Supporting Information for

Toward the two-step microdynamic phase transition mechanism of oligo(ethylene glycol) methacrylate-based copolymer with a LCST-type poly(ionic liquid) block

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GPC and ^{1}H NMR results of PMEO$_2$MA-*b*-P[P$_{4,4,4,4}$][SS]

^{1}H NMR spectra were recorded on a Varian Mercury plus 400 M spectrometer with CDCl$_3$ as solvent. A gel permeation chromatograph (GPC) instrument with a G1362A refractive index detector was used to identify the weight-average molecular weights (M$_w$), number-average molecular weights (M$_n$), and the polydispersity index (PDI, M$_w$/M$_n$). N,N-Dimethylformamide (DMF) was used as the eluent at a flow rate of 1.0 mL min^{-1} and monodispersed poly(methyl methacrylate) (PMMA) was used as the standard for the calibration curve.

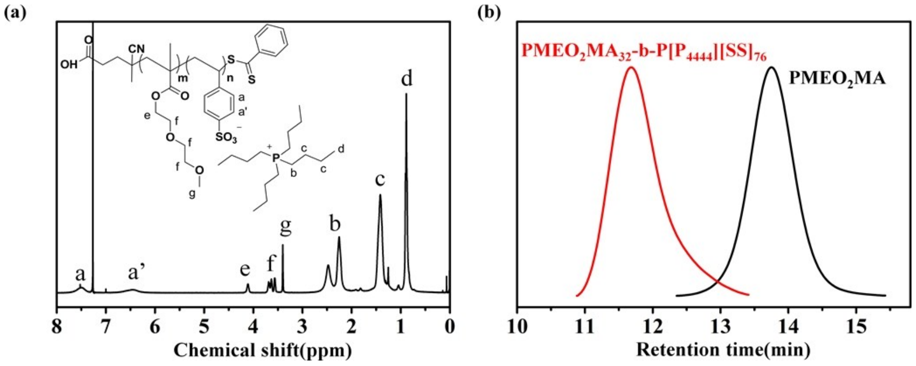

Fig. S1. (a) ^{1}H NMR spectra of PMEO$_2$MA-*b*-P[P$_{4,4,4,4}$][SS] copolymer (CDCl$_3$), (b) GPC curves of PMEO$_2$MA-*b*-P[P$_{4,4,4,4}$][SS] and PMEO$_2$MA with DMF as solvent.

Z-Average size distributions of PMEO$_2$MA-*b*-P[P$_{4,4,4,4}$][SS]

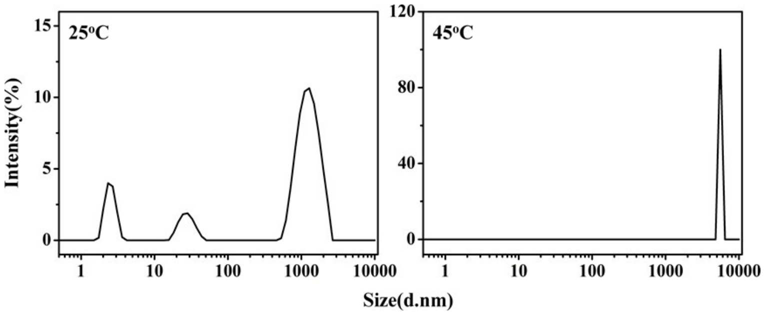

Fig. S2 Size distributions of PMEO$_2$MA-*b*-P[P$_{4,4,4,4}$][SS] (10 wt%) in water at 25 and 45 °C.

Specific contrast of ^{1}H NMR spectra at 20 and 55 °C

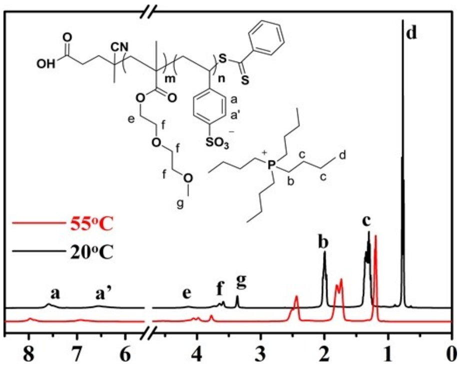

Fig. S3. Normalized ^{1}H NMR spectra of PMEO$_2$MA-*b*-P[P$_{4,4,4,4}$][SS] copolymer (20 wt% in D$_2$O) at 20 and 55 °C.

