SUPPLEMENTARY MATERIAL

Periodically clickable polyesters: Study of intra-chain self-segregation induced folding, crystallization and mesophase formation

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EXPERIMENTAL SECTION

and Materials Methods: Sodium hydride, Lithium aluminium hydride, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iododecane (FC iodide), propargyl bromide (80 wt.% in toluene) were purchased from Aldrich Chemical and used as such. Eicosanedioic acid was purchased from Tokyo Chemical Industry and used as such without purification. Diethyl malonate, thionyl chloride, potassium hydroxide, N,N-diisopropylethylamine and allyl bromide were purchased from Spectrochem Chemical Company and were used as such, except for thionyl chloride. Thionyl chloride was refluxed in presence of sulphur for 12 h and then distilled before use. Pyridine was purchased from Merck Chemicals and was dried in presence of KOH and distilled before use. All the solvents were dried and distilled prior use if necessary, following standard procedures. 1-Azido-1H,1H,2H,2Hperfluorodecane was synthesised using reported procedure.²¹ Eicosanedioic acid chloride was synthesised using a reported procedure.²² ¹H NMR spectroscopy was used to confirm the structure of all the monomers and polymers. NMR spectra of all the molecules were recorded using a Bruker AV400 MHz spectrometer in suitable deuterated solvents using TMS as internal standard. GPC studies were carried out using Shimadzu GPC system with UV-PDA detector. The separation of the polymers was achieved using PLgel 5 µm MIXED-C (Mixed gel, Varian) column operated at 35° C and CHCl₃ as the eluent. Molecular weights were calculated using standard calibration curve based on the data from UV-PDA detector using narrow polystyrene standards. All the DSC studies were carried out using a Mettler Toledo DSC1 instrument. All the samples were first heated to melt and then cooled to room temperature to remove any thermal history present in the samples. The heatingcooling cycle were subsequently run at a heating rate of 10°C/min. To confirm the reproducibility, the heating-cooling cycles were repeated thrice and the overlay of the 2nd and 3rd scans was checked. All the POM studies were carried out using an Olympus BX-51 polarizing microscope. All the samples were first heated to melt where there was no birefringence and then slowly cooled (5°C/min) to room temperature with 2 min isotherm at each temperature for equilibration prior to capturing the images. The X-ray diffraction (XRD) studies were performed using the PANalytical X'Pert PRO MP X-ray diffractometer. The diffractometer consists of a focusing elliptical mirror and a fast high resolution detector (PIXCEL); the wavelength

of the radiation employed was 0.15418 nm. To perform the XRD studies, samples were filled in Lindemann capillary tube and annealed above the second melting transition observed in the DSC thermogram. XRD profiles were recorded as a function of temperatures by cooling the samples from the melt at a cooling rate of 1deg/min. SAXS data were collected after equilibration at each temperature for ~10 mins. The TEM bright field (BF) images, dark field (DF) images, selected area electron diffraction (SAED) were recorded using a JEOL 2100F instrument at 200 kV operational mode. The samples for TEM were prepared by drop-casting a dilute chloroform solution (0.25mg/mL) on 400 mesh carbon coated Cu-grid. Variable temperature IR studies were carried out using a Perkin Elmer Spectrum One FTIR spectrometer. The samples for the studies were prepared by drop casting a CHCl₃ solution (2 mg/ml) of the sample on to a KBr pellet; the films were dried under vacuum and annealed above the clearing temperature for 1h prior to recording the spectrum. The pellets were mounted in a Specac variable temperature setup and heated to the required temperature; the sample was allowed to equilibrate for 5 min at each temperature, prior to recording its spectrum.

MONOMER (A)

Diethyl 2-(prop-2-yn-1-yl)malonate

Sodium hydride (5 g, 60 wt % in mineral oil, 125 mmol) was taken in dry THF, and the solution was cooled to 0°C. Diethylmalonate (60 g, 375 mmol) was then added dropwise to the ice-cold solution, and the reaction mixture was allowed to stir for 2 h at room temperature. To this solution propargyl bromide (15 g, 125 mmol) was added dropwise at 0°C and the solution was allowed to warm to room temperature with continuous stirring. The stirring was continued for 24 h. The THF was removed using a rotary evaporator, 50 ml water was added and the entire solution was extracted thrice with ethyl acetate. The combined organic layer was then concentrated in reduced pressure. The crude mixture contained both diethylmalonate and mono-propargyl functionalized diethylmalonate. The required product was separated from the diethylmalonate under reduced pressure by fractional distillation in vigreux column at 80°C. The distillation resulted in colourless oil yielding 70% pure product.

