Electronic Supplementary Information for

Thermoresponsivity of Polymer Solution Derived from Self-Attractive Urea unit and Self-Repulsive Lipophilic Ion Unit

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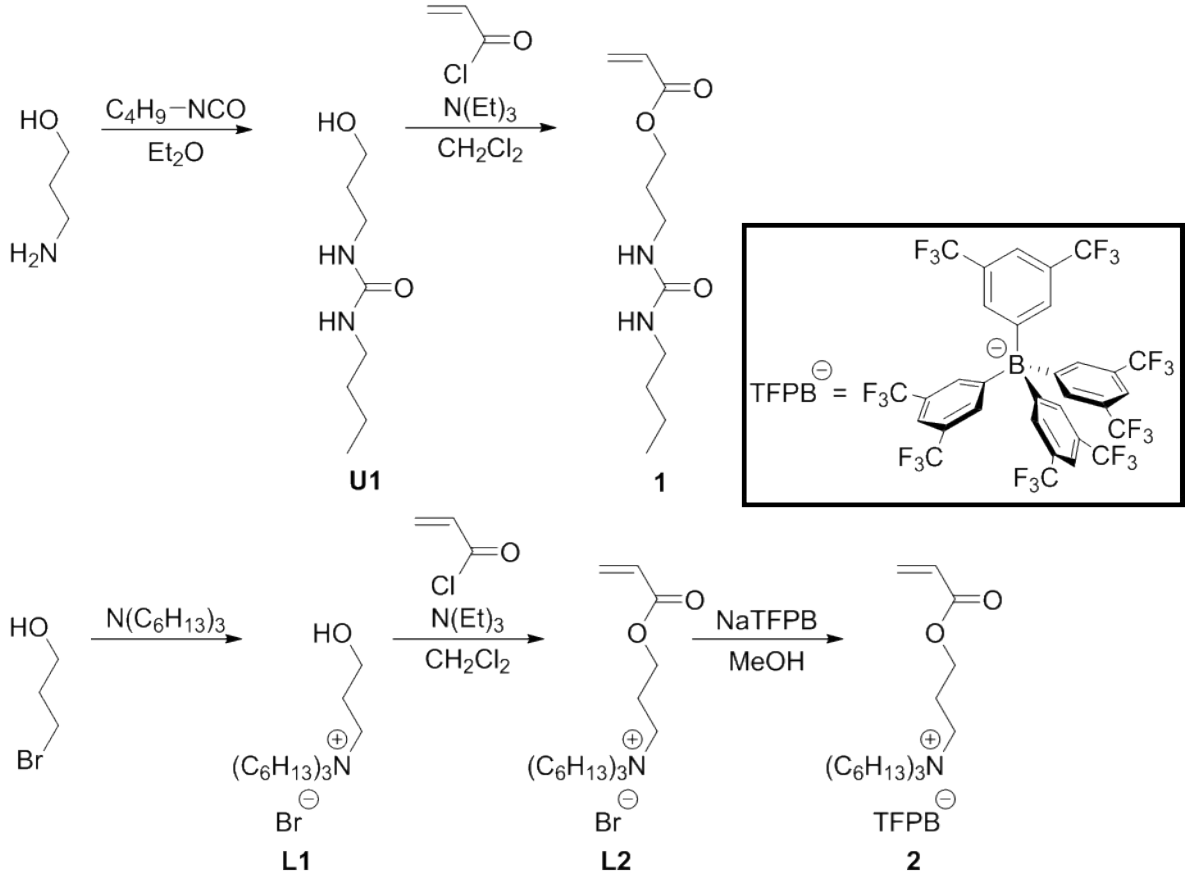
Experimental Section

