

ELECTRONIC SUPPLEMENTARY INFORMATION

Amphiphilic double-brush polymers based on Itaconate diesters

Saheli Chakraborty, S. G. Ramkumar and S. Ramakrishnan*

Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 560012 INDIA

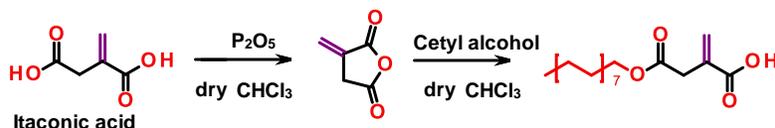
Experimental section –

Materials

Itaconic acid, triethyleneglycol monomethyl ether, tetraethylene glycol, tosyl chloride, 1H,1H,2H,2H-perfluorodecanol, 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure – 2959) were purchased from Sigma Aldrich Chemical Co. and most of the chemicals were used without further purification. Phosphorus pentoxide, cetyl alcohol, Benzyl chloride, sodium hydroxide, sodium bicarbonate, pyridine were purchased from Spectrochem chemical company and were used without further purification. All the solvents were dried and distilled before use.

Synthesis

Synthesis of monocetyl itaconate¹



Scheme S1. Preparation of monocetyl itaconate

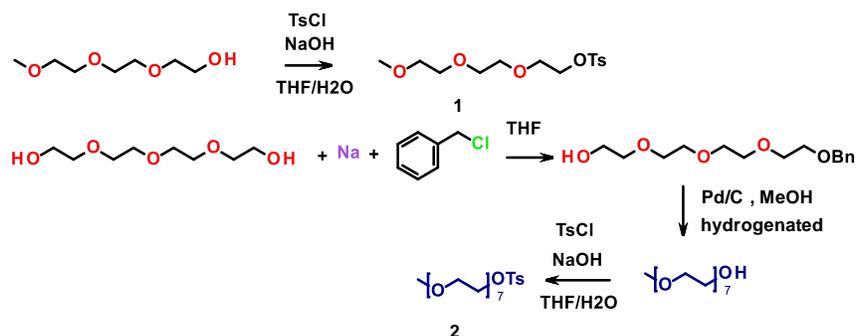
Itaconic anhydride – 10 g of Itaconic acid (76 mmol) was dispersed in 150 mL dry chloroform and 11 g (38.5 mmol) of phosphorus pentoxide was added to it. The solution was refluxed for 8 hours. It was then cooled and filtered. The filtrate was concentrated up to one third of its volume and kept in the freeze. White crystals were formed. The crystals were collected and dried to obtain pure product. Yield – 96%; mp – 68°C

NMR (400 MHz, δ ppm, CDCl₃): 3.62 (2H, t, -CH₂C-), 5.92 (1H, t, C=CHH'), 6.57 (1H, t, C=CHH')

Monocetyl itaconate – 10 g (41 mmol) of cetyl alcohol and 4.1 g (36.9 mmol) of itaconic anhydride were taken in 150 mL dry chloroform and refluxed for 12 hours. After that chloroform was evaporated to obtain white solid. It was then recrystallized twice from n-hexane to obtain pure product. Yield – 90%; mp – 72°C

NMR (400 MHz, δ ppm, CDCl₃) : 0.87 (3H, t, CH₃-CH₂-), 1.25 (26H, m, CH₃-(CH₂)₁₃CH₂), 1.61 (2H, m, -CH₂-CH₂COO), 3.33 (2H, s, COO-CH₂-C), 4.09 (2H, t, -CH₂-CH₂COO), 5.82 (1H, s, C=CHH'), 6.44(1H, s, C=CHH')

Synthesis of heptaethyleneglycol monomethyl ether tosylate²



Scheme S2. Preparation of heptaethyleneglycol monomethyl ether tosylate

Triethylene glycol monomethyl ether tosylate: 20 g of Triethylene glycol monomethyl ether (121.9 mmol) was taken in 50 mL of THF solution and cooled in an ice bath. 9.75 gm of NaOH solution (243.8 mmol, 50% aqueous solution) was added and stirred for 30 minutes. Tosyl chloride (34.8 g, 182.9 mmol) was dissolved into 100 mL of THF and added dropwise in the reaction mixture under ice-cold condition. The reaction was carried out for next 24 hours at room temperature. After 24 hours, 20 mL of water was added and stirred for another 30 minutes. The THF layer was then collected and passed through anhydrous NaSO₄ and evaporated and dried thoroughly. The liquid thus obtained was dissolved in diethyl ether where the excess tosic acid precipitated out as white solid and the ether layer was filtered and evaporated to obtain the pure product. Yield – 80%