1H NMR (δ, CDCl₃): 1.28 (t, 6H, −OCH₂CH₃); 2.01 (t, 1H, CCH); 2.78 (dd, 2H, CCH₂); 3.56 (t, 1H, CH₂CH); 4.23 (m, 4H, −OCH₂CH₃)

S3

2-(Prop-2-yn-1-yl)propane-1,3-diol

Lithium aluminium hydride (LAH) (3.8 g, 101 mmol) was taken in dry diethyl ether, and the solution was cooled to 0°C. Diethyl 2-(prop-2-yn-1-yl)malonate (20 g, 101 mmol) was then added dropwise to the ice-cold solution with continuous stirring. The temperature was then allowed to come to room temperature and the stirring was continued for 36 h. After that a 5% NaOH solution was added slowly to the reaction mixture to quench the unreacted LAH. Once the quenching is completed (cease of hydrogen gas evolution) the reaction mixture was filtered through Buchner funnel, the residue was washed twice again with diethyl ether. The filtrate was collected and the diethyl ether removed under reduced pressure. The crude product was then distilled in Kugelrohr at 120°C under high vacuum. The product was a colourless viscous liquid with a yield of 50%.

1H NMR (δ, CD₃OD): 3.64 (m, 4H, -**CH**₂OH); 2.3 (dd, 2H, C**CH**₂); 2.26 (t, 1H, C**CH**); 1.86 (m, 1H, CH₂**CH**)

MONOMER (B)

Diethyl 2,2-di(prop-2-yn-1-yl)malonate

Sodium hydride (14.25 g, 60 wt % in mineral oil, 356.3 mmol) was taken in dry THF, and the solution was cooled to 0°C. Diethylmalonate (28 g, 178 mmol) was then added dropwise to the ice-cold solution, and the reaction mixture was allowed to stir for 2 h at room temperature. To this solution propargyl bromide (53 g, 445.4 mmol) was added dropwise at 0°C and allowed to reach room temperature with continuous stirring. The stirring was continued for 24 h. THF was removed using a rotary evaporator, 50 ml water was added and the entire solution was extracted thrice with ethyl acetate. The combined organic layer was then concentrated under reduced pressure. The crude product was then distilled under reduced pressure at 120°C which resulted in a colourless liquid with a yield of 90%.

1H NMR (δ, CDCl₃): 4.23 (q, 4H, -O**CH**₂CH₃); 2.99 (d, 4H, C**CH**₂); 2.04 (t, 2H, C**CH**); 1.28 (t, 6H, CH₂**CH**₃)

2,2-Di(prop-2-yn-1-yl)propane-1,3-diol

Lithium aluminium hydride (LAH) (4 g, 116.6 mmol) was taken in dry diethyl ether, and the solution was cooled to 0°C. Diethyl 2,2-(prop-2-yn-1-yl)malonate (25 g, 106 mmol) was then added dropwise to the ice-cold solution with continuous stirring. The

temperature was then allowed to come to room temperature and the stirring was continued for 36 h. After that a 5% NaOH solution was added slowly to the reaction mixture to quench the unreacted LAH. Once the quenching is over (cease of hydrogen gas evolution) the reaction mixture was filtered through Buchner funnel, the residue was washed twice again with diethyl ether. The filtrate was collected and the diethyl ether removed under reduced pressure. The crude product was then distilled in Kugelrohr at 140°C under high vacuum. The product was a white crystalline solid with a yield of 60%

1H NMR (δ, CDCl₃): 3.8 (d, 4H, -**CH**₂OH); 2.4 (d, 4H, C**CH**₂); 2.1 (t, 2H, C**CH**)

MONOMER (C)

Diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate

Sodium hydride (6.67 g, 60 wt % in mineral oil, 167.2 mmol) was taken in dry THF, and the solution was cooled to 0°C. Diethyl 2-(prop-2-yn-1-yl)malonate (30 g, 152 mmol) was then added dropwise to the ice-cold solution, and the reaction mixture was allowed to stir for 2 h at room temperature. To this solution allyl bromide (28 g, 227 mmol) was added dropwise at 0°C and allowed to reach room temperature with continuous stirring. The stirring was continued for 48 h. THF was removed using a rotary evaporator, 50 ml water was added and the entire solution was extracted thrice with ethyl acetate. The combined organic layer was then concentrated under reduced pressure. The crude product was then distilled under reduced pressure at 120°C which resulted in a colourless liquid with a yield of 90%.

