Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and UCST-Type Phase Behavior of α-Helical Polypeptides with Y-Shaped and Imidazolium Pendant

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Materials. Poly(γ-allyl-L-glutamate) (PALG, M_n =6200 , M_w/M_n = 1.2, DP = 37), 3-butyl-1-propargylimidazolium bromide (BPIB), and poly(γ-propyl-L-glutamate) *N*-butylimidazolium bromide conjugate (PPLG-ImBr) were synthesized according to reported procedures.[1] Anhydrous *N,N*-dimethylformamide (DMF, 99.9%) was dried over molecular sieves before use. Chloroform-*d* ($CDCl_3$, D.99.8%) + silver foil was purchased from Cambridge Isotope Laboratories, Inc. Copper bromide (CuBr, 99%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), deuterium oxide (D_2O, D.99.9%), *N*-butylimidazole (98%), NaI (98%), and $NaBF_4$ (98%) were purchased from Energy Chemical. Sodium azide (NaN_3, 99.5%) and dimethyl sulfoxide-d_6 (DMSO-d_6, 99.9 atom % D, contains 0.03% v/v TMS) were purchased from Sigma-Aldrich. Allyl alcohol was purchased from Kegonghua (Beijing) Chemical Technology Co. Ltd. Bromine (99.5%) and all other chemicals were purchased from Aladdin and used as received. Deionized water (DI-H_2O) was obtained from Aquapro AR1-100L-P11 water-purification-system (Ever Young Enterprises Development Co., Ltd., P. R. China).

Instrumentation. ^{1}H and ^{13}C nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were recorded on a Bruker ARX400 MHz spectrometer at room temperature. Chemical shifts (δ) were reported in the units of ppm and referenced to the protio impurities. The polymer solutions with concentrations of ~15 mg·mL^{-1} for NMR test prepared by directly mixing and shaking at room temperature. Gel permeation chromatography (GPC) measurements were performed on a PL-GPC120 setup equipped with a column set consisting of two PL gel 5 μm MIXED-D columns (7.5

mm × 300 mm, effective molar mass range of 0.2-400.0 kg·mol^{-1}) and PL-RI differential refractive index (DRI) detector. DMF containing 0.01 M LiBr was used as the eluent at 80 °C at a flow rate of 1.0 mL·min^{-1}. Narrowly distributed polystyrene standards in the molar mass range of 0.5-7.5 × 10^{4} kg·mol^{-1} (PSS, Mainz, Germany) were utilized for calibration. Polymer solutions for the GPC test with a concentration of 5 mg·mL^{-1} in 0.01 M LiBr/DMF were prepared by directly mixing and shaking at room temperature. FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with an attenuated total reflection (ATR) sample holder. Solid samples were placed on the diamond crystal window and pressed with a metal probe. Spectral measurements were carried out in the transmittance mode (scan range = 4000-600 cm^{-1}, resolution = 2 cm^{-1}, number of scans = 2, 25 °C). Circular dichroism (CD) measurements were carried out on a JASCO J-810 spectrometer. The polymer aqueous solutions were diluted to 0.2 mg·mL^{-1} and placed in a quartz cell with a path length of 0.1 cm. CD data were collected with the high tension voltage (i.e., the voltage applied to the photomultiplier) less than 600 V. Two scans were conducted and averaged between 185-250 nm with a resolution of 0.5 nm. The data were processed by subtracting the solvent (i.e., DI-H_2O) background. The CD spectra were reported in mean residue ellipticity (MRE) (unit: deg·cm^{2}·dmol^{-1}) which was calculated by the equation $[\theta]_{\lambda} = \mathrm{MRW} \times \theta_{\lambda}/10 \times \mathrm{d} \times \mathrm{c}$, where MRW is the mean residue weight (MRW = the molecular weight of polypeptide repeating unit), θ_{λ} is the observed ellipticity (mdeg) at the wavelength λ (i.e., 222 nm), d is the path length (mm) and c is the concentration (mg·mL^{-1}).[2] The fractional helicity (f_{H}) of the polypeptides was calculated using the equation $f_{\mathrm{H}} = (-[\theta]_{222} + 3{,}000)/39{,}000$ to allow for a quantitative comparison of the relative helical content, where $[\theta]_{222}$ is the mean residue ellipticity at 222 nm.[3] Ultraviolet–visible (UV–vis) spectra were measured using an Agilent Cary 100 spectrometer. The polymer solutions were prepared by stirring at temperatures above respective UCST-type phase transition temperature (T_{pt}), and then placed in a quartz cell with a path length of 1.0 cm. The transmittances of solutions were collected at the wavelength of 500 nm. Neat methanol, ethanol, and DI-H_2O at 25 °C were set to be 100% of transmittance for methanol, ethanol, and aqueous solutions, respectively. The solutions were cooled from high temperatures to low temperatures for UCST-type transitions with initial stabilization of 20 min. T_{pt} was determined at 50% of transmittance in the cooling cycle. For ionic strength dependent studies, the salt concentration was adjusted by the addition of NaX (X = Cl, I, or BF_4) and mixing at the temperature above respective T_{pt}.

