3O-$[CH_2CH_2O]_n$-CH_2CH_2O-Ar-**CH_3**)

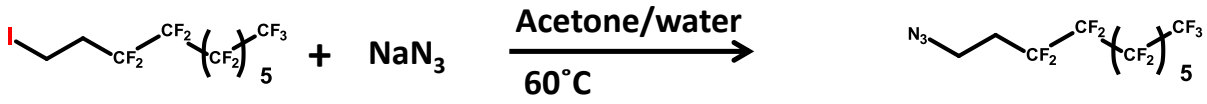
PEG750 thiol monomethylether (12)

10 g (11 mmol) PEG750 tosylate (11) and 1.26 g (16.57 mmol) thiourea were taken in 150 mL absolute ethanol and refluxed for 24 h under nitrogen environment. The solution was cooled to room temperature and purged with nitrogen gas for 15 min. 0.89 g (22.1 mmol) sodium hydroxide was added and the contents were stirred to reflux under nitrogen atmosphere for 24 h. Subsequently, pH of the solution was brought down to 4-5 by adding 2 (N) HCl. Ethanol was removed completely under vacuum. 100 mL DCM was poured in to the mixture and washed twice

(2 x 50mL) with water. Organic layer was dried over sodium sulfate and concentrated to give pale yellow product with 62 % (5.35 g) yield.

^{1}H NMR (δ, $CDCl_3$): 3.61 (m, CH_3O-[**CH_2CH_2**O]$_n$-CH_2CH_2SH); 3.35(s, 3H, **CH_3**O-[CH_2CH_2O]$_n$-CH_2CH_2-SH); 2.67 (m, 2H, CH_3O-[CH_2CH_2O]$_n$-CH_2**CH_2**SH); 1.59 (t, 1H CH_3O-[CH_2CH_2O]$_n$-CH_2CH_2**SH**)

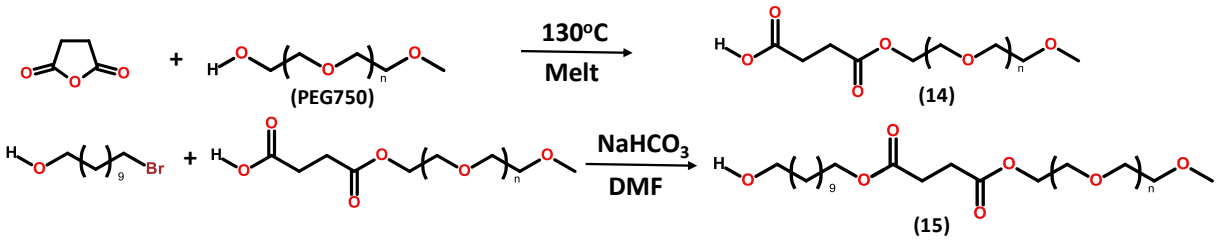
Perfluoroazide (13)



Scheme 6: preparation of fluorocarbon azide from fluorocarbon iodide

Fluorocarbon azide was prepared using synthetic procedure reported by Narsaiah et. all[2]. 6 g (10.4 mmol) perfluoro iodide and 2.72 g (41.8 mmol) sodium azide were taken in 40 mL 1:3 mixture of water and acetone. The contents were heated at 60 ˚C for 3 days with continuous stirring. Acetone was removed from the mixture and 50 mL water was added. The product, fluorocarbon azide was extracted in 150 mL hexane (3 x 50 mL) and dried over sodium sulfate. The final product was obtained upon concentrating the solution with 90 % (4.6 g) yield.

^{1}H NMR (δ, $CDCl_3$): 3.61 {t, 2H, N_3**CH_2**$CH_2(CF_2)_7CF_3$}; 2.39 {m, 2H, N_3CH_2**CH_2**$(CF_2)_7CF_3$}



Scheme 7: PEG750 (ω-hydoxyundecanyl) succinate (15)

PEG750 succinate (14)

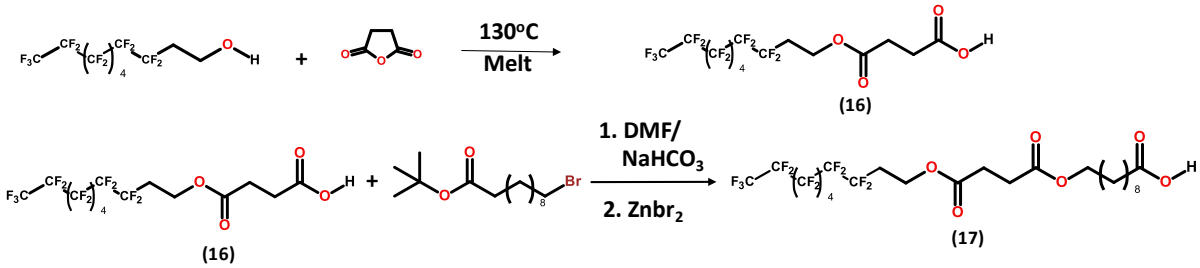
1.07 g (10.7 mmol) freshly prepared succinic anhydride and 4 g (5.33 mmol) dry PEG750 monomethyl ether were placed in Kugelrohr and reaction was carried out at 130 °C for 4 h. Subsequently excess succinic anhydride was removed under vacuum at 130 °C in Kugelrohr. 4.26 g PEG750 succinate was obtained (94 % yield).

^{1}H NMR (δ, $CDCl_3$): 4.24 {t, 2H, CH_3O-$(CH_2CH_2O)_n$ -CH_2**CH_2**-O-}; 3.63 { m, 62 H, CH_3O-(**CH_2CH_2**O)$_n$-CH_2CH_2O-}; 3.36 {s,3H, **CH_3**O-$(CH_2CH_2O)_n$-OH}; 2.63 {m, 4H, -OC(O)-**CH_2CH_2**-(O)CO-}

PEG750 (ω-hydoxyundecanyl) succinate (15)

2.2 g (2.59 mmol) PEG750 succinate (14) and 1.09 g (12.97 mmol) sodium bicarbonate were taken in 100 mL round bottom flask. 50 mL DMF was added to it and stirred at RT for 10 min. Subsequently 0.78 g (3.10 mmol) 11-bromoundecanol was added to it and reaction mixture was stirred at 45 ^{o}C for 3 days. 100 mL chloroform was added to it and DMF was removed my extraction with 300 mL (3 x 100 mL) water. Chloroform containing product was passed through sodium sulfate. Product was obtained by removal of organic solvent. The crude product was purified by washing twice with hexane. Finally, 1.74 g viscus liquid product was obtained with 66 % yield.

^{1}H NMR (δ, $CDCl_3$): 4.22 (q, 2H, PEG-CH_2-**CH_2**-O-); 4.04 (t, 2H, HO-$CH_2(CH_2)_9$**CH_2**O-); 3.61{ m, 62 H, CH_3O-(**CH_2CH_2**O)$_n$-O-}; 3.36 {s, 3H, **CH_3**O-(CH_2CH_2O)$_n$-OH}; 2.60 {m, 4H, -OC(O)-**CH_2CH_2**-(O)CO-} ; 1.57 {m, 4H, HO-CH_2-$(CH_2)_8$-**CH_2**CH_2O-S}; 1.26 {S, 14 H, HO-CH_2CH_2-**$(CH_2)_7$**-CH_2-CH_2-O}



Scheme 8: Synthesis of Perfluoro ω-carboxyundecanyl succinate

Perfluoro succinate (16)

2 g (4.3 mmol) perfluoro alcohol and 0.86 g (8.62 mmol) freshly prepared succinic anhydride were taken in Kugelrohr and heated at 130 ^{o}C. The reaction was carried out at 130 ^{o}C for 4 h. Excess succinic anhydride was removed at high vacuum. 2.25 g Perfluoro succinate was obtained with 92 % yield.

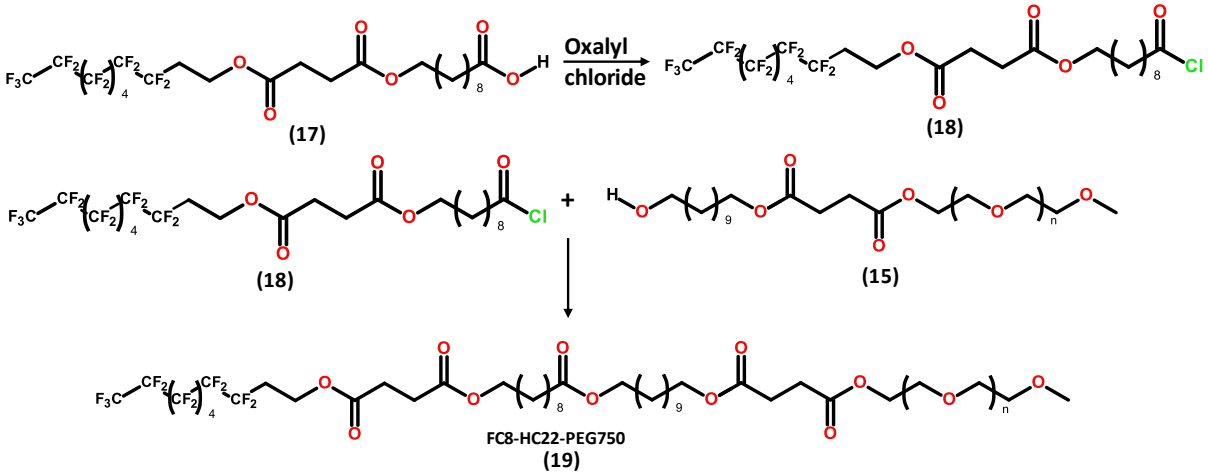
^{1}H NMR (δ, $CDCl_3$): 4.42 (t, 2H, C_8F_{17} -CH_2**CH_2**O-); 2.69 {m, 4H, -OC(O)-**CH_2CH_2**-(O)CO-}; 2.48 (m, 2H, C_8F_{17} -**CH_2**CH_2O-)

Perfluoro ω-carboxyundecanyl succinate (17)

2 g (3.55 mmol) perfluoro succinate (16) and 1.1 g (13.09 mmol) sodium bicarbonate were taken in 100 mL RB. 50 mL DMF was added to it. The mixture was stirred at RT for 10 min. 1.36 g (4.25 mmol) 11-bromo-t-butylundecanoate was added to it. The reaction mixture was stirred at 45 ^{o}C for 3 days. 100 mL chloroform was added to it and DMF was removed by extracting with 300 mL (3 x 100mL) water. Chloroform layer was dried by passing it through sodium sulfate and removal

of solvent under reduced pressure yielded white viscus liquid product. The product was dissolved in 30 mL dry DCM and 2.36 g zinc bromide (10.47 mmol) was added to it. The mixture was stirred at RT for 24 h at air-tight condition. DCM was washed twice with 100 mL (2 x 50mL) water and concentrated to yield white solid product. The product was purified by recrystallization from hexane. Yield 1.48 g (56 %).