1H NMR (δ, CDCl₃): 5.7 (m, 1H, CH₂CHCH₂); 5.2 (m, 2H, -CH₂CHCH₂); 4.26 (q, 4H, CH₂CH₃), 2.86 (d, 2H, -CH₂CCH; d, 2H, -CH₂CHCH₂); 2.06 (t, 1H, CCH); 1.3 (t, 6H, CH₂CH₃)

2-Allyl-2-(prop-2-yn-1-yl)propane-1,3-diol

Lithium aluminium hydride (LAH) (4.6 g, 120 mmol) was taken in dry diethyl ether, and the solution was cooled to 0°C. Diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate (26 g, 109.1 mmol) was then added dropwise to the ice-cold solution with continuous stirring. The temperature was then allowed to come to room temperature and the stirring was continued for 36h. After that a 5% NaOH solution was added slowly to the reaction mixture to quench the unreacted LAH. Once the quenching is over (cease of hydrogen gas evolution) the reaction mixture was filtered through Buchner

funnel, the residue was washed twice again with diethyl ether. The filtrate was collected and the diethyl ether removed under reduced pressure. The crude product was then distilled in Kugelrohr at 120°C under high vacuum. The product was colourless liquid with a yield of 50%.

1H NMR (δ , CDCl₃, D₂O): 5.82 (m, 1H, CH₂CHCH₂); 5.16 (m, 2H, -CH₂CHCH₂); 3.65 (q, 4H, CH₂OH), 2.27 (d, 2H, -CH₂CCH); 2.16(d, 2H, -CH₂CHCH₂); 2.04 (t, 1H, CCH)

TYPICAL POLYMERIZATION PROCEDURE

Eicosane diacidchloride was prepared from the corresponding diacid by refluxing overnight in freshly distilled thionyl chloride. The excess thionyl chloride was removed by pump under reduced pressure. The freshly prepared diacidchloride was then used directly for the polymerization.

Typical polymerization

A mixture of diacid chloride (2 g) and either of the diols B or C (in exactly 1:1 molar ratio mixture) was dissolved in 8 ml of dry toluene and was heated at 90°C for 24 h under continuous stirring. The progress of the reaction was monitored by the evolution of HCl gas (detected by holding a pH paper at the mouth of guard tube). When the evolution of HCl stopped, the reaction mixture was quenched by pouring methanol into it which results into the precipitation of the polymer from the solution. The solid polymer was dissolved again in CHCl₃ and reprecipitated thrice into methanol. The polymer was dried under high vacuum.

PE-DP: ¹H NMR (δ, CDCl₃): 4.1 (s, 4H, OCH₂); 2.4 (d, 4H, CCH₂); 2.33 (t, 4H, O₂CCH₂(CH₂)₁₆CH₂CO₂); 2.04 (t, 2H, CCH); 1.6 (t, 4H, O₂CCH₂CH₂(CH₂)₁₄CH₂CH₂CO₂); 1.24 (S, 28H, O₂CCH₂CH₂CH₂(CH₂)₁₄CH₂CH₂CO₂);

PE-AP: ¹H NMR (δ, CDCl₃): 5.76 (m, 1H, CH₂CHCH₂); 5.15 (m, 2H, -CH₂CHCH₂); 4.01 (s, 4H, OCH₂); 2.33 (t, 4H, O₂CCH₂(CH₂)₁₆CH₂CO₂); 2.26 (d, 2H, -CH₂CCH; d, 2H, -CH₂CHCH₂); 2.02 (t, 2H, CCH); 1.6 (t, 4H, O₂CCH₂CH₂(CH₂)₁₄CH₂CH₂CO₂); 1.25 (S, 28H, O₂CCH₂CH₂(CH₂)₁₄CH₂CH₂CO₂)

Modified procedure for polymerization using monomer A.

Though the polymerization is quite straight forward, it did not work well for the monomer A. A slightly modified procedure was used where the polymerization was carried out in the presence of pyridine to capture the HCl released.

In presence of pyridine (2.1 equivalents), the reaction mixture (1:1 mixture of the monomer A and the diacidchloride in toluene) was stirred at room temperature for 2 h, and then it was heated at 70° C for 24 h with continuous stirring. The purification of the polymer was done in the same way as earlier.

