Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPLEMENTARY INFORMATION

Precise control of grafting density in periodically grafted amphiphilic copolymers: An alternate strategy to fine-tune the lamellar spacing in the sub-10 nm regime

Ramkrishna Sarkar[a], E. Bhoje Gowd[b], and S. Ramakrishnan*[a]

[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, INDIA

[b] Material Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram – 695019, Kerala, INDIA

e-mail: raman@iisc.ac.in

Table of contents

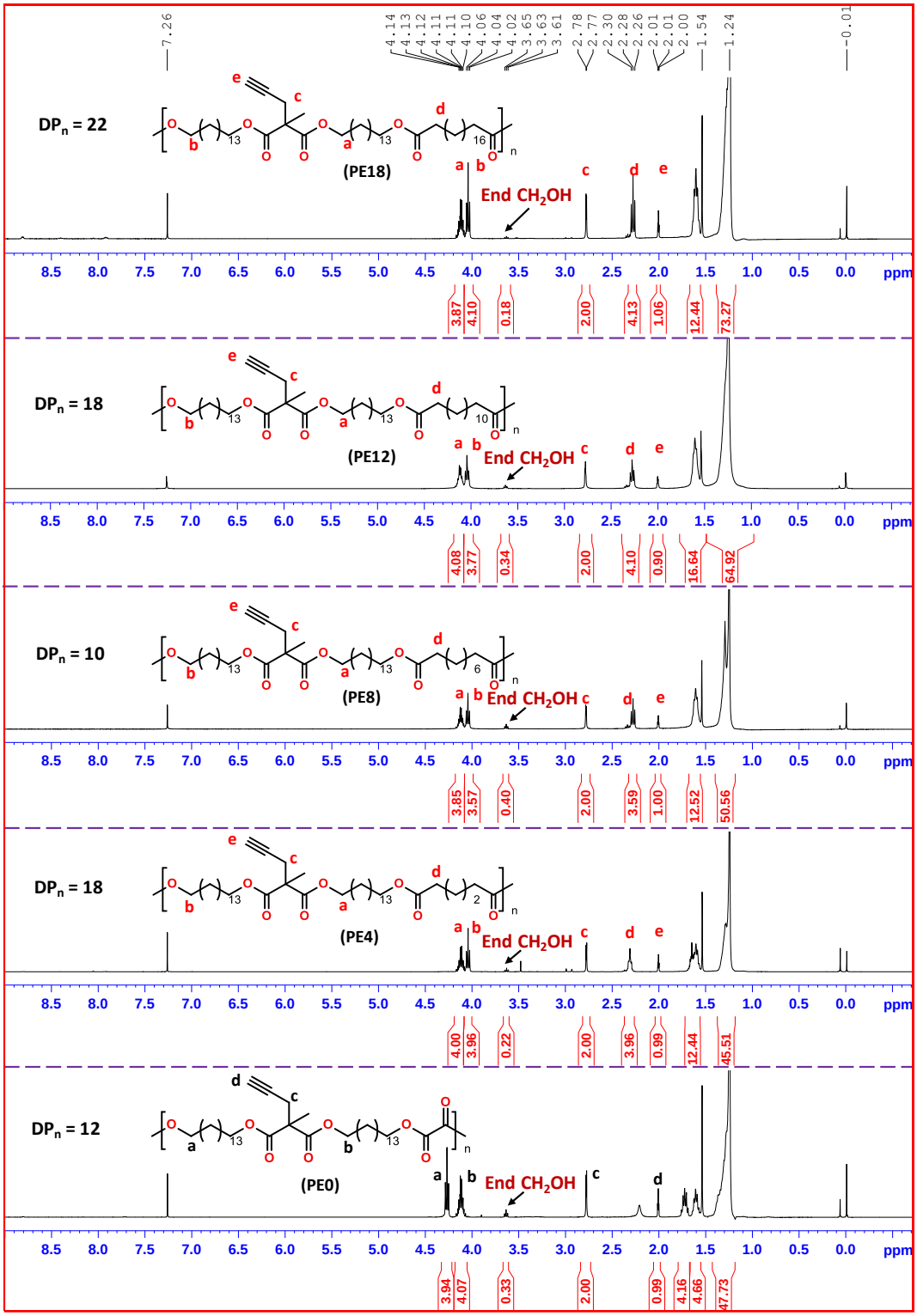


***Figure S1**: Stacked ^{1}H NMR spectra of parent polymers (PEx) derived from propargyl bearing diol and diacid chlorides of variable lengths. The average degree of polymerization (DP_n) of the polymers was estimated using the intensity of the C**H**$_2$-OH end group peaks (at ~3.65 ppm), assuming that each chain, on an average, has a single C**H**$_2$-OH end group; the values thus obtained are listed against each spectrum.*

