Supporting Information for

# The role a unique spatial structure plays in the volume phase transition behavior of poly(N-isopropylacrylamide)-based interpenetrating polymer network microgel including a thermosensitive poly(ionic liquid)

*Lan Ma[ab] and Peiyi Wu[ab]**

[a]*Key Laboratory of Science and Technology of Eco-Textiles, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China. E-mail: wupeiyi@dhu.edu.cn*

[b]*The State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China. E-mail: peiyiwu@fudan.edu.cn*

**$^1$H NMR measurements**

In order to keep a well comparability for the PNIPAM/P[$P_{4,4,4,6}$][MC3S] IPN and polymer mixture samples, linear PNIPAM and linear P[$P_{4,4,4,6}$][MC3S] were mixed based on the component proportion of IPN sample with excess PIL moiety. The integral area of different characteristic peaks in IPN: δ = 4.32-4.00 (t, 3.02H, $H_d$), 1.23-1.01 (d, 5.89H, $H_m$); For polymer mixture: δ = 4.3-3.8 (t, 2.83H, $H_d$), 1.15-0.94 (d, 6.03H, $H_m$). The integral area of $H_l$ was normalized.

In this part, we chose $H_m$ in PNIPAM and $H_d$ in P[$P_{4,4,4,6}$][MC3S] to calculate the

IPN composition. According to the integrations of peak area, in the PNIPAM/ P[$P_{4,4,4,6}$][MC3S] IPN solution, the $H_m/H_d$ ratio is 2:1, indicating the molar ratio of NIPAM/[$P_{4,4,4,6}$][MC3S] repeat units is 2:3. Given the molar weight ratio of NIPAM/[$P_{4,4,4,6}$][MC3S] repeat units is 113:494, it can be inferred that the actual weight ratio of NIPAM/[$P_{4,4,4,6}$][MC3S] repeat units in IPN microgels is 1:6.6, which is also the weight ratio of PNIPAM and P[$P_{4,4,4,6}$][MC3S] moieties in IPN solution. According to this weight ratio, PNIPAM and P[$P_{4,4,4,6}$][MC3S] homopolymers synthesized before were mixed. As the Figure S1 shows, in the PNIPAM/P[$P_{4,4,4,6}$][MC3S] polymer mixture solution, $H_m/H_d$ ratio is 2.13:1, which is close to that of IPN solution. This polymer mixture was used as a comparison to investigate the volume phase transition mechanism of IPN microgels in FTIR section. Moreover, the relaxation delay is 6 s.

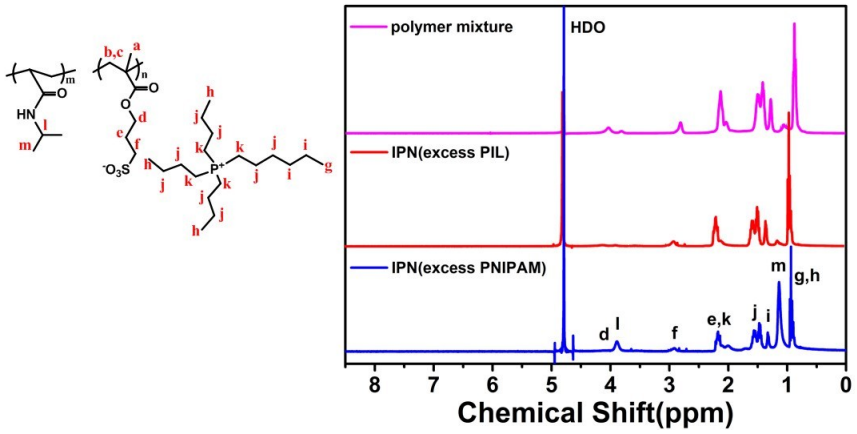


**Figure S1.** $^1$H NMR spectra of PNIPAM/P[$P_{4,4,4,6}$][MC3S] IPN with different composition ratios and PNIPAM/P[$P_{4,4,4,6}$][MC3S] polymer mixture in $D_2O$.

**Temperature-variable FTIR measurements**

In this article, All the temperature-dependent FTIR spectra were recorded on a Nicolet Nexus 6700 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The mirror velocity is 0.6329 cm·s$^{-1}$ and the wavenumber range is 4000-500 cm$^{-1}$. The FTIR measurements of all sample solutions were conducted in transmission geometry.

In order to make it easy for sample to be detected and get a premium IR spectrum, a small piece of poly(tetrafluoroethylene) (PTFE) sealing tape was cut and placed on the edge of ZnS tablet. Then, a drop of sample solution (10 μL) with a pipette was put

on the center of tablet and covered with the other ZnS tablet rapidly to keep the droplet away from air contact. Finally, the ZnS tablets were sealed with sealing tapes as quickly as possible. By adding PTFE sealing tapes with same size, all sample solutions exhibited a wedge shape in the ZnS tablets which ensured the unified and proper thickness of the samples.

The cell holder used was commercially available. After placing the sample in the cell holder, the cell holder connected with a thermocouple thermometer which made the ZnS tablets directly in touch with thermocouple. Thus, the thermocouple thermometer displayed the real temperature value of our sample. Meanwhile, the cell holder was linked with a temperature controller which attached to the computer. It is noteworthy that the temperature readings that temperature controller showed were different from that thermocouple thermometer showed and we only focused on the readings on the latter. By applying the temperature program of software OMNIC, specifically, setting the starting temperature, ending temperature and ramp time, could the automatic heating process be accomplished.

