Electronic Supplementary Material (ESI) for Soft Matter

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

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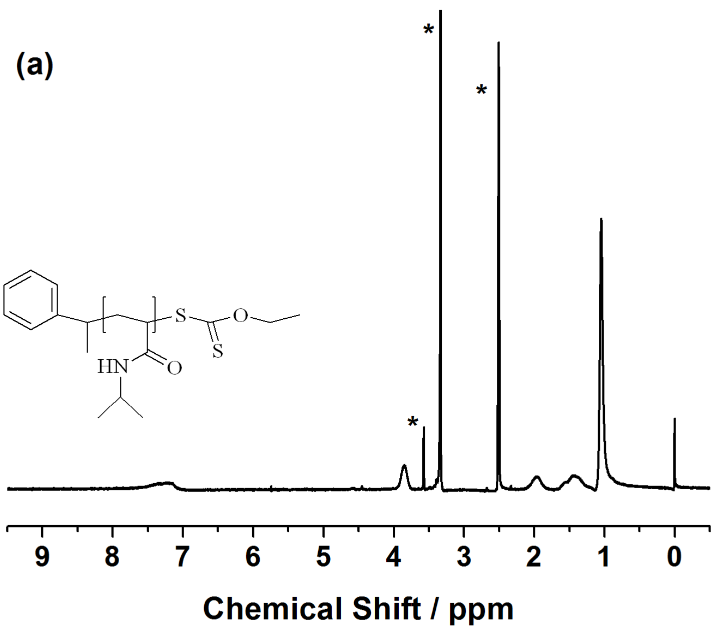
A. Synthesis of 1-Butyl-3-vinylimidazolium Bromide (BVImBr)

BVImBr was synthesized by the reaction of 1-vinylimidazole with correspondingalkyl bromides. In a typical experiment, 6.90 mL of 1-bromobutane (8.80 g, 0.0642 mol) was added dropwiseto 4.81 mL of 1-vinylimidazole (5.00 g, 0.0531mol) at 0 °C. The reaction mixture was kept for stirring and stopped after 24h. 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.^{1}H NMR (DMSO-d_6):δ 9.6 (s, 1H, -N-C*H*-N-), 7.9(s, 1H,-N-C*H*CH-N-), 7.6 (s, 1H,-N-CHC*H*-N-), 7.4 (dd,1H, CH_2=C*H*-N-), 6.0 (dd 1H,CH_2=CH-N-), 5.4 (dd, 1H, CH_2=CH-N-), 4.2 (t, 2H, -N-CH_2-CH_2-), 1.3 (m, 2H, -CH_2-CH_2-CH_2), 1.8 (m, 2H, -CH_2-CH_2-CH_3), 0.9 ppm (t, 3H, -CH_3).

B.^{1}H-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 ^{1}H-NMR spectra of Poly(NIPAM-b-BVImBr) is showed in Fig. S1b.



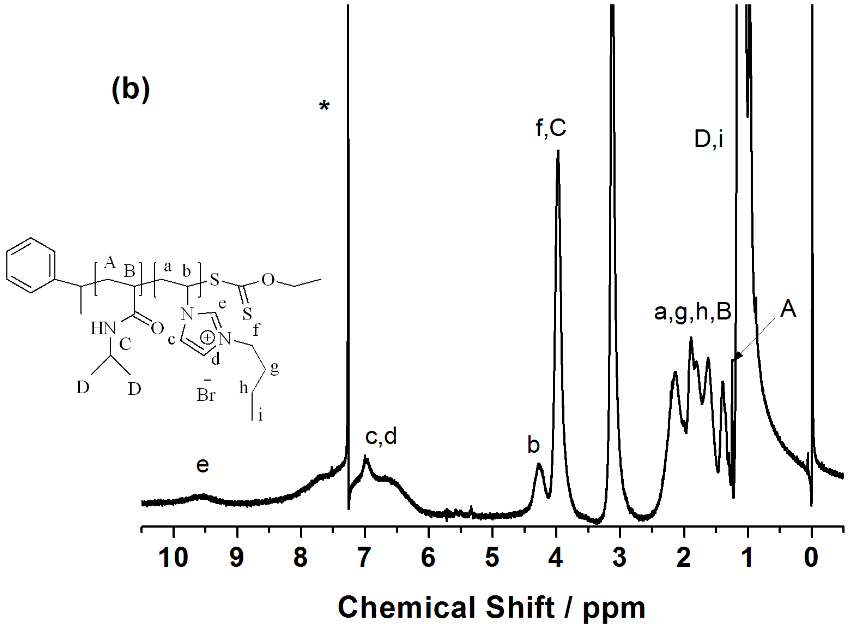


Fig. S1 [1]H-NMR spectra of (a) PNIPAM macro-CTA (DMSO-d_6) and (b) poly(NIPAM-*b*-BVImBr) ($CDCl_3$).

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 "autopeaks", which are always positive, indicating that the peak at the same wavenumber changes greatly under theexternal perturbation. The Off-diagonal peaks ($\Phi(v_1, v_2)$) are cross peaks, which may be positive or negative. The positive cross-peaks ($\Phi(v_1, v_2)$) demonstrate that both peaks $v_1$and v_2 change in the same direction (both increase or decrease) under the perturbation, whereas negative cross-peaks infer that the intensities of peaks v_1 and v_2 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 (v_1, v_2, and assume $v_1 > v_2$) in the synchronous and asynchronous maps has the same sign (both positiveor negative), the change of peak v_1 may occur prior to that of v_2, and vice versa. Hence, combined with synchronous and asynchronous spectra, some useful information about the temporal sequence of events can be obtained.