Materials and Measurements. Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used without further purification. The polymerization initiator, 2,2'-azobis(isobutyronitrile) (AIBN), was recrystallized using methanol before usage. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure. The RAFT reagent, cumyl dithiobenzoate (**3**),[1] were synthesized according to reported procedure. Size exclusion chromatography (SEC) was carried out on a SHIMADZU LC-9A system (SHODEX KD-805 and K-804 column) with a SHIMADZU RID-10A refractive index detector using DMF (10 mM LiBr) as an eluent at 30 °C, after calibration with the standard polystyrene samples. Turbidity measurements were recorded on a JASCO V-570 spectrophotometer with a JASCO ETC-50ST temperature controller, in various organic solvents at the concentration of 25 g/L at room temperature. Cloud points of the polymer solutions were determined from the transmittance at 700 nm on cooling at 1.0 °C/min as the temperature with 90% transmittance. Scanning electron microscopy (SEM) observation was conducted with a JEOL JSM-7400F microscope. ^{1}H and ^{13}C NMR measurements were recorded on a Bruker AV300, Bruker 600 MHz NMR, and JEOL JNM-AL300 instruments. MALDI-TOF spectra were recorded on a Perspective Voyager RP. FT-IR ATR spectra was recorded by using a JASCO FT/IR 4100 instrument.



Scheme S1. Synthetic route for monomers **1** and **2**.

Synthesis of N-butyl-N'-(3-hydroxypropyl)-urea (U1).[2] n-Butyl isocyanate (9.91 g, 100 mmol) was added to a solution of 3-amino-1-propanol (7.51 g, 100 mmol) in dry diethyl ether (45 mL) with vigorous stirring. The reaction mixture was stirred for 1 h at room temperature, and filtered off. The resulting solid was washed diethyl ether and obtained **U1** as a white powder (16.98 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard, r.t.): δ (ppm) 0.92 (t, J = 7.2 Hz, 3H, -CH_3), 1.28-1.40 (m, 2H, -CH_2CH$_3$), 1.41-1.52 (m, 2H, -CH_2CH$_2$CH$_3$), 1.65 (quin, J = 5.8 Hz, 2H, -NHCH$_2$CH_2CH$_2$OH), 3.15 (q, J = 6.6 Hz, 2H, -NHCH_2CH$_2$CH$_2$CH$_3$), 3.35 (q, J = 6.0 Hz, 2H, -NHCH_2CH$_2$CH$_2$OH), 3.65 (q, J = 5.7 Hz, 2H, -NHCH$_2$CH$_2$CH_2OH), 3.77 (t, J = 6.2 Hz, 1H, -OH), 4.71 (s, 1H, -NHCH$_2$CH$_2$CH$_2$CH$_3$), 4.90 (s, 1H, -NHCH$_2$CH$_2$CH$_2$OH).

Synthesis of 3-(3-butylureido)propyl acrylate (1).[2] To a solution of *N*-butyl-*N*'-(3-hydroxypropyl)-urea (8.71 g, 50 mmol) and triethylamine (5.57 g, 55 mmol) in dry CH_2Cl_2 (150 mL), acryloyl chloride (4.98 g, 55 mmol) was slowly added at 0 °C. After the mixture was stirred for additional 3 h at room temperature, it was poured into the water. The reaction mixture was washed with $NaHCO_3$ aq., water, and dried over anhydrous Na_2SO_4, followed by evaporation to dryness. The residue was purified by silica column chromatography (CH_2Cl_2 /acetone= 9:1 (v/v)) to obtain **1** as a white solid (6.44 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard, r.t.): δ (ppm) 0.92 (t, J = 7.2 Hz, 3H, -CH_3), 1.27-1.40 (m, 2H, -CH_2CH$_3$), 1.41-1.54 (m, 2H, -CH_2CH$_2$CH$_3$), 1.88 (quin, J = 6.3 Hz, 2H, -NHCH$_2$CH_2CH$_2$O-), 3.15 (q, J=6.6 Hz, 2H, -NHCH_2CH$_2$CH$_2$CH$_3$), 3.27 (q, J = 6.4 Hz, 2H, -NHCH_2CH$_2$CH$_2$O-), 4.26 (t, J = 6.2 Hz, 2H, -NHCH$_2$CH$_2$CH_2O-), 4.35 (s, 1H, NH, -NHCH$_2$CH$_2$CH$_2$CH$_3$), 4.70 (s, 1H, -NHCH$_2$CH$_2$CH$_2$O-), 5.85 (dd, J = 10.2, 1.5 Hz, 1H, alkene H), 6.12 (dd, J = 17.4, 10.5 Hz, 1H, alkene H), 6.42 (dd, J = 17.1, 1.5 Hz, alkene H). FTIR (ATR, cm^{-1}): 3324, 2966, 2932, 2874, 1717, 1617, 1580, 1480, 1415, 1295, 1200, 1049, 983, 811. Anal. Calcd. for $C_{11}H_{20}N_2O_3$ C 57.87, H 8.83, N 12.27. Found: C 57.82, H 8.83, N 12.27. HRMS (EI): m/z calcd. for $C_{11}H_{20}N_2O_3$ $[M]^+$: 228.1474; found: 228.1465.

