

Zwitterionic Amphiphilic Homopolymer Assemblies

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(† Authors contributed equally)

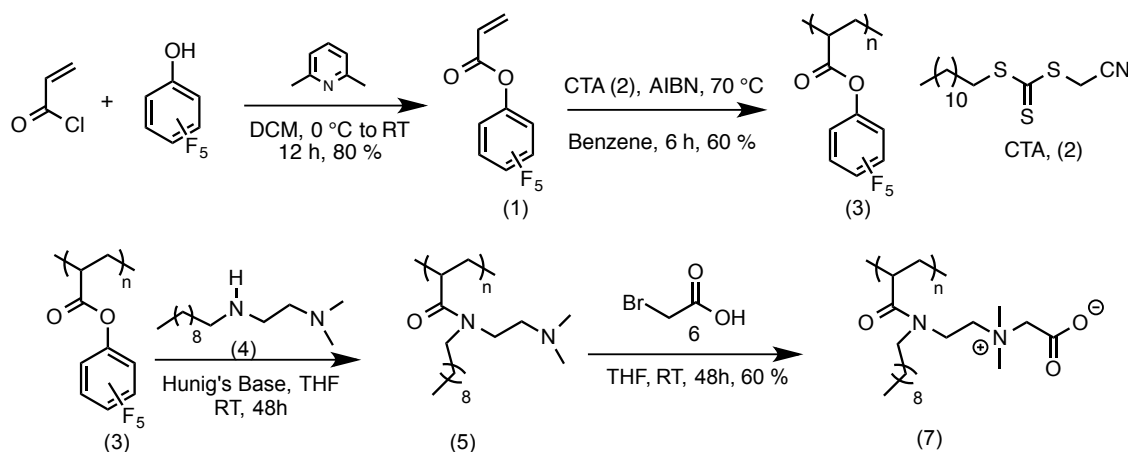
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Materials and Methods:

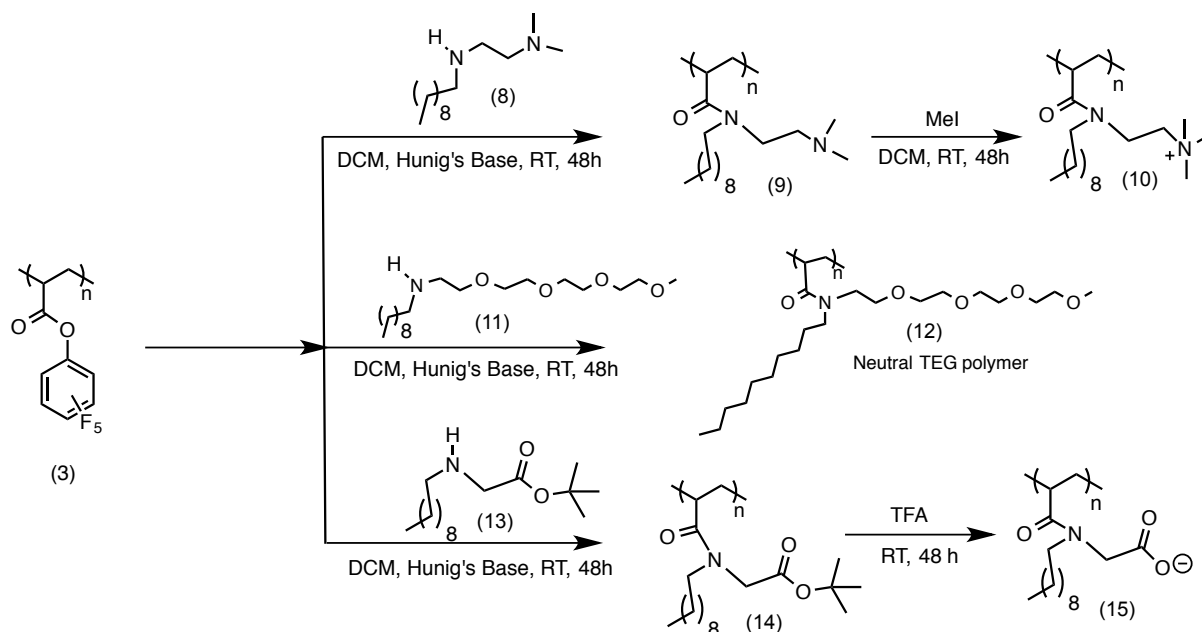
All chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise mentioned. ^1H NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer, while ^{19}F -NMR spectra were collected on a 300 MHz Bruker NMR Spectrometer using the residual proton resonance of 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; bs, broad singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using carbon signal of the deuterated solvent as the internal standard. Molecular weight of the polymers was measured by gel permeation chromatography (GPC, THF) using a PMMA standard with a refractive index detector. THF was used as eluent with a flow rate of 1mL/min. Dynamic light scattering (DLS) measurements were performed using a Malvern Nanozetasizer. FTIR spectra were recorded on a Perkin Elmer Spectrometer.