1. Q. Hu, Y. Deng, Q. Yuan, Y. Ling and H. Tang, *J. Polym. Sci. Part A: Polym. Chem.*, 2014, **52**, 149-153.
2. S. M. Kelly, T. J. Jess and N. C. Price, *Biochim. Biophys. Acta*, 2005, **1751**, 119-139.
3. J. A. Morrow, M. L. Segall, S. Lund-Katz, M. C. Phillips, M. Knapp, B. Rupp and K. H. Weisgraber, *Biochemistry*, 2000, **39**, 11657-11666.

Table S1 Solubility of PPLG-ImX and PPLG-$(ImX)_2$ (X = Br, I, or BF_4) in various solvents

Solvent	PPLG-ImX			PPLG-$(ImX)_2$		
	X = Br	X = I	X = BF_4	X = Br	X = I	X = BF_4
DMSO	*S*	*S*	*S*	*S*	*S*	*S*
DMF	*S*	*S*	*S*	*S*	*S*	*S*
H_2O	*S*	*S*	*U*	*S*	*S*	*U*
MeOH	*S*	*S*	*U*	*S*	*S*	*U*
EtOH	*S*	*U*	*I*	*S*	*U*	*I*
THF	*I*	*I*	*I*	*I*	*I*	*I*
EAc	*I*	*I*	*I*	*I*	*I*	*I*
DEE	*I*	*I*	*I*	*I*	*I*	*I*
TCM	*I*	*I*	*I*	*I*	*I*	*I*
DCM	*I*	*I*	*I*	*I*	*I*	*I*
Hexane	*I*	*I*	*I*	*I*	*I*	*I*

DMSO = dimethyl sulphoxide; DMF = *N*,*N*-dimethylformamide; MeOH = methanol; EtOH = ethanol; THF = tetrahydrofuran; EAc = ethyl acetate; DEE = diethyl ether; TCM = trichloromethane (chloroform); DCM = dichloromethane; *S* = soluble; *I* = insoluble; *U* = UCST-type phase transition (polymer concentration = 10 mg·mL^{-1}). Note: the maximum polymer concentration for polypeptides in EtOH was 4 mg·mL^{-1}.

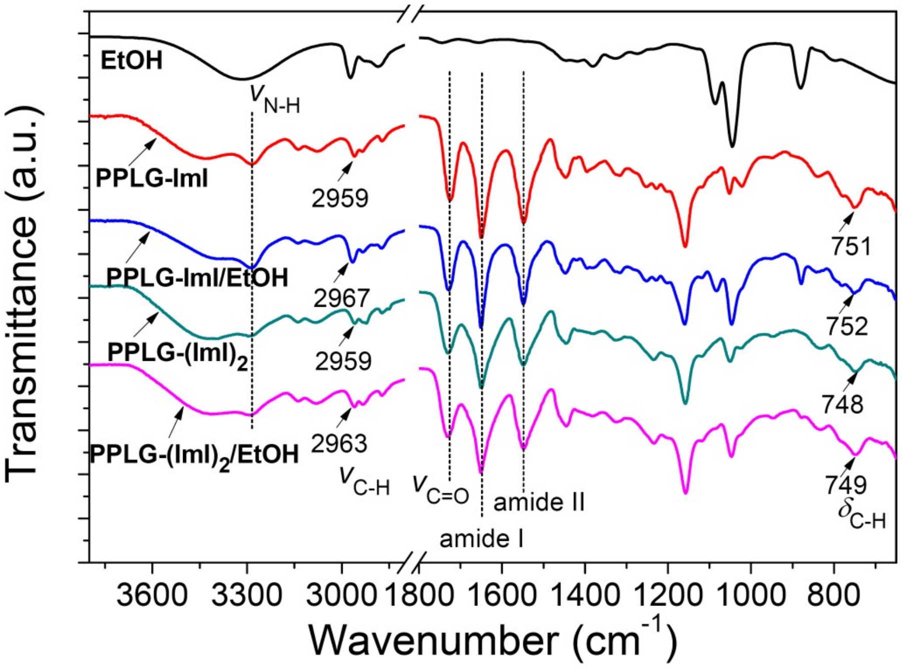

Figure S1. FTIR spectra of neat EtOH, PPLG-ImI, PPLG-$(ImI)_2$, PPLG-ImI/EtOH mixture, and PPLG-$(ImI)_2$/EtOH mixture (25 °C). Polymer/solvent mixtures were prepared by cooling the polymer solution from temperatures above the T_{pt} to room temperature, followed by collecting the wet polymer precipitate for FTIR measurement.