Synthesis of *N*-(3-hydroxypropyl)-*N*,*N*,*N*-trihexylammonium bromide (L1).[3] A mixture of tri-(n-hexyl)amine (11.9 g, 44.2 mmol) and 3-bromo-1-propanol (12.3 g, 88.5 mmol) was stirred at 60 °C for 24 h under Ar atmosphere. The viscous liquid was purified by reprecipitation into excess amount of diethyl ether and obtained **L1** as a white powder (7.84 g, 46%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard, r.t.) δ = 0.91 (t, J = 6.4 Hz, 9H, -NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3), 1.3 (m, 12H, -NCH$_2$CH$_2$CH$_2$CH_2CH_2CH$_3$), 1.38 (m, 6H, -NCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 1.70 (m, 6H, -NCH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 2.00 (m, 6H, NCH$_2$CH_2CH$_2$OH), 3.19 (t, J = 8.3 Hz, 6H, NCH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.71 (t, J = 8.1 Hz, 2H, NCH$_2$CH$_2$CH_2OH), 3.81 (m, 2H, NCH_2CH$_2$CH$_2$OH), 4.50 (m, 2H, NCH$_2$CH$_2$CH$_2$OH). MS (MALDI-TOF): m/z calcd for $C_{21}H_{48}NO$ $[(M\text{-}TFPB)^+]$: 328.60; found: 328.32.

Synthesis of *N*-[3-(acryloyloxy)propyl]-*N*,*N*,*N*-trihexylammonium bromide (L2).[3] The compound **L1** (4.00 g, 9.82 mmol) was dissolved in 100 mL of dry dichloromethane in a two-necked round bottom flask under Ar atmosphere. The flask was cooled in an ice-bath and triethylamine (2.72 mL, 19.6 mmol) was added to the stirring solution. Acryloyl chloride (1.59 mL, 19.6 mmol) was added dropwise to the solution over a period of 10 min. The mixture was further stirred for 5 h at room temperature. The reaction mixture was washed with saturated $NaHCO_3$ aq., water, and dried over anhydrous $MgSO_4$. The solvent was removed by a rotary evaporator to **L2** as a viscous liquid (3.32 g, 73%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS standard, r.t.) δ= 0.90 (t, *J* =6.7 Hz, 9H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.33 (m, 12H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.41 (m, 6H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.68 (m, 6H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 2.24 (m, 6H, -$NCH_2CH_2CH_2O$-), 3.39 (t, *J* = 8.4 Hz, 6H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 3.48 (m, 2H, -$NCH_2CH_2CH_2O$-), 4.34 (t, *J* = 6.3 Hz, 2H, -$NCH_2CH_2CH_2O$-), 5.87 (d, *J* =10.5 Hz, 1H, alkene *H*), 6.13 (dd, J = 10.5, 17.3 Hz, 1H, alkene *H*), 6.44 (d, J = 17.3 Hz, 1H, alkene *H*).