Synthetic Schemes:

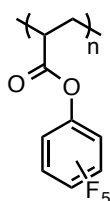
Synthesis of zwitterionic polymer from reactive monomer:



Synthesis of anionic and neutral TEG based amphiphilic polymers:



Synthesis of reactive polymer, 3:



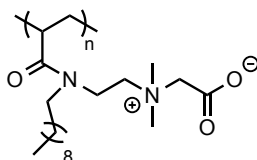
The pentafluorophenylacrylate monomer, 1 was synthesized following the known protocol.¹

The acrylate monomer (500 mg, 2.1 mmol) was added to a 20 mL vial with dry benzene (1.5 mL), chain transfer agent cyanomethyl dodecyl trithiocarbonate, 2 (14 mg), AIBN (3.4 mg, 0.21 mmol) and the resulting reaction mixture is purged with Argon for 2 min and immediately capped it under argon conditions. This reaction mixture is stirred at 70 °C for 6 hours. This reaction mixture is precipitated in hexanes to obtain pure product (60 % yield).

GPC (PMMA/THF): $M_n = 12$ K Da, $M_w = 14$ K Da, Dispersity = 1.1; $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ

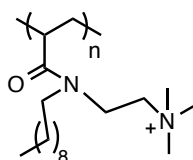
3.20-3.00 (br s, 1H), 2.20-1.90 (br s, 2H). ^{19}F -NMR (300 MHz; CDCl_3): -150.00 (s, 2F), -154.00 (s, 1F), -160.00 (s, 2F).

Synthesis of zwitterionic polymer, 7:



To the resulting reaction mixture Hunig's base (0.46 mL, 2.52 mmol) was added as base and stirred for 48 hr and purified by dialyzing it in DCM using a regenerated cellulose membrane with a MW cut off 3.5 kDa. IR and NMR confirm the conversion of activated ester polymer to intermediate tertiary amine species. To this tertiary amine polymer, excess bromoacetic acid was added and stirred for 48, then the reaction was precipitated several times in ethyl acetate followed by dialysis in DCM using a regenerated cellulose membrane with a MW cut off 3.5 kDa to get pure zwitterionic polymer (60 % yield). ^1H -NMR (400 MHz; CDCl_3): δ 4.36 (t, $J = 35.1$ Hz, 2H), 3.78-3.46 (m, 7H), 3.00 (d, 2H), 1.68 (d 2H), 1.28 (s, 14H), 0.90 (t, $J = 5.8$ Hz, 3H).

Synthesis of anionic cationic amphiphilic polymer, 10:

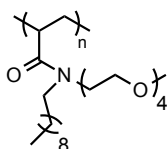


To the solution of reactive polymer (100 mg, 0.42 mmol) in dry THF (2 mL), tertiary amine, 8 (310 mg, 1.26 mmol) and Hunig's base (0.23 mL, 1.26 mmol) was added and stirred for 48 hr. To this crude reaction mixture excess of MeI was added and stirred for another 48 hrs at room temperature, then the reaction mixture is concentrated by rotary evaporation and

precipitated three times in DCM. The product formation is confirmed by NMR spectroscopy.

$^1\text{H-NMR}$ (400 MHz; MeOD): δ 4.36 (m, 2H), 3.80-3.64 (m, 9H), 3.1 (m, 2H), 1.68 (br s, 2H), 1.45-1.30 (br, 17H), 0.91 (t, $J = 5.9$ Hz, 3H).

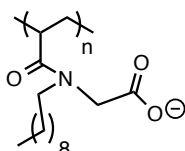
Synthesis of neutral TEG amphiphilic polymer, 12:



To the solution of reactive polymer (100 mg, 0.42 mmol) in dry THF (2 mL), TEG secondary amine, 11 (543 mg, 1.26 mmol) and Hunig's base (0.23 mL, 1.26 mmol) was added and stirred for 48 hr. This reaction mixture is purified by dialysis (Mol. Wt cut off: 3500 Da) in MeOH/DCM (25/75, v/v) mixture. The product formation is confirmed by NMR spectroscopy.