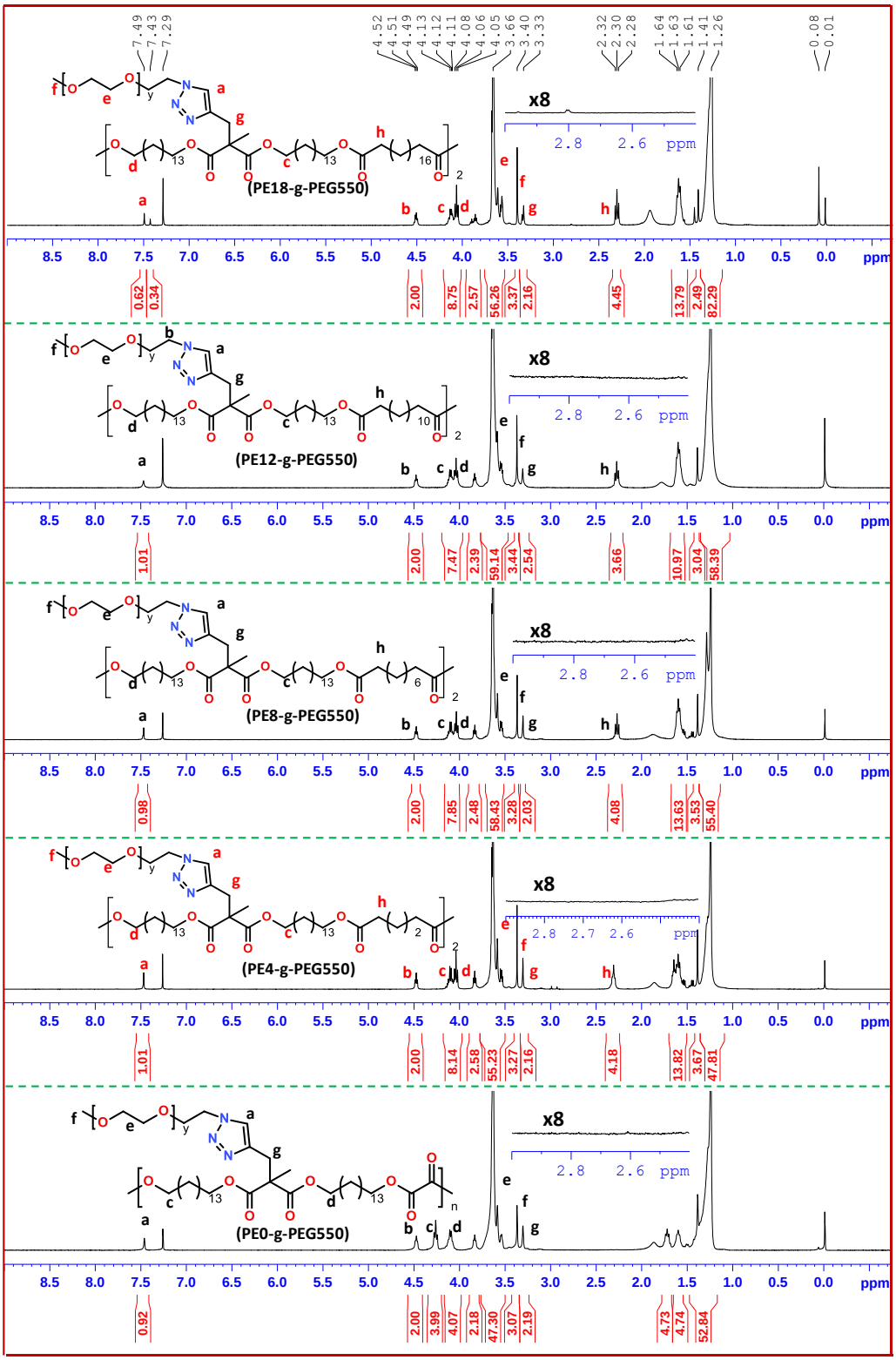


***Figure S2**: Stacked ^{1}H spectra of PEG550 grafted copolymers (PEx-g-PEG550). The inset shows a Y-expanded region to reveal the complete disappearance of propargyl peak after alkyne-azide click reaction. The end-group signals are no longer visible since there is an overlap with the PEG550 segments; hence, the DP_n values were not estimated. Since the click reactions is not expected to cause any chain degradation, the DP values could be taken to be the same as that of the parent polyesters.*

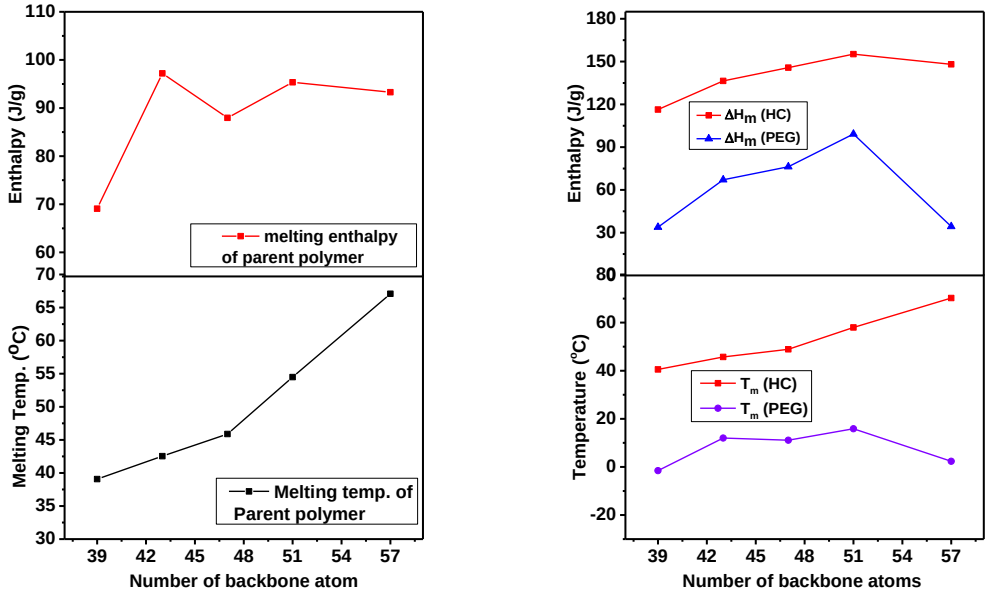


***Figure S3**: Variation of melting temperature and associated enthalpies of parent polymers (PEx) with total number of backbone atoms. (Enthalpies are not normalized). Right side shows variation of melting temperature and associated enthalpies (normalized w.r.t weight fractions of the segments) in graft copolymers (PEx-g-PEG550) with total number of backbone atoms. An increment in melting and crystallization temperature was observed with increasing backbone chain length.*