NMR (400 MHz, δ ppm, CDCl₃): 2.44 (3H, s, -ArCH₃), 3.37 (3H, s, -OCH₃), 3.52-3.69 (10H, m, -OCH₂CH₂O-), 4.15 (2H, t, Ar-O-CH₂CH₂O-), 7.35 (2H, d, ArH), 7.80 (2H, d, ArH)

Tetraethylene glycol monobenzylate: 20 g of tetraethylene glycol (103 mmol) was dissolved in 100 mL of dry THF and small pieces of 1.18 g sodium (51 mmol) were added into the reaction mixture and it was refluxed for 12 hours. 12.9 g (103 mmol) of benzyl chloride was dissolved in dry THF and added dropwise into the reaction mixture and was refluxed for another 12 hours. After cooling the reaction mixture, THF was evaporated and 50 mL of water was added to the residue. The product was then extracted from 5X25 mL of ethyl acetate. The organic layer was passed through anhydrous NaSO₄ and finally evaporated by rotary evaporator to obtain yellow liquid. Pure compound was obtained by vacuum distillation at 200 °C at 0.1 mm of Hg as colorless liquid. Yield – 60%

NMR (400 MHz, δ ppm, CDCl₃): 3.59-3.72 (16H, m, -OCH₂CH₂O-), 4.57 (2H, s, Ar-CH₂-), 7.26-7.35 (5H, m, ArH)

Heptaethyleneglycol monomethyl ether

10 g (35 mmol) of tetraethylene glycol monobenzylate was dissolved in 100 mL dry THF and 2.9 g of KOH (51 mmol) was added into it. The reaction mixture was refluxed until all the KOH dissolved. 11.2 g (35 mmol) of Triethylene glycol monomethyl ether tosylate was dissolved in 50 mL dry THF and added dropwise to the reaction mixture. The solution was further refluxed for 24 hours. After cooling, THF was

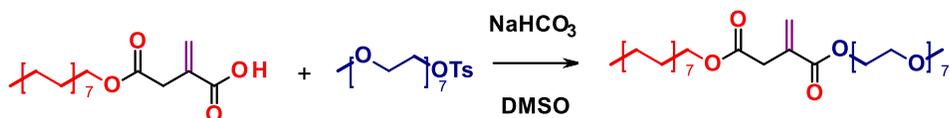
evaporated and the product was extracted from ethyl acetate. The organic layer was passed through anhydrous sodium sulfate and concentrated. The crude product thus obtained was hydrogenated without further purification. 15g of the crude compound was dissolved in 100 mL of MeOH and 250 mg of palladium catalyst (10 wt% palladium in charcoal) and one drop of concentrated HCl was added to it under inert N₂. The solution was hydrogenated using Parr hydrogenation apparatus at 55 psi hydrogen pressure at room temperature for 5 hours. After that the solution was neutralized by adding NaHCO₃ and it was then filtered and evaporated to obtain light yellow colored liquid. Distillation at 220 °C under 1 mm Hg of pressure in Kugel rohr apparatus gave the colorless pure product. Overall yield – 80%

NMR (400 MHz, δ ppm, CDCl₃): 3.36 (3H, s, -OCH₃), 3.52-3.70 (28H, m, -OCH₂CH₂O-)

Heptaethylene glycol monomethyl ether tosylate - 10 g (29.4 mmol) of heptaethylene glycol monomethyl ether was dissolved in 50 mL THF and 2.35 g of NaOH solution (58.8 mmol, 50 wt% aqueous solution) was added to it. The mixture was stirred for 30 minutes in ice cold condition. 8.4 g (44.1 mmol) of tosyl chloride was dissolved in 60 mL of THF and added dropwise into the ice-cold reaction mixture. It was further stirred in room temperature for 24 hours. After that 20 mL water was added and stirred for another 30 minutes. Then THF layer was collected and passed through anhydrous NaSO₄ and finally evaporated using rotary evaporator. The dried liquid was dissolved in 100 mL of diethyl ether where excess tosic acid precipitated out. The ether layer was evaporated to obtain pure product. Yield – 80%

NMR (400 MHz, δ ppm, CDCl₃): 2.44 (3H, s, -ArCH₃), 3.36 (3H, s, -OCH₃), 3.53-3.72 (28H, m, -OCH₂CH₂O-), 4.15 (2H, t, Ar-O-CH₂CH₂O-), 7.35 (2H, d, ArH), 7.80 (2H, d, ArH)

