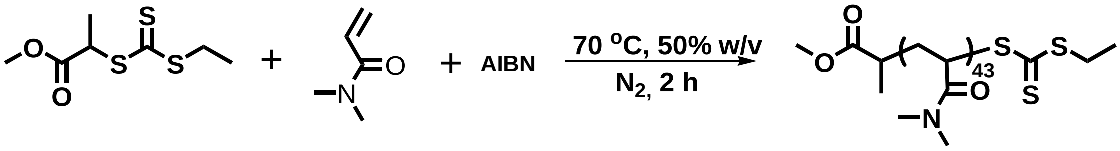
Supporting Information

Materials

2-Ethylsulfanylthiocarbonylsulfanylpropionic acid methyl ester (CTA) was synthesized according to a previously reported procedure (W. Zhou, Q. Qu, Y. Xu and Z. An, *ACS Macro Letters*, 2015, 4, 495-499). 1-Butylimidazole (98%), 4-vinylbenzyl chloride (90%) and *N*,*N*-dimethylacrylamide (DMA, 99%) were purchased from J&K Scientific. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 99%) was purchased from Sigma-Aldrich (recrystallized from ethanol). *N*,*N*-Dimethylformamide (DMF, 99.5%), ethanol (EtOH, 99.7%), diethyl ether anhydrous (99.7%) were purchased from Sinopharm Chemical Reagent Co. Ltd. The monomers were passed through a column of Al_2O_3 to remove the inhibitor before use.

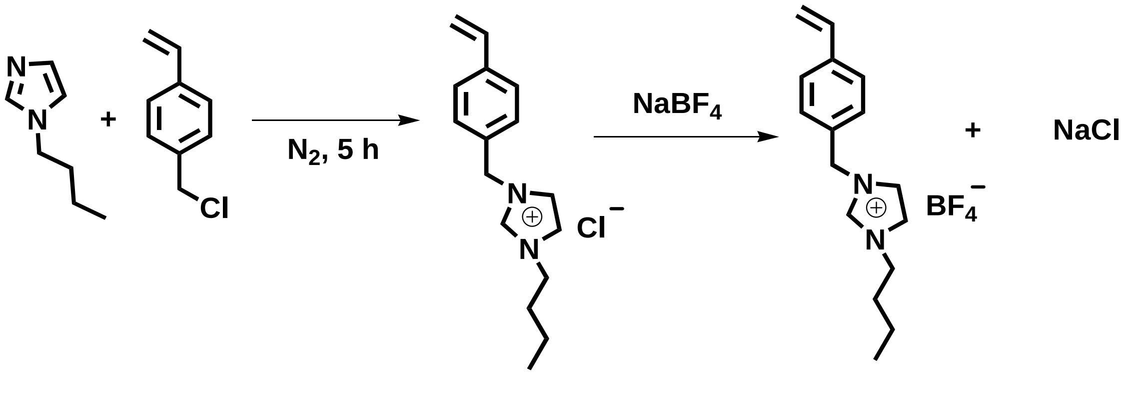
Characterization

The monomer conversions and synthesized polymers were analyzed by ^1H NMR spectroscopy on a Bruker AV 500 MHz spectrometer and chemical shifts were reported relative to the solvent residue. Transmission electron microscopy (TEM) analysis of nanoparticles was conducted on a Jeol 200CX microscope at 200 kV. TEM samples were prepared by diluting the as-synthesized colloidal solutions to generate 0.025-0.05% w/v dispersions, which were carefully dropped onto carbon-coated copper grids and dried overnight at 40 °C under vacuum. Dynamic light scattering (DLS) was performed on a Malvern ZS90 at a detection angle of 90° at 25 °C, which was equipped with a He-Ne laser (633 nm, 4 mW). The samples were prepared with concentrations of 0.025%-0.05% w/v, and z-average diameters were reported. Molar mass and dispersity of polymers were analyzed on a Waters Alliance e2695 GPC system equipped with a Styragel guard column (WAT054415, 30 × 4.6 mm), two Org separation columns D2500 (300 × 8 mm) and D5000 (300 × 8 mm). Multi-detection was made with a 2414 refractive index detector (Waters Alliance), a Viscotek 302/305 UV detector (Malvern Instruments), and a Viscotek TDA 305-020 LALS/RALS detector (Malvern Instruments). DMF (HPLC grade, 1.75 mg/mL LiBr) was used as the eluent at a flow rate of 0.7 mL/min. A differential scanning calorimeter DSC 822^e thermal analysis system (Mettler Toledo Instruments Inc. Switzerland) was used to determine the glass transition temperature of polymer samples under protection of N_2 at a scanning rate of 10 °C/min. The samples (6-8 mg) were placed in an aluminum crucible with a lid, and the change in heat flow was measured with respect to an empty aluminum crucible. The temperature was cycled in the range 0-150 °C, and the samples were held at 150 °C for 5 min to erase any thermal history.