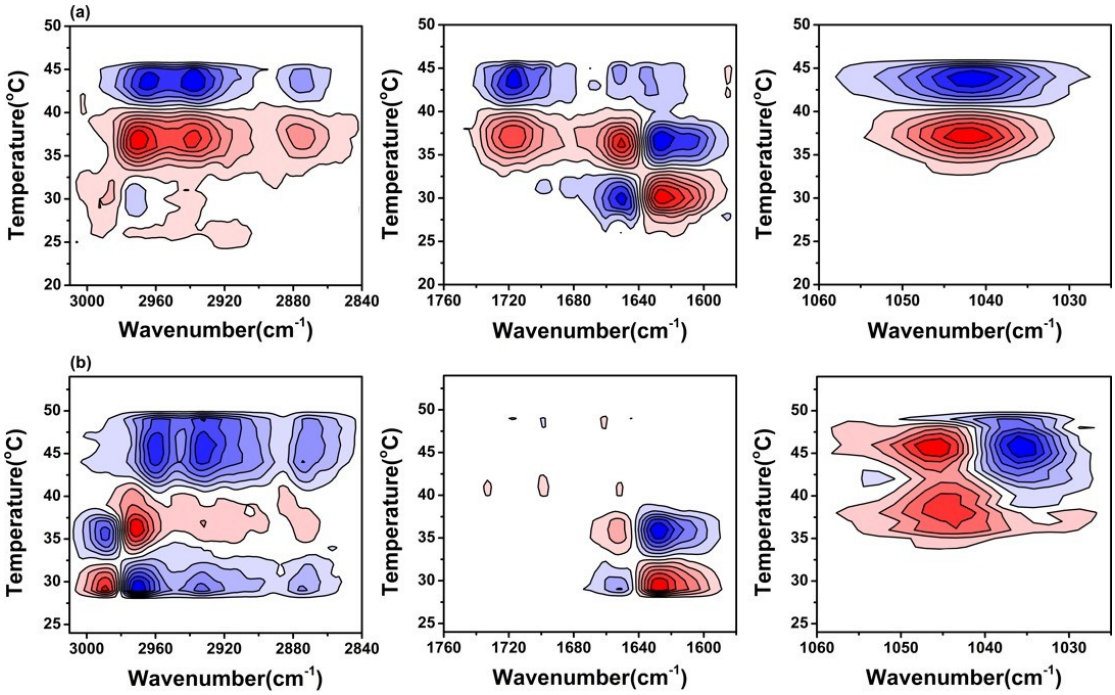


**Figure S2.** PCMW asynchronous spectra of (a) PNIPAM/P[$P_{4,4,4,6}$][MC3S] IPN microgels and (b) polymer mixture in $D_2O$ (20% (w/v)).

**Table S1.** Final results of multiplication on the signs of each cross-peak in the synchronous and asynchronous spectra of (a) PNIPAM/P[$P_{4,4,4,6}$][MC3S] IPN microgels from 20 to 50 $^{o}$C and (b) PNIPAM/P[$P_{4,4,4,6}$][MC3S] polymer mixture from 24 to 54 $^{o}$C.

**(a)**

| | 2985 | 2978 | 2958 | 2943 | 2932 | 2884 | 2874 | 1729 | 1716 | 1649 | 1626 | 1618 | 1601 | 1047 | 1040 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1040 | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| 1047 | + | + | - | - | - | - | - | - | - | + | + | - | + | | |
| 1601 | + | - | - | - | - | - | - | - | + | + | - | - | | | |
| 1618 | + | + | - | - | - | - | - | - | + | + | + | | | | |
| 1626 | + | - | - | - | - | - | - | - | - | + | | | | | |
| 1649 | - | - | - | - | - | - | - | - | - | | | | | | |
| 1716 | + | - | - | - | - | - | - | - | | | | | | | |
| 1729 | + | + | - | + | - | + | - | | | | | | | | |
| 2874 | + | + | + | + | + | + | | | | | | | | | |
| 2884 | + | + | - | + | - | | | | | | | | | | |
| 2932 | + | + | + | + | | | | | | | | | | | |
| 2943 | + | - | - | | | | | | | | | | | | |
| 2958 | + | + | | | | | | | | | | | | | |
| 2978 | + | | | | | | | | | | | | | | |
| 2985 | | | | | | | | | | | | | | | |

**(b)**

| | 2987 | 2974 | 2958 | 2943 | 2930 | 2884 | 2863 | 1735 | 1718 | 1649 | 1626 | 1614 | 1047 | 1042 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1042 | + | - | - | + | - | + | + | + | + | + | + | + | + | + |
| 1047 | + | - | - | + | - | - | - | + | - | + | + | + | | |
| 1614 | - | - | - | - | - | - | - | - | - | - | + | | | |
| 1626 | - | - | - | - | - | - | - | - | - | - | | | | |
| 1649 | + | - | - | - | - | - | - | - | - | | | | | |
| 1718 | + | - | - | + | - | + | - | + | | | | | | |
| 1735 | + | - | - | - | - | - | - | | | | | | | |
| 2863 | + | - | - | + | - | + | | | | | | | | |
| 2884 | + | - | - | + | - | | | | | | | | | |
| 2930 | + | + | - | + | | | | | | | | | | |
| 2943 | + | - | - | | | | | | | | | | | |
| 2958 | + | + | | | | | | | | | | | | |
| 2974 | + | | | | | | | | | | | | | |
| 2987 | | | | | | | | | | | | | | |