Synthesis of surfmer C16-Ita-HEG

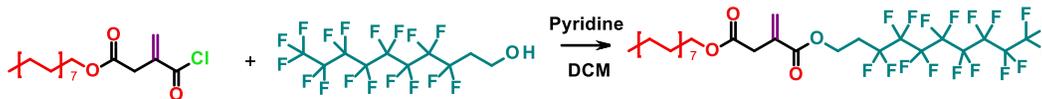


Scheme S3. Synthesis of the C16-Ita-HEG

3.5 g (9.8 mmol) of cetyl itaconate was dissolved in 10 mL of dry DMSO and 1.2 g (14.7 mmol) of NaHCO₃ was added to it. The mixture was stirred at 40°C for 30 minutes. 5.3 g (10.6 mmol) of hepta ethylene glycol monomethyl ether tosylate was dissolved in 10 mL of dry DMSO and added to the reaction mixture. The solution was stirred at 45°C for 4 days. After the reaction 100 mL of DCM was added to it and the organic layer was washed thoroughly with brine solution to remove the DMSO and finally it was passed through anhydrous Na₂SO₄ and evaporated to obtain the pure the product. Yield – 65%

NMR (400 MHz, δ ppm, CDCl₃): 0.87 (3H, t, -CH₂CH₃), 1.25 (26H, m, CH₃-(CH₂)₁₃CH₂), 1.61 (2H, m, -CH₂-CH₂COO), 3.33 (2H, s, COO-CH₂-C), 3.37 (3H, s, -OCH₃), 3.53-3.68 (26H, m, -OCH₂CH₂O-), 4.09 (2H, t, -CH₂-CH₂COO), 4.3 (2H, t, -OCH₂CH₂COO), 5.72 (1H, s, C=CHH'), 6.35 (1H, t, C=CHH')

Synthesis of C16-Ita-FC

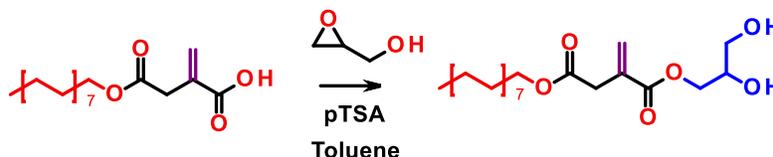


Scheme S4 – Synthesis of C16-ita-FC

Since 1-iodo-1H,1H,2H,2H-perfluorodecane is extremely unreactive towards nucleophilic substitution, the esterification was performed by making acid chloride of the cetyl itaconate. 1 g (2.8 mmol) of cetyl itaconate was dissolved in 10 mL dry DCM. 250 micro lit (4.2 mmol) of oxalyl chloride was added to the reaction mixture along with a drop of DMF. The reaction was carried out at room temperature for 4 hours. After that 1.5 g (3.2 mmol) of 1H,1H,2H,2H-perfluorodecanol was added to it along with 370 micro lit (4.2 mmol) pyridine and the solution was heated at 50°C for overnight. The organic layer was then washed with 1N HCl then passed through anhydrous Na₂SO₄ and evaporated in rotary evaporator. The solid thus obtained was recrystallized twice from methanol to obtain pure product. Yield – 60%

NMR (400 MHz, δ ppm, CDCl₃): 0.87 (3H, t, -CH₂CH₃), 1.25 (26H, m, CH₃-(CH₂)₁₃CH₂), 1.61 (2H, m, -CH₂-CH₂COO), 2.50 (2H, m, CH₂CH₂(CF₂)₇) 3.33 (2H, s, COO-CH₂-C), 4.07 (2H, t, -CH₂-CH₂COO), 4.47 (2H, t, -COOCH₂CH₂(CF₂)₇), 5.75 (1H, s, C=CHH'), 6.34 (1H, t, C=CHH')

Synthesis of C16-Ita-gly³

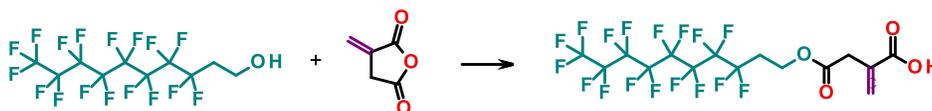


Scheme S5 – Synthesis of C16-Ita-Gly

2 g (5.6 mmol) of cetyl itaconate and 2.5 g (33.8 mmol) glycidol was taken in dry toluene and refluxed for 5 hours in presence of 48 mg (5 mol%) p-TSA. Pure product was obtained by column purification of the crude (PET ether/ EtOAc - 3:1) product. Yield – 50%