Temperature-variable ^{1}H NMR of PMEO$_2$MA$_{32}$ homopolymer

As for PMEO$_2$MA$_{32}$ homopolymer, the phase separation fraction p of the proton signal H_e close to C=O groups occurs to increase firstly at *ca.* 24°C, and shows the value of *ca.* 0.6 at high temperature. The peaks (H_f and H_g) attributing from the aliphatic side chains of PMEO$_2$MA segment shows a relatively slower phase separation degree change.

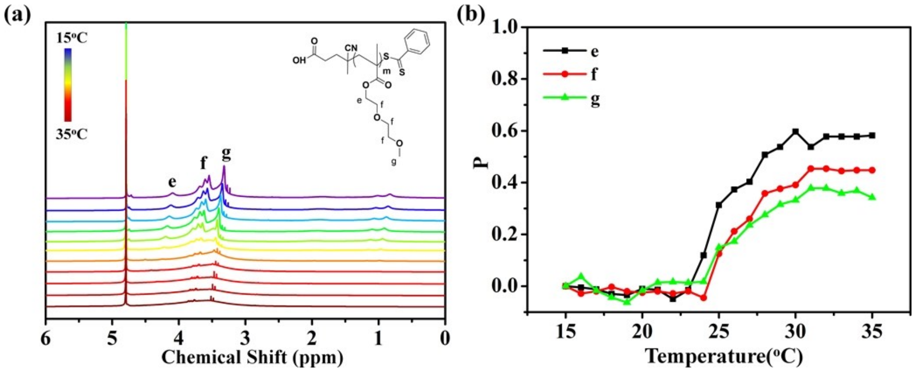

Fig. S4. (a) Normalized temperature-variable ^{1}H NMR spectra of $PMEO_2MA_{32}$ in D_2O (20 wt%) with an increment of 2 °C (b) Temperature-dependences of phase separated fraction *p* for different protons in $PMEO_2MA_{32}$ homopolymer.

Temperature-variable FTIR of $PMEO_2MA_{32}$ homopolymer

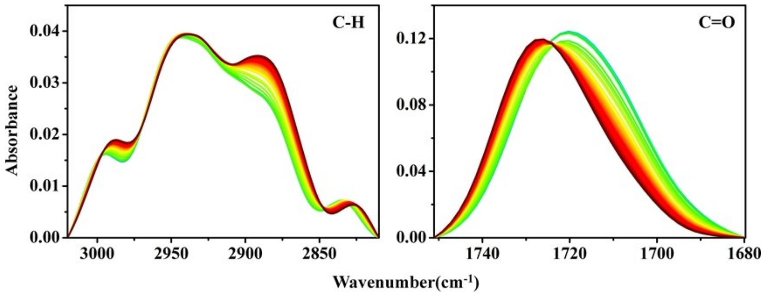

Fig. S5. Temperature-dependent FTIR spectra of $PMEO_2MA_{32}$ (15-35 °C) in D_2O (20 wt%) with an interval of 1 °C in the regions of 3020-2810 cm^{-1}, 1751-1679 cm^{-1}.

Perturbation Correlation Moving Window (PCMW)

PCMW is a newly developed technique which was originally proposed by Thomas and Richardson[1] and later improved into much wider applicability through introducing the perturbation variable into correlation equation by Morita et al.[2] Together with its ability to determine transition points as conventional moving window did, PCMW can also monitor the sophisticated spectral changes along the perturbation direction, additionally. PCMW synchronous spectra can provide information about transition points of different chemical groups, and asynchronous spectra offer details about the transition temperature region.

From the synchronous map, it is observed that the transition point of $PMEO_2MA_{32}$ is around 23 °C, which parallels well with the turbidity and DLS results. And there exists a transition temperature range almost from 20 to 26 °C of different groups from the asynchronous spectral map.

