Supplementary Information

Polymerization-induced self-assembly enables access to diverse highly ordered structures through kinetic and thermodynamic pathways

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EXPERIMENTAL DETAILS

Materials. Styrene (> 99%), 2-hydroxyethyl acrylate (HEA; > 95%), N,Ndicyclohexylcarbodiimide (DCC; > 97%), 4-dimethylaminopyridine (DMAP; > 99%), dichloromethane, and 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65; initiator; >95%) were purchased from FUJIFILM Wako Pure Chemical (Osaka, Japan). Styrene and HEA were passed through a column of activated alumina to remove polymerization inhibitors, and dichloromethane dried molecular sieves before 2was over use. (Dodecylthiocarbonothioylthio)-2-methylpropionic acid (CTA; > 98%) was purchased from Sigma-Aldrich. Polyethylene glycol (PEG) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) were purchased from Tokyo Chemical Industry (Tokyo, Japan). The nominal molecular weight of the uniform PEG was 2,000, as confirmed by SAXS and size-exclusion chromatography (SEC). One terminal of PEG is a methyl group, and the other terminal is a hydroxy group (*i.e.*, α -methyl- ω -hydroxypolyethylene glycol). The nominal purity of $[BMIM][PF_6]$ is > 98%; ¹H NMR spectroscopy confirmed the absence of detectable impurities. Unless otherwise specified, all materials were used as received.

Preparation of macro-CTA. Steglich esterification, a well-established method, ^{S1–S3} was employed to prepare macro-CTA (Scheme S1) as follows. PEG (4.93 g, 2.47 mmol), CTA (4.39 g, 12.0 mmol), DMAP (0.072 g, 0.59 mmol), and dichloromethane (28 g) were mixed in a brown glass vial for 20 min, followed by the addition of DCC (2.4 g, 11.6 mmol). This mixture was stirred for 24 hours at 4 °C. The resulting precipitate (urea from DCC) was removed by filtration, and dichloromethane was evaporated. The solution was kept in brown vials at below 15 °C throughout the process of the filtration and evaporation. To remove unreacted CTA, the solution was

dialyzed against methanol using a dialysis tube (MWCO 1000, Spectra/Por 7, Repligen, Waltham, MA) in a 2 L brown beaker at 4 °C for 2.5 days, with fresh methanol being exchanged every half-day. After evaporating off the methanol, the product was dried under vacuum at *ca*. 15 °C for 3 days and stored at –20 °C. Complete functionalization (> 99%) was confirmed by ¹H NMR (Fig. S1) as well as the UV spectroscopy for the macro-CTA and the raw material [2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid] (Fig. S2).



Scheme S1 Chemical reaction to synthesize macro-CTA



Fig. S1 ¹H NMR spectrum of macro-CTA in deuterated chloroform.



Fig. S2 (a) UV spectra for CTA and macro-CTA in ethyl acetate at 25 °C, where the pathlength of a quartz cell was 2 mm. Absorbance of the solvent (ethyl acetate) is also shown as a grey curve. (b) Absorbance at the wavelength of 308 nm as a function of molar concentration for CTA (turquoise circle) and macro-CTA (pink circle).

PISA synthesis of PEG-PHEA and PEG-PS. Macro-CTA, V-65, and HEA or styrene were dissolved in [BMIM][PF₆] in a vial with a rubber septum. The total solute concentration (macro-CTA, and HEA or styrene) was 40 wt%. Unless otherwise specified, the molar ratio of CTA:V-65 was 3:1 in all PISA synthesis in this study. The volume of the solution was typically 1 g. The monomer:CTA ratio was adjusted according to the target degree of polymerization. To remove dissolved oxygen, nitrogen gas was bubbled through the solution for 10 min. Subsequently, the vial was placed in an oil bath at 60 °C for 3 hours. The reaction was quenched by placing the vials in an ice bath and exposing them to air.

Molecular characteristics. After the PISA synthesis, the reaction mixtures were dissolved in appropriate solvents for subsequent measurements; *i.e.*, [BMIM][PF₆] was not removed before the nucleic magnetic resonance (NMR) and size-exclusion

chromatography (SEC) measurements. For ¹H NMR spectroscopy, samples were dissolved in deuterated chloroform with a polymer concentration of approximately 0.1 wt%. The measurements were performed using a JNM-ECA600 or ECA500 spectrometer (JEOL, Akishima, Japan) at 25 °C. SEC measurements were performed using a Prominence SEC system (Shimadzu, Kyoto) with two serially connected columns (GF-7M HQ, Shodex, Showa Denko, Tokyo) and a refractive index detector (RID-20A). *N,N*-Dimethylformamide containing 0.2 M LiBr was used as the eluent with a flow rate of 0.5 mL/min, with the columns and detector maintained at 40 °C. The polymer concentration when injecting was *c.a.* 0.1 wt%. Poly(methyl methacrylate) standards (Agilent Technologies, Santa Clara, CA) were used for calibration to determine relative molecular weights. DSC was run using a DSC-60A calorimeter (Shimadzu, Kyoto). Aluminum pans with lids were used, and samples of *c.a.* 10 mg (mixture of polymer–ionic liquid) and an empty aluminum pan (reference) were simultaneously heated at a rate of 10 °C/min to measure heat flow under a constant nitrogen purge.