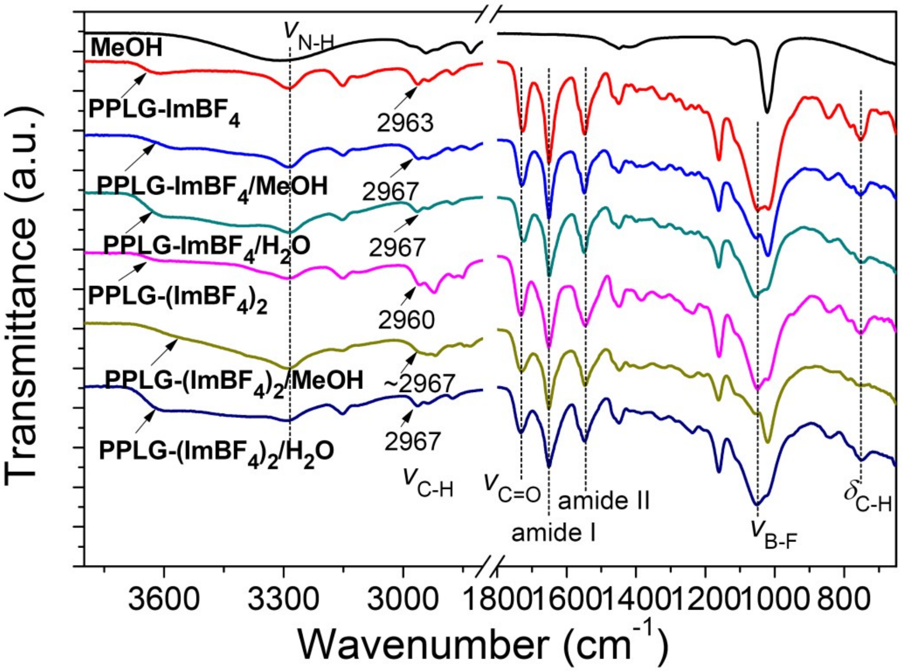

Figure S2. FTIR spectra of neat MeOH, PPLG-ImBF$_4$, PPLG-(ImBF$_4$)$_2$, PPLG-ImBF$_4$/MeOH mixture, PPLG-ImBF$_4$/H$_2$O mixture, PPLG-(ImBF$_4$)$_2$/MeOH mixture, and PPLG-(ImBF$_4$)$_2$/H$_2$O mixture (25 °C). Polymer/solvent mixtures were prepared by cooling the polymer solution from temperatures above the T_{pt} to room temperature, followed by collecting the wet polymer precipitate for FTIR measurement.

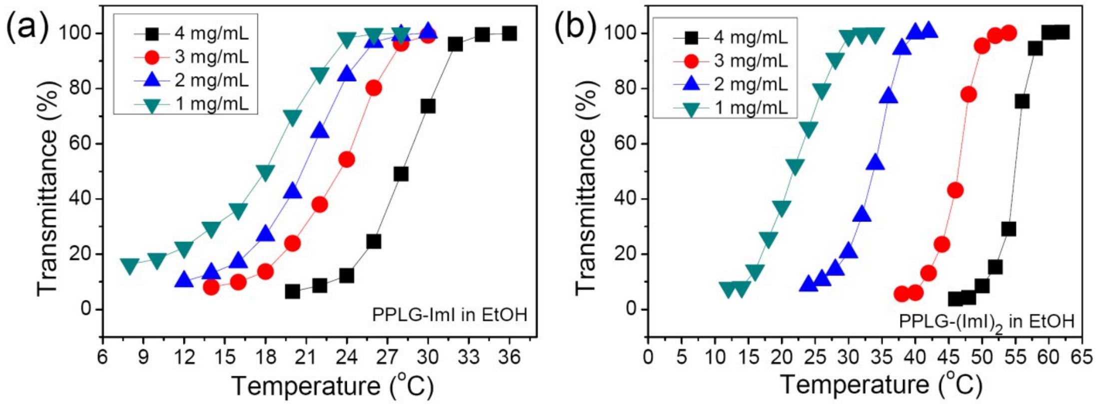

Figure S3. Plots of transmittance at λ = 500nm *versus* temperature for the ethanol solutions of (a) PPLG-ImI and (b) PPLG-(ImI)$_2$ at different polymer concentrations (1-4 mg·mL^{-1}).