NMR (400 MHz, δ ppm, CDCl₃):): 0.87 (3H, t, -CH₂CH₃), 1.25 (26H, m, CH₃-(CH₂)₁₃CH₂), 1.61 (2H, m, -CH₂-CH₂COO), 3.33 (2H, s, COO-CH₂-C), 3.56-3.74 (1H, m, -CH₂CH(OH)CH₂OH), 4.10 (2H, t, -CH₂CH(OH)CH₂OH), 4.21-4.39 (2H, m, -CH₂CH(OH)CH₂OH), 5.75 (1H, s, C=CHH'), 6.34 (1H, t, C=CHH')

Synthesis of F8-Ita-HEG

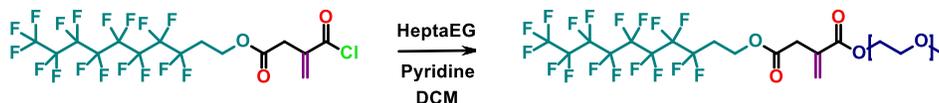


Scheme S5 – Synthesis of F8-Ita-HEG

2 g (4.3 mmol) 1H,1H,2H,2H-perfluorodecanol and 0.72 g (6.4 mmol) itaconic anhydride was reacted at 120°C under melt condition for 5 hours. After that 20 mL of distilled water was added to it in which excess unreacted itaconic anhydride dissolved. The solid thus obtained was filtered and dried to get the pure product. Yield – 95%

(400 MHz, δ ppm, DMSO-d₆): 2.66 (2H,m, CH₂-CH₂-(CF₂)₇) 3.32 (2H,s, COO-CH₂-C) 4.42 (2H,t, -COOCH₂CH₂(CF₂)₇), 5.74 (1H, s, C=CHH'), 6.16 (1H, t, C=CHH')

Synthesis of FC-Ita-HeptaEG



Scheme S6 – Synthesis of FC-Ita-HeptaEG

The fluoro-itaconate was unreactive towards nucleophilic substitution with PEG-tosylate. Hence it was prepared via acid chloride method. 1 g (1.7 mmol) of fluorocarbon itaconate was taken in 15 mL dry DCM and 157 micro lit (2.2 mmol) oxalyl chloride was added to it along with one drop of DMF. The solution was warmed at 40°C and the reaction was carried out for 4 hours. After that 0.7 g of dry hepta ethylene glycol mono methyl ether was added to it along with 230 micro lit (2.6 mmol) of pyridine. The reaction was refluxed for 12 hours and then it was collected and washed with 1N HCl. The organic layer was collected and passed through anhydrous Na₂SO₄ and evaporated to obtain the pure product. Yield = 70%

NMR (400 MHz, δ ppm, CDCl₃): 2.47 (2H,m, CH₂-CH₂-(CF₂)₇) 3.36 (2H, s, COO-CH₂-C), 3.36-3.38 (26H, m, -OCH₂CH₂O-), 4.31 (2H, t, -OCH₂CH₂COO), 4.40 (2H, t, COOCH₂CH₂(CF₂)₇), 5.75 (1H, s, C=CHH'), 6.38 (1H, t, C=CHH')

NMR spectra of the polymers

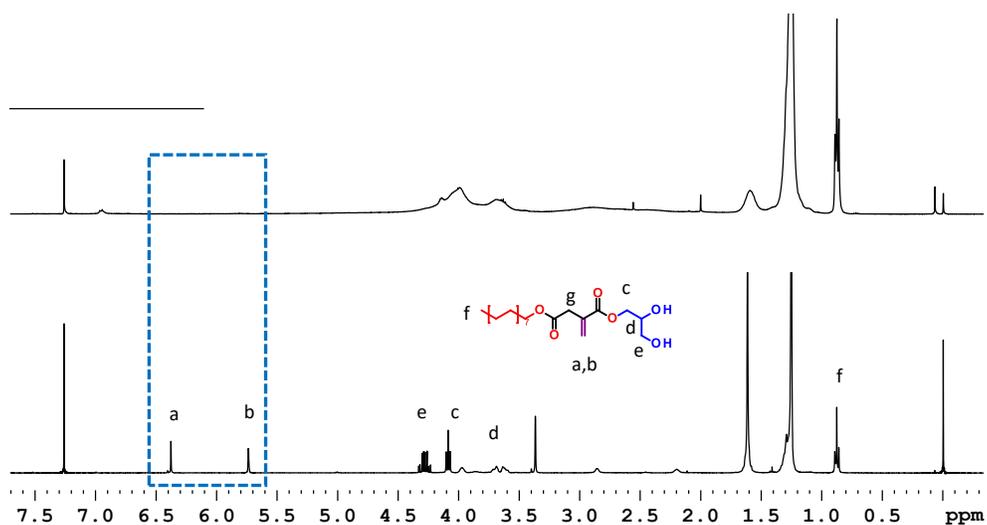


Figure S1. (a) – NMR spectra of C16-Ita-Gly (in CDCl₃) before (bottom) and after (top) the polymerization