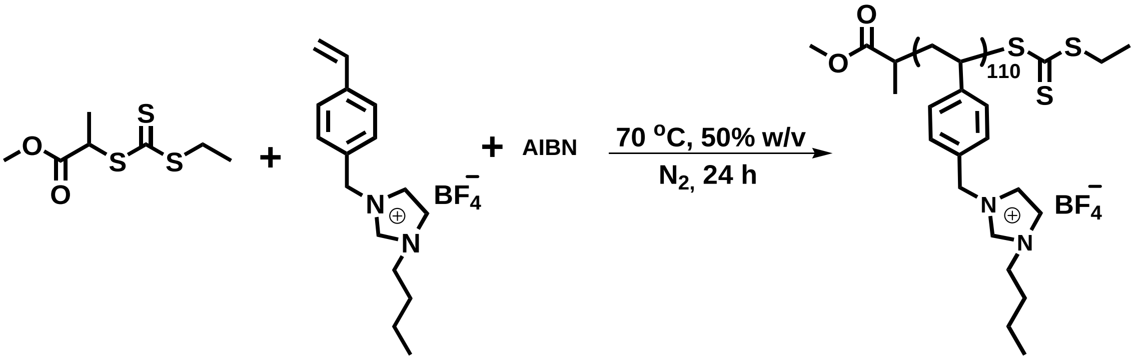
Synthesis of macromolecular chain transfer agent ($PDMA_{43}$)

2-Ethylsulfanylthiocarbonylsulfanylpropionic acid methyl ester (2.7660 g, 12.3 mmol) , DMA (67.3677 g, 679.6 mmol) and AIBN (0.0406 g, 0.247 mmol) were added into a glass vial and dissolved in 140 mL DMF. After the solution was stirred for 10 min, 100 μL solution was taken as the reference sample (0 min) for ^{1}H NMR spectroscopy analysis. After the solution was purged with nitrogen for 30 min, it was immersed into a preheated oil bath at 70 °C. After 2 h polymerization under nitrogen, the monomer conversion was determined to be 79% by ^{1}H NMR spectroscopy. A yellow polymer solid was obtained via precipitation in excess cold diethyl ether three times and dried at 45 °C under vacuum. Theoretical molar mass was calculated from monomer converson: $M_{\mathrm{n,theory}} = M_{\mathrm{CTA}} + (\text{target DP} \times M_{\mathrm{DMA}}) \times \text{conversion} = 4487$ g/mol; molar mass calculated from ^{1}H NMR spectroscopy analysis of purified polymer: $M_{\mathrm{n,NMR}} = (I_e/6)/(I_b/2) = 4487$; Triple-detection GPC: $M_n = 4545$ g/mol, $Đ = 1.05$.



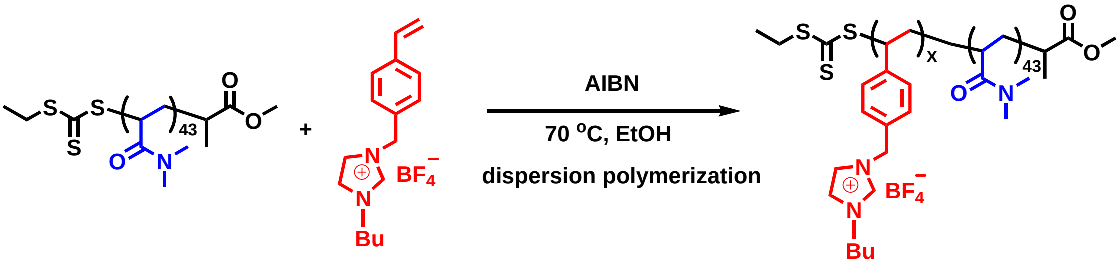
Synthesis of 1-butyl-3-(4-vinylbenzyl)imidazolium tetrafluoroborate ([BVBIm][BF_4])

The monomer 1-butyl-3-(4-vinylbenzyl)imidazolium tetrafluoroborate was synthesized according to Yan et al. (*Chemistry of Materials*, 2013, 25, 1858-1867). 1-Butyl-3-(4-vinylbenzyl)imidazolium chloride was first synthesized by stirring a mixture of 1-butylimidazole (24.836 g, 0.2 mol) and 4-vinylbenzyl chloride (33.58 g, 0.22 mol) at room temperature under N_2 protection for 5 h. The product was dissolved with a minimum amount of water and washed five times (6 × 150 mL) with ethyl ether. A solution of $NaBF_4$ (98.83 g, 0.6 mol) was slowly added to the obtained imidazolium hydrochloride. After stirring for 12 h the suspension was filtered and the cake was washed with water (3 × 20 mL). After drying at 45 °C under vacuum for two days, a white powder was obtained.