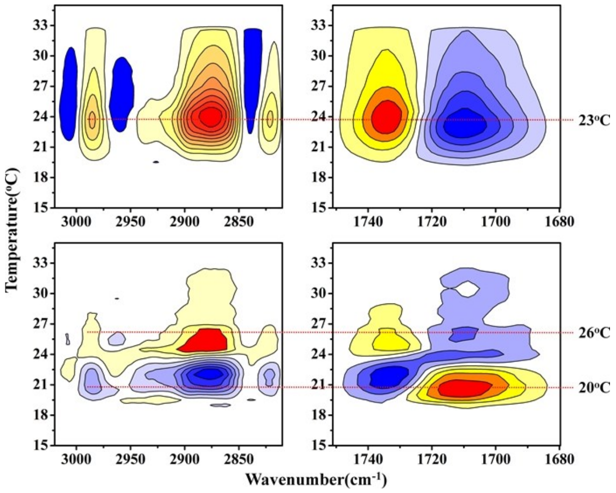

Fig. S6. PCMW synchronous and asynchronous spectra of $PMEO_2MA_{32}$ in D_2O (20 wt%) on heating. Warm colors (red and yellow) are defined as positive intensities, while cool colors (blue) are defined as negative intensities.

Sample preparation for $P[P_{4,4,4,4}][SS]$ homopolymer and $PMEO_2MA$/ $P[P_{4,4,4,4}][SS]$ Mixture

In order to make a better comparison, and $P[P_{4,4,4,4}][SS]$ homopolymer was synthesized by free radical polymerization in methanol with AIBN as the initiator according to previous report.[3] The number-average molecular weight (Mn) is 5.9×10^4 g mol^{-1}, and the polydispersity index (PDI=1.71) of the $P[P_{4,4,4,4}][SS]$ was determined by GPC measurements with a $NaNO_3$ solution as the eluent phase. Calorimetric measurements were taken using a Mettler-Toledo differential scanning calorimetry (DSC) thermal analyzer at a scanning rate of 10 °C min^{-1}. The aqueous solution (10 wt%) of PMEO$_2$MA/P[P$_{4,4,4,4}$][SS] mixture (repeat unit molar ratio of 1:1) was prepared for turbidity and DLS measurements.

Calorimetric measurements of P[P$_{4,4,4,4}$][SS] homopolymer

According to the DSC results, the transition temperature of the P[P$_{4,4,4,4}$][SS] aqueous solution (10wt%) is about 58^{o}C. Besides, the transition point undergoes a slight decrease with the range from 10 wt% to 20 wt% concentration.

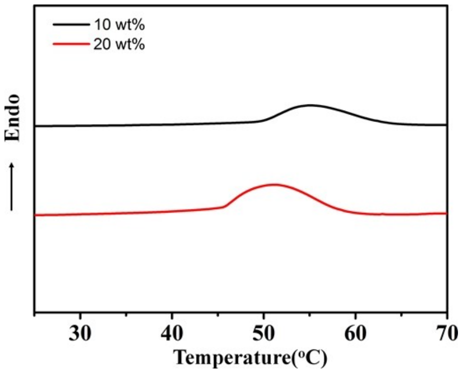

Fig. S7. DSC heating curves of [P$_{4,4,4,4}$][SS] solutions (10 wt% and 20 wt%) at the scanning rate of 10 ^{o}C min^{-1}.

Temperature-variable ^{1}H NMR, FTIR of P[P$_{4,4,4,4}$][SS] homopolymer

For P[P$_{4,4,4,4}$][SS] homopolymer, obviously, the resonant signals $H_{a,a'}$ corresponding to the anions of PIL show the beginning of slow dehydration at *ca.* 45°C. In contrast, the *p* changes of the signals $H_{b,c,d}$ mainly belonging to the cations are inconspicuous and appear to exhibit linear variation.

