Thermo-Sensitive Ionic Microgels with pH Tunable Degradation via In-Situ Quaternization Crosslinking

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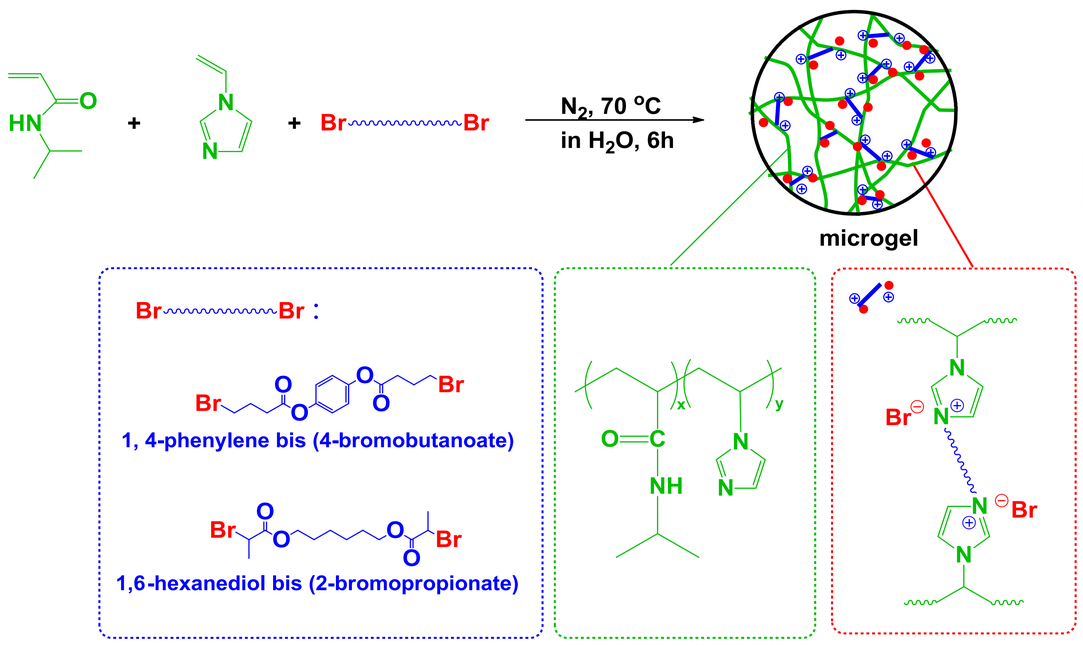
BACKGROUND

- Microgels are polymeric colloidal particles with three-dimensional cross-linked networks that are swollen in good solvents.
- Various di-functional or multi-functional monomers such as *N,N'*-methylenebisacrylamide (BIS), ethyleneglycol-dimethacrylate (EGDMA), divinylbenzene (DVB) were used as cross-linkers for the syntheses of microgels.
- The size, structure and properties of microgels could be controlled by designing the structure of cross-linkers. Here, we reported the thermo-sensitive ionic microgels with pH tunable degradation.

METHOD

Degradable thermo-sensitive ionic microgels were synthesized via surfactant-free emulsion polymerization (SFEP) of *N*-isopropylacrylamide (NIPAm) and 1-vinylimidazole (VIM) at 70 °C with degradable 1,4-phenylene-bis(4-bromobutanoate) or 1,6-hexanediol-bis(2-bromopropionate) as quaternized cross-linkers.



RESULTS AND DISCUSSION

1. Morphology of Microgels

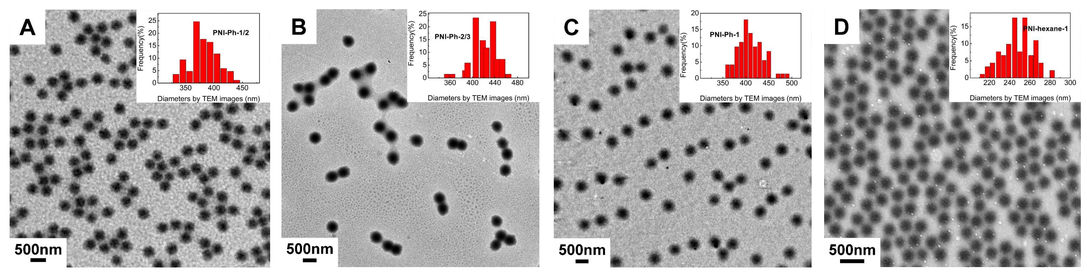


Figure 1. The representative TEM images and the corresponding size distributions of the degradable thermo-sensitive ionic microgels. (A) PNI-Ph-1/2, (B) PNI-Ph-2/3, (C) PNI-Ph-1, and (D) PNI-hexane-1.