^{1}H NMR (δ, $CDCl_3$): 4.40 (q, 2H, C_8F_{17} -CH_2**CH_2**-O-); 4.08 {t, 2H, -O**CH_2**$(CH_2)_8CH_2$-CO_2H}; 2.64 {m, 4H, -OC(O)-**CH_2CH_2**-(O)CO-} ; 2.48 (m, 2H, C_8F_{17} -**CH_2**CH_2-O); 2.34 {m, 4H, HO_2C-**CH_2**$(CH_2)_8$-CH_2-O-}; 1.65 {m, 4H, HOO_2C-CH_2**CH_2**$(CH_2)_6$**CH_2**CH_2O-}; 1.28{s,12H, HOO_2C-CH_2CH_2**$(CH_2)_6$**CH_2 CH_2O-}



Scheme 9: Synthesis of model compound (FC8-C22-PEG750)

FC8-HC-22-PEG750 (19)

0.53 g (0.708 mmol) Perfluoro ω-carboxyundecanyl succinate (17) was taken in 50 mL RB fitted with calcium chloride guard tube and 10 mL dry DCM was added to it. 0.27 g (2.12 mmol) oxalyl chloride was then added. One capillary drop DMF was added and the reaction mixture was heated at 40 ^oC for 3 h. Transformation of acid to acid chloride was indicated by the change of reaction color to pale yellow. DCM was then removed at reduced pressure. 6 mL dry chloroform was added to it and 0.94 g (0.92 mmol) PEG750 ω-hydoxyundecanyl succinate (15) was added to it. The mixture was stirred at RT for 30 min. Then 0.8 g pyridine was added, and reaction mixture was heated to 70 ^oC for 12 h. Solvent was removed under reduced pressure to yield solid product. Product was purified by reprecipitation from diethyl ether and then from hexane. Final product was obtained 0.56 g, 45 % yield.

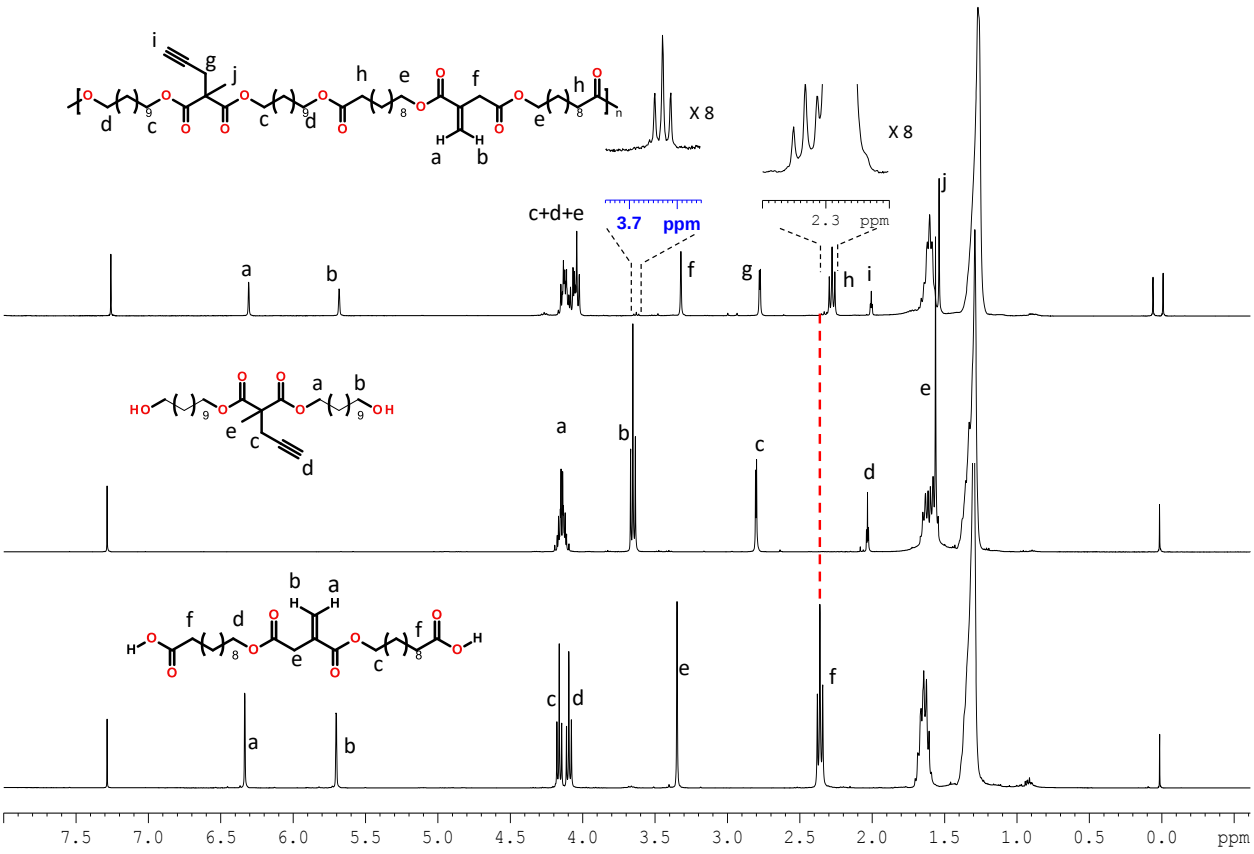


Figure S1: ^{1}H NMR spectrum of itaconate bearing diacid, propargyl bearing di-ol and parent polymer. Intensities of the peaks are accordance to the structures. Expanded region shows presence of- **CH_2**OH and -**CH_2**CO_2H end groups in parent polymer. Red dotted line shows the coincidence of the -**CH_2**CO_2H peak in the monomer and parent polymer.

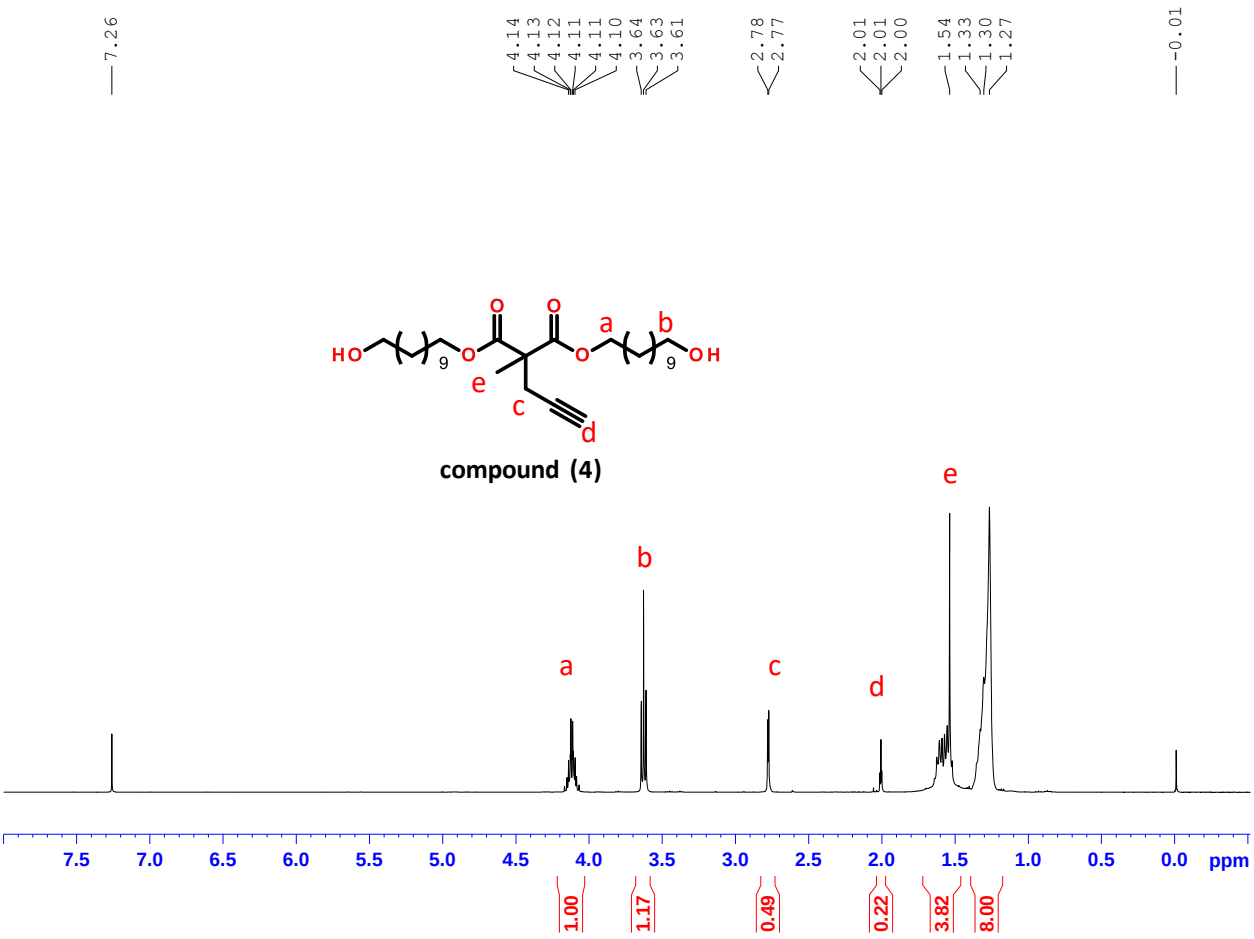


Figure S2: NMR spectrum of propargyl bearing diol monomer (**I**) recorded in $CDCl_3$.