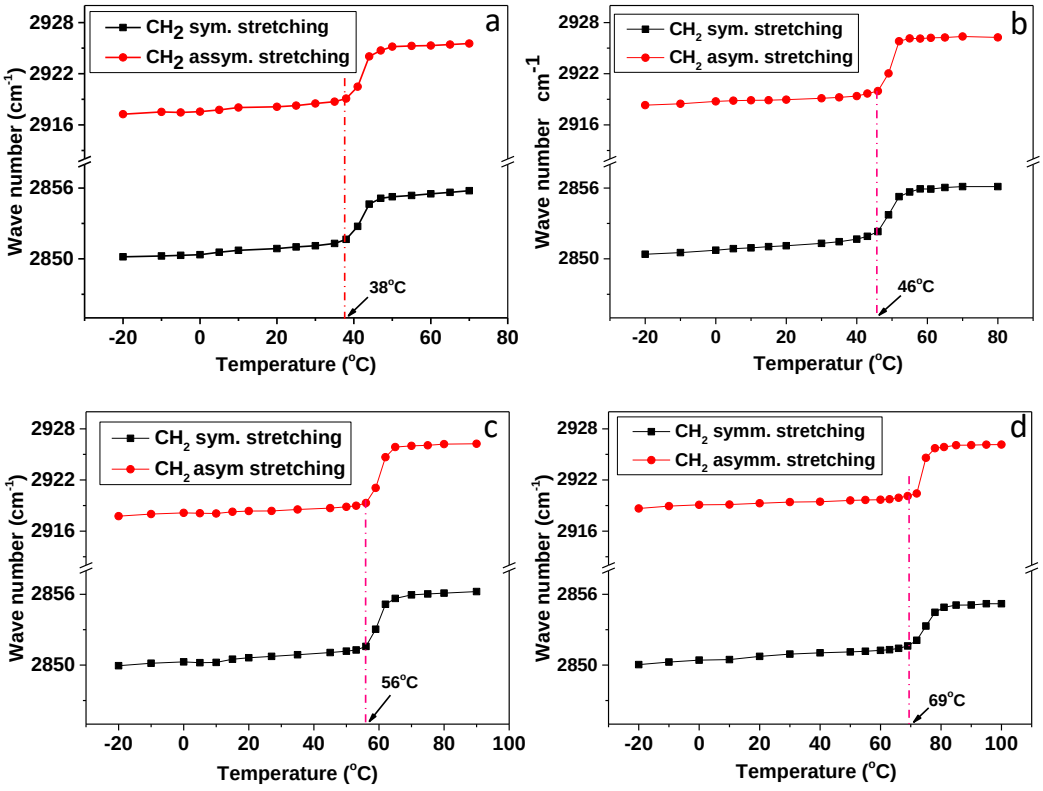


***Figure S4**: Variation of CH_2 symmetric and asymmetric stretching frequencies with temperature for PEG550 grafted copolymers, PEx-g-PEG550. The onset temperature matches with DSC onset temperature of higher temperature peaks, confirming that the higher temperature peak is due to the HC segment. a=PE0-g-PEG550, b=PE8-g-PEG550, c=PE12-g-PEG550, d=PE18-g-PEG550.*

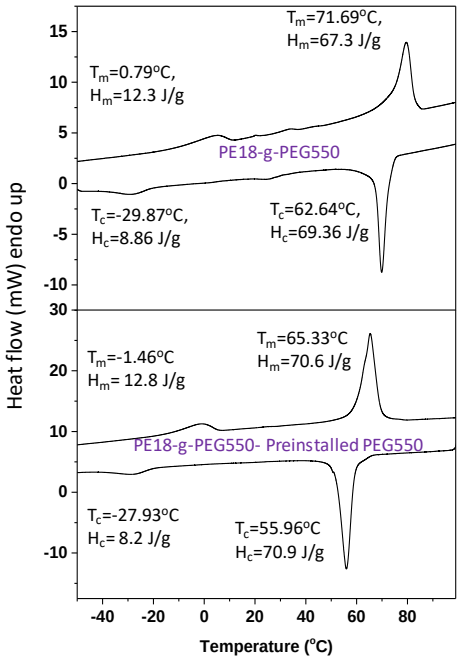


***Figure S5**: DSC stack plot of the PE18-g-PEG550 prepared via condensation of the diol bearing preinstalled PEG550 with corresponding acid chloride; and the polymer (PE18-g-PEG550) prepared by thermal alkyne-azide click reaction of the parent polymer (PE18) with PEG550 azide. The melting/crystallization temperatures as well as their associated enthalpies of these two polymers are not significantly different, confirming that the influence of regiospecificity is limited, if any.*

