环境响应性离子微凝胶的制备及应用*

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研究背景

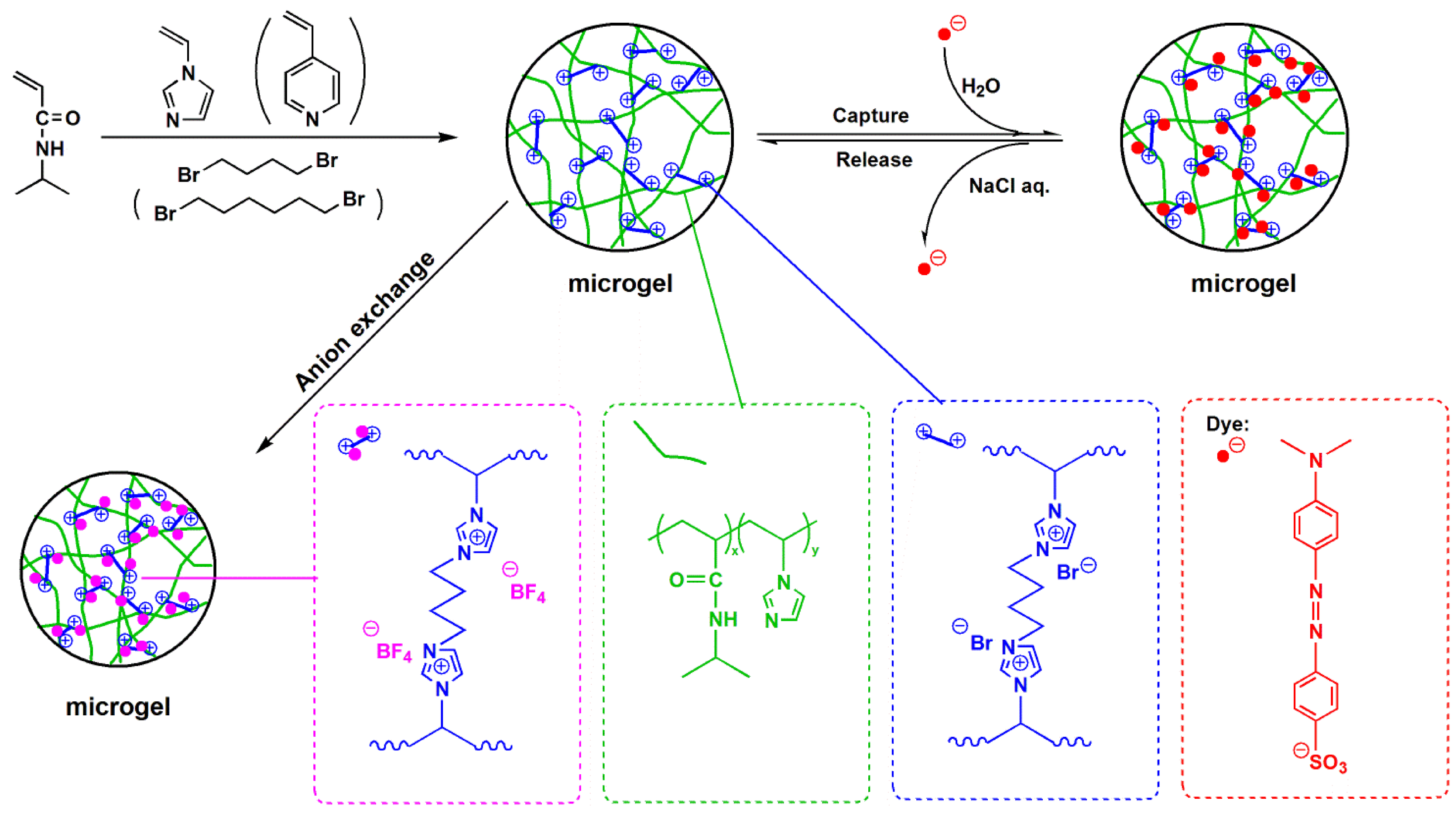
●温度响应性微水凝胶是交联的聚合物粒子，在良溶剂中溶胀而不溶解，当外界温度变化时，会表现出相应的响应行为，体现在体积的膨胀或收缩，可应用于药物控释、催化剂、化学分离、生物传感器等各领域。

●离子液体具有良好的化学和电化学稳定性、低可燃性、低蒸气压和高离子导电率，可作为聚合过程中的绿色溶剂，生物大分子的特种溶剂，引发剂或助催化剂，甚至作为功能性单体，获得聚离子液体。