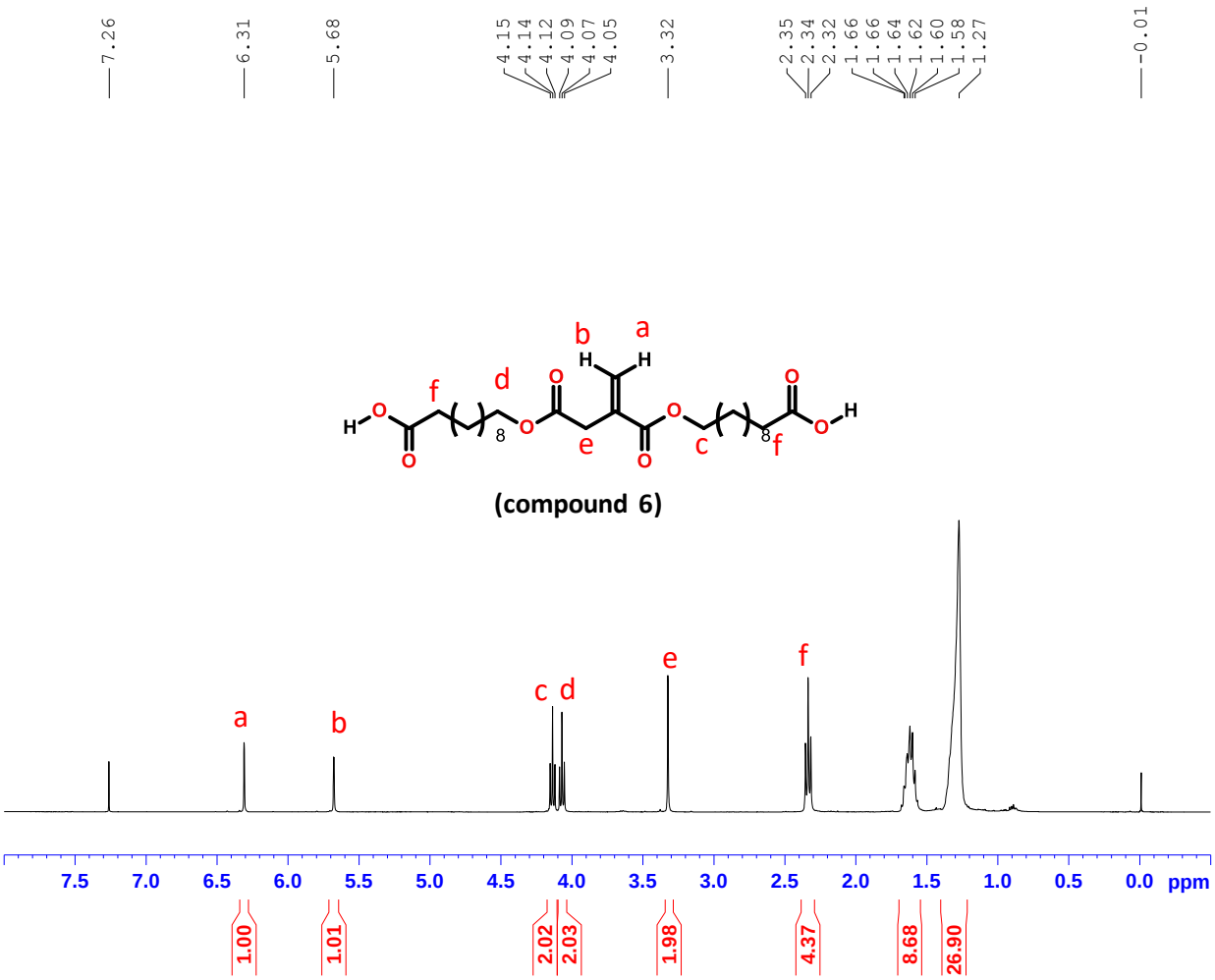


Figure S3: NMR spectrum of itaconate bearing diacid monomer (**II**) recorded in $CDCl_3$.

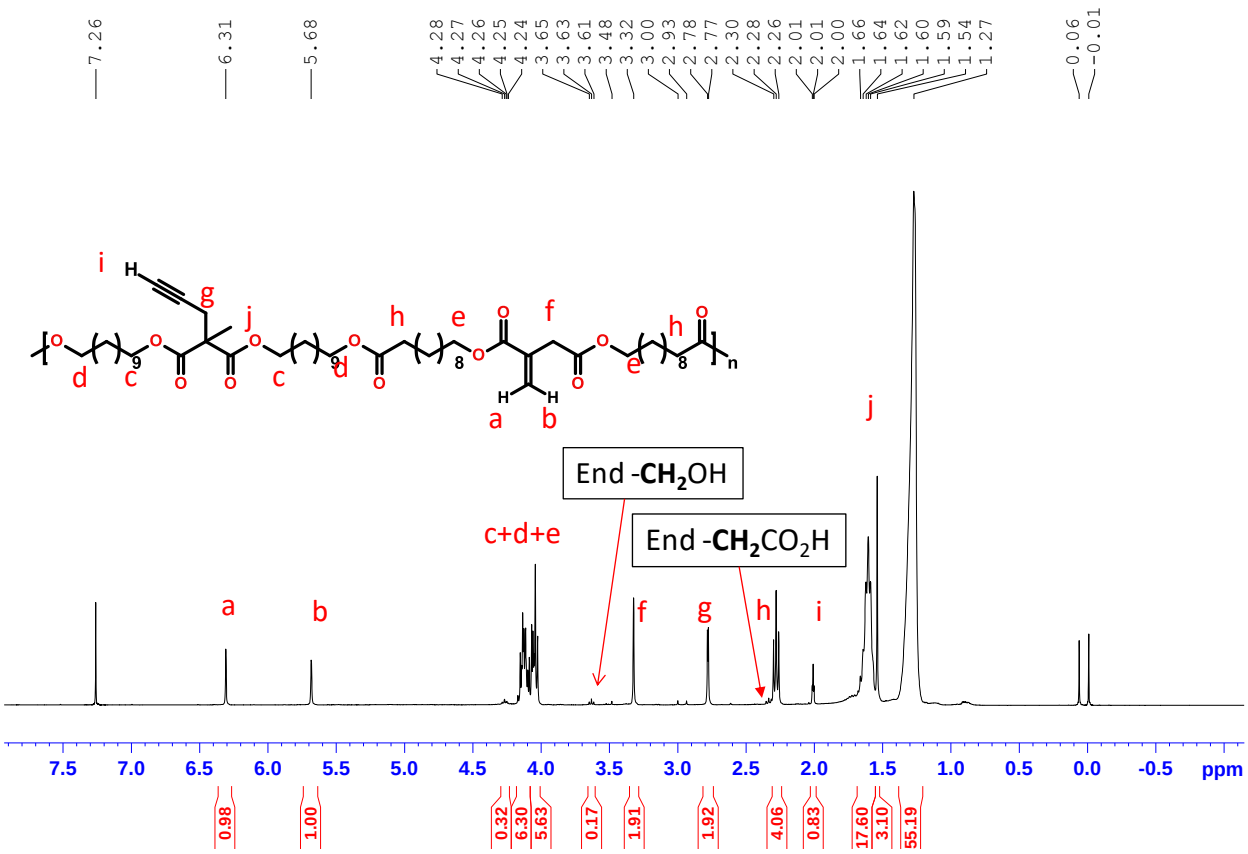


Figure S4: NMR spectrum of parent polymer (OCPE) recorded in $CDCl_3$.

^{1}H NMR (δ, $CDCl_3$): 6.31 {s, 1H, -OCOC(=C**H$_2$**)CH_2CO_2-}; 5.68 {s, 1H, -OCOC(=C**H$_2$**)CH_2CO_2-}; 4.25 (m, 12H , -O**CH$_2$**CH_2CH_2 -); 3.63 (t, 2H , end-**CH$_2$**OH); 3.32 {s, 2H, -OCO**CH$_2$**C(=CH_2)CO_2- }; 2.70 (d, 2H, -**CH$_2$**CCH); 2.30 (t, 4H, -CH_2CH_2**CH$_2$**$CO_2CH_2CH_2$-); 2.01 (t, 1H, -CH_2C**CH);** 1.54 (s, 3H, -**CH$_3$**).

Intensities of peaks a/b and g/i suggests equimolar propargyl and itaconate units.

Estimation of degree of polymerization (DP_n) and M_n by NMR end group analysis.

DP_n = Intensity of single proton in the repeating unit / intensity of single proton of the end group.