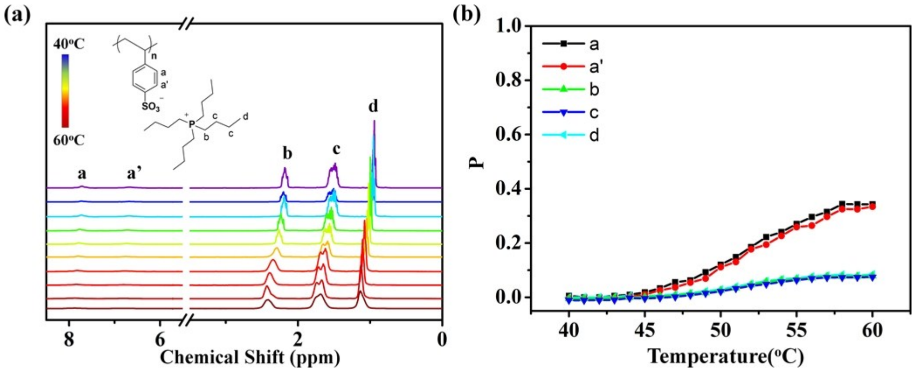

Fig. S8. (a) Normalized temperature-variable ^{1}H NMR spectra of P[$P_{4,4,4,4}$][SS] in D_2O (20 wt%) with an increment of 2 °C (b) Temperature-dependences of phase separated fraction *p* for different protons in P[$P_{4,4,4,4}$][SS] homopolymer.

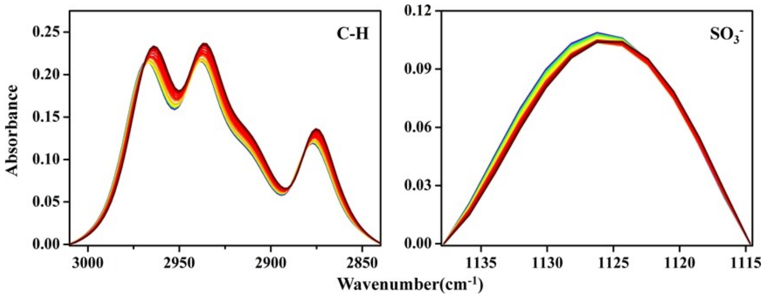

Fig. S9. Temperature-dependent FTIR spectra of P[$P_{4,4,4,4}$][SS] (40-60 °C) in D_2O (20 wt%) with an interval of 1 °C in the regions of 3010-2840 cm^{-1}, 1138-1114 cm^{-1}.

PCMW analysis of P[$P_{4,4,4,4}$][SS] homopolymer

From the synchronous map, it is observed that the transition point of P[$P_{4,4,4,4}$][SS] homopolymer is about 53 °C. And the transition temperature range is approximately from 48 to 55 °C for different groups from the asynchronous spectral map.

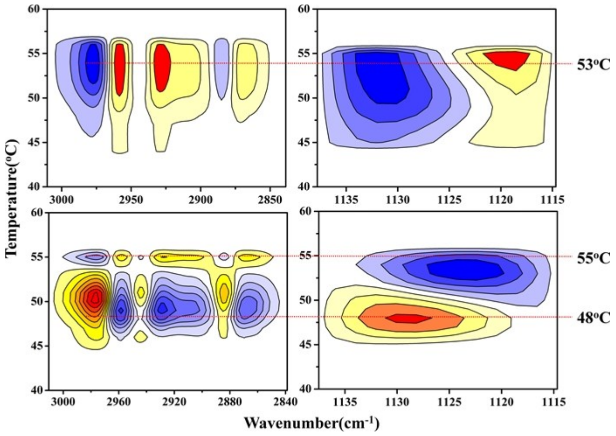

Fig. S10. PCMW synchronous and asynchronous spectra of P[$P_{4,4,4,4}$][SS] in D_2O (20 wt%) on heating. Warm colors (red and yellow) are defined as positive intensities, while cool colors (blue) are defined as negative intensities.

Thermal behavior of the $PMEO_2MA_{32}$/P[$P_{4,4,4,4}$][SS] mixture (1:1)

The thermal behavior of the $PMEO_2MA_{32}$/P[$P_{4,4,4,4}$][SS] mixture (10 wt% in water) is investigated by turbidity and DLS measurements, as shown in Fig. S11. In turbidity curve, it is observed that the mixture exhibits a sharp LCST-type phase transition with the transition point of 25 ^{o}C. While from the DLS curves, obviously, the D_h sizes undergo a two-step increase at *ca.* 25 ^{o}C and 40 ^{o}C, respectively, which might corresponds to the LCST transition points of the two homopolymers upon heating. It could be found that the LCST transition point of P[$P_{4,4,4,4}$][SS] homopolymer is slightly decreased because of the existence of $PMEO_2MA_{32}$, revealing that there might exist weak intermolecular interaction between $PMEO_2MA_{32}$ and P[$P_{4,4,4,4}$][SS] homopolymers in the solution of the $PMEO_2MA_{32}$/P[$P_{4,4,4,4}$][SS] mixture.

