Supporting Information for:

Supramolecular Assemblies from Amphiphilic Homopolymers: Testing the Scope

Elamprakash N. Savariar, Sivakumar V. Aathimanikandan, and S. Thayumanavan[*]

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

Experimental Section:

^{1}H-NMR spectra were recorded on a 400 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; b, broad. ^{13}C-NMR spectra were proton decoupled and recorded on a 100 MHz NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. EI mass spectra were obtained at the Coordinated Instrumentation Facility at University of Massachusetts. Flash chromatography was performed with 37-75 μm silica gel. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by UV lamp or using an iodine chamber. THF and toluene were distilled over Na/Ph_2CO. All other chemicals were obtained from commercial sources and used as received, unless otherwise mentioned.

General procedure for the esterification of bromoalkanoic acids (I):

Appropriate bromo alkanoic acid (1 equiv) was dissolved in methanol and a catalytic amount of conc. H_2SO_4 (0.1 mL / g) was added and the reaction mixture was refluxed overnight. Upon completion of reaction, methanol was removed in rotary evaporator and the crude product was washed with aq. $NaHCO_3$, brine solution and extracted with ethyl acetate. The product was used further without column purification.

General procedure for amine alkylation (II):

Glycine ethyl ester hydrochloride (2 equiv), triethylamine (4 equiv), and the appropriate aliphatic methyl bromoacetate or aliphatic alkyl halide (1 equiv) were mixed together in ethanol and the reaction mixture was refluxed for 24 h under argon atmosphere. After the solvent removal, the residue was added to water and extracted using dichloromethane. Solvent was removed and the crude reaction mixture was purified through silica-gel column chromatography to get the monoalkylated glycine ester.

General procedure for the synthesis of acrylamide monomer (III):

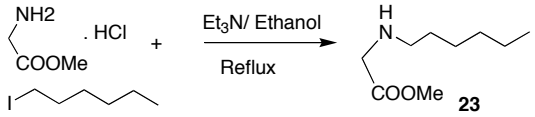
Appropriate monoalkylated glycine ethyl ester (1 equiv), triethylamine (1.2-1.3 equiv), and small amount of *p*-methoxy phenol were mixed together in dry dichloromethane under argon atmosphere and the mixture was stirred at 40 °C. Acryloyl chloride (1.3-1.4 equiv) was added dropwise to the reaction mixture and the stirring was continued for 6 h. Then the crude reaction mixture was washed with 1N HCl, saturated $NaHCO_3$ and brine

solution. Solvent was removed from the reaction mixture, and the acrylate monomer was purified using silica gel column chromatography with ethyl acetate/hexane as the eluent.

General Procedure for hydrogenation of acrylamide monomer (IV):
Required amount of monomer was dissolved 25 mL ethyl acetate and transferred to a 500 mL shaker bottle, 15 wt% of 10% Pd-carbon was added to the bottle. Reaction was carried out under hydrogen at 35 psi pressure for 3 hrs. Then the reaction mixture was filtered through celite to remove the catalyst. The solvent was evaporated under reduced pressure and purified the reaction mixture through column chromatography using 20% ethyl acetate in hexane.

General Procedure hydrolysis of the monomer (V):
The hydrolysis was carried out by dissolving the compound in methanol, with 6 equiv. of KOH. The reaction mixture was stirred for 8 h and then the solvent was evaporated. This was then acidified with 3M HCl and extracted with ethyl acetate. Ethyl acetate layer was dried over sodium sulfate and evaporated under reduced pressure.

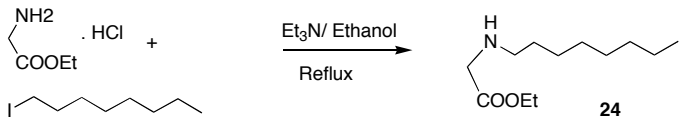
Compound 23



As per the general procedure (**II**), 1-iodohexane (16 g, 0.075 mol, 1 equiv), glycine methylester hydrochloride (19.0 g, 0.151 mol, 2 equiv) and triethylamine (42.0 mL, 0.302 mol, 4 equiv) were mixed up in ethanol (200 mL) and the reaction mixture was refluxed for 24 h under argon atmosphere. After the solvent removal, the residue was dissolved in water and extracted by using dichloromethane. Solvent was removed and the crude reaction mixture was subjected to silica gel column chromatography by using ethyl acetate (100 %) as the eluent to get the monoalkylated glycine ester (**23**). Yield (6.9 g, 49%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H), 3.31 (s, 2H), 3.21 (t, J = 6.8 Hz, 2H), 1.81 (s, 1H), 1.41 (quin, J = 6.8 Hz, 2H), 1.30-1.24 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 51.8, 49.6, 45.9, 31.7, 29.9, 26.8, 22.5, 14.0.

Compound 24

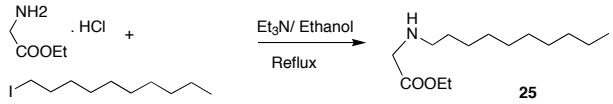


As per the general procedure (**II**), 1-iodooctane (40 g, 0.166 mol, 1 equiv), glycine ethyl ester hydrochloride (46.5 g, 0.333 mol, 2 equiv) and triethylamine (92.8 mL, 0.666 mol, 4 equiv) were mixed up in ethanol (400 mL) and the reaction mixture was refluxed for 24 h

under argon atmosphere. After the solvent removal, the residue was dissolved in water and extracted by using dichloromethane. Solvent was removed and the crude reaction mixture was subjected to silica gel column chromatography by using ethyl acetate (100%) as the eluent to get the monoalkylated glycine ester (**24**). Yield (16.5 g, 46%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.20 (q, *J* = 7.2 Hz, 2H), 3.37 (s, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 1.86 (s, 1H), 1.46 (quin, *J* = 7.2 Hz, 2H), 1.27-1.23 (m, 13H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 60.6, 50.8, 49.8, 31.7, 29.9, 29.3, 29.0, 27.1, 26.6, 22.5, 14.0.

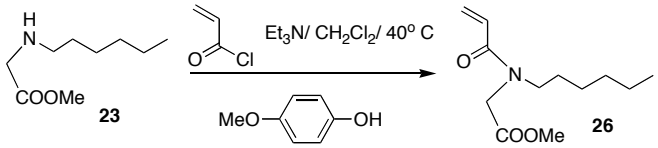
Compound 25



As per the general procedure (**II**), 1-iododecane (30 g, 0.12 mol, 1 equiv), glycine ethyl ester hydrochloride (31 g, 0.23 mol, 2 equiv) and triethylamine (45.3 g, 0.45 mol, 4 equiv) were mixed up in ethanol (250 mL) and the reaction mixture was refluxed for 24 h under argon atmosphere. After the solvent removal, the residue was dissolved in water and extracted by using dichloromethane. Solvent was removed and the crude reaction mixtures was subjected to silica gel column chromatography by using ethyl acetate/ hexane (80:20) as the eluent to get the monoalkylated glycine ester (**25**). Yield (13 g, 48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.1 (q, *J* = 7.2 Hz, 2H), 3.31 (s, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.75 (s, 1H), 1.40 (quin, *J* = 7.2 Hz, 2H), 1.22-1.17 (m, 18H), 0.80 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 60.5, 50.8, 49.5, 31.7, 29.8, 29.41, 29.38, 29.2, 29.1, 27.1, 26.6, 22.5, 14.1.