Synthesis of *N*-[3-(acryloyloxy)propyl]-*N*,*N*,*N*-trihexylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (2).[3] Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt dihydrate (1.47 g,1.66 mmol) and **L2** (0.74 g, 1.60 mmol) was dissolved in methanol (20 mL). Water was added dropwise to the stirring solution, and white solid gradually precipitated. The resulting mixture was stirred for 12 h. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO_2, hexane/acetone= 1:1, v/v) to obtain **2** as a white solid. (1.36 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS standard, r.t.) δ = 0.85 (t, *J* = 6.7 Hz, 9H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.27 (m, 18H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.56 (m, 6H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.98 (m, 6H, -$NCH_2CH_2CH_2O$-), 3.02 (t, *J* = 8.5 Hz, 6H, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 3.18 (t, *J* = 8.4 Hz, 6H, -$NCH_2CH_2CH_2O$-), 4.21 (t, *J* = 5.5 Hz, 2H, -$NCH_2CH_2CH_2O$-), 5.87(d, *J* = 10.4 Hz, 1H, alkene *H*), 6.13 (dd, *J* = 10.4, 17.2 Hz, 1H, alkene *H*), 6.64 (d, *J* = 17.3 Hz, 1H, alkene *H*), 7.53 (s, 4H, Ar-*H*), δ=7.70 (s, 8H, Ar-*H*). MS (MALDI-TOF): calcd for $C_{24}H_{48}NO_2$ [(M-TFPB)$^+$] 382.64; found 382.34, $C_{32}H_{12}BF_{24}$ [TFPB$^-$] 863.21; found 861.90. Anal. Calcd for $C_{56}H_{60}BF_{24}NO_2$: C 53.90, H 4.85, N 1.12; found: C 54.16, H 4.81, N 1.22.

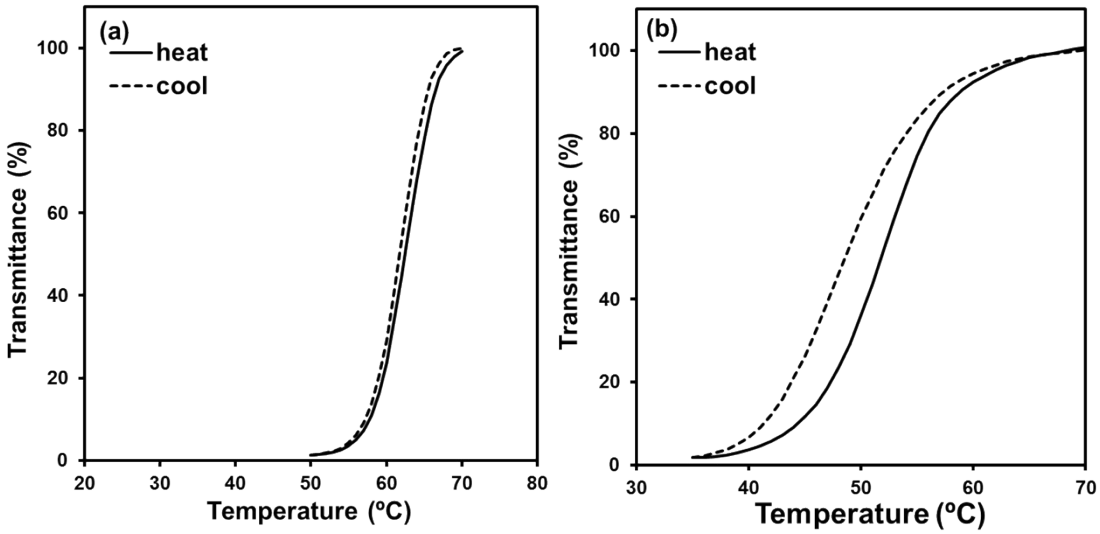


Fig. S1. Transmittance change of **PBPU-TFPB4** in (a) 1,2-dichloroethane (DCE) ([**PBPU-TFPB4**] = 25 g/L) and (b) acetonitrile (ACN) ([**PBPU-TFPB4**] = 100 g/L). Measured at 800 nm with 1 ºC/min scan rate.

Table S1. Monomer conversion and composition in polymer upon polymerization for **PBPU-TFPB5**.

Polymerization time (h)	Monomer conversion (%)[a]	*x* (%, obs.)[a]
2	5.2	5.8
4	9.2	4.3
8	26.4	5.1

[a] The monomer conversion of polymerization and composition of **PBPU-TFPB5** was estimated by ^{1}H NMR in DMSO-d_6.

