Electronic Supplementary Material (ESI) for Soft Matter

Supporting information for

Synthesis and unusual volume phase transition behaviorof poly(*N*-isopropylacrylamide)/poly(2-hydroxyethyl methacrylate) interpenetrating polymer network microgel

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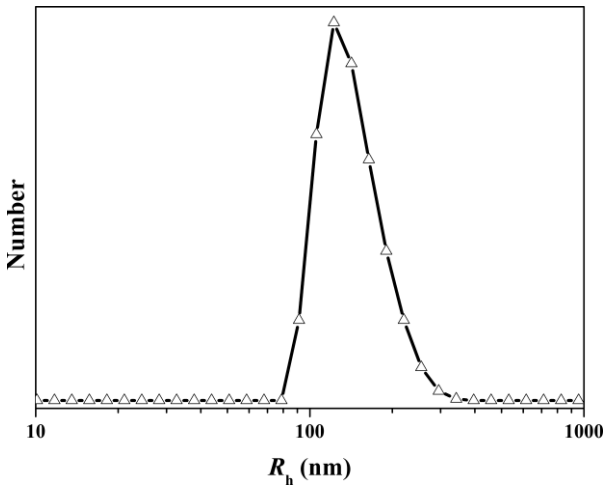

Fig.S1 Number distribution of hydrodynamic radius of IPN microgels at 25 °C. The polymer concentration of the IPN microgel dispersions was 5.0×10^{-6}g/mL with pH 7.

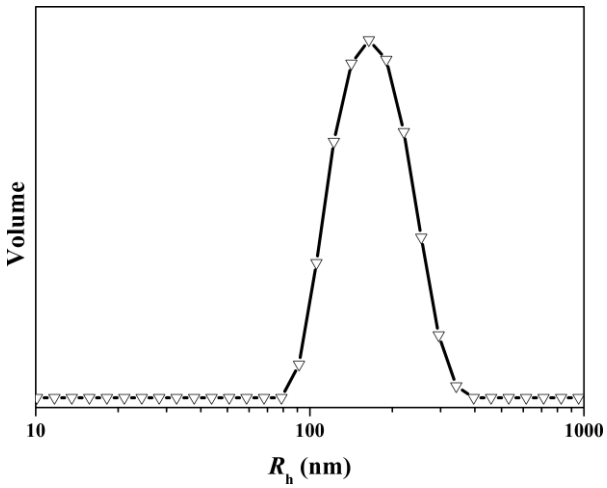

Fig.S2 Volume distribution of hydrodynamic radius of IPN microgels at 25 °C. The polymer concentration of the IPN microgel dispersions was 5.0×10^{-6}g/mL with pH 7.

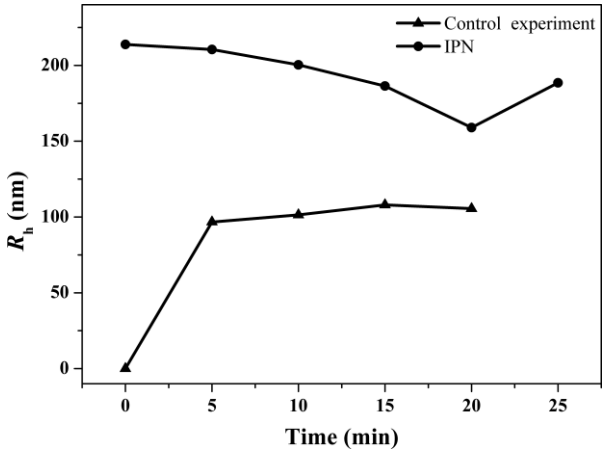

Fig.S3 Time-dependent hydrodynamic radius (R_h) of the particles during the control experiment and IPN microgel formation at 23 °C

Control experiment details: 0.05 g of MBAA and 0.415 g of HEMA were added into a three-neck flask. Distilled water was added to make the final solution volume into 35ml. The solution was kept at 4 °C for 2 days. The solution was bubbled for 1 h with nitrogen gas before further operation. The initiator (0.024 g of KPS) and accelerator (0.02 g of TEMED) were separately dissolved in water and added rapidly to the solution, making the final solution volume into 37 mL. The reaction lasted for 25 min under nitrogen atmosphere, and temperature was well regulated at 23 °C with a water bath. To gather reaction kinetic information, 5mL aliquots of solution were taken from the reaction container at different time after the reaction was started. All aliquots were dialyzed (MWCO 14000) for 1 week for future DLS analysis.