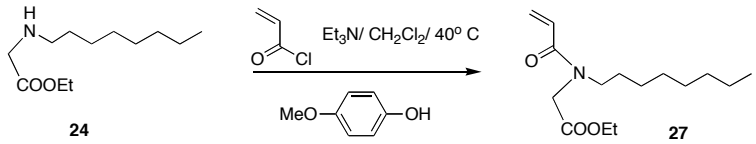
Compound 26



As per the general procedure (**III**), Compound (**23**) (4.0 g, 0.021 mol, 1 equiv), Et_3N (3.9 mL, 0.028 mol, 1.3 equiv), and small amount of *p*-methoxy phenol (10 mg) were mixed together in dry dichloromethane under argon atmosphere and the mixture was stirred at 40 °C. Acrolyl chloride (2.28 mL, 0.028 mol, 1.3 equiv) was added dropwise to the reaction mixture and the stirring was continued for 6h. Solvent was removed from the reaction mixture, and the acrylate monomer (**26**) was purified through silica gel column chromatography with ethyl acetate/hexane (25:75) as the eluent. Yield (4.8 g, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.06 (m, 1H), 6.48 (dd, *J* = 16.4 Hz, 2.4 Hz, 1H), 5.86 (dd, *J* = 10.2 Hz, 2.4 Hz, 1H), 3.99 (s, 2H), 3.66 (s, 2H) 3.37 (t, *J* = 6.8 Hz, 2H), 1.58 (quin, *J* = 6.8 Hz, 2H), 1.31 – 1.26 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 166.4, 130.5, 128.6, 126.7, 51.9, 49.2, 48.0, 31.4, 26.3, 22.3, 13.8.

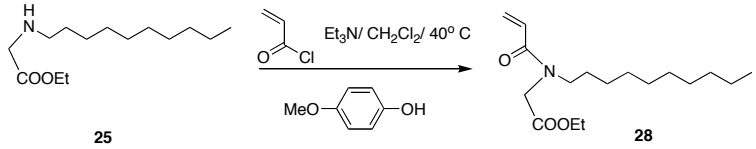
Compound 27



As per the general procedure (**III**), Compound (**24**) (5.75 g, 0.027 mol, 1 equiv), Et_3N (4.5 mL, 0.032 mol, 1.2 equiv), and small amount of *p*-methoxy phenol (10 mg) were mixed together in dry dichloromethane under argon atmosphere and the mixture was stirred at 40 °C. Acrolyl chloride (2.8 mL, 0.035 mol, 1.3 equiv) was added dropwise to the reaction mixture and the stirring was continued for 6h. Solvent was removed from the reaction mixture, and the acrylate monomer (**27**) was purified through silica gel column chromatography with ethyl acetate/hexane (25:75) as the eluent. Yield (6.6 g, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.08 (m, 1H), 6.44 (dd, *J* = 16.8 Hz, 2 Hz, 1H), 5.83 (dd, *J* = 10.4 Hz, 2 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 4.07 (s, 2H), 3.39 (t, *J* = 7.6 Hz, 2H), 1.53 (quin, *J* = 7.2 Hz, 2H), 1.26 – 1.23 (m, 14H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 166.4, 128.5, 126.7, 60.9, 49.2, 48.1, 31.6, 29.2, 29.1, 29.0, 26.5, 22.4, 14.0.

Compound 28

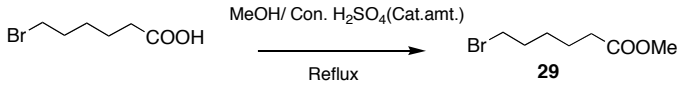


As per the general procedure (**III**), Compound (**25**) (12.3 g, 0.051 mol, 1 equiv), Et_3N (8.5 mL, 0.061 mmol, 1.2 equiv) and small amount of *p*-methoxy phenol (10 mg) were mixed together in dry dichloromethane under argon atmosphere and the mixture was stirred at 40 °C. Acrolyl chloride (5.4 mL, 0.066 mol, 1.3 equiv) was added dropwise to the reaction mixture and the stirring was continued for 6h. Solvent was removed from the reaction mixture, and the acrylate monomer (**28**) was purified through silica gel column chromatography with ethyl acetate/hexane (20:80) as the eluent. Yield (14.2 g, 94%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 – 6.50 (m, 1H), 6.34 (dd, *J* = 16.8 Hz, 2 Hz, 1H), 5.67 (dd, *J* = 10.4 Hz, 2 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.05 (s, 2H), 3.34 (t, *J* = 7.6 Hz, 2H), 1.53 (quin, *J* = 7.2 Hz, 2H), 1.24 – 1.19 (m, 17H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ 169.1, 166.6, 128.5, 126.7, 60.9, 49.2, 48.1, 31.7, 29.3, 29.2, 29.1, 29.0, 28.9, 26.5, 22.4, 14.0.

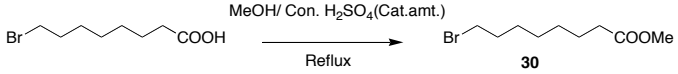
Synthesis of methyl 6-bromohexanoate (29)



As mentioned in the general procedure (**I**), 6-bromohexanoicacid (15 g, 76.9 mmol, 1 equiv) was dissolved in methanol (150 mL), and a catalytic amount of conc. H_2SO_4 (2 mL) was added and the reaction was carried out. The product was taken to next step without column purification. Yield 14.8 g (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.42-3.38 (m, 2H), 2.32 (t, J = 7.2 Hz, 2H), 1.90-1.83 (m, 2H), 1.68-1.61 (m, 2H), 1.50-1.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 173.9, 51.5, 33.8, 33.4, 32.3, 27.6, 24.0. EI/MS m/z (r.i.) 211(M+2, 98), 210(M+1, 8), 209(M+, 100), 178(16), 161(33), 129(51), 97(28), 87(9), 74(23), 69(23).

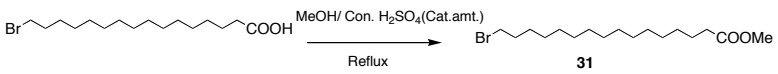
Compound 30



As per the general procedure (**I**), 8-bromooctanoicacid (10g, 44.8 mmol, 1 equiv) was dissolved in methanol (100 mL), and a catalytic amount of conc. H_2SO_4 (1.5 mL) was added and the reaction was carried out. The product was used further without column purification. Yield 10.1g (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H), 3.38 (t, J = 6.8 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H), 1.86-1.79 (m, 2H), 1.60-1.59 (m, 2H), 1.43-1.31 (m, 6H). ^{13}C NMR (100 MHz, CDCl3); δ 174.0, 51.3, 33.9, 33.8, 32.6, 28.8, 28.3, 27.8, 24.7. EI/MS m/z (r.i.) 239(M+2, 98), 238(M+1, 10), 237(M+, 100), 205(19), 189(38), 157(51), 125(48), 97(15), 74(41), 55(13).

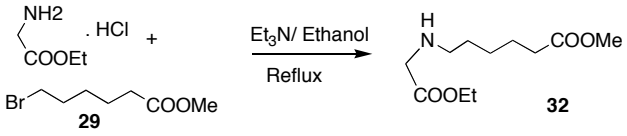
Synthesis of methyl 16-bromo hexadecanoate 31



As mentioned in the general procedure (**I**), 16-bromohexadecanoicacid (5 g, 14.9 mmol, 1 equiv) was dissolved in methanol (50 mL), and a catalytic amount of conc. H_2SO_4 (1 mL) was added and the reaction was carried out. The product was used further without column purification. Yield 4.68 g (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.40 (t, J = 6.8 Hz, 2H), 2.29 (t, J = 7.2 Hz, 2H), 1.84 (quin, J = 7.2 Hz, 2H), 1.61 (m, 2H), 1.41 (m, 2H), 1.27 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.3, 51.4, 34.1, 34.0, 32.8, 29.6, 29.5, 29.4, 29.2, 29.1, 28.7, 28.1, 24.9. EI/MS m/z (r.i.) 350(M+2, 34), 349(M+1, 8), 348(M+, 35), 319(9), 269(35), 143(16), 129(8), 87(60), 74(100), 55(26).