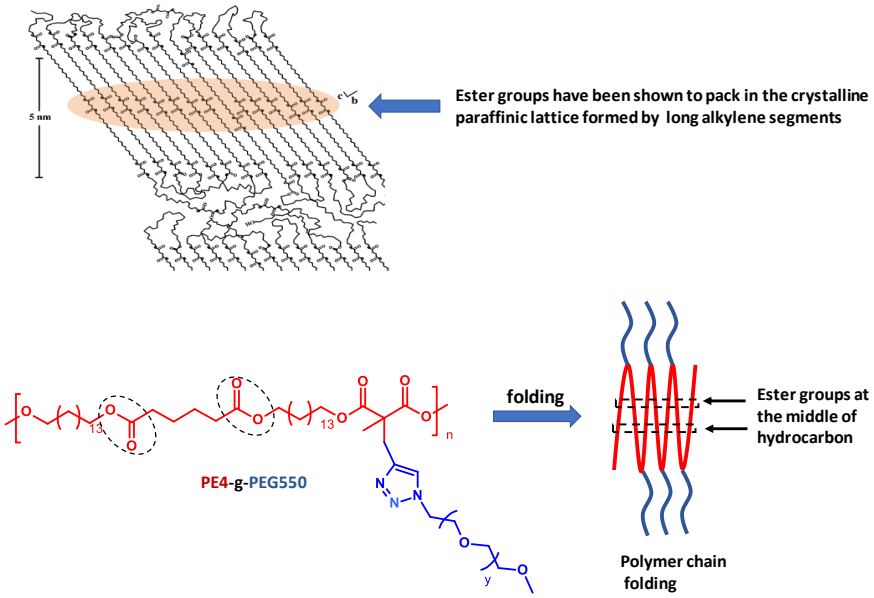


***Figure S6**: Top: schematic depiction of long chain polyester where ester groups are shown to be accommodated within paraffinic lattice. [Adapted from reference [1]] Bottom: Anticipated chain folding of a representative polymer, PE4-g-PEG550, where crystalline backbone contains ester groups at the middle.*

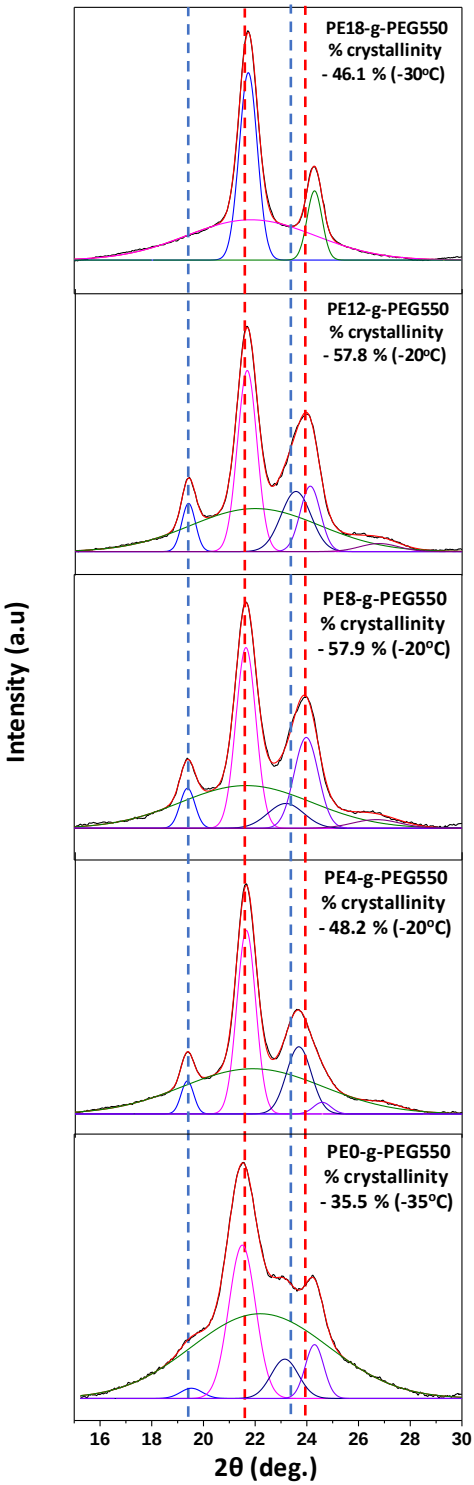


Figure S7*: Deconvoluted WAXS profiles of the graft copolymers (PEx-g-PEG550) recorded at lower temperature. Dotted lines provide visual guidelines; red lines denote HC peaks and blue denote PEG peaks. The crystalline PEG peak at 2ϑ ~23.5° is clearly revealed for PE0-g-PEG550, PE8-g-PEG550 and PE12-g-PEG550.*

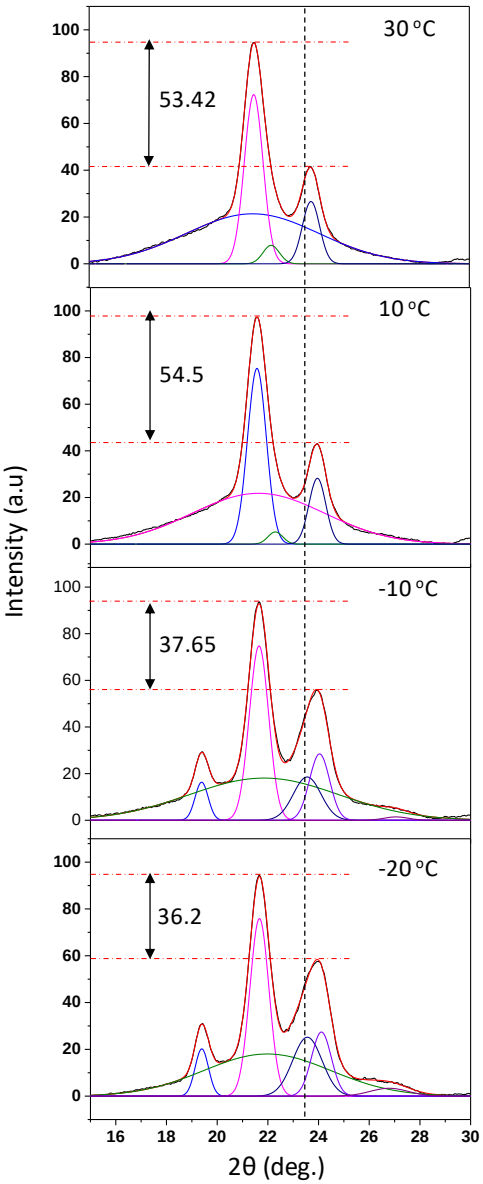


Figure S8: *Deconvoluted WAXS profiles of PE12-g-PEG550 recorded at temperature below (-20 °C, -10 °C) and above (10 °C, 30 °C) PEG melting. The crystalline peak at ~23.5 ° (visually guided by black dotted line) disappears above melting temperature of PEG, resulting a reduction of ~23.6 ° peak intensity as reflected by the intensity difference of the two peaks at ~21.5 ° and ~23.6 °.*