$^1\text{H-NMR}$ (400 MHz; CDCl_3): δ 4.2 (m, 2H), 3.31-3.10 (m, 8H), 2.74 (s, 3H), 1.68 (br s, 2H), 1.41-1.28 (br, 17H), 0.91 (br m, 3H).

Synthesis of neutral anionic amphiphilic polymer, 15:



To the solution of reactive polymer (100 mg, 0.42 mmol) in dry THF (2 mL), secondary amine ester, 13 (341 mg, 1.26 mmol) and Hunig's base (0.23 mL, 1.26 mmol) was added and stirred for 48 hr. This resulted in the formation of intermediate species, t -butyl protected ester. The reaction mixture is concentrated and re dissolved in DCM (2 mL). To this 0.5 mL TFA was added and stirred for 48 hrs. The reaction mixture is rotary evaporated several times by adding DCM to remove excess TFA, then precipitated in MeOH and repeated this process for two more times to get pure white solid of anionic polymer, product formation is confirmed

by NMR spectroscopy. $^1\text{H-NMR}$ (400 MHz; DMSO-d_6): δ 4.12 (br s, 2H), 3.42 (s, 2H), 2.58 (s, 1H), 2.10-1.28 (m, 17H), 0.88 (t, 3H).

^{19}F - NMR data

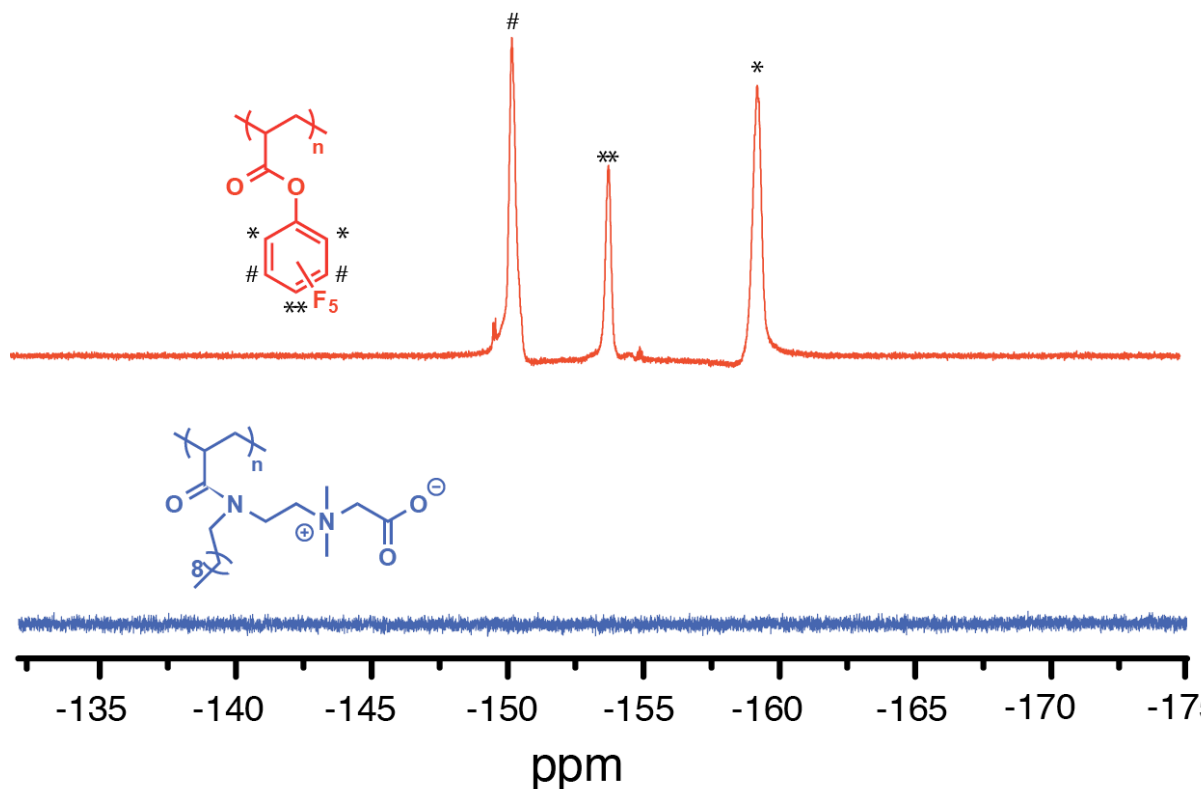


Fig S1. ^{19}F -NMR peaks corresponding to pentafluorophenyl group disappear upon conversion of reactive polymer to zwitterionic polymer, indicating the efficient post functionalization of reactive polymer.