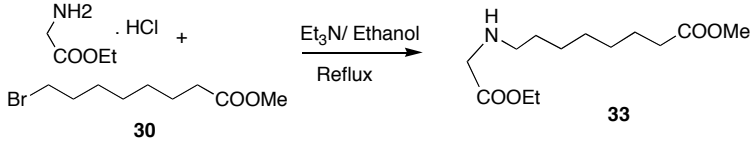
Compound 32



As per the general procedure (**II**), glycine ethyl ester hydrochloride (21.4 g, 153 mmol, 2 equiv), triethylamine (42.7 mL, 306 mmol, 4 equiv), and methyl 6-bromohexanoate (16 g, 76.5 mmol, 1 equiv) were mixed together in ethanol and reacted. Solvent was removed and the crude reaction mixture was purified through silica-gel column chromatography by using methanol/ethyl acetate (3:97) as the eluent to get the monoalkylated glycine ester (**32**). Yield 9.2 g (52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21-4.15 (m, 2H), 3.66 (s, 3H), 3.41-3.40 (m, 2H), 2.64-2.61 (m, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.67-1.59 (m, 2H), 1.55-1.51 (m, 2H), 1.40-1.32 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.0, 172.2, 60.6, 51.4, 50.7, 49.2, 33.8, 29.5, 26.6, 24.6, 14.1. EI/MS m/z (r.i.) 233(M+2, 5), 232(M+1, 13), 231(M+, 7), 200(5), 185(5), 158(100), 154(10), 116(26), 98(25), 69(7), 59(5).

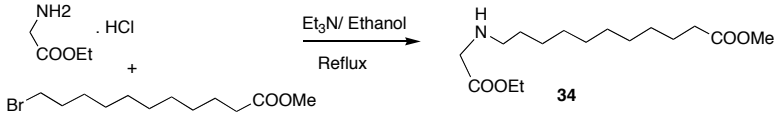
Compound 33



According to the general procedure (**II**), glycine ethyl ester (12.3g, 88.5 mmol, 2 equiv), triethylamine (25 mL, 177 mmol, 4 equiv), and Methyl 8-bromooctanoate (10.5g, 44.3 mmol, 1 equiv) were mixed together in ethanol and reacted. Solvent was removed and the crude reaction mixture was purified through silica-gel column chromatography by using methanol/ ethyl acetate (2:98) as the eluent to get the mono substituted glycine ester (1). Yield 6.4 g (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.20-4.15 (m, 2H), 3.65 (s, 3H), 3.40-3.39 (m, 2H), 2.61-2.58 (m, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.64-1.59 (m, 2H), 1.53-1.47 (m, 2H), 1.30-1.24 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.1, 172.3, 60.6, 51.3, 50.8, 49.5, 33.9, 29.8, 29.0, 28.9, 26.9, 24.7, 14.1. EI/MS m/z (r.i.) 260(M+1, 6), 259(M+, 5), 228(6), 186(100), 154(15), 116(26), 84(8), 55(5).

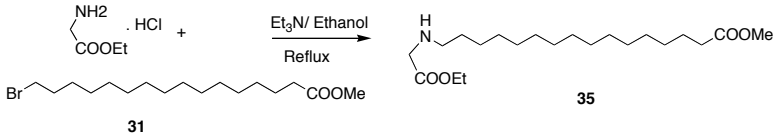
Compound 34



According to the general procedure (**II**), glycine ethyl ester hydrochloride (10 g, 71.6 mmol, 2 equiv), triethylamine (20 mL, 143.2 mmol, 4 equiv), and methyl 11-bromoundecanoate (10 g, 35.8 mmol, 1 equiv) were mixed together in ethanol and refluxed. Solvent was removed and the crude reaction mixture was purified through silica-gel column chromatography by using methanol/ethyl acetate (2:98) as the eluent to get the monosubstituted glycine ester (**34**). Yield 4.53 g (42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14 (q, *J* = 7.2 Hz, 2H), 3.61 (s, 3H), 3.34 (s, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 1.71 (s, 1H), 1.57-1.52 (m, 2H), 1.44-1.39 (m, 2H), 1.24-1.20 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.3, 172.5, 60.6, 51.5, 51.2, 50.9, 49.6, 34.0, 29.9, 29.4, 29.3, 29.0, 27.1, 24.8, 14.1. EI/MS m/z (r.i.) 303 (M+2, 5), 302(M+1, 19), 301(M+, 100), 270(5), 228(46), 196(5), 116(19), 84(8), 55(5).

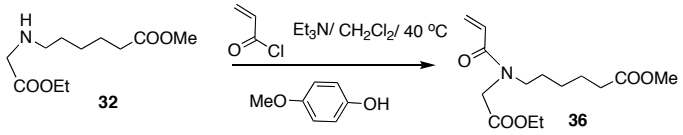
Compound 35



According to the general procedure (**II**), glycine ethyl ester hydrochloride (3.9 g, 28.6 mmol, 2 equiv), triethylamine (8 mL, 57.3 mmol, 4 equiv), and methyl 16-bromohexadecanoate (5 g, 14.3 mmol, 1 equiv) were mixed together in ethanol and reacted. Solvent was removed and the crude reaction mixture was purified through silica-gel column chromatography by using methanol/ethyl acetate (1:99) as the eluent to get the monoalkylated glycine ester (**35**). Yield 2.7 g (51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21-4.19 (m, 2H), 3.66 (s, 3H), 3.46-3.41 (m, 2H), 2.67 (m, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.62-1.57 (m, 4H), 1.29-1.24 (m, 25H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.3, 172.2, 60.7, 51.4, 50.7, 49.5, 34.1, 29.8, 29.6, 29.5, 29.4, 29.2, 29.1, 27.2, 24.9, 14.2. EI/MS m/z (r.i.) 373(M+2, 9), 372(M+1, 44), 371(M+, 16), 325(16), 298(100), 266(16), 238(16), 224(9), 116(51), 74(9), 55(9).

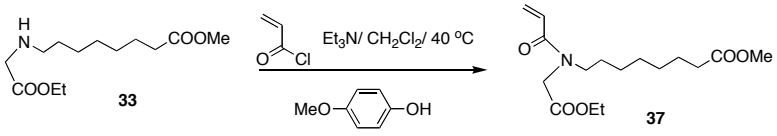
Compound 36



As mentioned in the general procedure (**III**), Compound **29** (4.76 g, 20.6 mmol, 1 equiv), triethylamine (3.7 mL, 26.7 mmol, 1.3 equiv), and small amount of *p*-methoxy phenol were mixed together in dry dichloromethane under argon atmosphere and the mixture was stirred at 40 °C. Acryloyl chloride (2.3 mL, 28.7 mmol, 1.4 equiv) was added drop wise to the reaction mixture and the stirring was continued for 6 h. Then the crude acrylate monomer (**36**) was purified through silica gel column chromatography with ethyl acetate/hexane (25:75) as the eluent. Yield 4.83 g (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57-6.50 (m, 1H), 6.36-6.28 (m, 1H), 5.70-5.64 (m, 1H), 4.19-4.11 (m, 2H), 4.05-4.03 (m, 2H), 3.63 (s, 3H), 3.41-3.34 (m, 2H), 2.27 (t, J = 6.8 Hz, 2H), 1.64-1.49 (m, 4H), 1.33-1.20 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 173.7, 169.1, 166.6, 128.9, 126.7, 61.1, 51.4, 49.0, 48.3, 33.8, 28.7, 26.3, 24.5, 14.0. EI/MS m/z (r.i.) 286(M+1, 5), 285(M+, 13), 254(10), 230(24), 212(42), 200(14), 158(100), 116(25), 98(13), 69(9), 55(42).

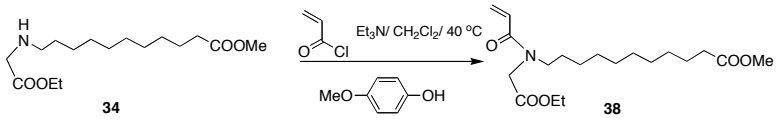
Compound 37



As mentioned in the general procedure (**III**), compound **33** (3.34g, 12.9 mmol, 1 equiv), Et_3N (2.33 mL, 16.7 mmol, 1.3 equiv), and small amount of p-methoxy phenol were mixed together in dry dichloromethane under argon atmosphere and the mixture was stirred at 40° C. Acrolyl chloride (1.36 mL, 16.7 mmol, 1.3 equiv) was added dropwise to the reaction mixture and the stirring was continued for 6h. Then the crude acrylate monomer (1) was purified through silica gel column chromatography with ethyl acetate/hexane (25:75) as the eluent. Yield 3.54g (87%).