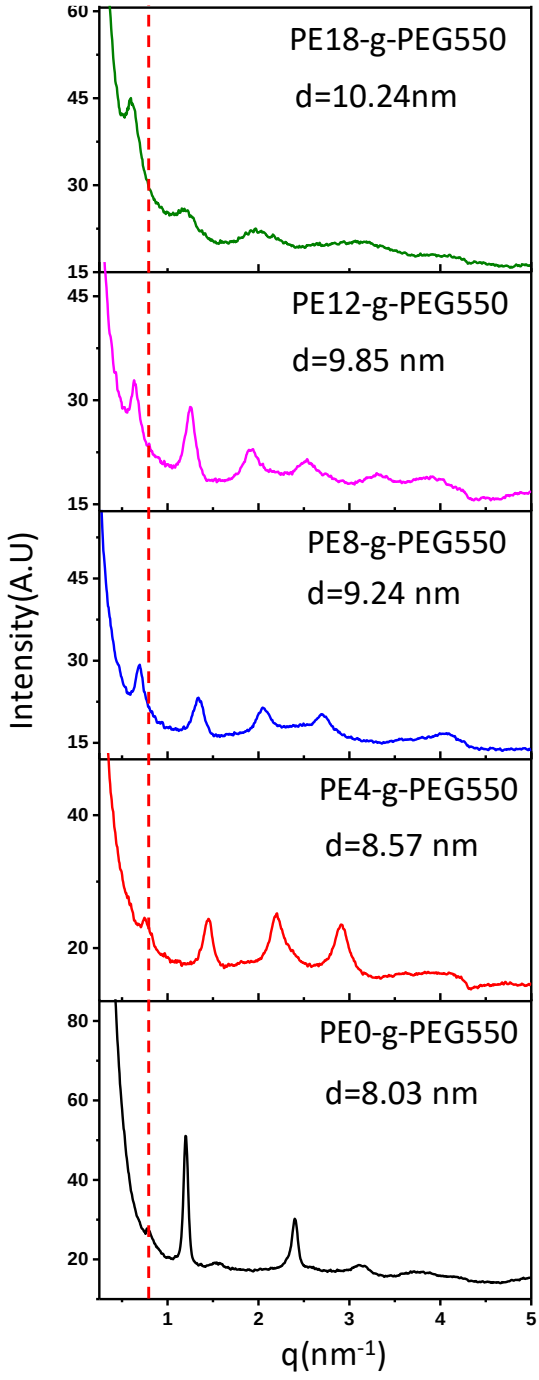


Figure S9: *Stack plot of the SAXS profiles of various PEx-g-PEG550 samples recorded at 25°C; the dashed line provides a guide to reveal the increase of d-spacing (decrease of q-value) as a function of backbone segment length. The d-spacing was calculated based on the average of q values obtained from the first and higher orders peaks. In the case of PE0-g-PEG550, the weaker set of peaks corresponding to the longer d-spacing is used to estimate the increment per methylene unit (Figure 6); this is based on the assumption that in this lamellar organization the backbone is in a crystalline lattice adopting an extended all-trans conformation.*

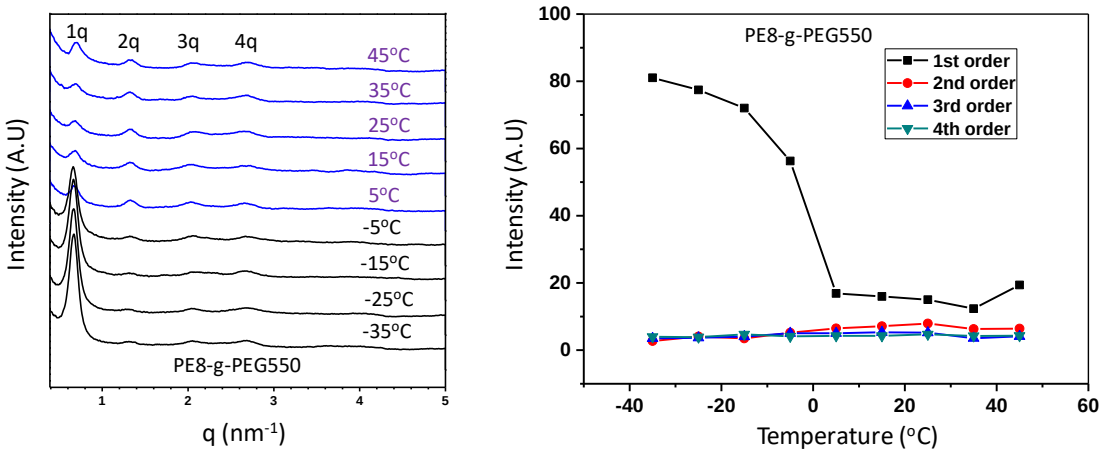


Figure S10: *Variable temperature SAXS profiles of PE8-g-PEG550. The sample was first cooled to -35°C and then heated to 45°C; at each temperature it was allowed to equilibrate for 5 min before data collection. Plot on the right depicts variation of the peak intensities with temperature; a drastic reduction in the intensity of the first order peak upon melting of PEG segments is observed, along with a small increase in the 2nd order peak.*