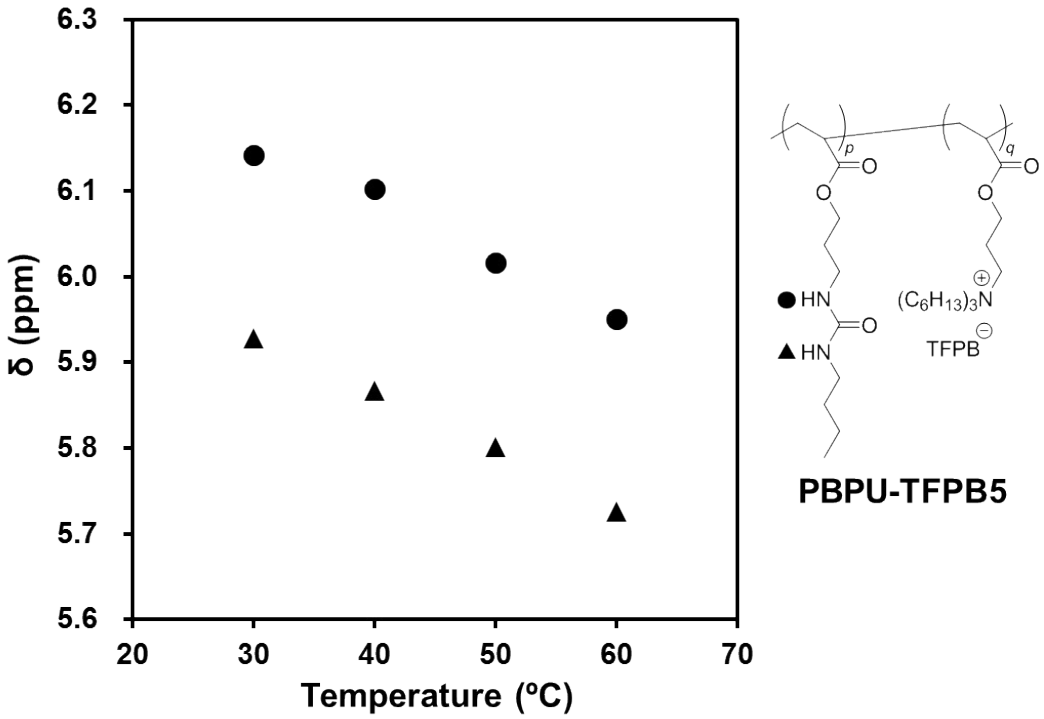


Fig. S2 ^{1}H NMR chemical shift variation of urea group in **PBPU-TFPB5** upon heating in 1,2-dichloroethane-d_4 (DCE-d_4) ([**PBPU-TFPB5**] = 25 g/L).

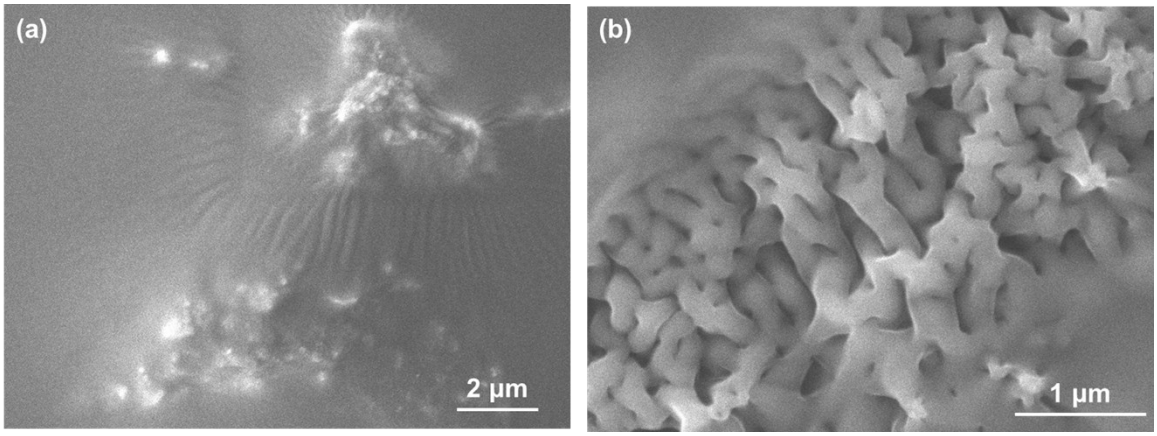


Fig. S3 SEM images of **PBPU-TFPB5** dried from (a) 1,2-dichloroethane (DCE) and (b) acetonitrile (ACN) at room temperature.

References

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