^{1}H NMR (400 MHz, CDCl3): δ 6.57-6.50 (m, 1H), 6.35-6.27 (m, 1H), 5.69-5.64 (m, 1H), 4.16-4.11 (m, 2H), 4.05-4.02 (m, 2H), 3.61 (s, 3H), 3.39-3.33 (m, 2H), 2.26 (t, J = 7.2 Hz, 2H), 1.56-1.45 (m, 4H), 1.27-1.20 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.0, 169.2, 166.6, 128.7, 126.7, 61.1, 51.4, 49.2, 48.2, 33.9, 29.0, 27.3, 26.6, 26.4, 24.7, 14.0. EI/MS m/z (r.i.) 314(M+1, 5), 313(M+, 12), 282(18), 258(22), 240(51), 226(9), 186(100), 170(18), 154(9), 116(26), 84(23), 55(33).

Compound 38

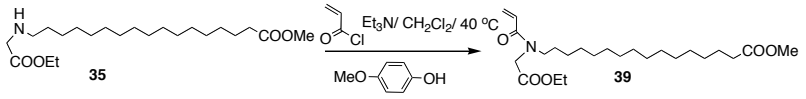


As mentioned in the general procedure (**III**), compound **34** (12.4 g, 39.3 mmol, 1 equiv), triethylamine (7.1 mL, 51.1 mmol, 1.3 equiv), and small amount of *p*-methoxy phenol were mixed together in dry dichloromethane under argon atmosphere and the mixture

was stirred at 40 °C. Acryloyl chloride (3.8 mL, 47.2 mmol, 1.2 equiv) was added drop wise to the reaction mixture and the stirring was continued for 6 h. Then the crude acrylate monomer (**38**) was purified through silica gel column chromatography with ethyl acetate/hexane (20:80) as the eluent. Yield 12 g (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60-6.53 (m, 1H), 6.39-6.35 (m, 1H), 5.72-5.69 (m, 1H), 4.20-4.16 (m, 2H), 4.08-4.05 (m, 2H), 3.64 (s, 3H), 3.39-3.35 (m, 2H), 2.27 (t, J = 7.2 Hz, 2H), 1.60-1.57 (m, 4H), 1.26-1.23 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.2, 169.2, 166.6, 128.7, 126.8, 61.1, 51.4, 49.3, 48.3, 34.0, 29.4, 29.3, 29.2, 29.1, 29.0, 26.9, 26.6, 24.8, 14.1. EI/MS m/z (r.i.) 356(M+1, 3), 355(M+, 9), 324(20), 300(26), 282(67), 250(9), 228(100), 212(8), 170(21), 116(21), 98(9), 55(33).

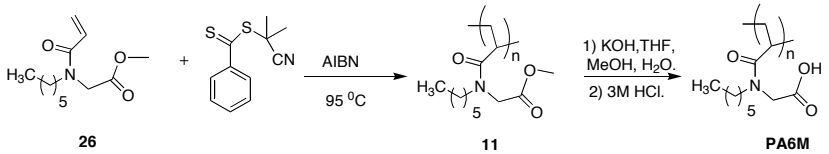
Compound 39



As mentioned in the general procedure (**III**), compound **35** (2 g, 5.4 mmol, 1 equiv), triethylamine (1.0 mL, 7.0 mmol, 1.3 equiv), and small amount of *p*-methoxy phenol were mixed together in dry dichloromethane under argon atmosphere and the mixture was stirred at 40 °C. Acryloyl chloride (0.6 mL, 7.5 mmol, 1.4 equiv) was added drop wise to the reaction mixture and the stirring was continued for 6h. Then the crude acrylate monomer (**39**) was purified through silica gel column chromatography with ethyl acetate/hexane (15:85) as the eluent. Yield 1.9 g (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.51 (m, 1H), 6.39-6.35 (m, 1H), 5.73-5.70 (m, 1H), 4.20-4.17 (m, 2H), 4.09-4.06 (m, 2H), 3.66 (s, 3H), 3.40-3.36 (m, 2H), 2.28 (t, J = 7.6 Hz, 2H), 1.60-1.58 (m, 4H), 1.27-1.24 (m, 25H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.3, 169.3, 166.6, 128.8, 126.8, 61.1, 51.4, 49.3, 48.3, 34.1, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.9, 26.7, 24.9, 14.1. EI/MS m/z (r.i.) 426(M+1, 5), 425(M+, 13), 394(18), 371(26), 320(12), 298(100), 266(9), 212(12), 170(25), 116(22), 98(13), 55(31).

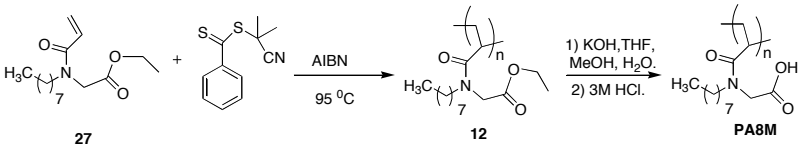
Polymer PA6M



2,2′-Azobisisobutyronitrile (AIBN) (0.001 g, 0.006 mmol), 2-cyanoisopropyl dithiobenzoate, (0.004 g, 0.017 mmol), monomer **26** (0.5 g, 2.1 mmol) were added to a dry Schlenk flask, flushed with nitrogen and degassed by freeze-pump-thaw cycles. The reaction mixture was kept at room temperature for 15 min, and it was transferred to a preheated oil bath at 95 °C and stirred for 45 min. Then the reaction mixture was dissolved in THF (3 mL), and precipitated in methanol. This precipitation was repeated thrice, and then the precipitate was collected and vacuum dried. Yield 90%, M_n-23,000,

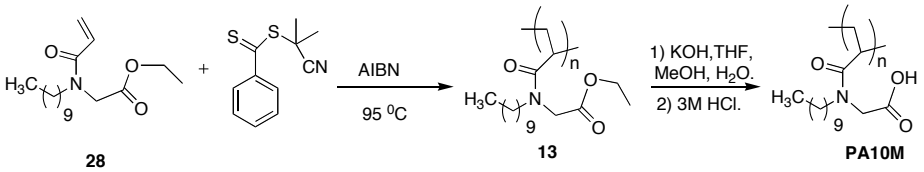
PDI- 1.36. Then potassium hydroxide (0.6 g, 10.70 mmol) was added to polymer **11** (0.42 g) in THF, methanol and water mixture (8 mL: 2 mL: 1 mL), heated in a round bottom flask at 50 ˚C for 20 h, and evaporated the solvents and 10 ml of water was then added. This solution was heated at 50 ˚C for 12 h, and then the reaction mixture was cooled to RT, and then neutralized with 3 M HCl solution to precipitate the polymer. The polymer was filtered and vacuum dried. Yield 0.3 g (90%) ^{1}H-NMR (400 MHz, DMF-d_7) δ 4.15 (bs, 2H), 3.40 (bs, 2H), 2.51 (bs, 1H), 2.12-1.18 (m, 10H), 0.83 (s, 3H),