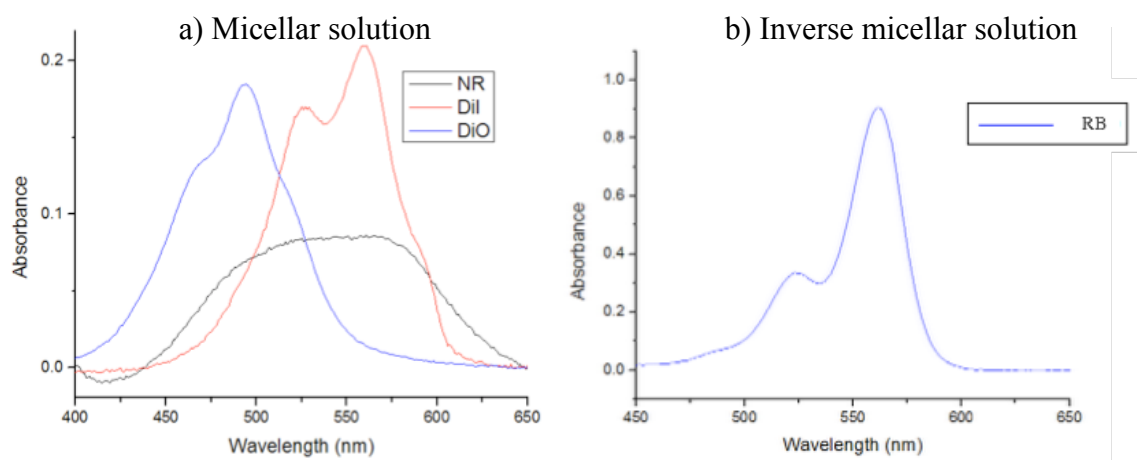


Fig S2. a). Absorbance spectra of hydrophobic and hydrophilic guest molecules (Nile Red, DiI, and DiO) encapsulated in micellar assemblies; b). hydrophilic guest molecule, Rose Bengal in inverse micellar assemblies.

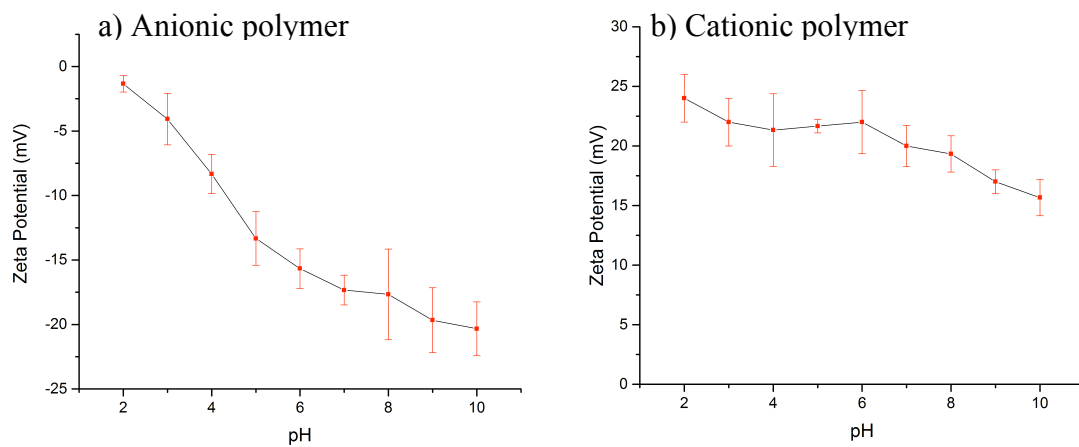


Fig S3. Zeta potential changes with the changes in pH of the solution were monitored for ionic polymers: a) Anionic polymers, b) Cationic polymers

(1) Eberhardt, M.; Mruk, R.; Zentel, R.; Théato, P. *Eur. Polym. J.* **2005**, *41*, 1569-1575.