PE-MP: ¹H NMR (δ, CDCl₃): 4.14 (s, 4H, OCH₂); 2.33 (7H, -CH₂CCH, CH₂CH, O₂CCH₂(CH₂)₁₆CH₂CO₂); 2.01 (t, 2H, CCH); 1.6 (t, 4H, O₂CCH₂(CH₂)₁₄CH₂CH₂CO₂); 1.25 (S, 28H, O₂CCH₂CH₂(CH₂)₁₄CH₂CH₂CO₂)

POST POLYMERIZATION MODIFICATION USING AZIDE-ALKYNE CLICK CHEMISTRY

Two approaches were used for the azide-alkyne click chemistry-

- 1. In the approach-I, $(Ph_3P)_3CuBr$ was used as the catalyst
- 2. In the approach-II, Cu(I)I was used as the catalyst

PE-MP-F: 200 mg (0.48 mmol) of the parent polyester and 352 mg (0.72 mmol) of FC azide were dissolved in 5 ml chloroform and purged with N₂ gas. 44 mg (0.048 mmol) (Ph₃P)₃CuBr and 120 μ l (0.48 mmol) DIPEA were then added into the solution and again purged with N₂ gas. After degassing, the reaction mixture was stirred at 50°C for 3 days. The reaction mixture was then concentrated and reprecipitated twice in methanol to give a light brown coloured polymer. The yield of the polymer was 95%

1H NMR (δ, CDCl₃): 7.44 (1H, s, triazole ring); 4.65 (2H, t, CH**CH**₂C); 4.1 (4H, m, -O**CH**₂CH); 2.8 (2H, m, CF₂CH₂**CH**₂, 2H, m, CF₂ **CH**₂); 2.47 (1H, M, CH₂**CH**); 2.3 (4H, t, -OCO**CH**₂); 1.58 (4H, t, -OCOCH₂**CH**₂ **&** H₂**O**); 1.23 (28H, s, (-**CH**₂-)_n)

PE-DP-F: 100 mg (0.22 mmol) of the parent polyester and 320 mg (0.65 mmol) of FC azide were dissolved in 3ml chloroform and purged with N₂ gas. 41 mg (0.044 mmol) (Ph₃P)₃CuBr and 112 μ l (0.44 mmol) DIPEA were then added into the solution

and again purged with N_2 gas. The reaction conditions and the purification procedure were same as mentioned earlier. The polymer was light brown in color with a yield of 90%

1H NMR (δ, CDCl₃): 7.44 (1H, s, triazole ring); 4.67 (4H, t, C**CH**₂C); 3.9 (4H, s, -O**CH**₂CH); 2.8 (4H, m, CF₂CH₂**CH**₂, 4H, m, CF₂ **CH**₂); 2.36 (4H, t, -OCO**CH**₂); 1.6 (4H, t, -OCOCH₂**CH**₂ & H₂**O**); 1.23 (28H, s, (-**CH**₂-)_n)

PE-PA-F: 1 g (2.2 mmol) of the parent polyester and 1.6 g (3.25 mmol) of FC azide were dissolved in 10 ml chloroform and purged with N₂ gas. 46 mg (0.23 mmol) Cu(I)I and 560 μ I (2.2 mmol) DIPEA were then added into the solution and again purged with N₂ gas. The reaction conditions and the purification procedure were same as mentioned earlier. The polymer was light brown in color with a yield of 94%

1H NMR (δ , CDCl₃): 7.4 (1H, s, triazole ring); 5.85 (1H, m, CH₂CHCH₂), 5.1 (2H, m, -CH₂CHCH₂), 4.67 (2H, t, CHCH₂C); 4.0 (4H, m, -OCH₂CH); 2.8 (2H, m, CF₂CH₂CH₂, 2H, m, CF₂CH₂); 2.35 (4H, t, -OCOCH₂); 2.3 (2H, m, -CH₂CHCH₂); 1.6 (4H, t, -OCOCH₂CH₂ & H₂O); 1.24 (28H, s, (-CH₂-)_n)



Figure S1(a): ¹H NMR spectra of 2-propargyl-1,3-propanediol in CD₃OD and of the parent polymer **PE-MP** in CDCl₃. The marked region shows the absence of the end group in the polymer



Figure S1(b): ¹H NMR spectra of 2,2-dipropargyl-1,3-propanediol and the parent polymer **PE-DP** in CDCl₃. The marked region shows the absence of the end group in the polymer.