●若能将聚离子液体的特点引入到微凝胶中，则可以使新型微凝胶同时拥有二者的优良特性，并通过二者的协同作用，发挥出新功能，从而扩展了微凝胶的潜在应用领域。

实验方法

- 采用无皂乳液聚合法以*N*-异丙基丙烯酰胺(NIPAm)为主单体，1-乙烯基咪唑(VIM)或4-乙烯基吡啶(4VP)为共单体，1，4-二溴丁烷或1，6-二溴己烷为交联剂，利用季铵化交联反应一锅合成温敏性离子微凝胶；
- 通过阴离子交换反应在微凝胶中引入具有不同疏水基团的反阴离子；
- 考察温敏性离子微凝胶对阴离子染料的包封和释放。



4. 阴离子交换反应

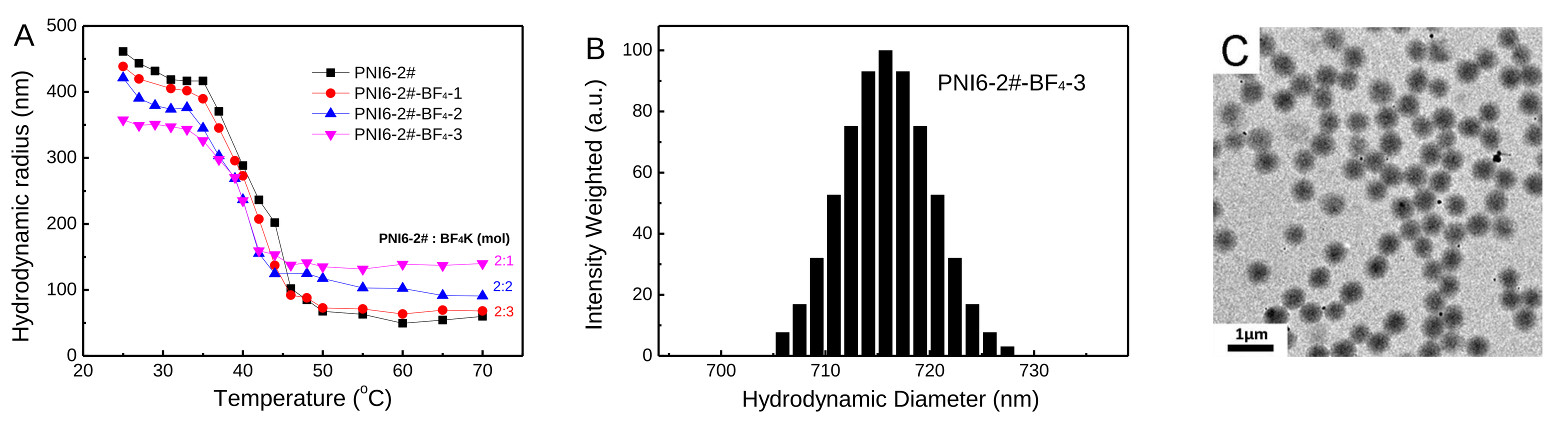


Figure 4. (A) The hydrodynamic radii of the PNI6-2# microgels measured by DLS as a function of measuring temperature before and after anionic exchange reactions with BF_4K. (B) Size distribution and (C) TEM images of the PNI6-2# microgels after anionic exchange reactions with BF_4K.