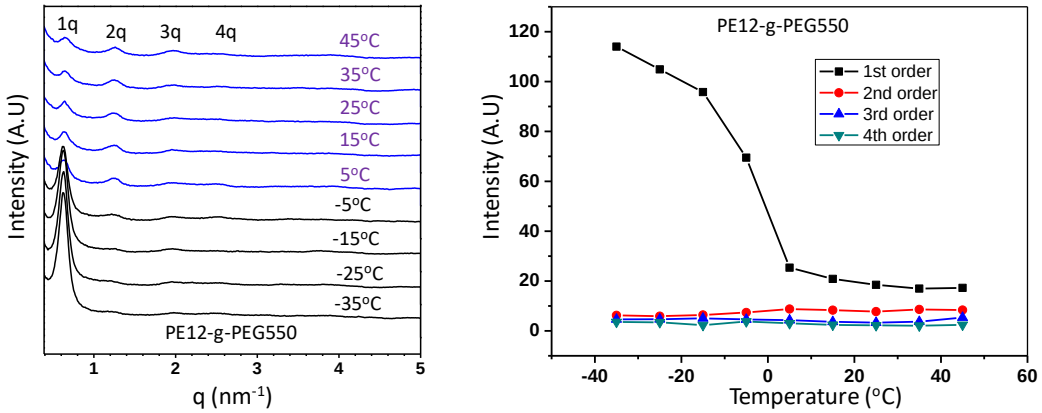


Figure S11: *Variable temperature SAXS profile of PE12-g-PEG550. The sample was first cooled to -35°C and then heated to 45°C; at each temperature it was allowed to equilibrate for 5 min before data collection. Plot on the right depicts variation of the peak intensities with temperature; a drastic reduction in the intensity of the first order peak upon melting of PEG segments is observed, along with a small increase in the 2nd order peak.*

Estimating the PEG550 layer thickness in PGACs based on earlier studies by Chandra et al.[5]

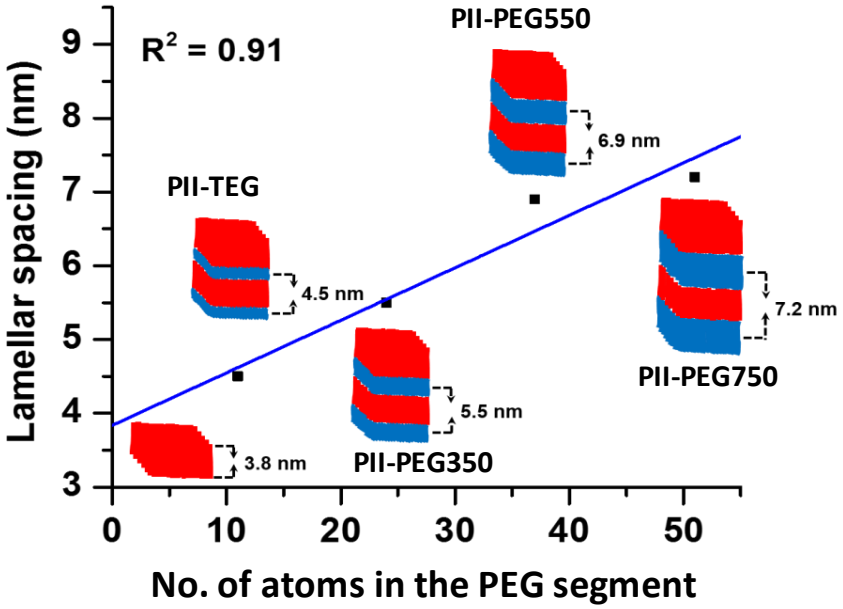


Figure S12: *Variation of inter-lamellar spacing in PGACs bearing long crystallizable hydrocarbon segment (20 backbone methylene), as function of PEG chain length. The extrapolated value (3.8 nm) yielded folded backbone length which matches well with the theoretically estimated values [adapted from reference[5]] .*

Lamellar spacing of the PGAC, poly(icosylene itaconate), containing 20 methylene hydrocarbon backbone and PEG550 as the pendant segment was 6.9 nm at room temperature, which is above the melting temperature of PEG segment and below that of the backbone HC segment. Contribution of backbone segment to the observed lamella is estimated to be 3.8 nm by extrapolation; hence, the contribution of amorphous PEG550 segment to lamella can be calculated to be: (6.9-3.8) = 3.1 nm. This value matches reasonably well with contribution of PEG550 segments to the lamellar spacing of 3.27 nm, in the present study.