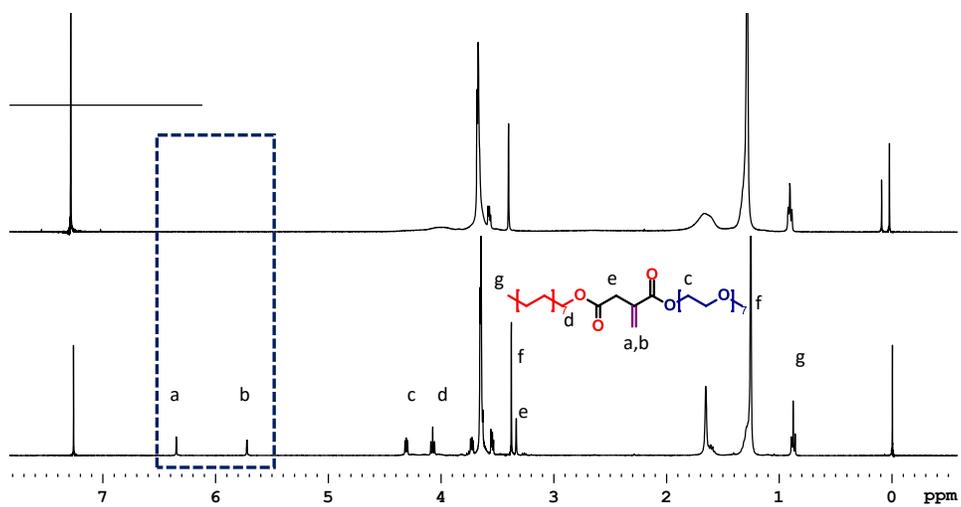


Figure S1. (b) – NMR spectra of C16-Ita-HEG (in CDCl₃) before (bottom) and after (top) polymerization

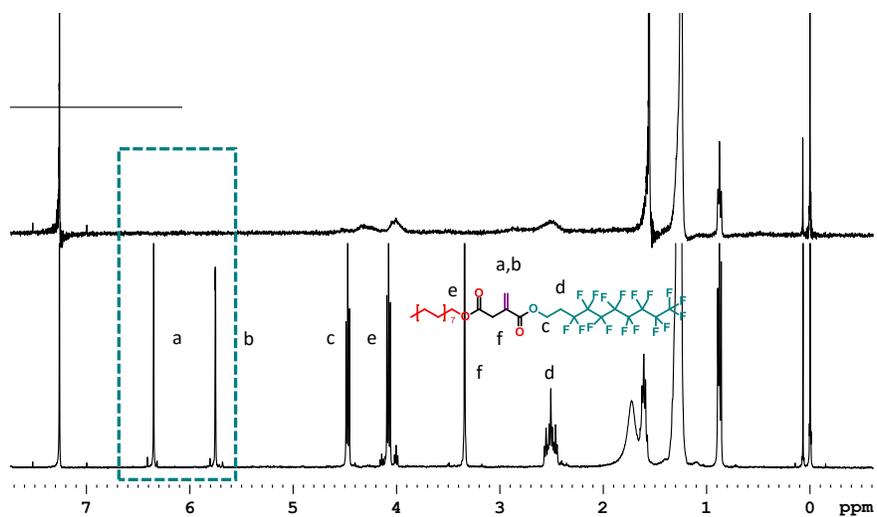


Figure S1. (c) - NMR spectra of C16-Ita-F8 (in CDCl₃) before (bottom) and after (top) polymerization