5. 染料包封与释放

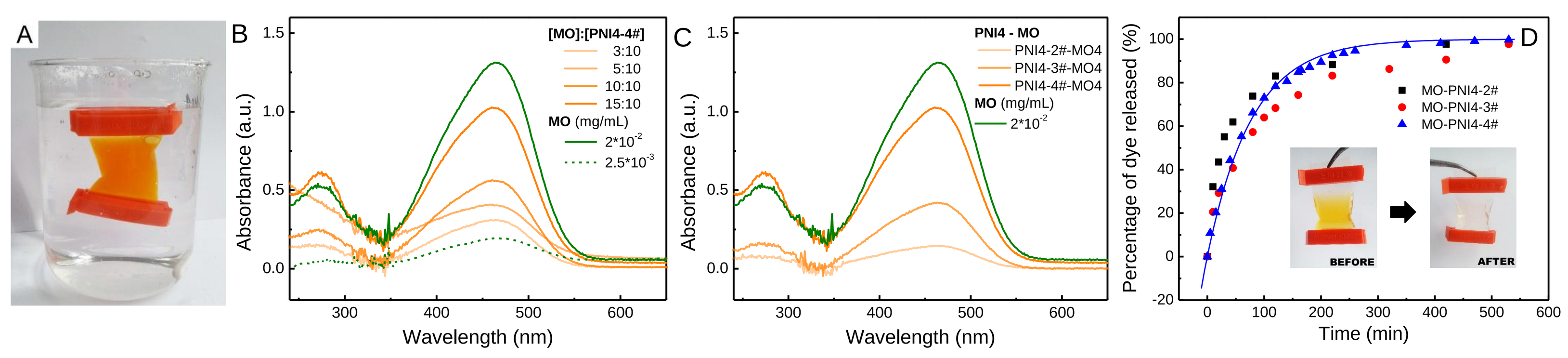


Figure 5. (A) Photo image of PNI4-4#-MO4 microgels with encapsulation of methyl orange (MO). (B) UV absorption spectra of MO-encapsulated PNI4-4# microgels with various feeding molar ratios of MO to quaternized imidazole moieties of PNI4-4#, i.e. $[MO]/[VIM^+]$ = 3/10, 5/10, 10/10, and 15/10, respectively. (C) UV absorption spectra of MO-encapsulated PNI4 microgels with fixed amounts of MO and various quaternization ratios of 1/2 (PNI4-2#), 2/3 (PNI4-3#) and 1 (PNI4-4#). (D) Release profiles of MO from the MO-encapsulated PNI4-2#-MO4, PNI4-3#-MO4 and PNI4-4#-MO4 microgels as a function of dialysis time in 0.1 M NaCl aqueous solutions.

结果与讨论

1. P(NIPAm-*co*-VIM)/1, 4-dibromobutane 微凝胶的形貌

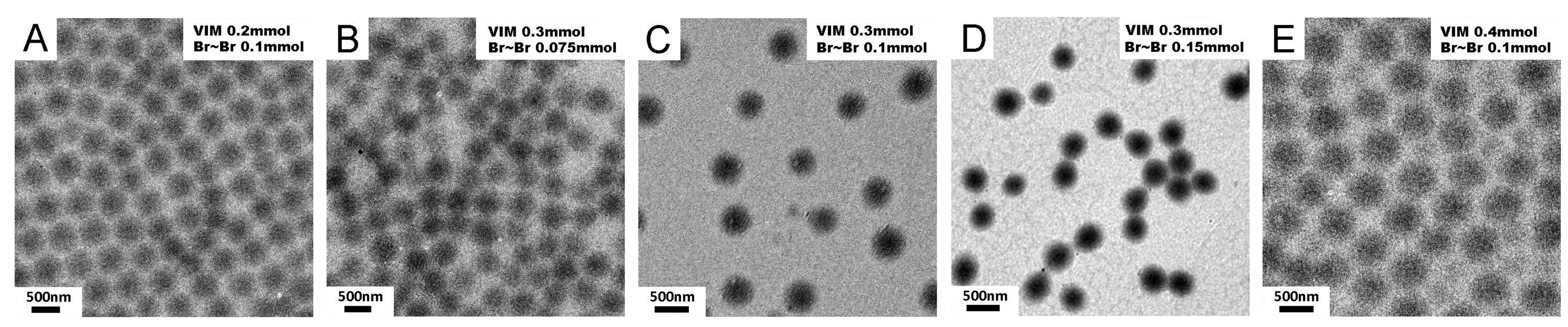


Figure 1. The representative TEM images of P(NIPAm-*co*-VIM)/1, 4-dibromobutane microgels with various amounts of VIM and quaternization ratios.