Synthesis of poly(1-butyl-3-(4-vinylbenzyl)imidazolium tetrafluoroborate) homopolymer

2-Ethylsulfanylthiocarbonylsulfanylpropionic acid methyl ester (0.0098 g, 4.37×10^{-2} mmol), 1-butyl-3-(4-vinylbenzyl)imidazolium tetrafluoroborate (1.7175 g, 5.23 mmol) and AIBN (0.0035 g, 0.0213 mmol) were added into a glass vial and dissolved in 3 mL DMF. After the solution was stirred for 10 min, 100 μL solution was taken for ^1H NMR spectroscopy analysis. After the solution was purged with nitrogen for 30 min, it was immersed into a preheated oil bath at 70 °C. After 24 h polymerization under nitrogen, the monomer conversion was determined to be 92% by ^1H NMR spectroscopy analysis. The polymer was purified in a dialysis bag (MWCO 1.0 kg/mol) against ethanol for two days. After drying under vacuum at 60 °C for two days, the polymer was isolated after removal of solvent.



Synthesis of poly(dimethylacrylamide)–*b*–poly(1-butyl-3-(4-vinylbenzyl)imidazolium tetrafluoroborate) block copolymer nano-objects via RAFT dispersion polymerization

The synthesis of $PDMA_{43}$–*b*–$P([BVBIm][BF_4])_x$ nano-objects via RAFT dispersion polymerization in ethanol was systematically investigated at 20-40% solids by varying the target DP of the PIL block in the range 30-140 (see **Table S1**). The synthesis of $PDMA_{43}$–*b*–$P([BVBIm][BF_4])_{90}$ is given as a representative procedure. 1-Butyl-3-(4-vinylbenzyl)imidazolium tetrafluoroborate ($[BVBIm][BF_4]$, 0.3472 g, 1.06 mmol) and $PDMA_{43}$ (0.0528 g, 1.18×10^{-2} mmol) were weighed into a 20 mL glass vial. A certain amount of ethanol (2 mL in this case) was added to dissolve all the reagents to form a homogeneous solution. After the reaction mixture was purged with nitrogen for 20 min in an ice/water bath, the vial was placed into an oil bath at 70 °C with a stirring speed of 500 rpm. Then a certain amount of AIBN ($AIBN/PDMA_{43} = 0.5$) dissolved in 100 μL ethanol was added via a syringe. After 24 h polymerization under nitrogen, the monomer conversion and block copolymer composition were determined by ^1H NMR spectroscopy in DMSO-d_6, the size and morphology were analyzed by DLS and TEM.

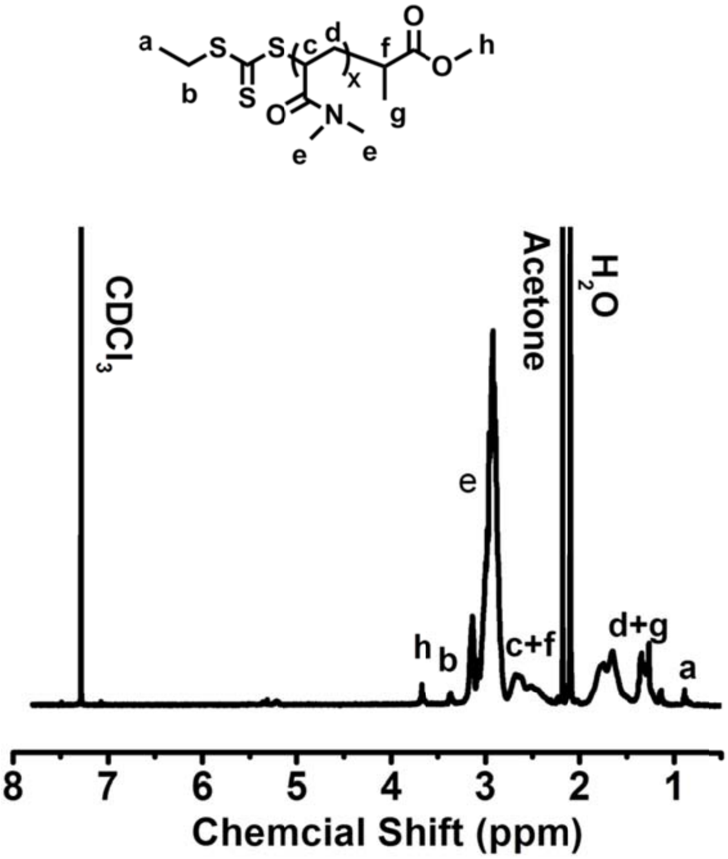


Fig. S1 ^{1}H NMR spectrum of PDMA$_{43}$ macro-CTA in CDCl$_3$.