Polymer PA8M



2,2′-Azobisisobutyronitrile (AIBN) (0.001 g, 0.006 mmol), 2-cyanoisopropyl dithiobenzoate, (0.005 g, 0.023 mmol), monomer **27** (1 g, 3.7 mmol) were added to a dry Schlenk flask, flushed with nitrogen and degassed by freeze-pump-thaw cycles. The reaction mixture was kept at room temperature for 15 min, and it was transferred to a preheated oil bath at 95 °C and stirred for 45 min. Then the reaction mixture was dissolved in THF (3 mL), and precipitated in methanol. This precipitation was repeated thrice, and then the precipitate was collected and vacuum dried. Yield 70%, M_n-23,000, PDI- 1.18. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.18 (bs, 4H) 3.25 (bs, 2H), 2.65 (bs, 1H), 2.12-1.20 (m, 17H), 0.87 (s, 3H). Then 0.7 g (12.48 mmol) of potassium hydroxide was added to the polymer **12** (0.5 g) in THF, methanol and water mixture (8 mL: 2 mL: 1 mL), heated in round bottom flask at 50 ˚C for 20 h, and evaporated the solvents and 10ml of water was then added. This solution was heated at 50 ˚C for 12 h, and then the reaction mixture was cooled to RT, and neutralized with 3 M HCl solution to precipitate the polymer. The polymer was filtered and vacuum dried. ^{1}H-NMR (400 MHz, DMF-d_7) δ 4.20 (bs, 2H), 3.40 (bs, 2H), 2.52 (bs, 1H), 2.08-1.18 (m, 14H), 0.80 (s, 3H)

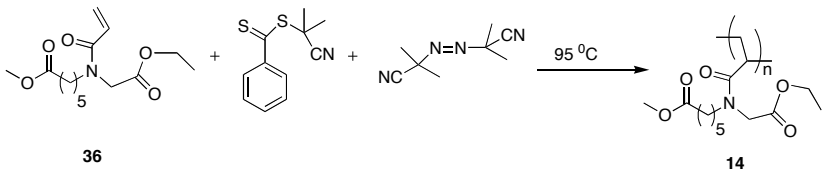
Polymer PA10M



2,2′-Azobisisobutyronitrile (AIBN) (0.0005 g, 0.003 mmol), 2-cyanoisopropyl dithiobenzoate, (0.003 g, 0.013 mmol), monomer **28** (0.8 g, 2.7 mmol) were added to a dry Schlenk flask, flushed with nitrogen and degassed by freeze-pump-thaw cycles. The reaction mixture was kept at room temperature for 15 min, and it was transferred to a preheated oil bath at 95 °C and stirred for 45 min. Then the reaction mixture was dissolved in THF (3 mL), and precipitated in methanol. This precipitation was repeated thrice, and then the precipitate was collected and vacuum dried. Yield 0.7 g (70%), M_n-

19,000 PDI- 1.28. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 3H), 2.15-1.21 (m, 21H), 2.58 (bs, 1H), 3.28 (bs, 2H), 4.22 (bs, 4H). Then 1 g of potassium hydroxide was added to the polymer **13** (0.6 g) in THF, methanol and water mixture (8 mL: 2 mL: 1 mL), heated in round bottom flask at 50 °C for 20 h, and evaporated the solvents and 10 mL of water was then added. This solution was heated at 50 °C for 12 h, and then the reaction mixture was cooled to RT, and then neutralized with 3 M HCl solution to precipitate the polymer. The polymer was filtered and vacuum dried. Yield 0.45 g (83%) ^{1}H-NMR (400 MHz, DMF-d_7) δ 4.10 (bs, 2H), 3.48 (bs, 2H), 2.56 (bs, 1H), 2.10-1.21 (m, 18H), 0.87 (s, 3H).

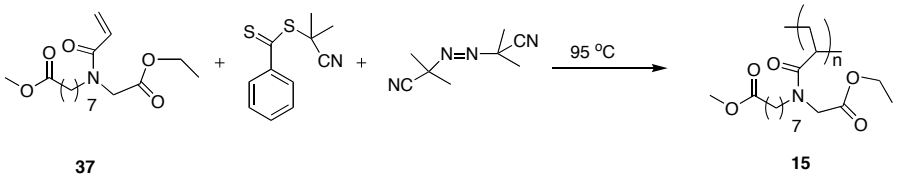
Polymer 14



36 **14**

2,2′-Azobisisobutyronitrile (AIBN) (0.002 g, 0.012 mmol), 2-cyanoisopropyl dithiobenzoate, (0.008 g, 0.036 mmol), **36** (1 g, 3.5 mmol) were added to a dry Schlenk flask, flushed with nitrogen and degassed by freeze-pump-thaw cycles The reaction mixture was kept at room temperature for 15 min, and it was transferred to a preheated oil bath at 95 °C and stirred for 45 min. Then the reaction mixture was dissolved in THF (3 mL), and precipitated in hexane. This precipitation was repeated thrice, then the precipitate was collected and vacuum dried. Yield 0.93 g, (93 %), M_n-24000, PDI- 1.30. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.09 (bs, 4H), 3.66 (s, 3H), 3.24 (bs, 2H), 2.57 (bs, 1H), 2.28 (bs, 2H), 2.14-1.23 (m, 11H).

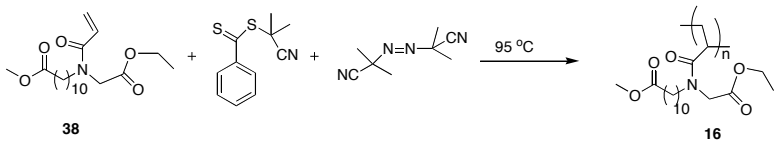
Polymer 15



37 **15**

2,2′-Azobisisobutyronitrile (AIBN) (0.001 g, 0.006 mmol), 2-cyanoisopropyl dithiobenzoate (CIDB), (0.004 g, 0.018 mmol), **37** (1 g, 3.190 mmol) were added to a dry Schlenk flask, flushed with nitrogen and degassed by freeze-pump-thaw cycles. The reaction mixture was kept at room temperature for 15 minutes, and transferred the reaction flask to oil bath, which was preheated at 95° C and, stirred at this temperature for 45 minutes. Then the reaction mixture was dissolved in THF (3 mL), and precipitated in hexane and the precipitation was repeated twice and the filtrate was decanted, precipitate (kind of gel) was vacuum dried. Yield 0.85 g, 85%, Mn-27000, PDI- 1.32. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.42-3.8 (m, 4H), 3.65 (s, 3H), 3.25 (bs, 2H), 2.82 (bs, 2H), 2.62 (bs, 1H), 2.15-1.12 (m, 14H).

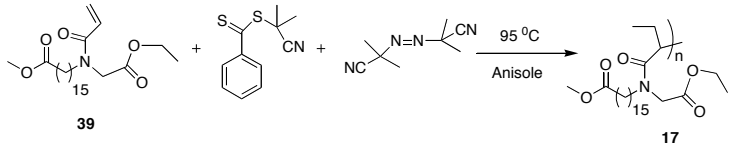
Polymer 16



38 16

2,2′-Azobisisobutyronitrile (AIBN) (0.0008 g, 0.005 mmol), 2-cyanoisopropyl dithiobenzoate (CIDB), (0.003 g, 0.014 mmol), **38** (0.5 g, 1.408 mmol) were added to a dry Schlenk flask, flushed with nitrogen and degassed by freeze-pump-thaw cycles. The reaction mixture was kept at room temperature for 15 min, and it was transferred to a preheated oil bath at 95 °C and stirred for 15 min. Then the reaction mixture was dissolved in THF (2 mL), and precipitated in hexane and the precipitation was repeated thrice. Then the supernatant was decanted and precipitate was vacuum dried. Yield 0.4g, (80 %), M_n-9800, PDI- 1.1. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.12 (bs, 4H), 3.64 (s, 3H), 3.25 (bs, 2H), 2.65 (bs, 1H), 2.26-2.30 (t, J = 7.2, 2H), 2.15-1.18 (m, 21H).

Polymer 17



39 17

2,2′-Azobisisobutyronitrile (AIBN) (0.001 g, 0.006 mmol), 2-cyanoisopropyl dithiobenzoate (CIDB), (0.004 g, 0.018 mmol), **39** (1 g, 2.35 mmol) anhydrous anisole (0.4 mL) were added to a dry Schlenk flask, flushed with nitrogen and degassed by freeze-pump-thaw cycles. The reaction mixture was kept at room temperature for 15 min and transferred to a preheated oil bath at 95 °C and stirred for 45 min. Then the reaction mixture was dissolved in THF (3 mL), and precipitated in hexane. The precipitation was repeated thrice and the precipitate was collected and vacuum dried. Yield 0.90 g, (90%), M_n-30000, PDI- 1.36. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.12 (bs, 4H), 3.65 (s, 3H), 3.25 (bs, 2H), 2.64 (bs, 1H), 2.30-2.27 (t, J = 7.6 Hz, 2H), 2.14-1.16 (m, 31H).