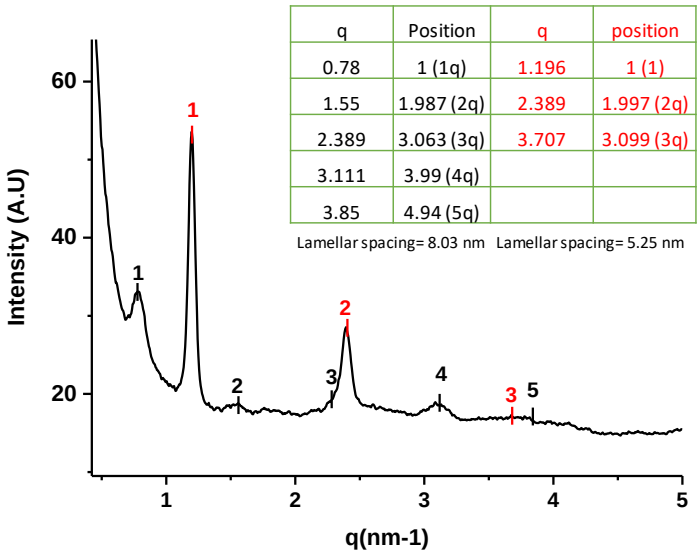
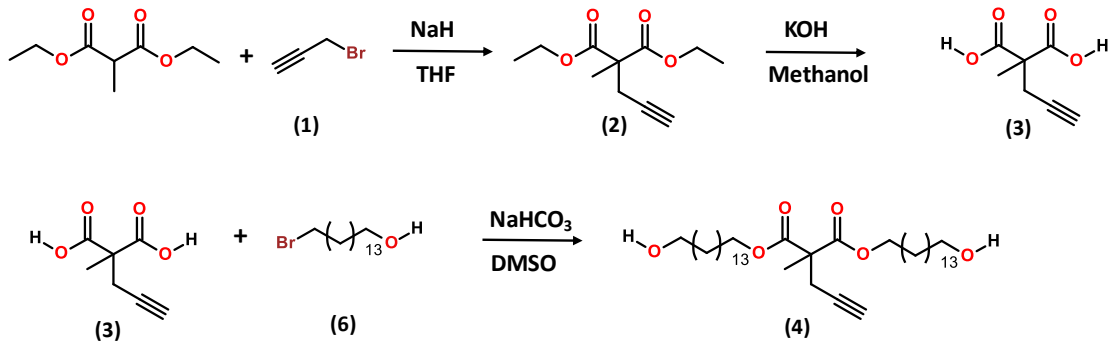


Figure S13: *SAXS profile of PE0-g-PEG550 at 25°C (cooled from melt). The two sets of peaks, one marked in black and the other in red, reveal the formation of two types of lamella with inter-lamellar spacings of 8.03 nm and 5.25 nm, respectively. The peaks marked in red are more intense and do not vary in intensity as a function of temperature (see figure 5, in the main manuscript). The weaker set of peaks (in black) corresponding to the longer d-spacing is used to estimate the increment per methylene unit (Figure 6); this is based on the assumption that in this lamellar organization the backbone is in a crystalline lattice adopting an extended all-trans conformation.*

Synthesis of the monomers and intermediates



Scheme S1*: Synthesis scheme of propargyl bearing diol*

Diethyl-2-methyl-2propargylmalonate (2)

A 500 mL round bottom charged with 7 g sodium hydride (60 wt. % in mineral oil, 175.07 mmol) and 200 mL dry-distilled THF was added to it. 20.31 g (116.57 mmol) diethyl methylmalonate was added dropwise to it while maintaining the temperature at 0 ˚C. The reaction mixture was stirred continuously for 2 h at 0 ˚C. Subsequently, 20.85 (175.2 mmol) propargyl bromide was added dropwise and reaction was continued at room temperature for 24 h. THF was removed using rotary evaporator and 200 mL ethyl acetate was added to it. The organic layer containing product was washed twice (2 x 100 mL) with water and passed through sodium sulphate. Finally, solvent was removed under reduced pressure to yield product, which was distilled in Kugelrohr at 85 ˚C under reduced pressure with a yield of 18.27 g colourless liquid product (74 % 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)

To a 250 ml round bottom flask, 13.12 g (233.84 mmol) potassium hydroxide was added and dissolved in minimum amount of water. 200 ml methanol was added to it. Subsequently, 8 g (37.68 mmol) diethyl-2-methyl-2-propargylmalonate (2) was added and the reaction was continued at 50 ºC for 24 h. Subsequently, 50 mL water was added to it and methanol was removed by rotary evaporation. pH of the solution made to ~4 by addition of HCl and product was extracted in 150 mL (3 x 50 mL) ethyl acetate. The organic solvent was dried over sodium

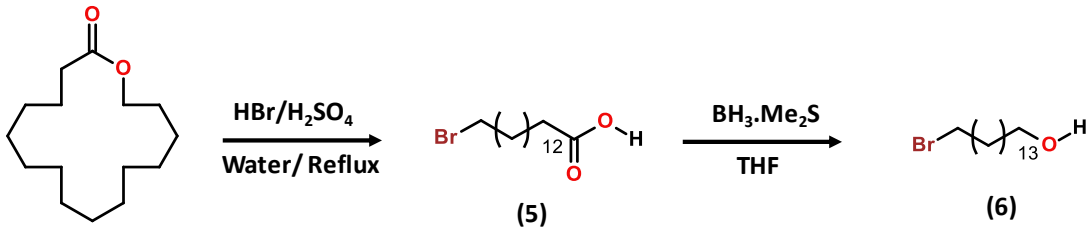
sulphate. Finally, removal of organic solvent under reduced pressure resulted 5.12 g solid product with 87 % yield.

^{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-hydroxypentadecanyl) 2- methyl-2- propargylmalonate (4)

2.5 g (16.23 mmol) 2-methyl-2propargylmalonic acid (3) and 8.72 g (103.8 mmol) sodium bicarbonate were taken in 100 mL DMSO. 16 g (52.11mmol) 15-bromopentadecanol along with catalytic amount potassium iodide were added to it. The resulted reaction mixture was stirred at 40 ˚C for 4 days. 150 mL chloroform 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 methanol with 55 % yield (5.37 g)

^{1}H NMR (δ, $CDCl_3$): 4.11 {(m, 4H, -CO_2**CH_2**(CH_2)$_{13}$$CH_2$OH)}X ; 3.63 {(t, 4H, HO**CH_2**(CH_2)$_{13}$$CH_2$-)}; 2.78 (d, 2H, -**$CH_2$**CCH); 2 (t, 1H, -$CH_2$C**CH**); 1.54 (s, 3H, -**CH_3**)



Scheme S2*: Synthesis scheme of 15-bromo-1-pentadecanol*

15-Bromopentadecanoic acid (5)