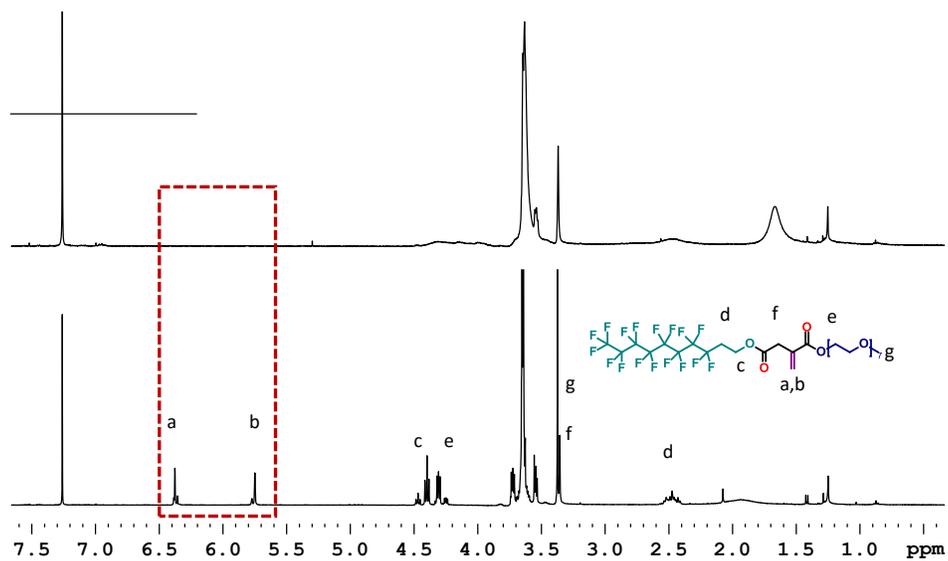


Figure S1. (d) - NMR spectra of F8-Ita-HEG (in CDCl₃) before (bottom) and after (top) polymerization

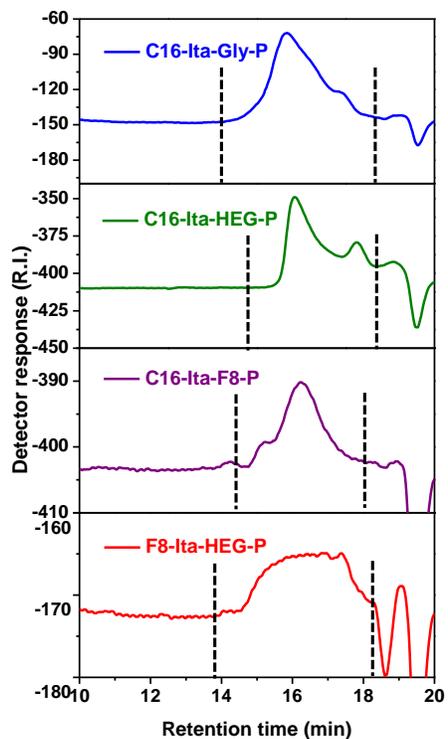


Figure S2. GPC of the double brush copolymers

Polymer	M _n	M _w	PDI
C16-Ita-Gly-P	3700	4700	1.2
C16-Ita-HEG-P	3600	4000	1.1
C16-Ita-F8-P	3500	4000	1.1
F8-Ita-HEG-P	3400	4600	1.3

Table 1. M_n, M_w and PDI of all the copolymers

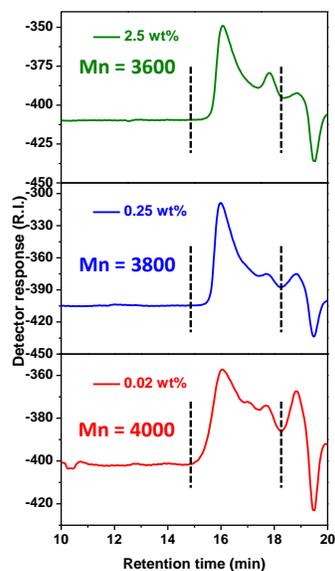


Figure S3. GPC of C16-Ita-HEG-P polymerized at different monomer concentrations. The molecular weight of the polymers did not vary much with the initial monomer concentrations.

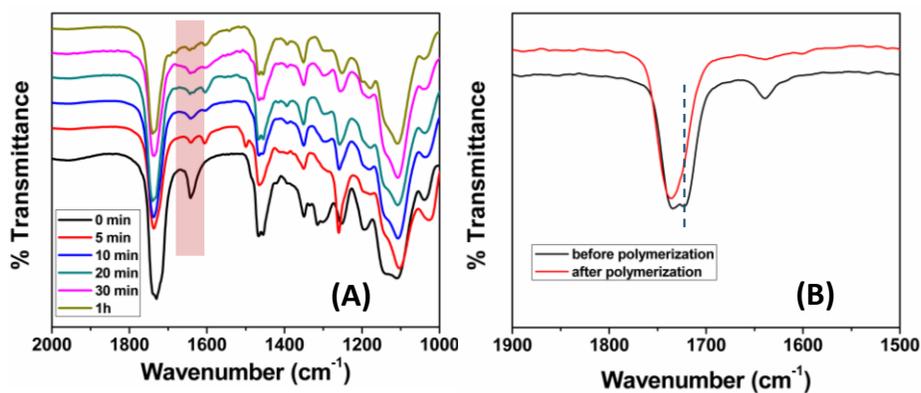


Figure S4. (A) IR spectra of the freeze-dried polymerization mixture of C16-Ita-EO7 as a function of polymerization time; (B) expanded carbonyl stretch region showing the apparent shift of the C=O stretching peak upon polymerization.