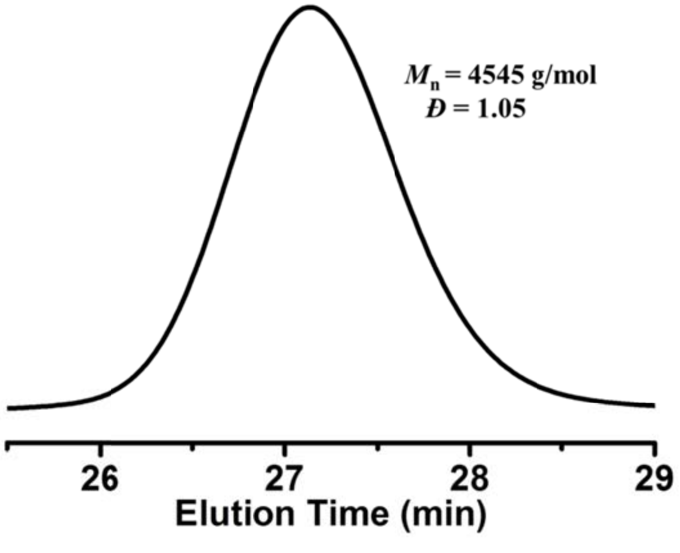


Fig. S2 GPC trace of PDMA$_{43}$ macro-CTA.