General procedure for hydrolysis of 14, 15, 16 and 17:

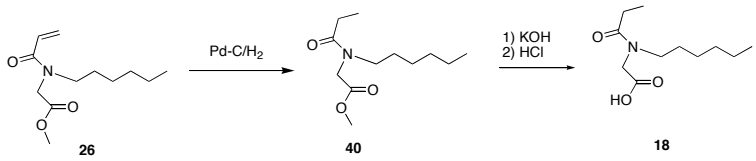
The polymer (1 equiv) dissolved in methanol was taken in a single neck round bottom flask, potassium hydroxide (5 equiv) was added and stirred at room temperature for 36 h under argon atmosphere. Methanol was removed under reduced pressure, the residue was dissolved in water and neutralized with 3M HCl. The precipitate was filtered and dried under vacuum. The obtained yield was 85 to 90%. The polymers were characterized by using H^1 NMR spectroscopy.

Polymer PA5V: ^{1}H-NMR (400 MHz, MeOD): δ 4.06 (bs, 2H), 3.42 (bs, 2H), 2.82 (bs, 1H), 2.36 (bs, 2H), 2.16-1.16 (m, 8H).

Polymer PA7V: ^{1}H-NMR(400 MHz, MeOD): δ 4.17 (bs, 2H), 3.26 (bs, 2H), 2.83 (bs, 1H), 2.34 (bs, 2H), 2.12-1.14 (m, 12H),

Polymer PA10V: ^{1}H-NMR (400 MHz, MeOD): δ 4.05 (bs, 2H), 3.29 (bs, 2H), 2.68 (bs, 1H), 2.30-2.34 (t, *J* = 6.4 Hz, 2H), 2.10-1.15 (m, 18H).
Polymer PA15V: ^{1}H-NMR (400 MHz, MeOD): δ 4.11 (bs, 2H), 3.27 (bs, 2H), 2.81 (bs, 1H), 2.33-2.30 (t, *J* = 7.2 Hz, 2H), 2.14-1.2 (m, 28H),

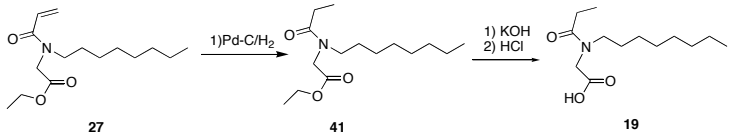
Compound 18



According to the general procedure (**IV**) the reaction was carried out with 1 mmol of **26**. The obtained yield was 0.2g.
Compound **40**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.98 (s, 2H), 3.65 (s, 3H), 3.25 (t, *J* = 7.6Hz, 2H), 2.34 (q, *J* = 7.2, 2H) 1.54-1.38 (m, 2H), 1.32-1.15 (m, 6H), 1.09 (t, *J* = 7.2Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 173.9, 169.9, 51.8, 48.9, 47.4, 31.4, 28.5, 26.4, 26.2, 22.4, 13.9, 13.8.

According to the general procedure (**V**) the reaction was carried out with 1 mmol of reduced compound. The obtained yield was 0.17 g (85%).
Compound **18**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 4.05 (s, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 2.39 (q, *J* = 7.6 Hz, 2H), 1.63-1.42 (m, 2H), 1.32-1.20 (m, 6H), 1.12 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); 175.5, 172.9, 49.4, 47.9, 31.5, 28.6, 26.5, 26.0, 22.6, 14.1, 9.4.

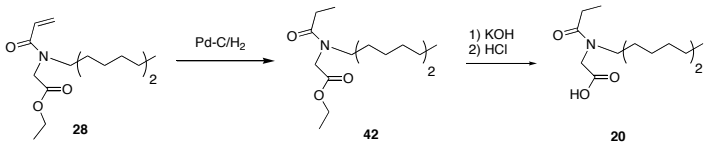
Compound 19



According to the general procedure (**IV**) the reaction was carried out with 0.45 g (1.66 mmol) of **27**. The obtained yield was 0.41 g (90%).
Compound **41**^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.2-4.1 (m, 2H), 4.02 (s, 2H), 3.34 (t, *J* = 7.6 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 1.60-1.45 (m, 2H), 1.35-1.18 (m, 12H), 1.14 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 6.8, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): 175.0, 169.6, 61.2, 49.5, 48.3, 31.7, 29.3, 29.19, 29.1, 22.6, 14.1, 9.35.

According to the general procedure (**V**) the reaction was carried out with 0.40 g (1.47 mmol) of compound **41**. The obtained yield was 0.34 g (92%).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 4.06 (s, 2H), 3.31 (t, *J* = 7.6Hz, 2H), 2.42 (q, *J* = 7.2 Hz, 2H), 1.62-1.42 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); 175.4, 172.9, 49.5, 48.2, 31.8, 29.3, 29.2, 28.6, 26.8, 26.0, 22.6, 14.1, 9.34.

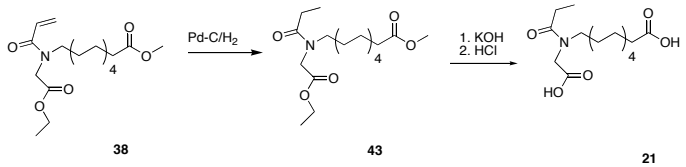
Compound 20



According to the general procedure (**IV**) the reaction was carried out with 0.5 g (1.67 mmol) of **28**. The obtained yield was 0.46 g (90%)
Compound **42**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.19-4.17 (m, 2H), 4.02 (s, 2H), 3.3 (t, *J* = 7.6 Hz, 2H), 2.39 (q, *J* = 7.2 Hz, 2H), 1.55-1.46 (m, 2H), 1.29-1.23 (m, 17H), 1.15 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 6.8Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); 173.4, 169.5, 61.1, 45.2, 43.6, 31.9, 29.6, 29.4, 28.8, 26.9, 26.0, 22.8, 14.2, 9.5.

According to the general procedure (**V**) the reaction was carried out with 0.45 g (1.5 mmol) of compound **42**. The obtained yield was 0.4 g (95%)
Compound **20**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.47 (s, 1H), 4.06 (s, 1H), 3.31 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.2, 2H), 1.60-1.48 (m, 2H), 1.33-1.2 (m, 14H), 1.15 (t, *J* = 7.2, 3H), 0.89-0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); 175.4, 173.5, 49.6, 48.2, 32.0, 29.6, 29.4, 28.7, 26.9, 26.1, 22.8, 20.9, 14.2, 9.4.

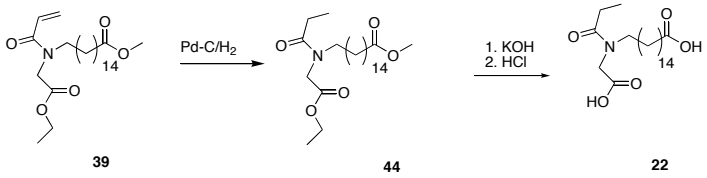
Compound 21



According to the general procedure (**IV**) the reaction was carried out with 0.5 g (1.44. mmol) of **38**. The obtained yield was 0.44 g (90%)
Compound **43.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.20-4.14 (m, 2H), 4.03 (s, 2H), 3.66 (s, 3H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.40 (q, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H) 1.61-1.39 (m, 4H), 1.40-1.22 (m, 15H), 1.17-1.14 (m, 3H).