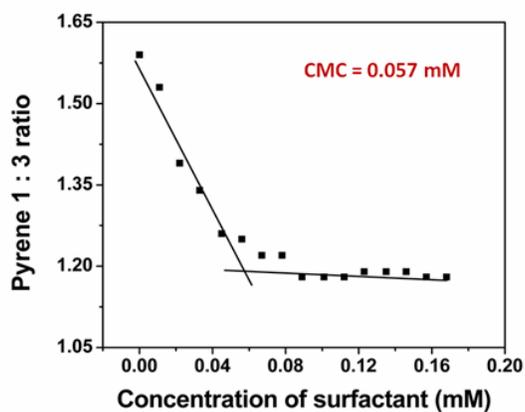


Figure S5. CMC of C16-Ita-HEG as determined by pyrene encapsulation technique⁴.

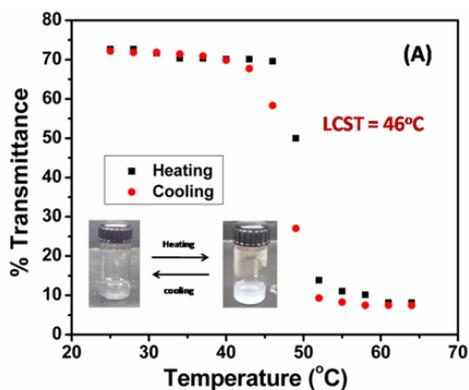


Figure S6. LCST of the C16-Ita-HEG. The measurements were carried out by monitoring % transmittance wavelength of 550 nm where the molecule exhibit no absorption. The LCST of C16-Ita-HEG is 46 °C

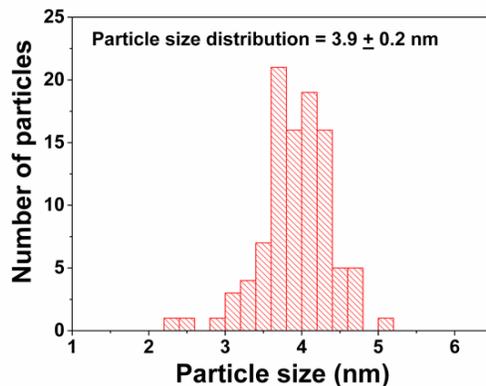


Figure S7. Histogram of the particle size distribution of the TEM image obtained from 0.02 wt% surfmer solution after polymerization. The histogram was drawn based on 100 particles.

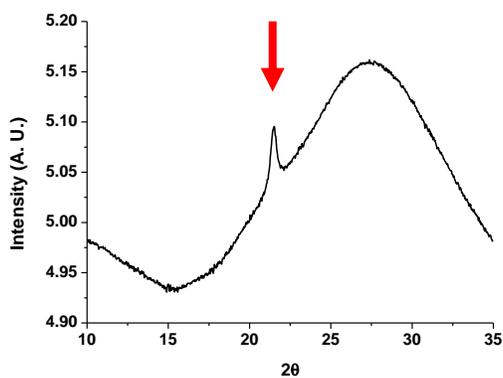


Figure S8. WAXS of hydrogel sample. Peak at $2\theta = 21.5^\circ$ corresponds to the hexagonally packed paraffinic lattice

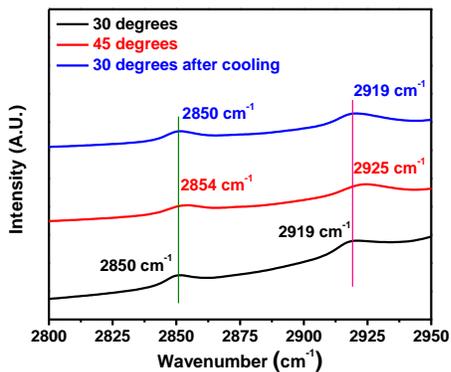


Figure S9. VT-IR of the hydrogel. The symmetric and anti-symmetric stretching frequency of crystalline C-H alkyl chains appeared at 2850 and 2919 cm^{-1} respectively at room temperature. Upon heating at 45 degrees both of them shifted towards higher wavenumber, 2854 and 2925 cm^{-1} respectively indicating melting of the crystalline alkyl chains. However upon cooling the gels the position of stretching frequencies were restored.