Figure S1(c): ¹H NMR spectra of 2-allyl-2-propargyl-1,3-propanediol in $CDCl_3 + D_2O$ and of the parent polymer **PE-AP** in $CDCl_3$. The marked region shows the absence of the end group in the polymer.



Figure S2 (a): Stack plot of the GPC chromatograms of the parent polyesters recorded using $CHCI_3$ as the eluent. The molecular weights were estimated using polystyrene-based standard calibration curve.



Figure S2 (b): Stack plot of the 1H NMR spectra of the three parent polymers; the expanded regions shows the peaks due to the end-groups. The DP is calculated by comparing the intensity of the peaks corresponding to the end group(s) with that of a backbone methylene peak at ~4.00 - 4.2 ppm. It is assumed that the end-groups are present on both ends of the polymer chain and hence this value provides the upper bound for the Mn.



Figure S3 (a): ¹³C NMR of the parent polymer, PE-MP in CDCl₃



Figure S3 (b): ${}^{13}C$ - ${}^{1}H$ Hetero-correlation of the parent polymer, **PE-MP**. From the correlation spectra it is evident that the peak 2.3 ppm corresponds to three different kinds of ${}^{1}Hs$.



Figure S4 (a): ¹H NMR spectra of the periodically grafted copolymer named PE-MP-F in $CDCI_3$



Figure S4 (b): ¹H NMR spectra of the periodically grafted copolymer named **PE-DP-F** in CDCl₃



Figure S4 (c): ¹H NMR spectra of the periodically grafted copolymer named **PE-AP-F** in CDCl₃



Figure S5: DSC thermograms of the FC modified periodically grafted copolymers. The scans were run at 10 ^oC min-1 and all the thermograms are completely reproducible. Both **PE-MP-F** and **PE-DP-F** exhibit two transitions corresponding to HC and FC domains but **PE-AP-F** shows only one transition with a shoulder in the cooling scan.



Figure S6 (a): POM images **PE-DP-F** recorded at various temperatures under crosspolar. POM images showed clear transition from an isotropic molten state to a LC mesophase.



Figure S6 (b): POM images **PE-MP-F** recorded at various temperatures under cross-polar. POM images showed clear transition from an isotropic molten state to a LC mesophase.



Figure S7: Variable temperature WAXS data of the FC modified periodically grafted copolymers. Both **PE-MP-F** and **PE-AP-F** exhibit two higher angle peaks corresponding to the lateral spacing of HC and FC. There is a sharpening of the peak corresponding to HC in case of **PE-MP-F** is observed prior to the melting of HC compared to that at room temperature. The peak corresponding to HC is absent in the case of **PE-DP-F**.



Figure S8: Variable temperature SAXS data of the polymer **PE-AP-F** showing strong 1st order scattering and weak higher order scattering.



Figure S9: All the structures were optimized using Gaussian 09 package. All the calculations were carried out using 6-31G* basis set.

The above structures serve as the **least constrained models** for the three polymers; the carbon atoms marked by arrows represent the locations at which the two adjacent repeat units, that form the polymer backbone, would be attached. Whereas these represent minimized structures in the gas phase, for packing in the solid state, the intervening carbon segments lying between the FC and HC units would need to reconfigure with some *gauche* states to permit the adjacent backbone HC segments and pendant FC segments to lie roughly parallel to each other, as would be required to pack in the solid state. Thus, adopting the zigzag folded form, would requires the carbon segments close to the quaternary (or tertiary in **PE-MP-F**) backbone carbon to adopt significant gauche states; this was also suggested by Hove et al. (ref **9a** - *Nature Materials* **2004**, *3*, 33).



Figure S10: Brightfield TEM image of **PE-DP-F** along with the inset showing the SAED pattern.



Figure S11 (a): Variable temperature IR spectra of **PE-DP-F** of the C-H stretching region that is sensitive to conformation of the polymethylene segment; the variation of the v_{sym} and v_{asym} C-H stretching vibrations is plotted as a function of temperature in the bottom panel.



Figure S11 (b): Variable temperature IR spectra of **PE-AP-F** of the C-H stretching region that is sensitive to conformation of the polymethylene segment; the variation of the v_{sym} and v_{asym} C-H stretching vibrations is plotted as a function of temperature in the bottom panel.