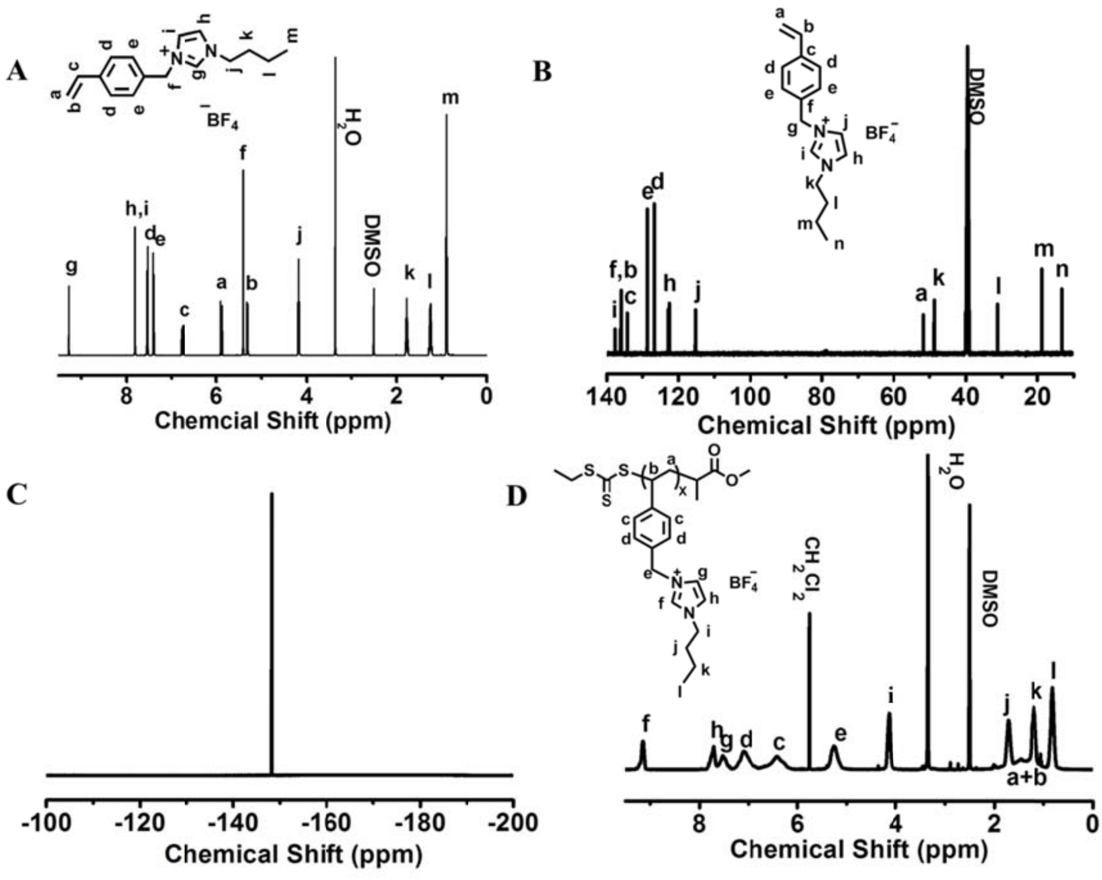


Fig. S3 ^{1}H, ^{13}C, ^{19}F NMR spectra of [BVBIm][BF$_4$] and ^{1}H NMR spectrum of P([BVBIm][BF$_4$]) in DMSO-d$_6$.

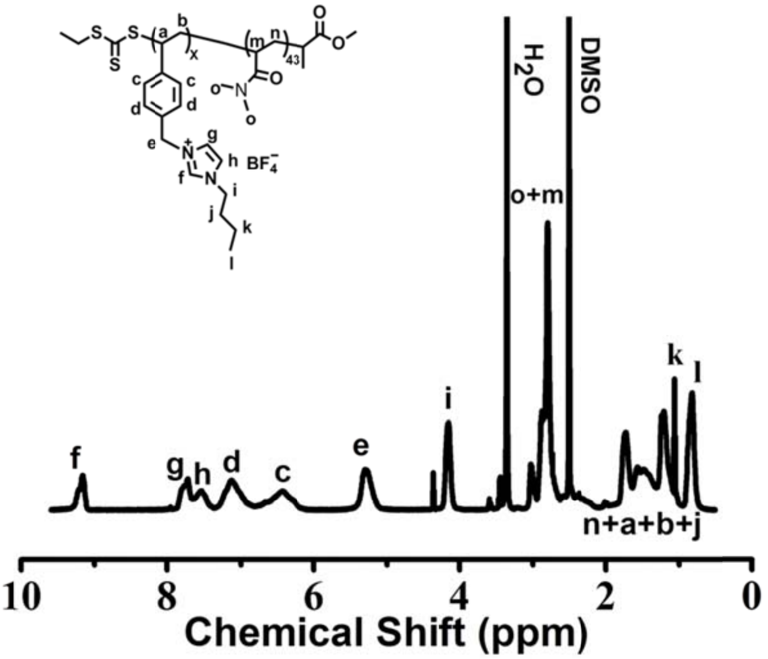


Fig. S4 ^{1}H NMR spectrum of PDMA–*b*–P([BVBIm][BF$_4$]) in DMSO-d$_6$.

Table S1 Summary of dispersion polymerization[a]

Entry	Solids (% w/v)	Target DP	conv.(%)[b]	D_h (nm)/PDI[c]	Morphology[d]
1	20	60	96	60.17 /0.186	S
2		80	98	208.7/0.214	W
3		90	96	225.7 /0.170	W+L
4		100	98	512.7 /0.230	L
5		120	96	350.3 /0.329	V
6		140	94	987.8 /0.148	V
7	25	30	92	22.67 /0.160	S
8		48	85	63.10 /0.170	S+W
9		60	96	502.9 /0.932	S+W
10		70	94	275.6 /0.061	W
11		90	99	698.2 /0.624	L
12		120	95	416.0 /0.191	V
13	30	30	98	27.02 /0.202	S
14		48	95	72.57 /0.152	S+W
15		60	96	193.5 /0.291	W
16		78	90	323.4 /0.141	W+L
17		90	96	400.0 /0.354	L+V
18		115	92	457.0 /0.392	V
19	40	30	98	76.28 /0.212	S
20		48	95	402.5 /0.492	W
21		78	93	365.8 /0.213	W+L
22		85	93	1346 /0.275	L+V
23		100	94	244.2 /0.065	V
24		135	93	300.5 /0.191	V

[a] RAFT dispersion polymerization of [BVBIm][BF_4] using $PDMA_{43}$ as the macro-CTA at 70 °C, 24 h, [AIBN]/[$PDMA_{43}$]=0.5. [b] Determined by ^1H NMR spectrum in DMSO-d_6. [c] z-average diameter and polydispersity index (PDI) determined by DLS at 25 °C in EtOH. [d] Determined by TEM.

