Supporting Information for

Influence of PIL Segment on Solution Properties of Poly(N-isopropylacrylamide)-b-poly(ionic liquid) Copolymer: Micelles, Thermal Phase Behavior and Microdynamics

Zhangwei Wang, Hengjie Lai and Peiyi Wu*

The State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People’s Republic of China

*corresponding author, email: peiyiwu@fudan.edu.cn
A. Synthesis of 1-Butyl-3-vinylimidazolium Bromide (BVImBr)

BVImBr was synthesized by the reaction of 1-vinylimidazole with corresponding alkyl bromides. In a typical experiment, 6.90 mL of 1-bromobutane (8.80 g, 0.0642 mol) was added dropwise to 4.81 mL of 1-vinylimidazole (5.00 g, 0.0531 mol) at 0 °C. The reaction mixture was kept for stirring and stopped after 24 h. The resultant yellow viscous oil was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h before use.¹H NMR (DMSO-d₆): δ 9.6 (s, 1H, -N-CH-N-), 7.9 (s, 1H, -N-CHCH-N-), 7.6 (s, 1H, -N-CHCH₂-N-), 7.4 (dd, 1H, CH₂=CH-N-), 6.0 (dd, 1H, CH₂=CH-N-), 5.4 (dd, 1H, CH₂=CH-N-), 4.2 (t, 2H, -N-CH₂-CH₂-), 1.3 (m, 2H, -CH₂-CH₂-CH₂), 1.8 (m, 2H, -CH₂-CH₂-CH₃), 0.9 ppm (t, 3H, -CH₃).

B. ¹H-NMR Spectra of PNIPAM Macro-CTA and Poly(NIPAM-b-BVImBr)

In the spectrum of PNIPAM macro-CTA (Fig. S1a), the resonances of protons in the phenyl group and –NH–CH– occur at δ=7.1–7.6 and 3.6–3.9 ppm, respectively. And ¹H-NMR spectra of Poly(NIPAM-b-BVImBr) is showed in Fig. S1b.
Fig. S1 $^1$H-NMR spectra of (a) PNIPAM macro-CTA (DMSO-$d_6$) and (b) poly(NIPAM-$b$-BVImBr) (CDCl$_3$).

**C. Rules of Perturbation Correlation Moving Window (PCMW)**

Two types of spectra (synchronous and asynchronous) can be generated by PCMW. The rules of PCMW are as follows: with the increment of perturbation, positive synchronous correlation stands for the increase of spectral intensities, while negative one for the decrease; positive asynchronous correlation corresponds to a convex spectral intensity variation while negative one to a concave variation.

**D. Rules of Two-Dimensional Correlation Analysis (2Dcos)**

Two types of correlation maps including synchronous and asynchronous spectra are obtained from a series of dynamic spectra, which are characterized by two independent “wavenumber” axes ($v_1$, $v_2$) and a correlation intensity axis. The correlation intensities in the synchronous and asynchronous maps reflect the relative degree of in-phase and out-of phase response, respectively.

On the 2D synchronous maps, peaks are symmetric with respect to the diagonal line in the correlation map. Peaks appearing along the diagonal are called “autoparks”, which are always positive, indicating that the peak at the same wavenumber changes greatly under the external perturbation. The Off-diagonal
peaks (Ψ(ν1, ν2)) are cross peaks, which may be positive or negative. The positive cross-peaks (Ψ(ν1, ν2)) demonstrate that both peaks ν1 and ν2 change in the same direction (both increase or decrease) under the perturbation, whereas negative cross-peaks infer that the intensities of peaks ν1 and ν2 change in opposite directions (one increases while the other one decreases).

In 2D asynchronous spectra, there is no autopeak but only off-diagonal cross-peaks, which can be either positive or negative. According to Noda’s rule, if cross-peak (ν1, ν2, and assume ν1>ν2) in the synchronous and asynchronous maps has the same sign (both positive or negative), the change of peak ν1 may occur prior to that of ν2, and vice versa. Hence, combined with synchronous and asynchronous spectra, some useful information about the temporal sequence of events can be obtained.