According to the general procedure (**V**) the reaction was carried out with 0.45 g (1.3 mmol) of **43**. The obtained yield was 0.38 g (93%)
Compound **21**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.23 (s, 2H), 4.07 (s, 2H), 3.31 (t, *J* = 7.4 Hz, 2H), 2.40 (q, *J* = 7.4 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.65-1.55 (m, 4H), 1.38-1.18 (m, 12H), 1.15 (t, *J* = 7.4 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$); δ 179.7, 175.2, 173.9, 49.4, 47.9, 34.0, 29.6, 29.3, 29.1, 29.0, 28.9, 28.5, 27.3, 26.7, 26.3, 9.3.

Compound 22



According to the general procedure (**IV**) the reaction was carried out with 0.25 g (0.6 mmol) of **39**. The obtained yield was 0.22 g (90%)
Compound **44**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.18 (q, *J* = 7.2 Hz, 2H), 4.02 (s, 2H), 3.65 (s, 3H), 3.3 (t, *J* = 8 Hz, 2H), 2.39 (q, *J* = 7.6 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.62-1.54 (m, 4H), 1.42-1.22 (m, 25H), 1.14 (t, *J* = 7.2 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$); 174.4, 174.14, 169.6, 61.0, 51.4, 49.1, 47.7, 34.1, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 26.8, 14.2, 9.4.
According to the general procedure (**V**) the reaction was carried out with 0.22 g (0.46 mmol) of compound **44**. The obtained yield was 0.18 g (90%.)
Compound **22**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.28 (s, 2H), 4.1 (s, 2H), 3.61-3.3 (m, 2H), 2.72-2.21 (m, 4H), 2.1-1.15 (m, 29H). ^{13}C NMR (100 MHz, $CDCl_3$); 179.8, 173.9, 49.6, 48.4, 34.1, 29.6, 29.5, 29.4, 29.3, 29.1, 28.7, 26.8, 26.1, 24.7, 9.3.

TEM Experiment:
TEM measurements were performed using a JEOL 100CX 100KV TEM. To prepare the samples for aqueous solutions of polymers, the polymers were dissolved in appropriate amount of Mili Q water with LiOH as the base. For each COOH unit present in the polymer 1.5 equiv of LiOH was added in order to form the carboxylate salts. This solution was then sonicated for 2 h. Then the solution was dialyzed against water using dialysis membrane (MWCO 1000 Da). To prepare the samples for doing TEM for inverted micelle-like assemblies, an appropriate amount of polymer was taken with calculated amount of toluene. To make the polymer soluble in toluene 1-2 equiv. of water and one equivalent of triethylamine were added to the polymer solution with respect to

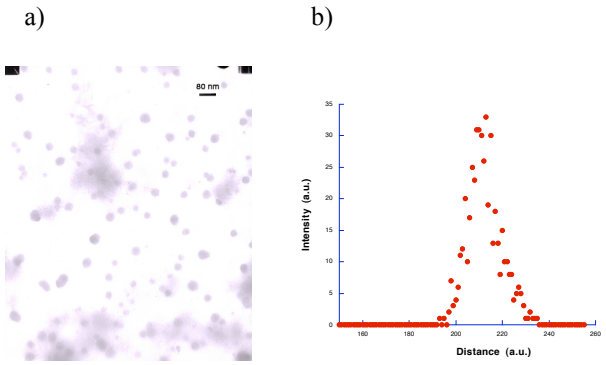


Figure **1**. a) TEM image obtained for aqueous solution of polymer **PA10M**. b) Histogram of particle from 'a' analyzed using "ImageJ" program.[1]

each carboxylic acid group present in the measured amount of polymer. This solution was

then sonicated for 4 h to get the homogeneous solution. Samples were prepared by dipping copper EM grids (pre-coated with the thin film of Formvar and then coated with carbon) in aqueous or toluene solutions of the polymers and dried at room temperature.
Figure 1a. shows the TEM image of polymer **PA10M**, where the average diameter was around 45 nm. Higher contrast in the center of the particle indicates that these are filled interior and micelle like particles. This was further supported by the histogram analysis as shown in Figure 1b.

Spectroscopic measurement:

The UV-Vis absorption spectra were recorded on a spectrophotometer using quartz cells. Fluorescence spectra were recorded on a fluorimeter. The spectra were recorded using a quartz cuvette.

Emission spectra of pyrene:

In order to measure I_1/I_3, 5X10^{-7} M solution of pyrene in acetone was made in a vial. The

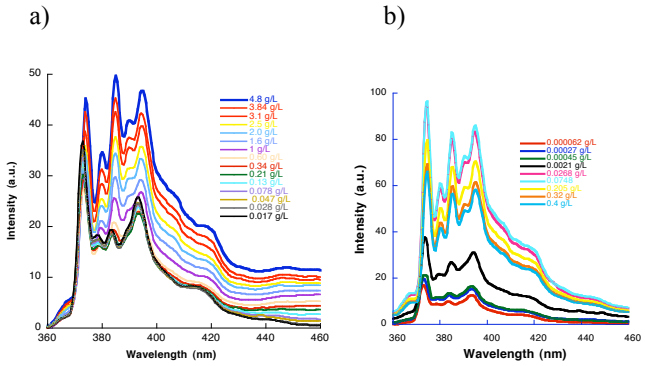


Figure 2. Emission spectra of pyrene at various concentrations of a) **18** and b) **PA10M**.

acetone was evaporated to dryness, and then aqueous solution of polymer was added and

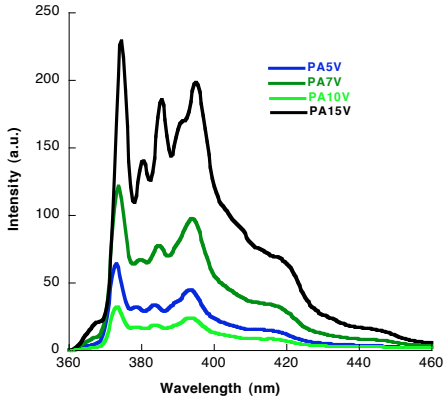


Figure 3. Plot of I_1/I_3 plot of pyrene in aqueous solutions of **PA5V**, **PA7V**, **PA10V** and **PA15V**.

then shaken well to mix. The obtained solution was excited at 339 nm, with the scan speed of 50 nm / min. Similar procedure was used for all the other compounds

CAC measurement:
$5X10^{-7}$ M solution of pyrene in acetone was made in a vial. The acetone was evaporated to dryness, and then aqueous solution of polymer or monomer was added and then shaken well to mix. For the excitation spectra the following instrumental parameters were used. λ_{em} = 374nm, Excitation bandwidth = 3 nm, emission bandwidth = 1 nm and the

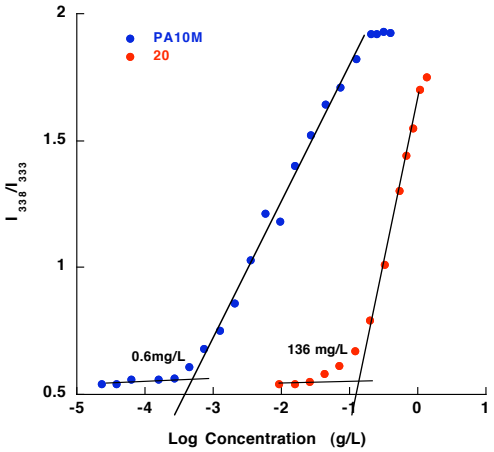


Figure 4. Plot of I_{338}/I_{333} vs concentration of **PA10M** and **20**.

scanning speed was 50 nm/min. The polymer or the monomer concentration was varied while keeping the pyrene concentration same ($5X10^{-7}$M). The ratio of I_{338}/I_{333} was used with various concentrations of polymer or the building blocks (monomer) to find out the CAC.[2] More specifically, the relative ratio of the first and the third peaks in the emission spectra of pyrene is sensitive to its microenvironment. One could utilize this to obtain the CMC of the polymer. However, a related and more common method of determining CMC involves the sensitivity of the excitation spectra of pyrene to its microenvironment. The red shift of the low energy band in the pyrene excitation spectra from 333 nm to 338 nm, in combination with decrease in I_1/I_3 in emission spectra at higher concentration of polymer indicates the partitioning of pyrene from an aqueous environment to hydrophobic environment. At lower concentrations of the polymer, the ratio of the intensity of the peaks at 338 and 333 nm (I_{338}/I_{333}) resembles that of pyrene in water. A plot of the log [polymer] *vs.* this intensity ratio clearly shows that there exists a sharp increase in the ratio at a certain concentration. The CMC for the polymer is obtained from the intersection of the tangent to the curve at the inflection point with the horizontal tangent through the points at low polymer concentrations. CMC of polymers **PA8M** and **PA10M** was determined in a similar manner. Figure 4 shows the plot I_{338}/I_{333} vs concentration of building block **20** and the polymer **PA10M**.