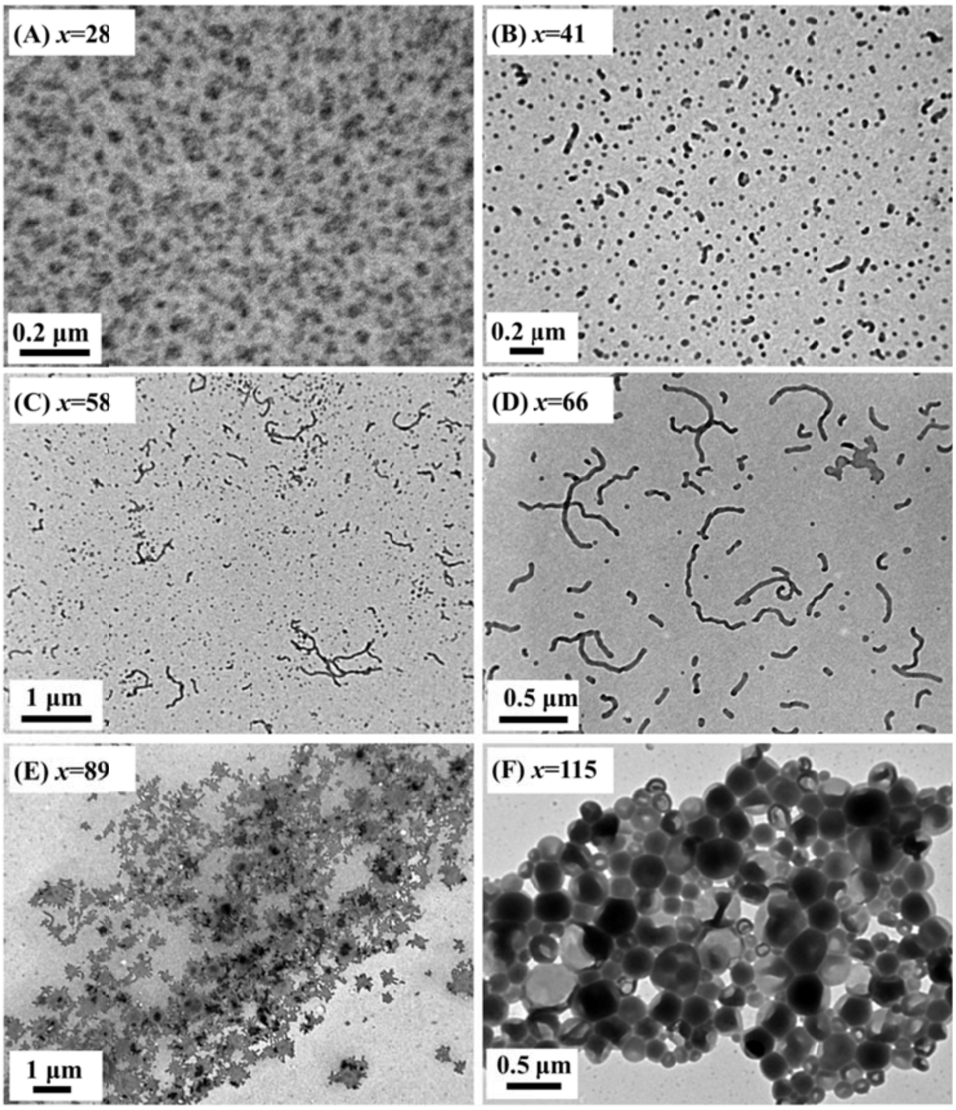


Fig. S5 TEM micrographs of PDMA$_{43}$–*b*–P([BVBIm][BF$_4$])$_x$ block copolymer nano-objects synthesized via RAFT dispersion polymerization of [BVBIm][BF$_4$] in ethanol at 70 °C using PDMA$_{43}$ as the macro-CTA at 25% w/v solids.