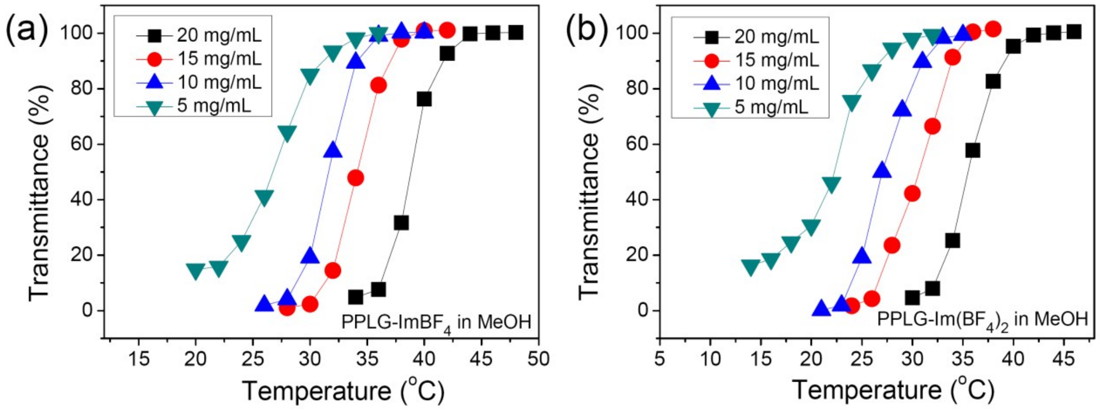

Figure S4. Plots of transmittance at λ = 500nm *versus* temperature for the methanol solutions of (a) PPLG-ImBF$_4$ and (b) PPLG-Im(BF$_4$)$_2$ at different polymer concentrations (5-20 mg·mL^{-1}).

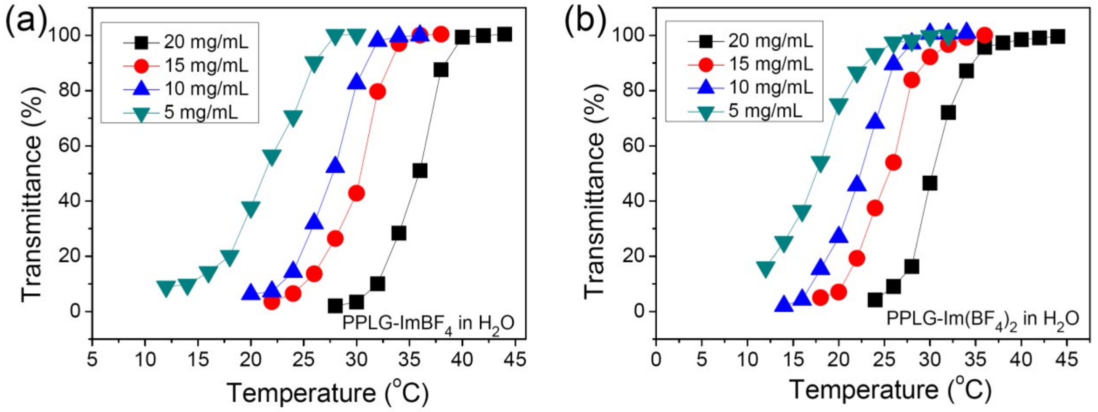

Figure S5. Plots of transmittance at λ = 500nm *versus* temperature for the aqueous solutions of (a) PPLG-ImBF$_4$ and (b) PPLG-Im(BF$_4$)$_2$ at different polymer concentrations in DI-H$_2$O (5-20 mg·mL^{-1}).