Water soluble dye encapsulation in aqueous solution of polymer PA10V:
To the dialyzed solution of **PA10V** the dye (R6G or calcein) was added and sonicated for 45 minutes then the resultant solution was dialyzed against water using dialysis membrane (6-8kDa MWCO). Dialysis was carried out for 15 h. The obtained solution was used for absorption and fluorescence spectroscopy.

Dye encapsulation in Reverse Micelle:

The polymer **PA10V** was dissolved in toluene ($5X10^{-6}$ M) by sonicating it for 2 h, and then 5 mg of R6G was added and sonicated it for 2 h at 40 ˚C. Then filtered the solution through 0.45 µm filter and used spectroscopic measurements. Same method was used for encapsulating R6G in polymer **PA6M** with the concentration of ($5X10^{-5}$ M) in toluene.

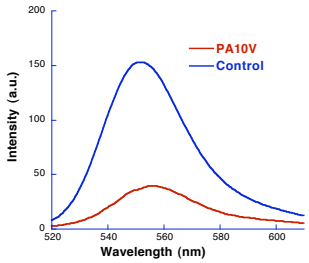


Figure 5. Absorption matched emission spectra of R6G in waster and toluene solution of **PA10V**.

Encapsulation of pyrene in Micelle:

The polymer solution (**PA6M**, 10^{-4} M) was added to the vial that contains 10^{-4} M pyrene obtained after evaporation of acetone. For the control, instead of polymer solution Mili Q water was added. And both the solutions were filtered separately using 0.45µ filter and used to measure the absorbance.

Dynamic and Static light scattering:

Dynamic light scattering experiments were performed by using a digital correlator and goniometer. The light source was solid-state laser system, operating at 514 nm. The temperature was kept constant at 25 ˚C throughout the experiment. Dust was eliminated

a) b)

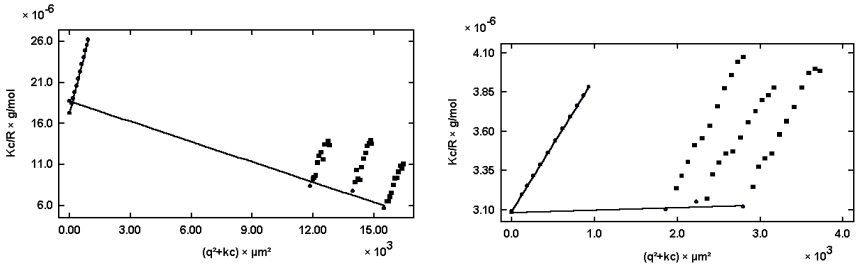


Figure 6. Zimm plot obtained for a) **PA6M** at the concentrations of 2, 1.8 and 1.5 mg/mL, the R_g was 41 nm. b) **PA10V** at the concentrations of 3, 2.4 and 2 mg/mL, R_g was 29 nm.

by filtering the solution through 0.22 µm filter. All the measurements were done at a correlation time of 1 min.

For static light scattering (SLS) the polymer was taken in three different concentrations and detected at different angles from 40˚ to 140˚ and measurements acquired during 30 seconds at every angle. Finally from the slope extrapolated to data at zero concentration,

the radius of gyration (R_g) was calculated using Zimm plot.[3] Figure 6a and 6b are Zimm plots for **PA6M** and **PA10V** respectively.

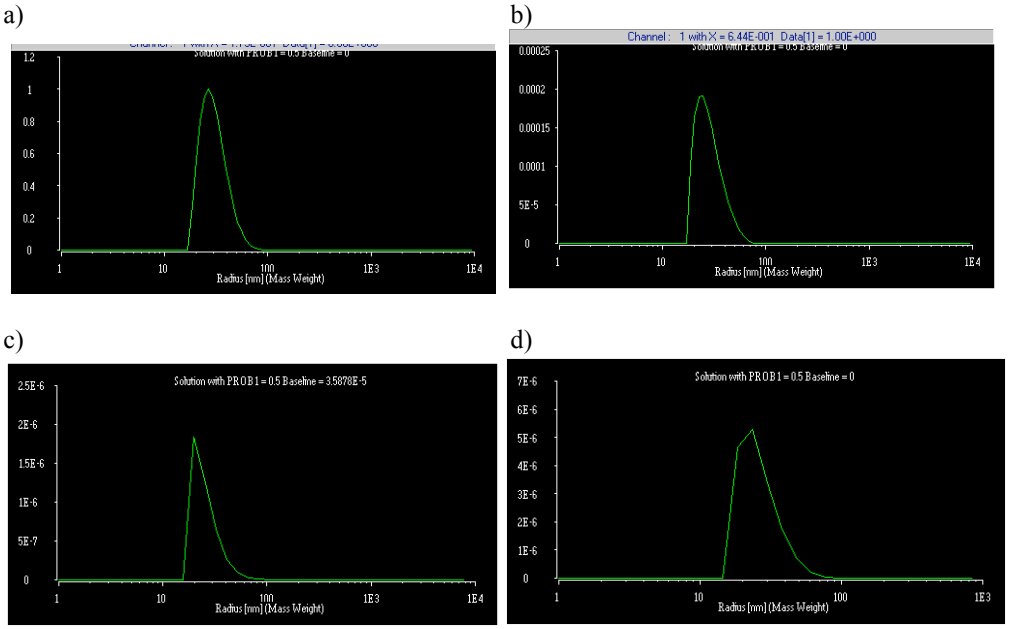


Figure 7. DLS of polymer **PA10V** at a) 30° b) 60° c) 90° d) 120°

The dynamic light scattering was also carried out at different angles. Figure 7 represents the DLS at few angles. The hydrodynamic radius was also checked at different concentration, and the size was almost same for all the tested concentrations as shown in Figure 8.

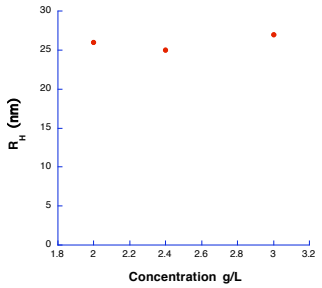


Figure 8. Hydrodynamic radius of polymer **PA10V** at different concentrations.

Effect of pH on the interior of the micelle:

The micellar was encapsulated with $5X10^{-7}$M of pyrene and the I_1/I_3 was checked as a function of pH. In all the cases the ratio decreases with decreasing the pH, which indicates the more nonpolar environment at low pH.

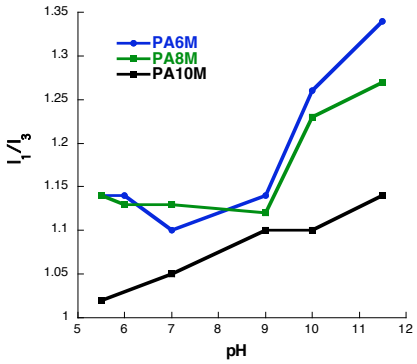


Figure 9. Plot of I_1/I_3 as function of pH for polymer **PA6M**, **PA8M**, and **PA10M**.

Reference:

(1) ImageJ program is a freeware downloaded from http://rsb.info.nih.gov/ij/.

(2) Wilhelm, M.; Zhao, C.-L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J.-L.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 1033-1040.

(3) For details refer Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Naghahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944-1947.