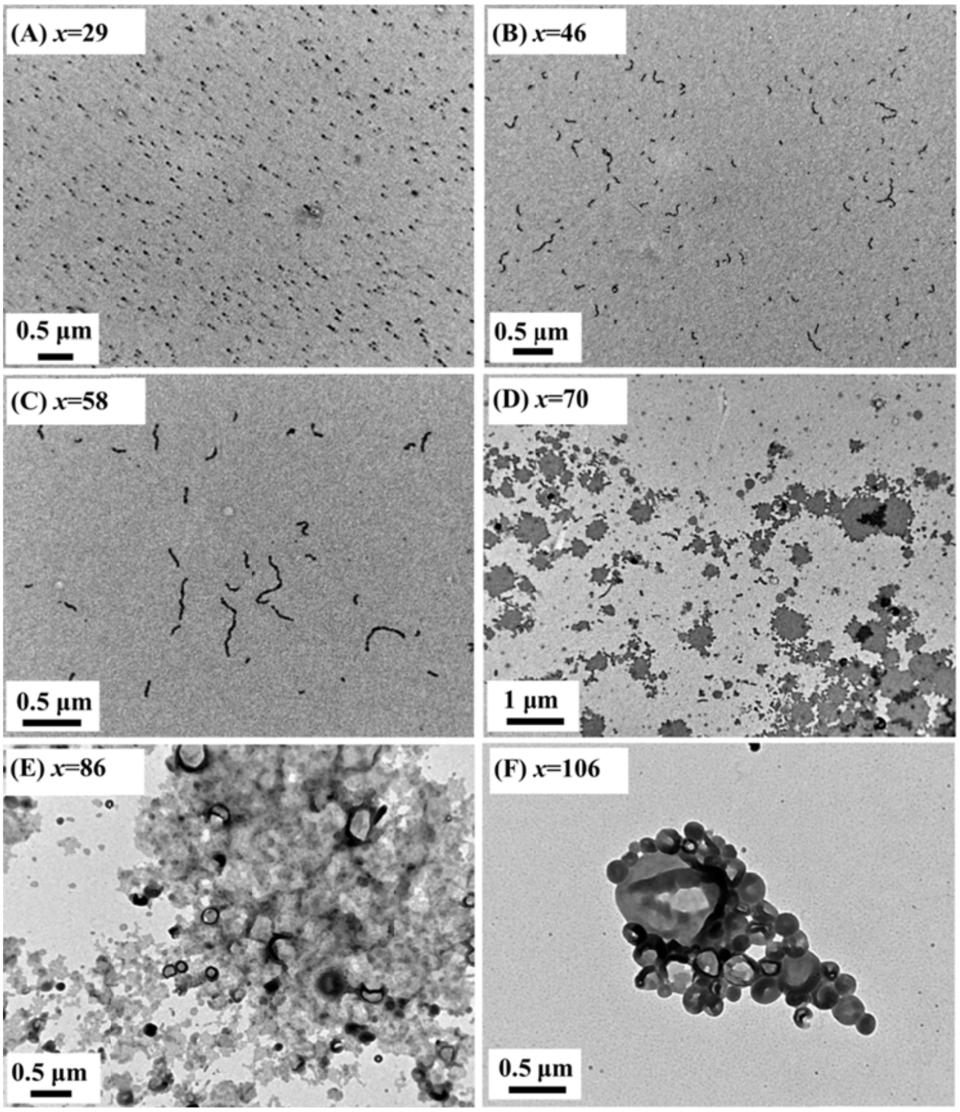


Fig. S6 TEM micrographs of $PDMA_{43}$–*b*–P([BVBIm][BF_4])$_x$ block copolymer nano-objects synthesized via RAFT dispersion polymerization of [BVBIm][BF_4] in ethanol at 70 °C using $PDMA_{43}$ as the macro-CTA at 30% w/v solids.