Discussion of the control experiment: As shown in Fig. S3, the bottom line is the time-dependent radius change of homo-PHEMA in the control experiment. After KPS

and TEMED were added to the system, homo-PHEMA microgel formed in less than 5 minutes. From 5 to 20 min, the size of homo-PHEMA microgel stayed at an almost constant value, while the amount of homo-PHEMA may increase with time because there were still many monomers in the solution. The value of $R_h$at 25 min is not given because obvious precipitation can be observed right after 20 min in the reaction process. Compared with the formation process of IPN microgel, the process of the control experiment and the IPN formation process are totally different. The value of R_h decreases slowly during the first 20min but increases quickly in the following 10min in the IPN formation process. Detailed comparison to explain the difference in depth is in the following parts. Homo-PHEMA formed much earlier in the control experiment (5 min) than that in the IPN formation process (25 min), this is because the concentration of free HEMA in the control experiment is much higher than that in the IPN formation process. Though same amount of HEMA monomer was added to the control experiment and IPN system, the distribution of HEMA monomer differs greatly in these two systems. In the control experiment, free HEMA is uniformly distributed in the whole volume. However, in the IPN system, because HEMA can form hydrogen bonds with PNIPAM microgel, the concentration of HEMA in

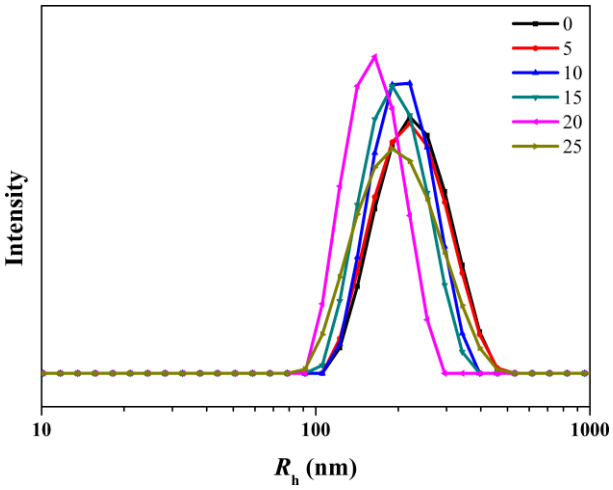

Fig.S4 Intensity distribution of hydrodynamic radius of IPN microgels taken out at different times at 23°C. The polymer concentration of the IPN microgel dispersions was 5.0×10^{-6}g/mL with pH 7.

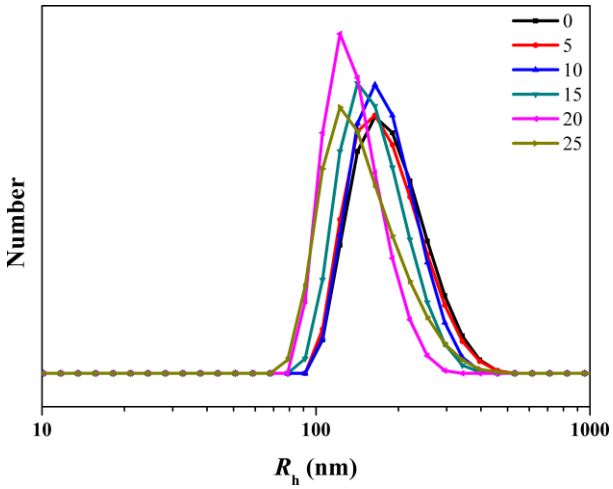

Fig.S5 Number distribution of hydrodynamic radius of IPN microgels taken out at different times at 23℃. The polymer concentration of the IPN microgel dispersions was 5.0×10^{-6}g/mL with pH 7.