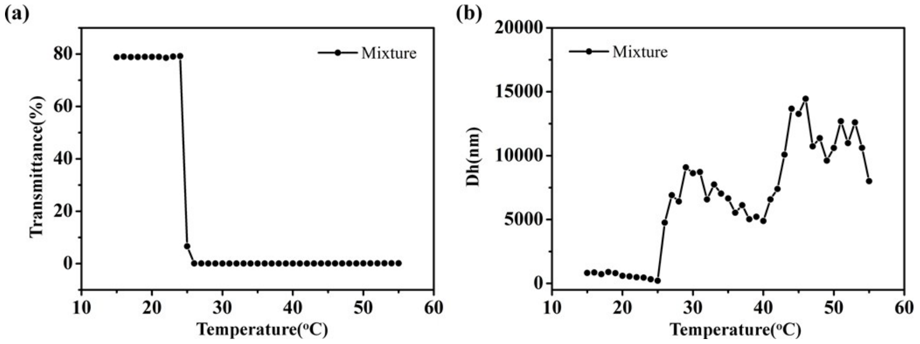

Fig. S11. (a) Turbidity analysis of $PMEO_2MA_{32}/P[P_{4,4,4,4}][SS]$ mixture (10 wt%) at the wavelength of 550 nm, heating rate 1°C min^{-1}. (b) DLS measurements of $PMEO_2MA_{32}/P[P_{4,4,4,4}][SS]$ mixture (10 wt%) with a heating rate of 1.0 ^{o}C min^{-1}.

Two-Dimensional Correlation Analysis (2Dcos).

Noda's rule: when the cross-peaks of v_1 and v_2 ($v_1 > v_2$) in synchronous and asynchronous spectra have the same symbol (both positive or negative), then the change at peak v_1 has an earlier response than that at peak v_2, and vice versa.

Table S1. Final results of multiplication on the signs of each cross-peak in the synchronous and asynchronous spectra of $PMEO_2MA$-*b*-$P[P_{4,4,4,4}][SS]$ from 20 to 40 ^{o}C.

1031	+	+	-	+	+	-	+	+	-	+	
1041	+	-	-	-	-	-	-	-	-		
1716	+	+	-	+	+	-	+	+			
1729	+	-	-	-	-	-	-				
2871	+	+	-	+	+	-					
2881	+	+	-	+	+						
2898	+	-	-	-							
2927	+	+	-								
2939	+	+									
2956	+										
2971											
	2971	**2956**	**2939**	**2927**	**2898**	**2881**	**2871**	**1729**	**1716**	**1041**	**1031**

Table S2. Final results of multiplication on the signs of each cross-peak in the synchronous and asynchronous spectra of PMEO$_2$MA-*b*-P[P$_{4,4,4,4}$][SS] from 40 to 55 ^{o}C.

	2973	2958	2940	2929	2898	2883	2869	1729	1710	1039	1031
1031	+	+	+	+	+	+	+	+	+	+	
1039	-	-	+	-	-	-	-	-	+		
1710	-	-	+	-	-	-	-	-			
1729	+	-	+	-	-	+	-				
2869	+	+	+	-	+	+					
2883	-	-	+	-	-						
2898	+	-	+	-							
2929	+	+	+								
2940	-	-									
2958	+										
2973											

REFERENCES

1. M. Thomas and H. H. Richardson, *Vib. Spectrosc.*, 2000, **24**, 137-146.
2. S. Morita, H. Shinzawa, I. Noda and Y. Ozaki, *Appl. Spectrosc.*, 2006, **60**, 398-406.
3. Y. Kohno and H. Ohno, *Aust. J. Chem.*, 2012, **65**, 91-94.