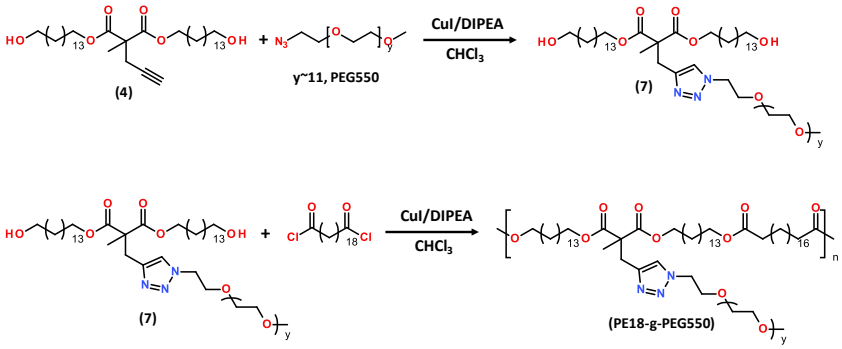
24 g (100 mmol) pentadecanolide were taken in a 500 ml round bottom flask. 200 ml 48% aqueous hydrobromic acid was added to it. 20 ml concentrated sulfuric acid was slowly added to it. The reaction mixture was refluxed for 48 h. Subsequently, product was extracted in 250 ml chloroform which was washed twice with water (2x100ml). The product containing organic layer was passed through sodium and concentrated to obtain 29.8 g solid 15-bromo-1-pentadecanoic acid with 93 % yield.

^{1}H NMR (δ, $CDCl_3$): 3.40 {(t, 2H, Br**CH_2**(CH_2)$_{12}$$CH_2CO_2H$)}; 2.34 {(t, 2H, $BrCH_2$(CH_2)$_{12}$**CH_2**CO_2H)}; 1.85 {(m, 2H, $BrCH_2$**CH_2**(CH_2)$_{11}$$CH_2CO_2H$)}; 1.63 {(m, 2H, $BrCH_2$ (CH_2)$_{12}$**CH_2**CH_2CO_2H)}

15-Bromo-1-pentadecanol (6)

14 g (43.6 mmol) 15-bromopentadecanoic acid (5) 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 g (65 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 11.6 g (87 % yield) product.

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



Scheme S3*: Synthesis scheme of PE18-g-PEG550 with preinstalled PEG 550 segment*

PEG550 grafted diol (7)

A reaction vessel was charged with 1 g (1.64 mmol) compound 4 and 1.18 g (1.95 mmol) PEG550 azide along with 10 ml chloroform. 31 mg copper(I) iodide and 0.3 ml DIPEA was added it. The reaction mixture was purged with nitrogen for 15 min and air tighten. The reaction was carried out at 50 ^oC for 3 days. Subsequently centrifugation was carried out for the removal of copper salt. The solution was concentrated and product was obtained by reprecipitation from methanol

^{1}H NMR (δ, $CDCl_3$): 7.53 (1H, s , triazole ring); 4.49 {2H, t, Triazole-**CH_2**$CH_2(CH_2CH_2O)_yCH_3$}; 4.29 {4H , t, -O(O)C**CH_2**$CH_2(CH_2)_{11}CH_2CH_2OH$ }; 3.62 {m, 50 H, Triazole-CH_2CH_2(**CH_2CH_2**O)$_y$$CH_3$}; 3.35 {s, 3 H, Triazole-$CH_2CH_2(CH_2CH_2O)_y$**CH_3**}; 3.32 {s, 2 H, -**CH_2**Triazole-$CH_2CH_2(CH_2CH_2O)_yCH_3$}

The polymer was prepared using similar polymerization procedure to that of PEx.

PEG-550-tosylate monomethyl ether

2.5 g (62.5 mmol) sodium hydroxide was taken in 250 ml round bottom flux and dissolved in minimum amount of water. 12 g (21.8 mmol) PEG 550 monomethyl ether and 150 ml THF was then added to it. The contents were kept in ice bath and subsequently, 6.24 g (32.7 mmol) tosyl chloride was added to it. The mixtures were stirred for 36 h at RT. 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 sulphate and concentrated under vacuum to yield product. Final product was obtained with 82 % (12.61 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**-Ar-CH_3);3.62 (S, CH_3O-[**CH_2CH_2**$O]_n$-CH_2CH_2 -Ar-CH_3); 3.35 (s,3H, **CH_3**O-$[CH_2CH_2O]_n$-CH_2CH_2-Ar-CH_3); 2.42 (s, 3H, CH_3O-$[CH_2CH_2O]_n$-CH_2CH_2-Ar-**CH_3**)

PEG-550 monomethyl azide

5 g (7.09 mmol) PEG 550 tosylate and 1.84 g (28.36 mmol) sodium azide were taken in 100 ml round bottom flask. 50 ml acetonitrile was added to it and the reaction was continued at reflux for 3 days. Acetonitrile was removed using rotary evaporator and 70 ml chloroform was added to it. The organic solvent containing product was washed twice (2x50 ml) with water and passed through sodium sulphate. Finally, removal of solvent under reduced pressure yielded 3.31 g product with 79 % yield.

^{1}H NMR (δ, $CDCl_3$): 3.62 (S, CH_3O-[**CH_2CH_2**$O]_n$-CH_2CH_2 -Ar-CH_3); 3.35 (s,3H, **CH_3**O-$[CH_2CH_2O]_n$-CH_2CH_2-Ar-CH_3).

References

(1) M. G. Menges, J. Penelle, C. Le Fevere de Ten Hove, A. M. Jonas, K. Schmidt-Rohr, *Macromolecules,* 2007, **40**, 8714-8725.

(2) S. Chanda, S. Ramakrishnan, *Macromolecules,* 2016, **49**, 3254-3263.