Here, DP_n= (Intensity of peak at 5.68 ppm, one of the hydrogens linked with itaconate double bond in the repeating unit) / (intensity of corresponds to single proton for -**CH$_2$**OH end at 3.63 ppm)

Therefore, DP_n= {1/ (0.17/2)} =11.76 and X_n (number degree of polymerization) = 11.76x2=23.53

Therefore, M_n= DP_n x Repeat unit molecular weight= 11.76x990 = 11647 Dalton

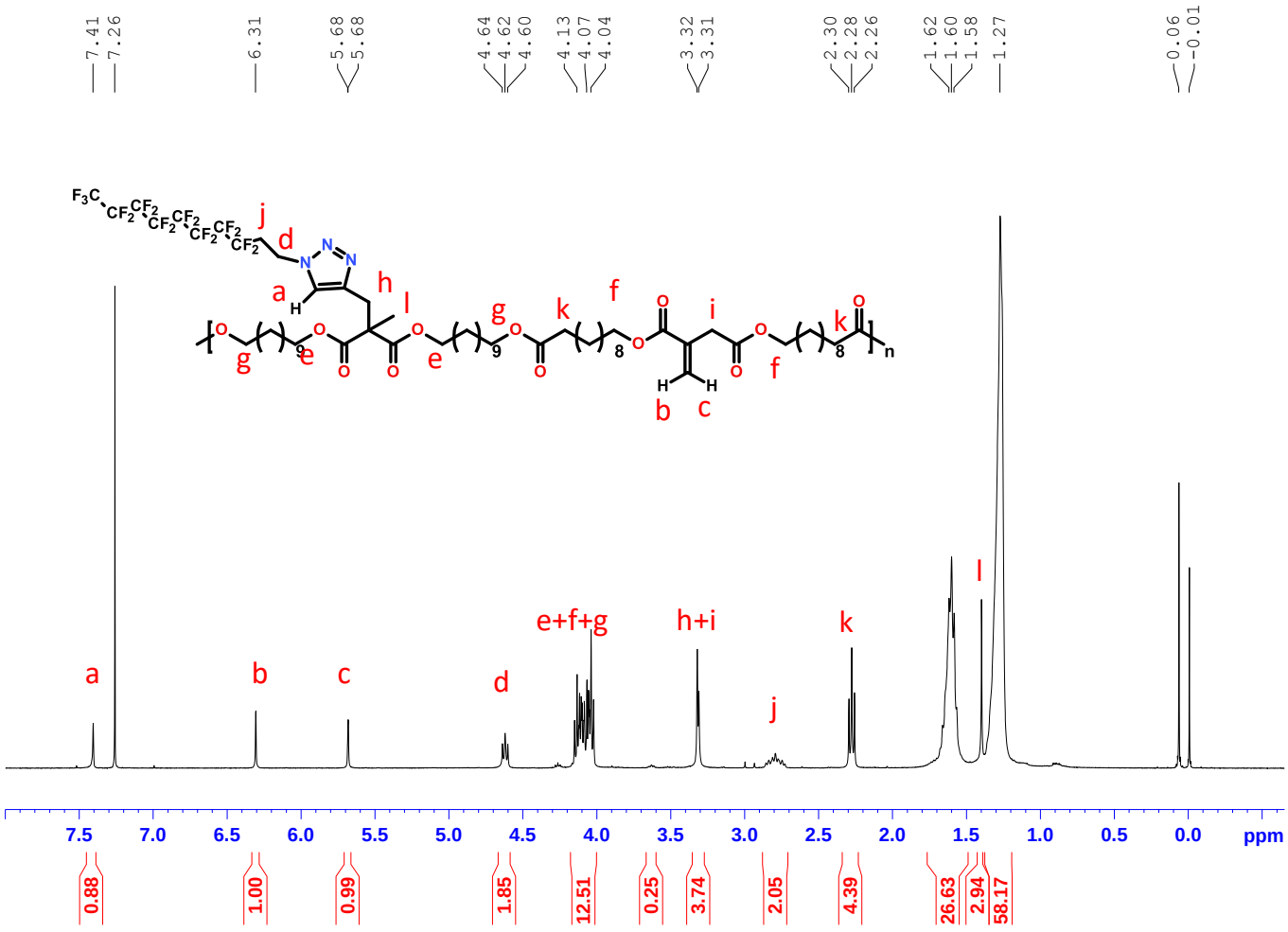


Figure S5: NMR spectrum of fluorocarbon grafted copolymer (OCPE-g-FC) recorded in $CDCl_3$.

^{1}H NMR (δ, $CDCl_3$): 7.41 (s,1H triazole ring proton); 6.31 {s, 1H, -OCOC(=C**H$_2$**)CH_2CO_2-}; 5.68 {d, 1H, -OCOC(=C**H$_2$**)CH_2CO_2-}; 4.62{t, 2H, -**CH$_2$**$CH_2(CF_2)_7CF_3$}; 4.15 (m, 12H , -O**CH$_2$**CH_2CH_2 -); 3.32 {d, 2H, -OCO**CH$_2$**$C(=CH_2)CO_2$-}; 3.32 {d, 2H, -CH_2**CH$_2$**-trizole-$(CF_2)_7CF_3$}; 2.79 {m, 2H, -CH_2**CH$_2$** $(CF_2)_7CF_3$}; 2.30 (t, 4H, -CH_2CH_2**CH$_2$**$CO_2CH_2CH_2$-); 1.54 (s, 3H, -**CH$_3$**)

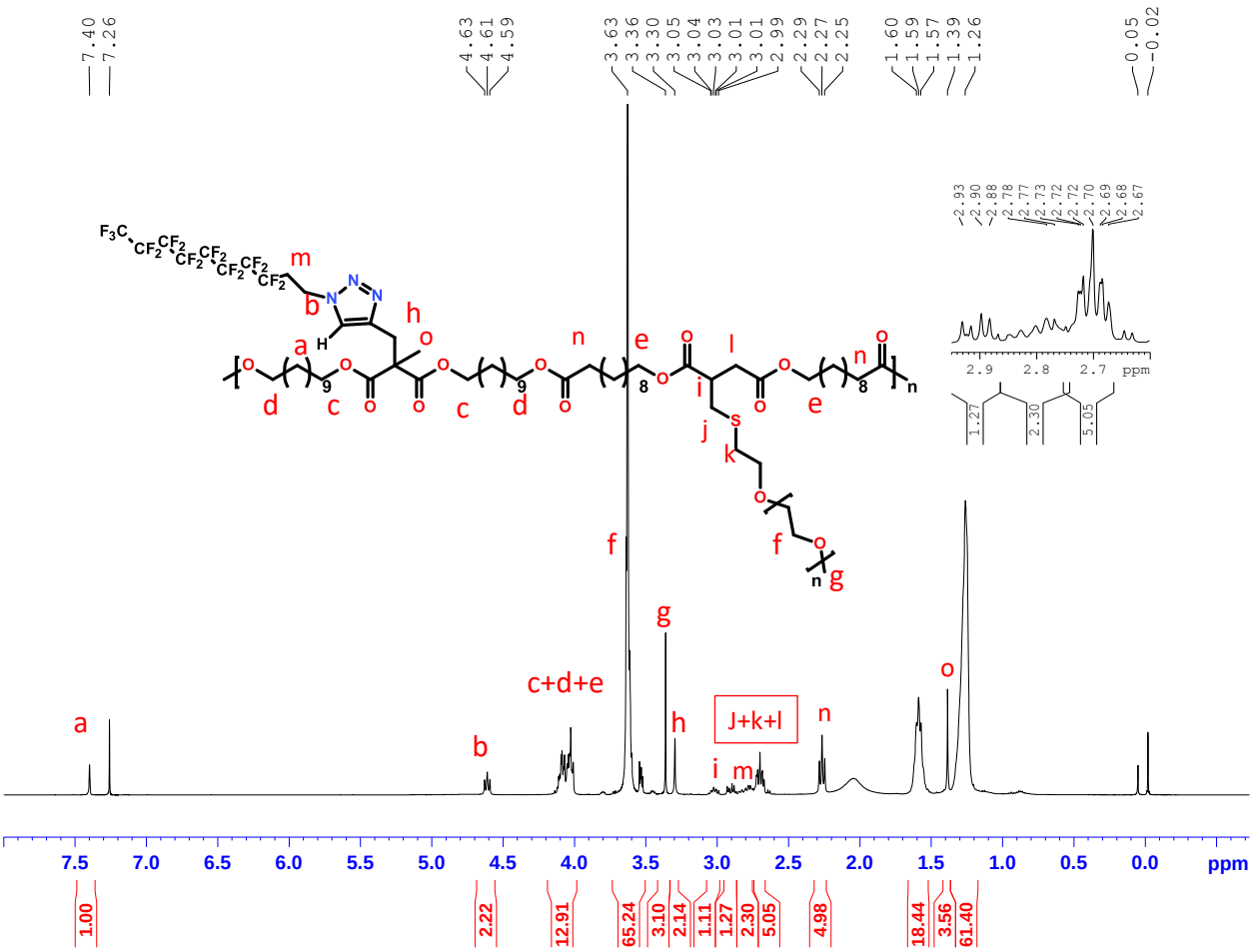
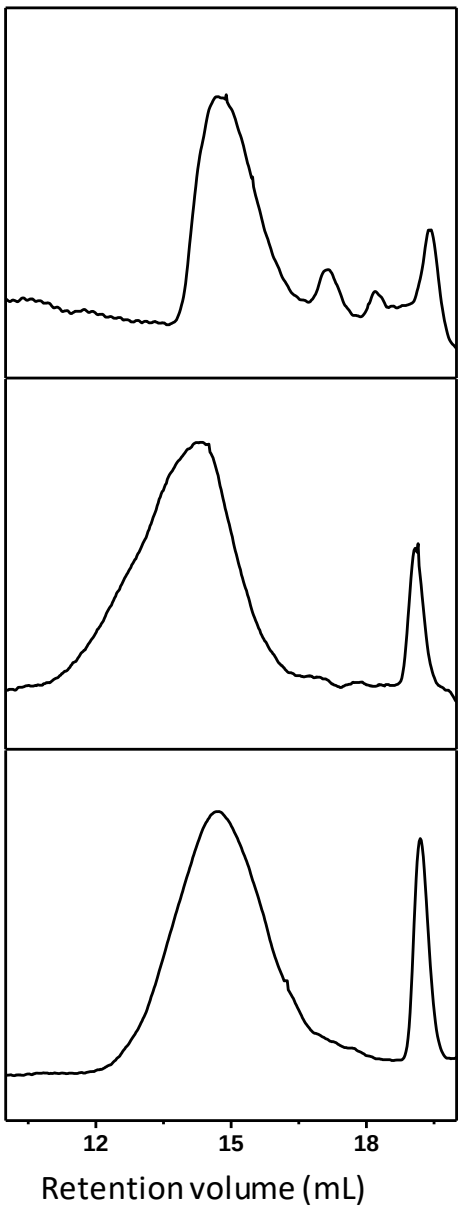


Figure S6: NMR spectrum of fluorocarbon and PEG grafted copolymer (OCPE-g-FC-g-PEG) recorded in $CDCl_3$. Inset shows expansion in region of 2.6 to 2.95 ppm.