2.不同季铵化程度、共单体含量微凝胶的温敏行为

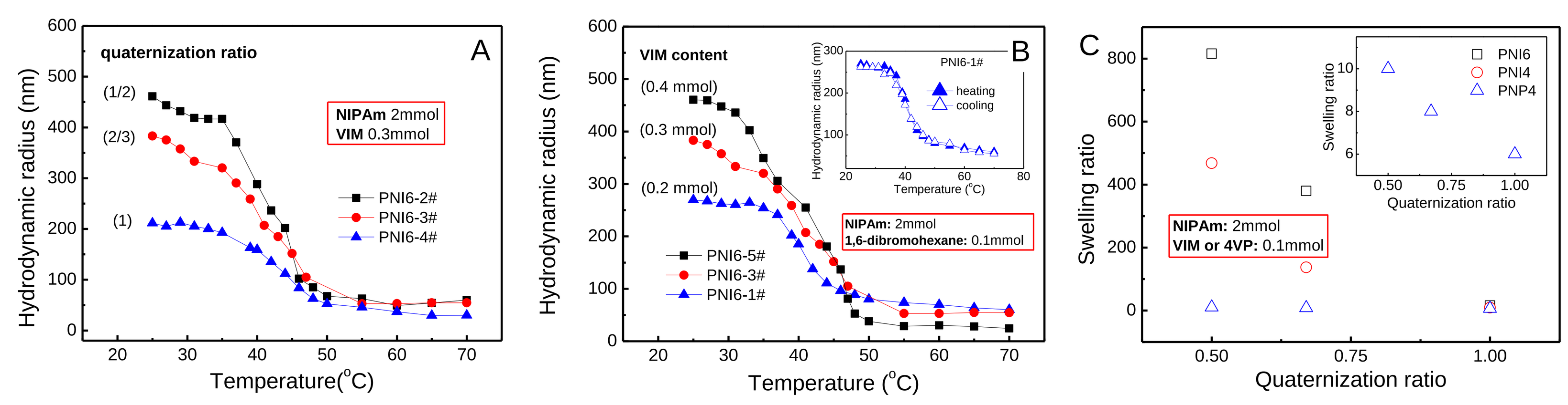


Figure 2. The hydrodynamic radii of P(NIPAm-*co*-VIM)/1, 6-dibromohexane microgels measured by DLS as a function of measuring temperature (A) with fixed amounts of VIM and various quaternization ratios. (B) with various amounts of VIM and fixed amounts of 1, 6-dibromohexane. (C) The swelling ratio of the PNI6, PNI4 and PNP4 series of microgels with fixed amounts of comonomer and various quaternization ratios. The inset of (B) was the evolution of hydrodynamic radius of PNI6-1# microgels during the heating and cooling cycles. The inset of (C) was the swelling ratio of PNP4 microgels with enlarged Y scale.

3.不同季铵化程度、共单体含量微凝胶的表面电位

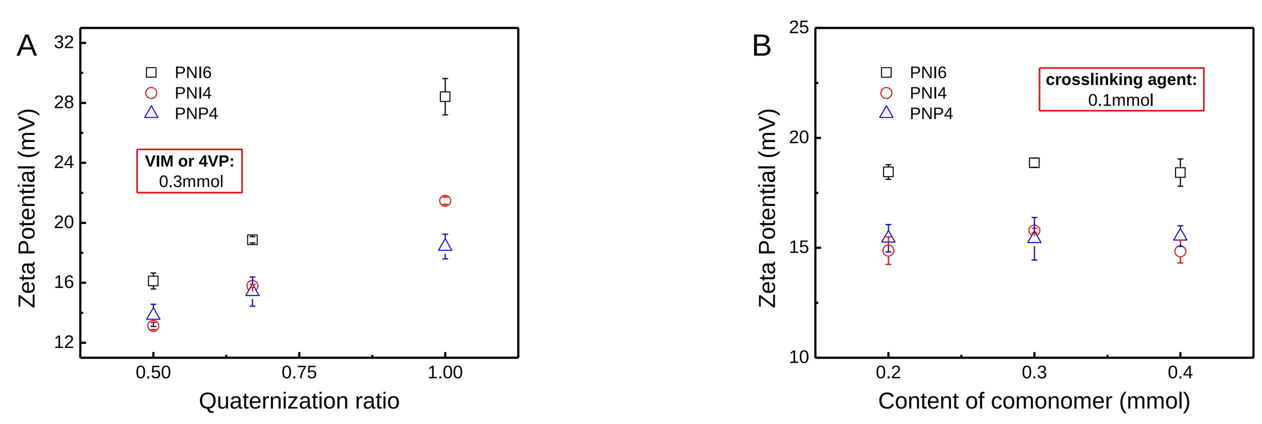


Figure 3. The Zeta potentials of the PNI6, PNI4, and PNP4 series of microgels (A) with fixed amounts of comonomer (VIM or 4VP) and various amounts of quaternized crosslinking agent (1, 6-dibromohexane or 1, 4-dibromobutane), i.e. with various quaternization ratios. (B) with fixed amounts of quaternized crosslinking agent and various amounts of comonomer. All the measurements of Zeta potential were performed at 25° C. The pH of the obtained ionic microgels was measured to be 7.04±0.07.

小结

●采用季铵化交联反应成功合成了尺寸均匀的温敏性离子微凝胶；

●通过控制季铵化程度、共单体浓度、反离子等可有效调控微凝胶的尺寸；

●实现了阴离子染料在温敏性离子微凝胶中的包封与可控释放。

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