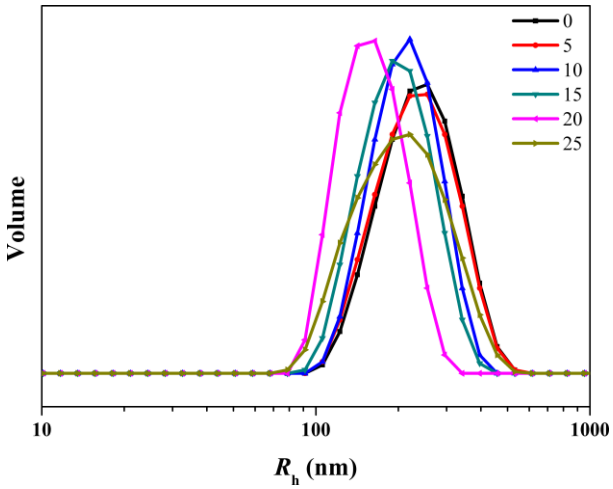

Fig.S6 Volume distribution of hydrodynamic radius of IPN microgels taken out at different times at 23℃. The polymer concentration of the IPN microgel dispersions was 5.0×10^{-6}g/mL with pH 7.

PNIPAM microgel is much higher than that in the control experiment, while the concentration of free HEMA in water is much lower than that in the control experiment. HEMA monomer is non-uniformly distributed in the IPN system. As is known, at the same reaction temperature, the reaction rate depends primarily on the concentration of the monomer. In the control experiment, polymerization occurs right after the addition of KPS and TEMED because HEMA is uniformly distributed in the whole volume. In the IPN system, the concentration of HEMA inside the microgel is much higher than that outside the microgel. Polymerization occurs inside the PNIPAM microgel first and homo-PHEMA formed after 20 min. obvious precipitation could be observed earlier in the control experiment (25 min) than that in the IPN system (30 min), which can also be attributed to the difference of the

concentration of free HEMA monomer. Precipitation is result of the aggregation of large amount of homo-PHEMA microgel. The concentration of free HEMA monomer in the IPN system is much lower than that in the control experiment, so the formation and aggregation of homo-PHEMA microgel is much later.

The intensity, numberandvolume distribution of all the samples taken out during the IPN formation process at 23 ^{o}C are shown in Fig. S4, S5 and S6.The uniform distributionsare apparent evidence for the majority of IPN microgel and negligible of homo-PHEMA.

Considering the non-uniform distribution of HEMA monomer in the IPN system, it is reasonable that polymerization occurs mainly inside the PNIPAM microgel firstly, while the amount of homo-PHEMA can be negligible because the concentration of free HEMA monomer is fairly low.

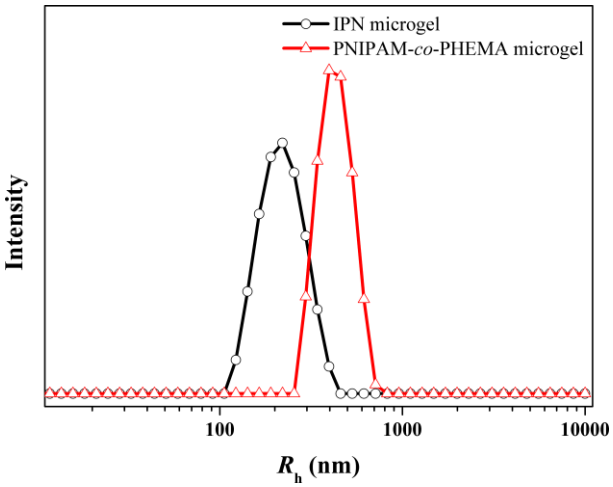

Fig.S7 Distribution of hydrodynamic radius of PNIPAM-co-PHEMA and IPNmicrogels at 25^{o}C. The polymer concentration of the PNIPAM-co-PHEMA andIPN microgel dispersions were the same as 5.0×10^{-6}g/mL withpH 7.

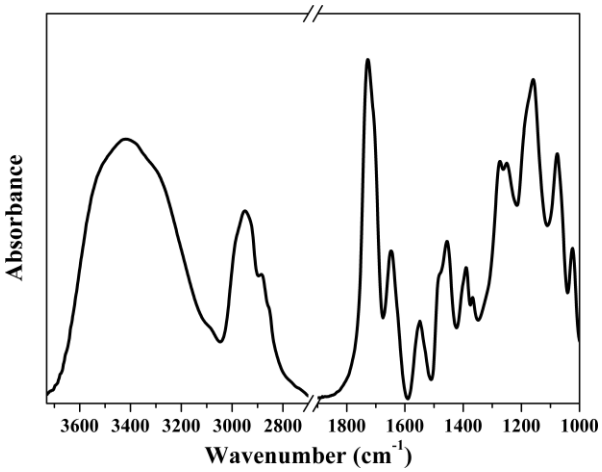

Fig.S8FT-IR spectraof PNIPAM-co-PHEMAmicrogel after drying.