^{1}H NMR (δ, $CDCl_3$): 7.41 {s,1H triazole ring proton); 4.61 {t, 2H, -**CH_2**CH_2-$(CF_2)_7CF_3$}; 4.15 (m, 12H , -O**CH_2**CH_2CH_2 -); 3.63 {m, 55H, -O(**CH_2CH_2**O)$_n$-CH_3}; 3.36 (s,3H, -O-$(CH_2CH_2O)_n$-**CH_3**}; 3.30 {s, 2H, -CH_2**CH_2**-trizole-$(CF_2)_7CF_3$}; 3.05 {m, 1H, -CO_2CH_2C**H**$(CH_2$-S-PEG$)CO_2$-}; 3.03 {m, 2H, -CH_2**CH_2**$(CF_2)_7CF_3$}; 2.28 (t, 4H, -CH_2CH_2**CH_2**$CO_2CH_2CH_2$-); 1.54 (s, 3H, -**CH_3**)



OCPE-g-FC-g-PEG

Mn - (Daltons) - 8,010
Mw - (Daltons) - 10,156
Mw / Mn - 1.268

OCPE-g-FC

Mn - (Daltons) - 16,099
Mw - (Daltons) - 41,125
Mw / Mn - 2.555

OCPE

Mn - (Daltons) - 7,471
Mw - (Daltons) - 15,335
Mw / Mn - 2.053

Figure S7: Stacked GPC plot of parent and graft copolymer using THF as an eluent. Molecular weight of polymers was determined against narrow standard polystyrene using RI calibration method**.** Molecular weight of the fluorocarbon grafted polymer expectedly increased from that of parent polymer but surprisingly enhancement in molecular weight of final graft copolymer was not prominent. Solubility parameter of the parents and graft copolymer could be the reason.

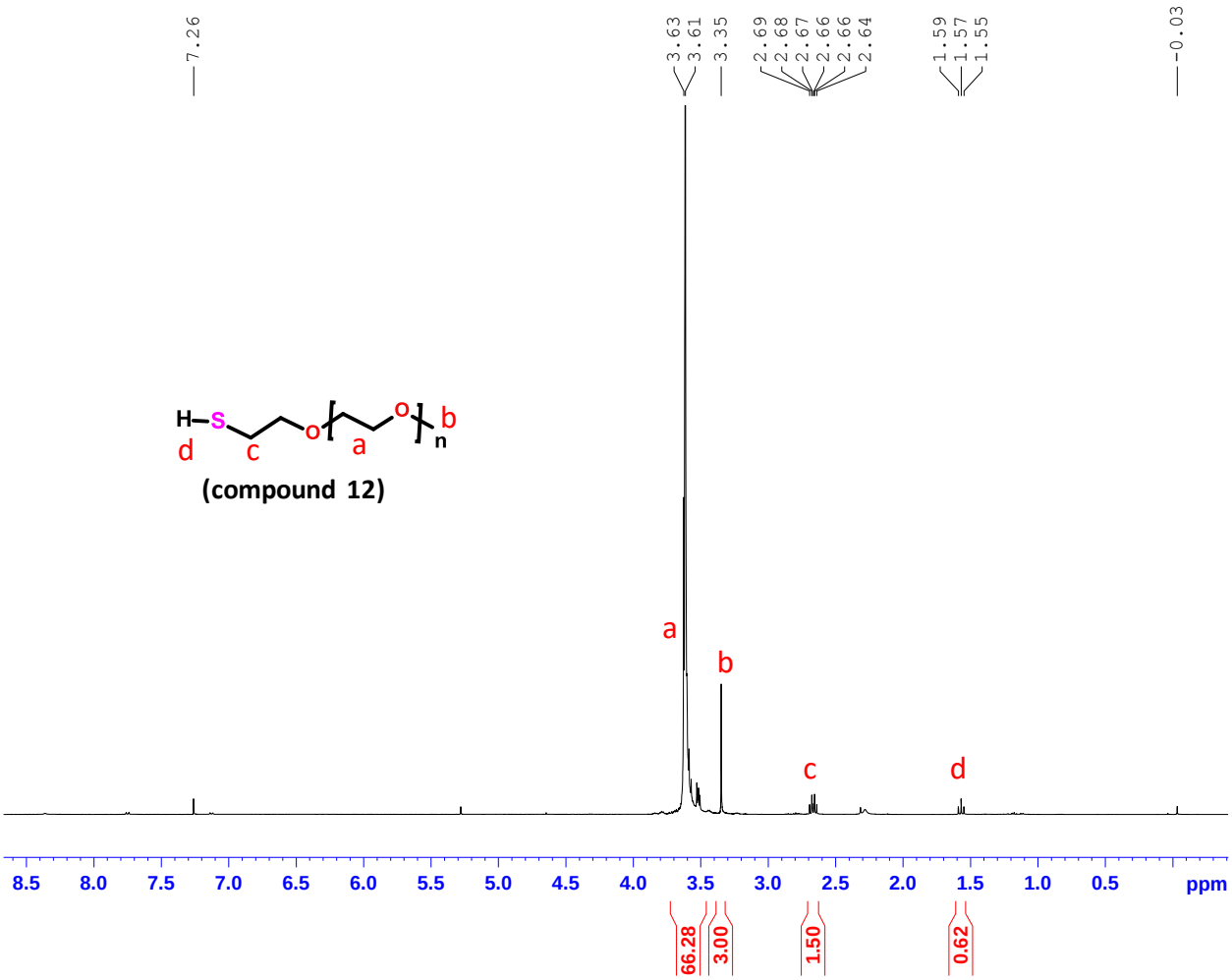


Figure S8: NMR spectrum of PEG-750 thiol recorded in $CDCl_3$.

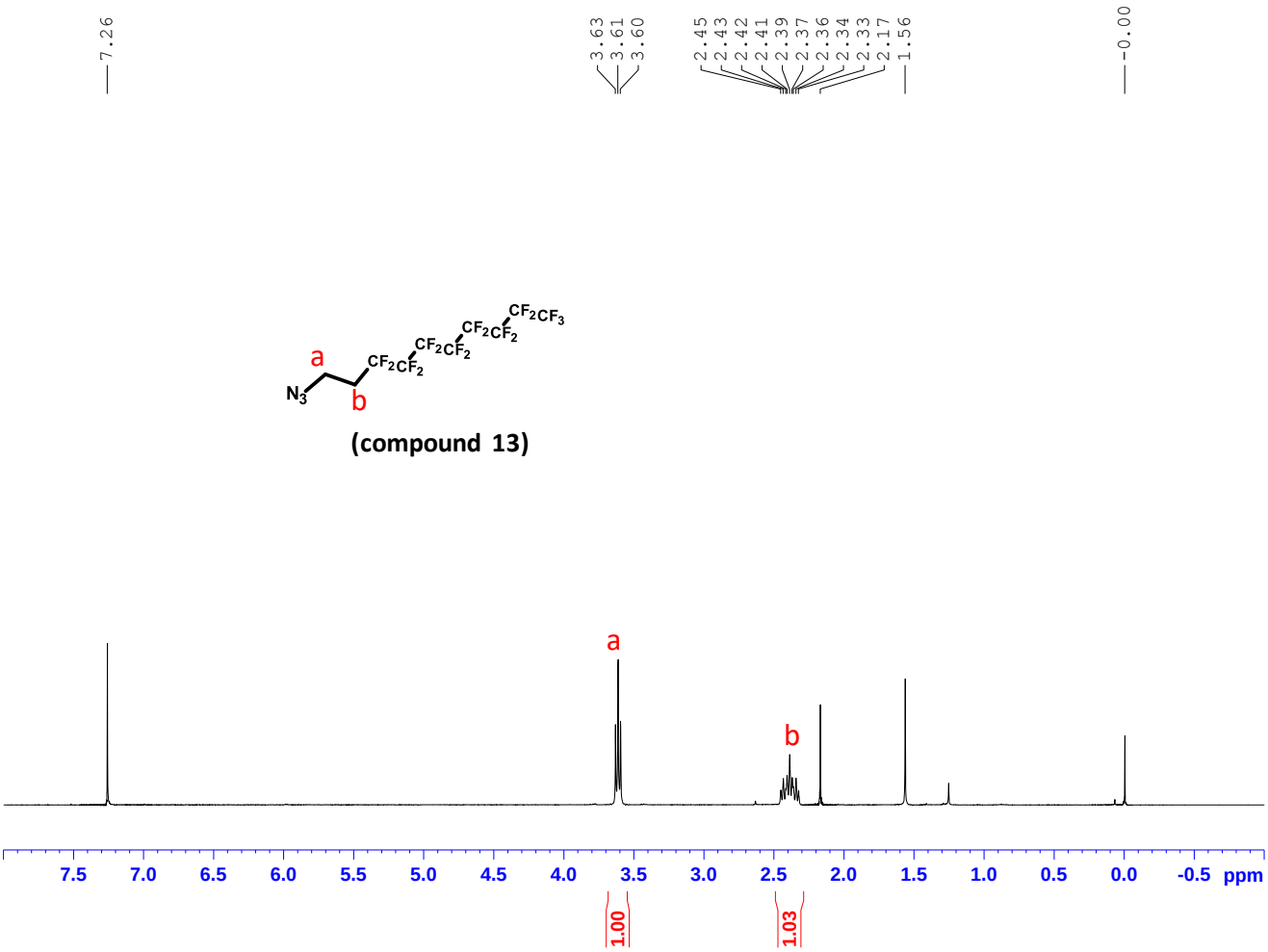


Figure S9: NMR spectrum of perfluorooctyl azide recorded in $CDCl_3$.