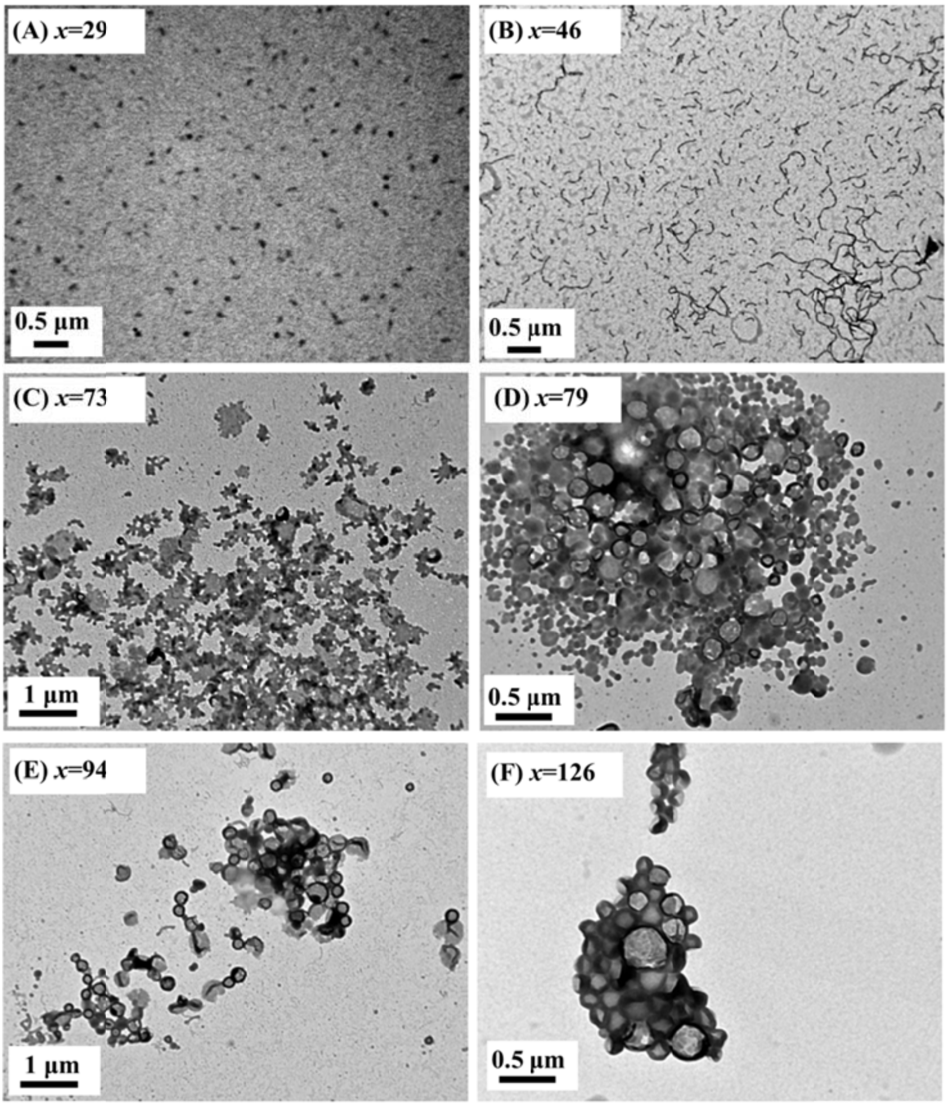


Fig. S7 TEM micrographs of $PDMA_{43}$–*b*–P([BVBIm][BF_4])$_x$ block copolymer nano-objects synthesized via RAFT dispersion polymerization of [BVBIm][BF_4] in ethanol at 70 °C using $PDMA_{43}$ as the macro-CTA at 40% w/v solids.

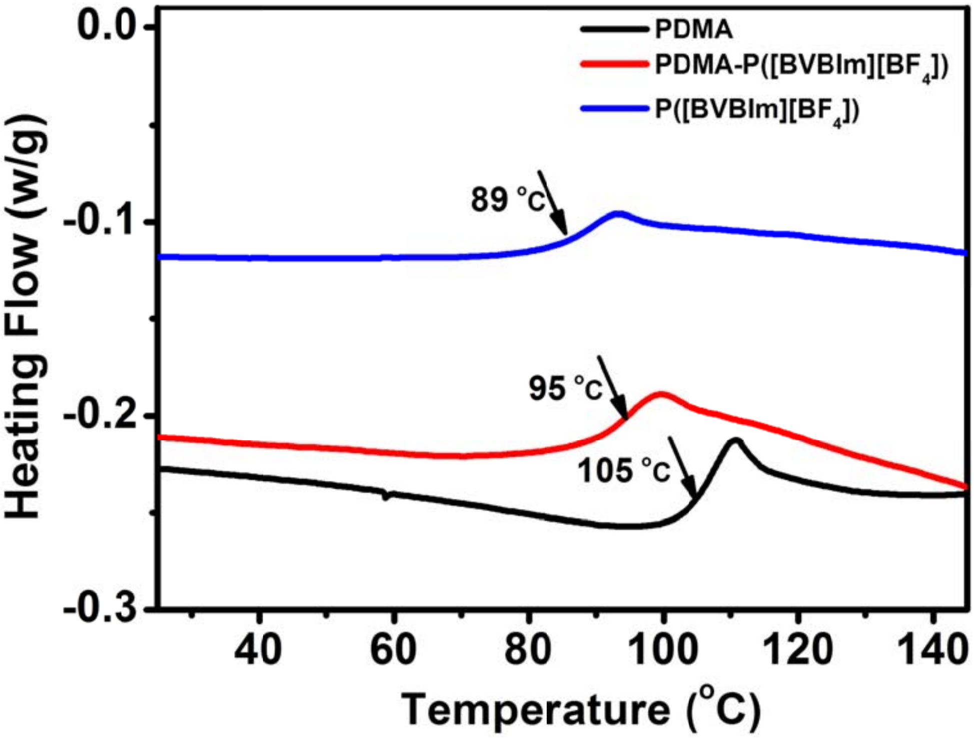


Fig. S8 DSC traces (second heating cycle) of $PDMA_{43}$, $P([BVBIm][BF_4])_{110}$, $PDMA_{43}$–*b*–$P([BVBIm][BF_4])_{80}$.