Comparison study of thermal response between PNIPAM-*co*-HEMA and PNIPAM/PHEMA IPN microgels.The experimental details are as follows: 0.233 g of *N*-isopropylacrylamide, 1.917g of 2-hydroxyethyl methacrylate, 0.033 g of *N*,*N*'-methylenebisacrylamide, and 0.075 g of sodium dodecyl sulfate (SDS) were dissolved in 120 g of distilled water. The solution was put into a three-neck flask equipped with a magnetic stirrer and a nitrogen feed. The solution was purged with nitrogen for 1h before being placed into a 70 ^{o}C hot bath. Potassium persulfate (0.083 g), which was dissolved in 10 mL of water, was then added to initiate the emulsion polymerization. The reaction lasted for 4 h under nitrogen atmosphere with the reaction temperature being kept at 70 ^{o}C. All PNIPAM particles were purified via dialysis (MWCO 14000) against frequent changes of stirring water for 1 week at room temperature.

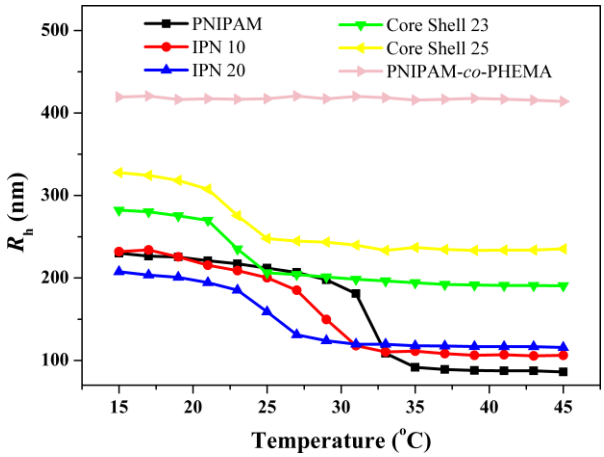

Fig. S9 Temperature-dependent hydrodynamic radius (R_h) of different particles.

DLS was performed to first estimate the size and distribution of the PNIPAM-*co*-PHEMA microgel, as shown in Fig. S7. Both the PNIPAM-*co*-PHEMA and IPN microgel are uniformly distributed. As shown in Fig. S8, the absorption peak at 1728 cm^{-1} is assigned to the carbonyl band of PHEMA and the absorption peak at 1648 cm^{-1} is the characteristic peak of the Amide I group of PNIPAM, which indicates the successful copolymerization of PNIPAM and PHEMA in the microgel.

A comparison study of thermal response between PNIPAM-PHEMA IPN microgel and PNIPAM-*co*-PHEMA microgel was also carried out. As shown in Fig. S9,

compared to other microgels, there was no significant change of the PNIPAM-*co*-PHEMA microgel size. Because the molar percentage of PNIPAM was only 12%, the majority of PNIPAM-*co*-PHEMA microgel was PHEMA. PHEMA possesses an "imperfect" ability for phase transition, because the phase transition only occurs when the molecular weight of PHEMA is very low or other hydrophilic monomer is incorporated in PHEMA and the phase transition is not obvious compared to PNIPAM,[1, 2] so it is reasonable that the microgel would not show response to temperature. Though the feed ratio of NIPAM: HEMA is the same in PNIPAM-PHEMA IPN microgel and PNIPAM-*co*-PHEMA microgel, the detailed process is totally different, which could account for the different temperature-responsive property. HEMA and NIPAM are uniformly distributed in PNIPAM-*co*-PHEMA microgel system, so the resultant microgel exhibits no response to temperature. In the IPN system, PNIPAM is first synthesized and exists as a soft ball in the system, which HEMA is non-uniformly distributed in the solution, as described before. Due to the special synthetic process of IPN microgel, as described before, the structure and the molar ratio of NIPAM: HEMA are different from those of the PNIPAM-*co*-PHEMA microgel, so it is reasonable that the thermal response between PNIPAM-*co*-HEMA and PNIPAM-PHEMA IPN microgels is totally different.