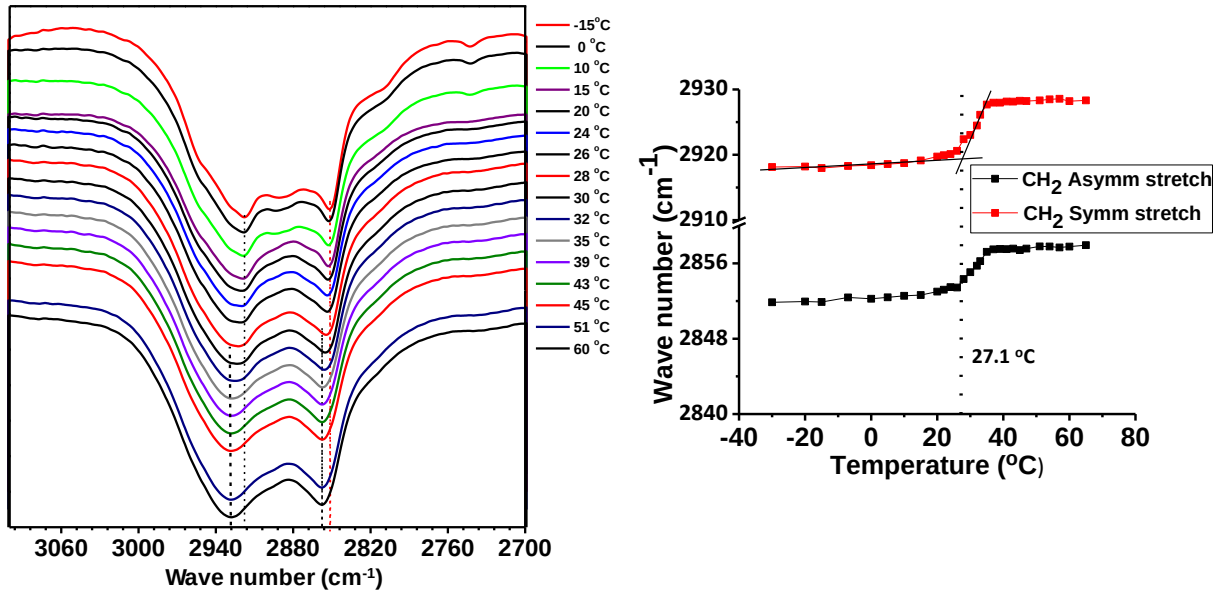


Figure S10. Variable temperature IR spectrum of OCPE-g-FC-g-PEG in the region of C-H stretching frequencies. At each temperature, the sample was allowed to equilibrate for ~5 min prior to data collection; the measurements were done by heating from the lower temperature to the higher temperature. On the right panel, the variation of -CH_2 symmetric and -CH_2 asymmetric stretching frequencies as a function of temperature is shown, which clearly reveals the onset (at ~ 27°C) of the melting of the paraffinic lattice formed by the central HC segment.

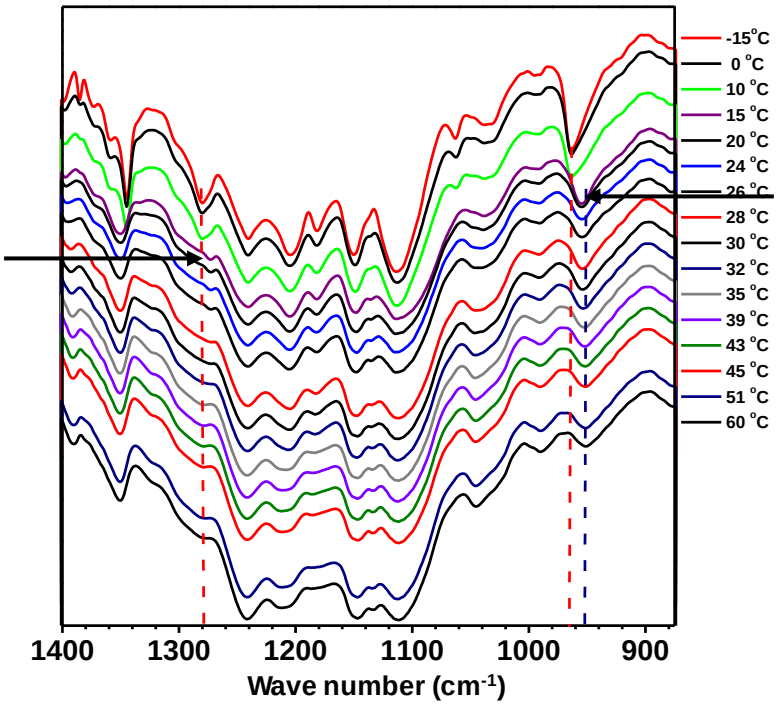


Figure S11. Variable temperature FT-IR of OCPE in the range of PEG stretching frequencies. At each temperature, the sample was allowed to equilibrate for 5 min before to data collection. The measurements were done by heating from the lower temperature to the higher temperature. At 15 °C, 1280 cm^{-1} peak, associated with the CH_2 twisting[3] motion in crystalline domains disappear and the peak at 963 cm^{-1} shifts to 950 cm^{-1} (rocking of gauche CH_2 in molten sate). The arrow at 15 °C, indicates the onset of lower temperature endothermic peak (25.8 °C) in DSC. Based on this, peak at 25.8 °C in DSC is assigned to the melting of PEG segments.

Reference 3: Matsuura, H.; Miyazawa, T., Vibrational analysis of molten poly(ethylene glycol). *Journal of Polymer Science Part A-2: Polymer Physics* **1969,** *7* (10), 1735-1744.

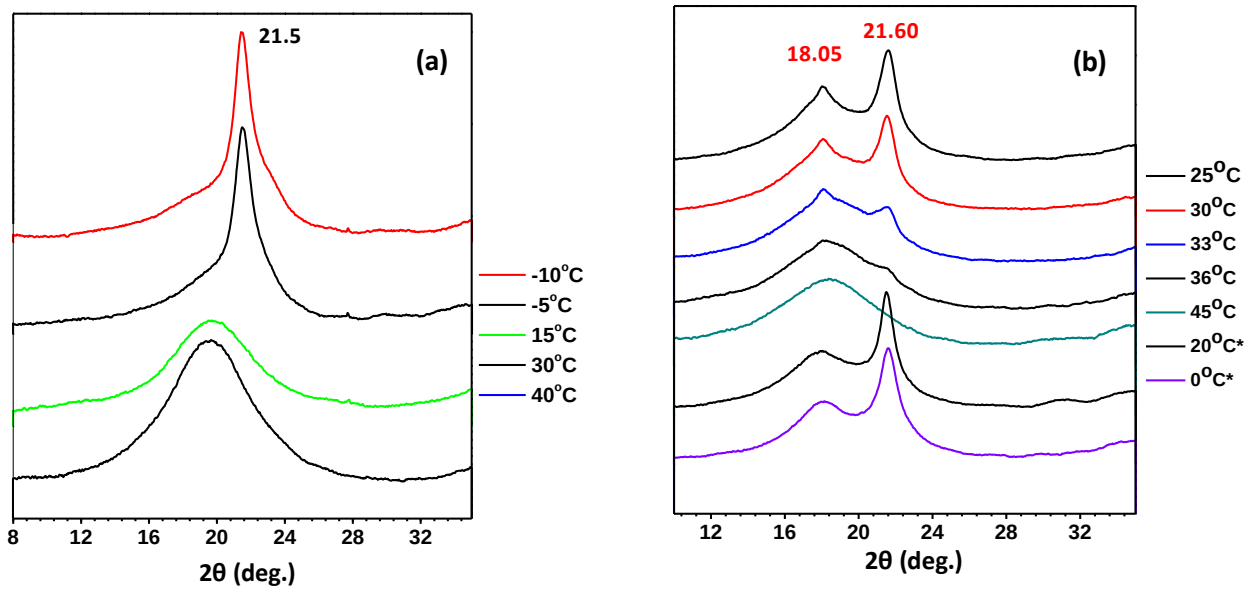


Figure S12: Variable temperature WAXS of a) OCPE b) OCPE-g-FC. Samples were heated from lower to higher temperature and then cooled (asterisk notation is used for cooling temperature) to lower temperature, at each temperature sample was allowed to equilibrate for ~5 min prior to data collection. Parent polymer (OCPE) exhibited strong crystallization peak (at 2θ=21.5 degree) at a temperature below the melting of hydrocarbon, subsequently emerged to a broad amorphous hallow at higher temperature. Fluorocarbon grafted polymer (OCPE-g-FC) showed two strong peaks where the lower peak value (2θ=18.05 degree) corresponds to interchain spacing of fluorocarbon and higher peak values (2θ=21.6 degree) for that of hydrocarbon. Interestingly, in both of the polymers, hydrocarbon crystallization peaks remain almost same position.

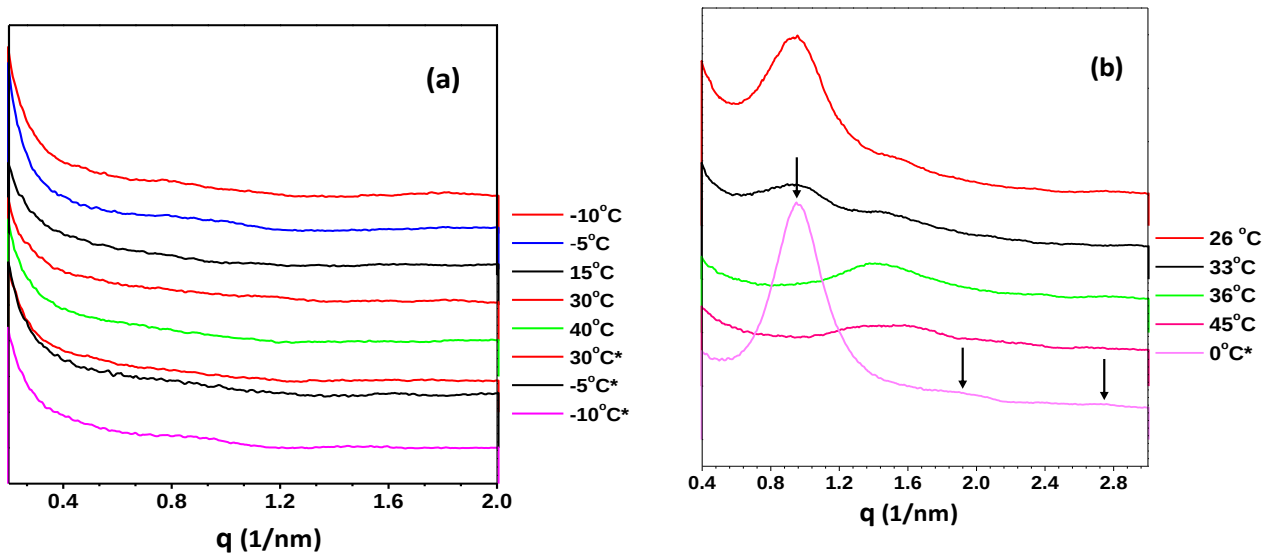


Figure S13: Variable temperature SAXS profile of a) OCPE b) OCPE-g-FC. In both of the cases samples were heated to the higher values then cooled to lower temperature. The asterisk denotation used to denote cooling temperature. Data were recorded after allowing ~5 min at each temperature. Parent polymer, lack of long-range ordering did not exhibit any SAXS pattern, whereas the fluorocarbon grafted polymer (OCPE-g-FC) exhibited a strong first order peak and weak second and third order peaks. The peak position in the ratio of 1:2:3 implies lamellar morphologies with lamellar height (d-spacing) of 6.8 nm.