2. Thermo-sensitive Behavior and Size Distribution of Microgels

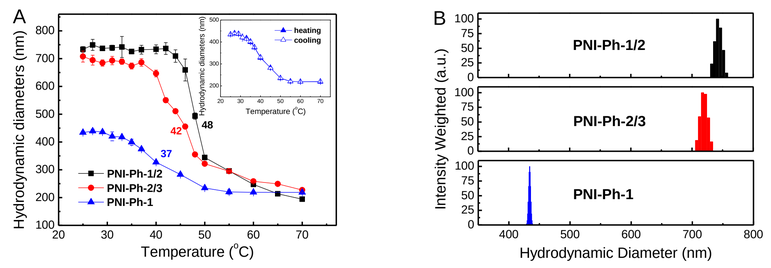


Figure 2. (A) The hydrodynamic diameters of the PNI-Ph series of microgels measured by DLS as a function of measuring temperature with different quaternization ratios. (B) The corresponding size distribution of the PNI-Ph series of microgels measured by DLS at 25 °C.

3. Degradation of Microgels

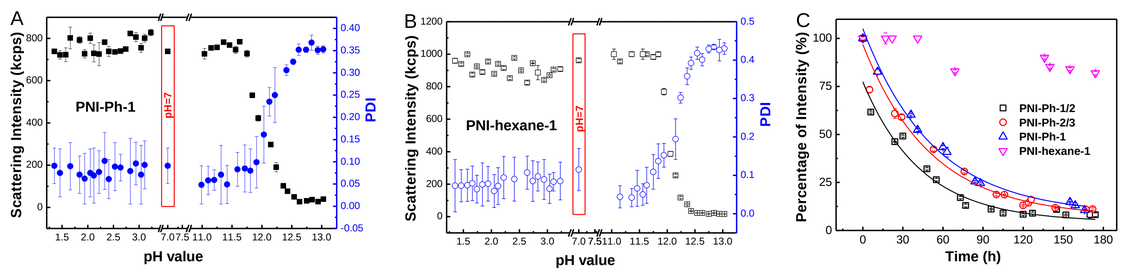


Figure 3. The degradation of PNI-Ph-1 (A) and PNI-hexane-1 (B) microgels as a function of pH value. (C) The degradation of PNI-Ph and PNI-hexane-1 microgels in neutral aqueous solution as a function of time.

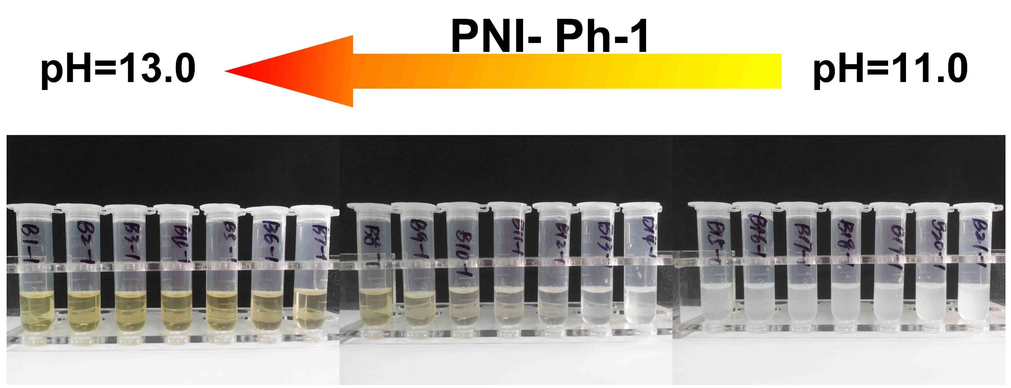


Figure 4. The photo pictures of PNI-Ph-1 microgels with solution pH value from 11.0 to 13.0.

4. Microgels as Degradable Templates for the Fabrication of Silica Nanostructures

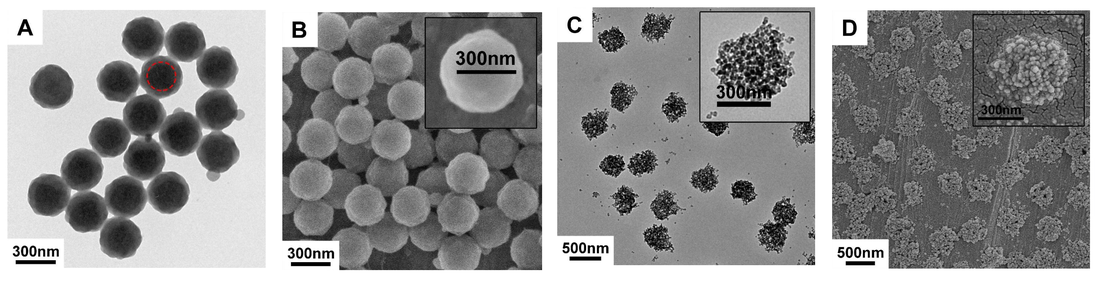


Figure 5. TEM and SEM images of SiO_2 nanoparticles prepared with PNI-Ph-1 microgels as the template at 50 °C (A, B) and 25 °C (C, D), respectively.

CONCLUSIONS

- The obtained microgels were spherical in shape with narrow size distribution and exhibited thermo-sensitive behavior and controllable degradation.
- The degradation rate of the obtained microgels could be regulated by tuning the pH value of microgel suspensions.
- Furthermore, such degradable thermo-sensitive ionic microgels could be used as templates for the fabrication of different silica nanostructures at various temperatures.

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