SAXS. SAXS experiments were carried out at BL40B2 beamline, SPring-8, Sayo, Japan. The incident X-ray energy and flux were 12.4 keV and 7×10^9 photons/s, respectively, and the spot size was approximately 0.2 mm diameter. A PILUTAS 2M detector was used with a sample-to-detector distance of 4.2 m. The sample cells consisted of two polyetherimide windows of 20 µm-thick (SUPERIO UT F-type, Mitsubishi Chemical, Tokyo, Japan) and a spacer, with a path length of 0.5 mm. Scattering from polyetherimide windows was subtracted from each data. The other experimental conditions were identical to those described in a previous study.^{S2}

TEM. Each Sample (mixtures of polymer and ionic liquid) was swollen with methanol and gently rubbed onto a Formvar-coated copper grid (PVF-C20-25; STEM,

Machida, Japan). The methanol was then removed under vaccum. TEM was performed using a JEM 2100 plus electron microscope (JEOL, Akishima, Japan) operating at an accelerating voltage of 200 kV. Images were aquired by an Orius SC200D CCD camera (Gatan, Pleasanton, CA).

Oscillatory rheology. The storage and loss moduli (G' and G'') as a function of angular frequency (ω) were obtained using an MCR302 rheometer (Anton Paar, Graz, Austria) equipped with a cone plate (25 mm diameter). The strain amplitude was adjusted for each sample to ensure measurements were performed within the linear viscoelastic regime. The plateau modulus was defined as the storage modulus at the minimum of the loss tangent ($\tan \delta = G''/G'$). If multiple minima were observed in $\tan \delta$, the highest ω value was used to estimate the plateau modulus.

Impedance spectroscopy. The impedance spectroscopy was performed according to a previously reported method.^{S4} Samples were filled into a cylindrical cell consisting of a fluoroplastic spacer and gold electrodes (20 µm-thick gold leaf; Nilaco, Tokyo, Japan; >99.95% purity). The inner thickness (*t*) and radius (*r*) of the cylindrical cell was 2 mm and 1.5 mm, respectively. The cell was placed on a thermostatic plate to maintain the sample temperature at 25 °C. An impedance analyzer (IM3590, Hioki, E. E., Ueda, Japan) was used to measure the absolute impedance, $|Z| = \sqrt{(Z^2 + Z''^2)}$, with *Z'* and *Z''* denoting the real and imaginary parts of the impedance, respectively. Measurements were done over a frequency range of 0.01 kHz to 200 kHz at a current of 1.00 mA. The electrical conductance (σ) was calculated by $\sigma = t/(\pi r^2 |Z|_p)$, where $|Z|_p$ stands for the plateau value of |Z| at high frequency regime in the |Z| *vs*. frequency plot, corresponding to the resistance.



Fig. S3 ¹H NMR spectra of PEG_{45} – PS_n in deuterated chloroform.



Fig. S4 ¹H NMR spectra of PEG_{45} -PHEA_n in deuterated chloroform.

Sample	Ð	Conversion / %	Structure	Nearest-neighbor	Plateau modulus / kPa	Electrical conductivity /
				domain spacing / nm		mS cm ^{-1}
PEG ₄₅ -PS ₂₃	1.08	98	BCC	13.6	47	0.33
PEG ₄₅ -PS ₄₅	1.06	> 99	НСР	19.0	27	0.32
PEG ₄₅ -PS ₇₅	1.04	97	GYR	41.7 ^{<i>a</i>}	25	0.63
PEG ₄₅ –PS ₉₁	1.14	96	DIS (VES+LAM)	25.4	25	0.31
PEG ₄₅ -PS ₁₃₆	1.12	92	DIS (VES+LAM)	30.2	3.9	0.35
PEG ₄₅ -PHEA ₂₉	1.16	> 99	DIS	12.2	_ <i>b</i>	0.27
PEG ₄₅ -PHEA ₃₄	1.12	> 99	HEX	15.4	69	0.27
PEG ₄₅ -PHEA ₄₅	1.15	> 99	HEX	16.8	22	0.28
PEG ₄₅ -PHEA ₇₅	1.15	95	GYR	50.5 ^a	40	0.30
PEG ₄₅ -PHEA ₁₃₆	1.21	> 99	LAM	27.1	4.8	0.26

 Table S1 Molecular weight and structural characteristics and physical properties

^{*a*} Unit cell parameter. ^{*b*} No plateau modulus was observed.

Table S2. Electron density of each component^a

	PS	PHEA	PEG	[BMIM][PF ₆]
Electron density / nm ⁻³	389	386	394	424

^{*a*} Calculated by $N_A\rho n_e/M$, where $N_{A,\rho}$, n_e , and M denote Avogadro's constant, mass density, number of electrons, and molar mass, respectively. ρ for PS, PHEA, and PEG are assumed to be 1.2 g/cm³.



Fig. S5 SAXS profiles of PEG₄₅–PS₄₅ in [BMIM][PF₆] at 25 °C prepared by "*ex situ* polymerization" as follows: Polymerization was performed in ethyl acetate (a good solvent for PEG, PS, and [BMIM][PF₆]), in the absence of [BMIM][PF₆]. [BMIM][PF₆] was then added to the solution, followed by evaporation of ethyl acetate at 60 °C under vacuum ([BMIM][PF₆] is a non-volatile solvent). The final polymer concentration was 40 wt%.



Fig. S6 Storage (a) and loss moduli (b), and loss tangent (c) plotted against angular frequency for PEG_{45} – PS_n in [BMIM][PF₆] at 25 °C, with the polymer concentration of 40 wt%.



Fig. S7 Storage (a) and loss moduli (b), and loss tangent (c) plotted against angular frequency for PEG_{45} –PHEA_n in [BMIM][PF₆] at 25 °C, with the polymer concentration of 40 wt%.



Fig. S8 Impedance spectra for PEG_{45} – PS_n in [BMIM][PF₆] at 25 °C, with the polymer concentration of 40 wt%. Each data is shifted vertically for clarity.



Fig. S9 Impedance spectra for PEG_{45} –PHEA_n in [BMIM][PF₆] at 25 °C, with the polymer concentration was 40 wt%. Each data is shifted vertically for clarity.

References

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