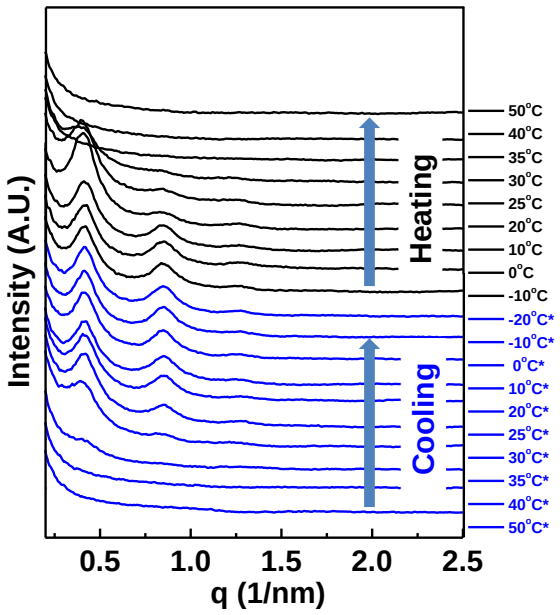


Figure S14. Variable temperature SAXS profiles of OCPE-*g*-FC-g-PEG; these profiles were recorded by first cooling the molten samples from 50 °C to -20 °C, and then the samples were reheated again to 50 °C, during which the data was collected; at each temperature the sample was equilibrated for ~5 mins prior to data acquisition.

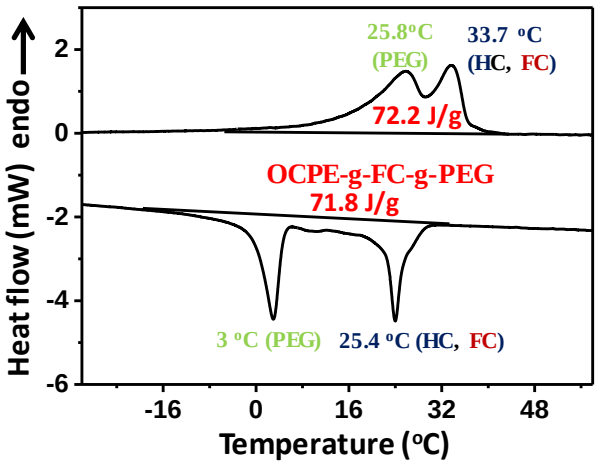
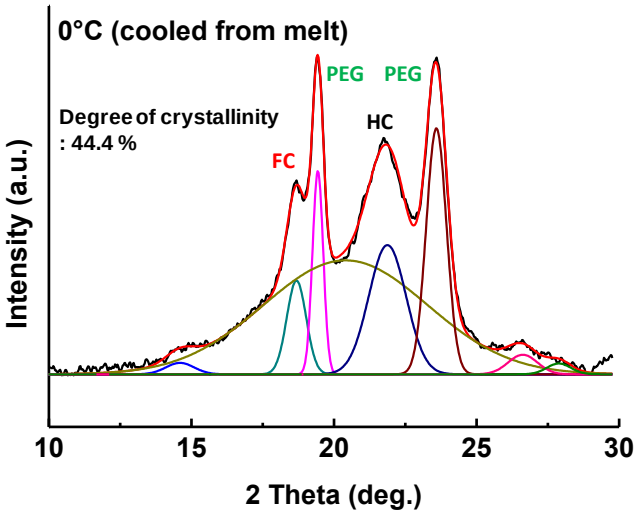


Figure S15: DSC of OCPE-g-FC-g-PEG750 with heating/cooling rate 10 deg./min. Sum of enthalpies (as shown area under the curve) associated with melting of both HC and FC and crystallization of both HC and FC matches resonably well.



Temperature (°C) (Cooled from melt)	Degree crystallinity (%)
-20	45
-10	46.5
0	44.4
10	36.5
25	26
30	13

Figure S16: Deconvoluted WAXS profile recorded at 0 °C shows crystallization peaks for FC, HC and PEG segments. Ratio of area under the sharp peaks to the total area reveals degree of crystallinity 44.4 %. Right table shows variation of degree of crystallinity with temperature.

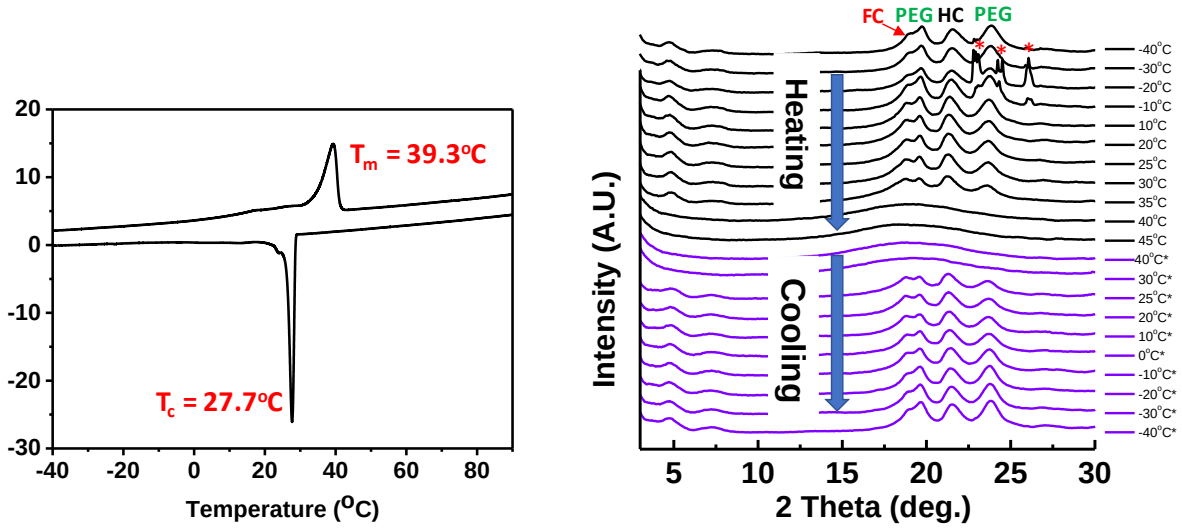


Figure S17: DSC and WAXS of model compound, FC8-HC22-PEG750. DSC was carried out at heating/cooling rate 10 deg/min. For variable temperature WAXS, sample were first heated to melt (up to 45°C) then cooled to -40 °C and heated again up to 45 °C, asterisk notation is used for cooling temperature, at each temperature sample was allowed to equilibrate for 5 min prior to data collection. Independent crystallization of PEG, hydrocarbon and fluorocarbon are evident from variable temperature WAXS but unlike polymer, all three segments melt and crystallize at a same temperature. Peaks denoted by asterisk arises due to crystallization of water at low temperature.

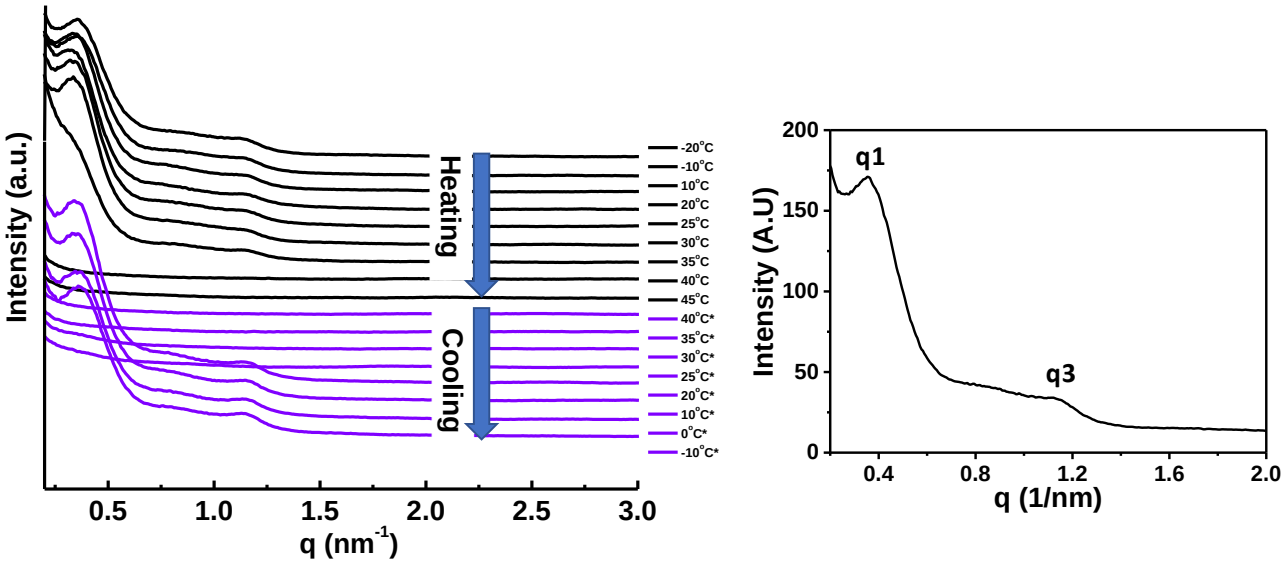


Figure S18: Variable temperature SAXS of model comp FC8-HC22-PEG750. Sample were first heated to melt (up to 45 °C) then cooled to -40 °C and heated again up to 45 °C; asterisk notation is used for cooling temperature, at each temperature sample was allowed to equilibrate for 5 min prior to data collection. SAXS profile exhibit intense first order peak and weak higher order peaks. Calculated inter-lamellar spacing is 17.4 nm, whereas that of the polymer, OCPE-g-FC-PEG750 it is 15.2 nm. Right panel shows SAXS profile recorded at -20 °C.