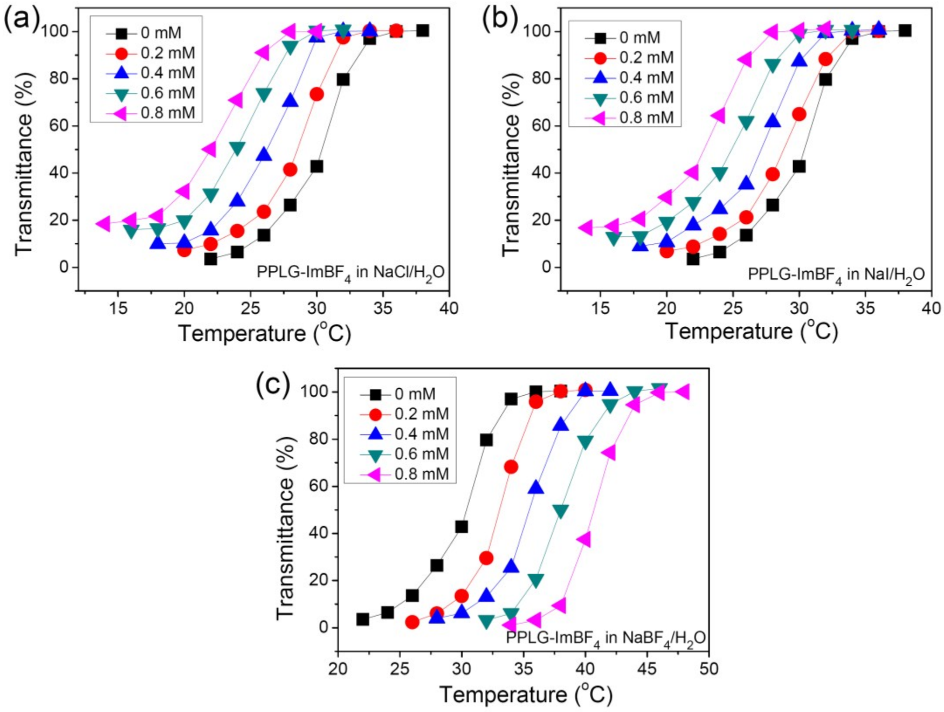

Figure S6. Plots of transmittance at λ = 500nm *versus* temperature for the (a) NaCl, (b) NaI, and (c) $NaBF_4$ aqueous solutions of PPLG-ImBF_4 at different salt concentration (0-0.8 mM, polymer concentration = 15 mg·mL^{-1}).

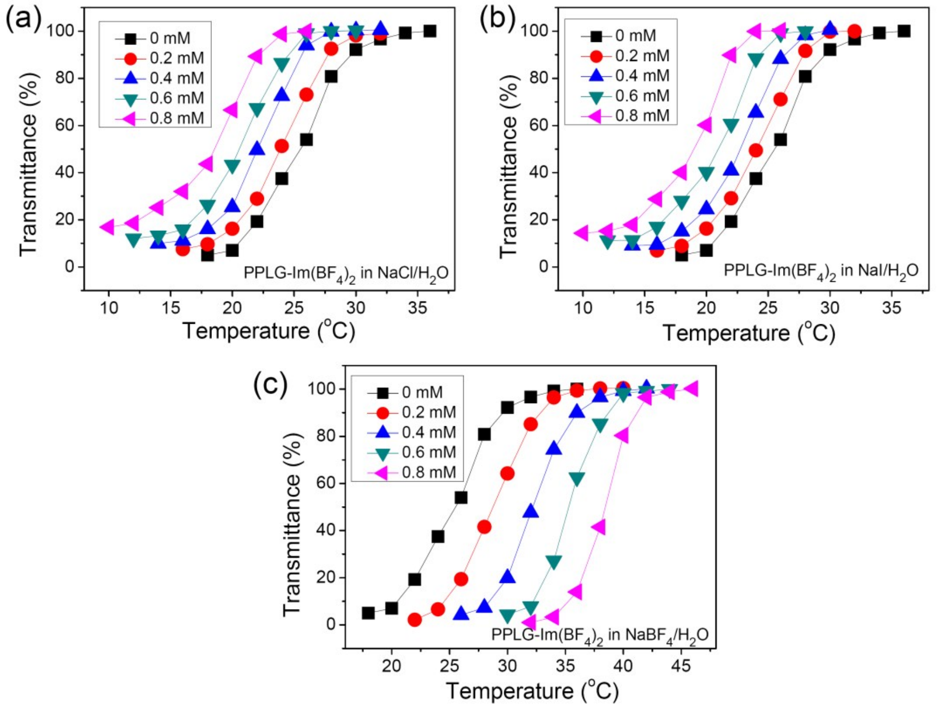

Figure S7. Plots of transmittance at λ = 500nm *versus* temperature for the (a) NaCl, (b) NaI, and (c) $NaBF_4$ aqueous solutions of PPLG-Im$(BF_4)_2$ at different salt concentration (0-0.8 mM, polymer concentration = 15 mg·mL^{-1}).