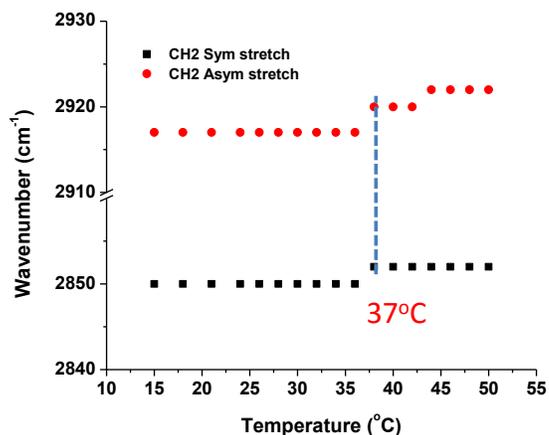


Figure S10. (a) For C16-Ita-Gly the variation of ν_{sym} and ν_{asym} C-H stretching frequency was plotted against the temperature. For an all *trans* configuration of alkylene chain the symmetric (ν_{sym}) and (ν_{asym}) C-H stretching frequency appear at 2850 cm^{-1} and 2919 cm^{-1} respectively, which upon melting shifts to 2855 cm^{-1} and 2924 cm^{-1} respectively⁵. Such variation is often used as a marker for hydrocarbon chain melting. From the graph it is clear that the onset occurs at 37°C which matches with that of DSC (34°C)

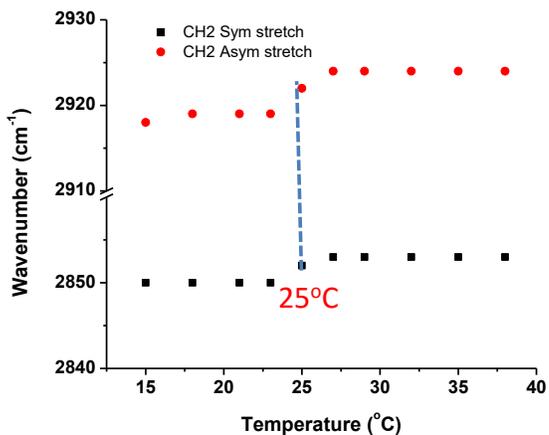


Figure S10. (b) For C16-Ita-HEG the onset of variation of ν_{sym} and ν_{asym} C-H stretching frequency starts at 25°C which resembles well with DSC (27°C)

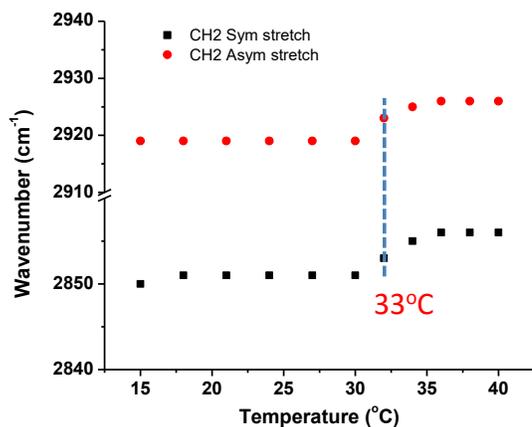


Figure S10. (c) For C16-Ita-F8 the onset of variation of ν_{sym} and ν_{asym} C-H stretching frequency starts at 33°C which matches exactly with DSC (33.5°C)



Figure S11 (a). The calculated length of cetyl chain considering extended all-*trans* conformation is 1.9 nm. This gives an estimate of bilayer thickness of minimum 3.8 nm, without considering the contribution from itaconate and glycerol segments. The experimentally observed value is 3.9 nm clearly revealing presence of gauche defect and/or interdigitation.

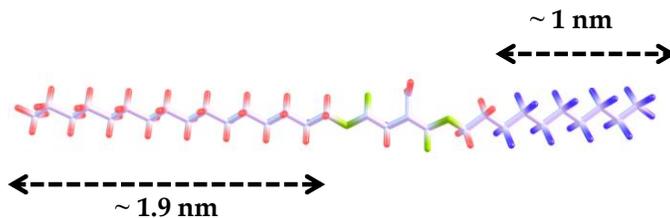


Figure S11 (b). The calculated bilayer thickness is 3.8 nm (from two C16 chains) + 2 nm (from two F8 chains) = 5.8 nm. This does not include the contribution from the itaconate unit. The calculation confirms that the observed length 5.8 nm is matching with that of the calculated one.

References

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