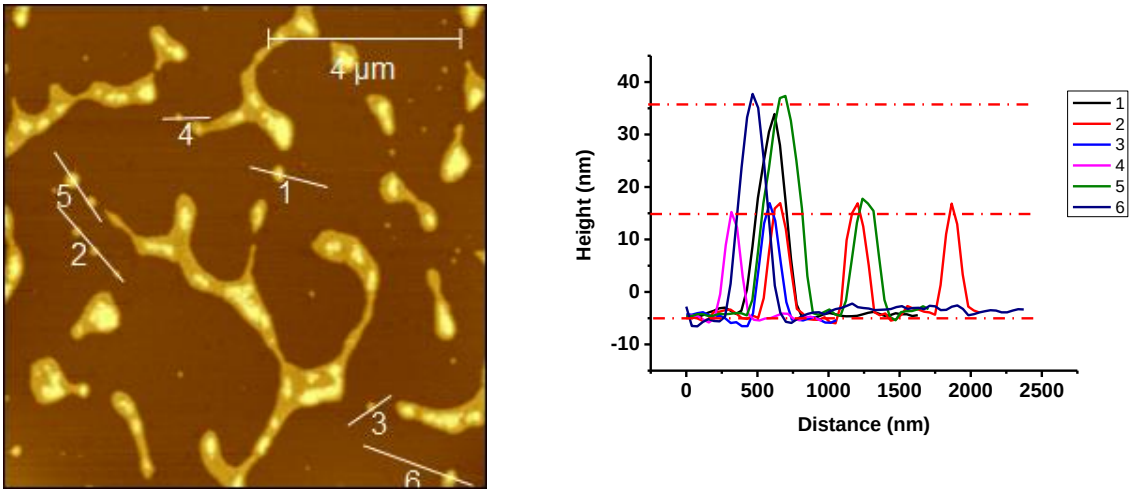


Figure S19: AFM height profile of OCPE-g-FC-g-PEG on freshly cleaved mica substrate. Right side: height profile of small sized (and some larger) dots are shown. Uniform bilayer height of ~20 nm (small dots) and occasionally double of bilayer height of ~40 nm (large dots) were observed.

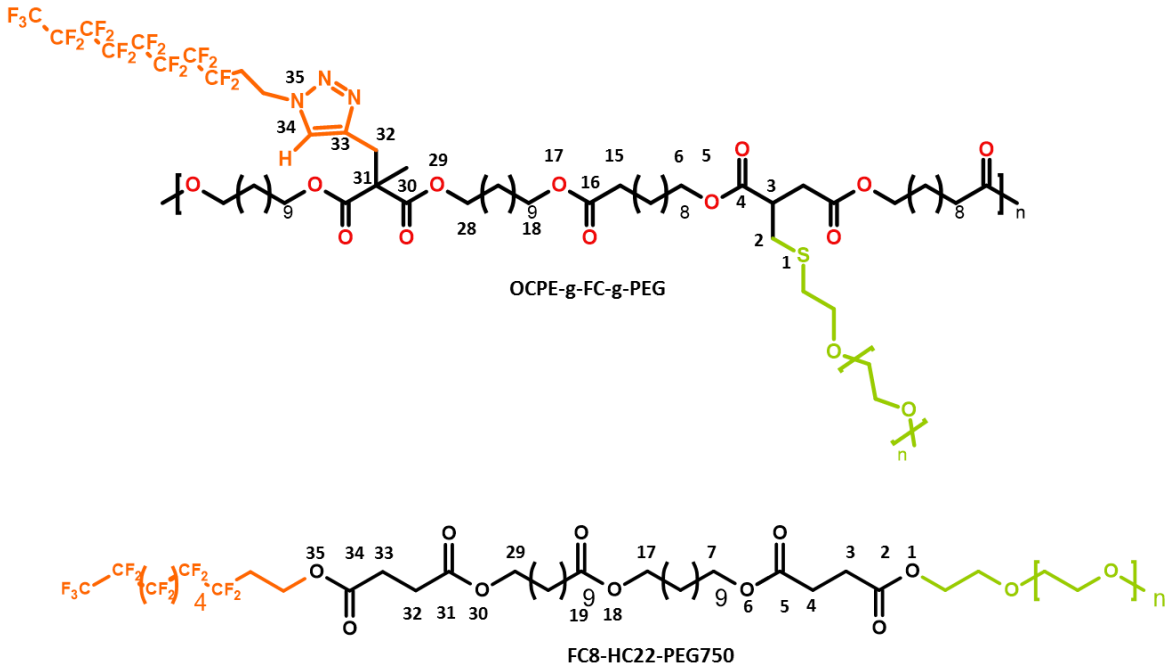
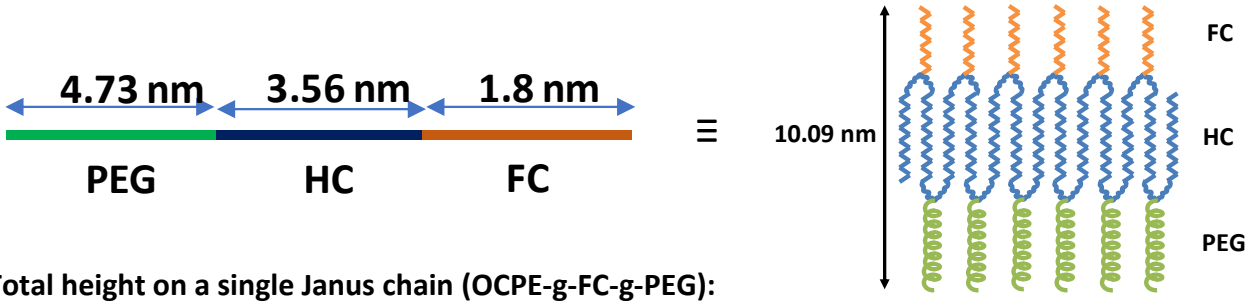


Figure S20: Counting the numbers of atoms in between PEG and fluorocarbon segments of graft copolymer and model compound; indicating the exact number of atoms (35) present in within FC and PEG segments in both of the cases.

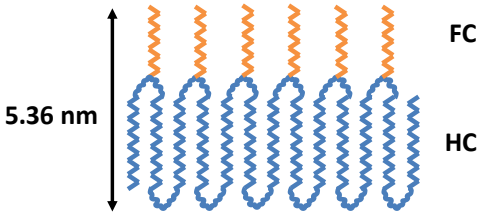
Estimating the sizes of the various segments



Total height on a single Janus chain (OCPE-g-FC-g-PEG):

4.73 + 3.56 + 1.8 = 10.09 nm
A bilayer height = 20.18 nm

Height before clicking PEG segment (OCPE-g-FC):



3.56 + 1.8 = 5.36 nm
A bilayer height = 10.72 nm

PEG segment:

PEG is known to form helical conformation in crystalline state. Where 1.95 nm is the length per 7 (-CH_2CH_2O-) repeat units in the helical crystalline organization (Takahashi et al. *Macromolecules*, 6, 672, **1973**). PEG 750 can be taken as having 17 repeat units; hence the estimated length would be (17/7) x 1.95 = **4.73 nm**

HC segment:

0.254 nm per pair of -CH_2-CH_2- in all-*trans* extended conformation adopted in a paraffinic lattice; The central HC segment carries 26 (+2) atoms; hence the estimated length would be 14 x 2.54 = **3.56 nm**

FC segment:

0.259 nm per pair of CF_2-CF_2 in twisted extended conformation adopted in a crystalline lattice; (Bunn et al. Nature, 174, 549, **1954**). The FC segment (F8) carries four pairs and, in addition to three pairs of methylenes (methines) units; hence the estimated length would be (4 x 0.259) + (3 x 0.254) = **1.8 nm**

References

1. Wright, S. W.; Hageman, D. L.; Wright, A. S.; McClure, L. D., Convenient preparations of t-butyl esters and ethers from t-butanol. *Tetrahedron Letters* **1997,** *38* (42), 7345-7348.
2. Sambasiva Rao, P.; Kurumurthy, C.; Veeraswamy, B.; Santhosh Kumar, G.; Poornachandra, Y.; Ganesh Kumar, C.; Vasamsetti, S. B.; Kotamraju, S.; Narsaiah, B., Synthesis of novel 1,2,3-triazole substituted-N-alkyl/aryl nitrone derivatives, their anti-inflammatory and anticancer activity. *European Journal of Medicinal Chemistry* **2014,** *80* (Supplement C), 184-191.
3. Matsuura, H.; Miyazawa, T., Vibrational analysis of molten poly(ethylene glycol). *Journal of Polymer Science Part A-2: Polymer Physics* **1969,** *7* (10), 1735-1744.
4. Menges, M. G.; Penelle, J.; Le Fevere de Ten Hove, C.; Jonas, A. M.; Schmidt-Rohr, K., Characterization of Long-Chain Aliphatic Polyesters: Crystalline and Supramolecular Structure of PE22,4 Elucidated by X-ray Scattering and Nuclear Magnetic Resonance. *Macromolecules* **2007,** *40* (24), 8714-8725.