由儿茶酚基团与自由基的反应制备微凝胶*

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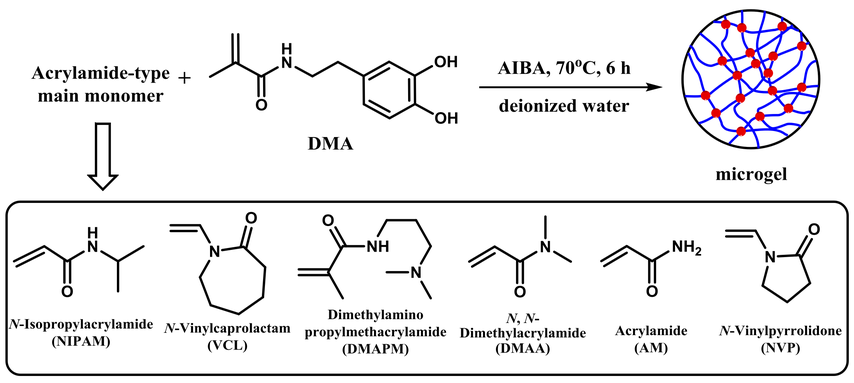
研究背景

- 无皂乳液聚合(SFEP)因其操作简单且无表面活性剂残留而被广泛用于微凝胶的制备，然而该法通常需要预聚物具备温敏性，即在水溶液中具有低临界相转变温度(LCST)；
- 儿茶酚是一种典型阻聚剂，可与自由基反应形成芳氧键；
- 若将含儿茶酚基团的共聚单体应用于SFEP法制备微凝胶，则有望大大拓宽其适用的主单体范围。

实验方法

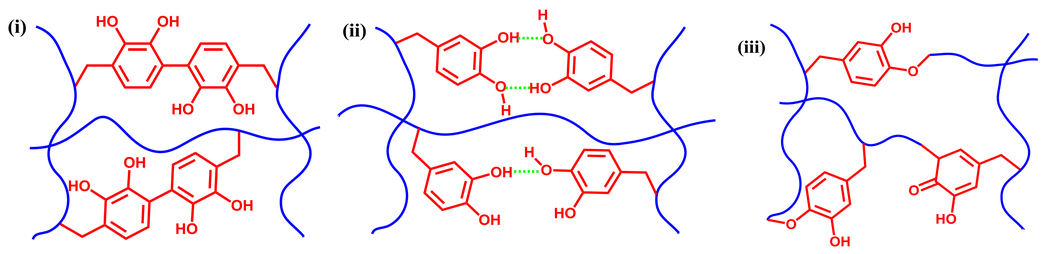
- 采用无皂乳液聚合方法(SFEP)，分别以*N*-异丙基丙烯酰胺(NIPAM)，*N*-乙烯基己内酰胺(VCL)，*N*,*N*-二甲基氨丙基甲基丙烯酰胺(DMAPM)，*N*,*N*-二甲基丙酰胺(DMAA)，丙烯酰胺(AM)， *N*-乙烯基吡咯烷酮(NVP)为主单体，多巴胺甲基甲基丙烯酰胺(DMA)为共单体，在70°C水溶液中由偶氮二异丁脒盐酸盐(AIBA)引发聚合特定时间后，一定量的DMA溶解在乙醇中加入反应体系中，反应持续 6 h。



Scheme 1. The schematic routine of microgels fabricated via SFEP at 70 ℃ in aqueous solution without addition of any other crosslinker by using acrylamide-type monomer as the scaffold monomer, and dopamine methacrylamide (DMA) bearing unprotected catechol group as the comonomer.

• DMA基微凝胶交联机理探究

• 三种交联机理假设



Scheme 2. Possible mechanisms for the formation of cross-linking network structure during the radical copolymerization of DMA and the acrylamide-type main monomer.

• 交联机理验证

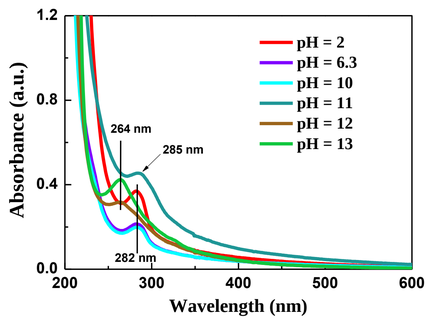


Figure 7. UV-visible spectra of Poly(NIPAM-*co*-DMA) microgel aqueous suspensions (0.15 mg/ml) with different pH values.

Figure 8. Photo of poly(NIPAM-*co*-DMA) microgel aqueous suspensions with different pH values from 2 to 13.

微凝胶在紫外-可见光吸收曲线中没有出现264nm处特征吸收峰，只在pH调至≥12时才会发生儿茶酚基团间氧化偶合，机理(i)可排除

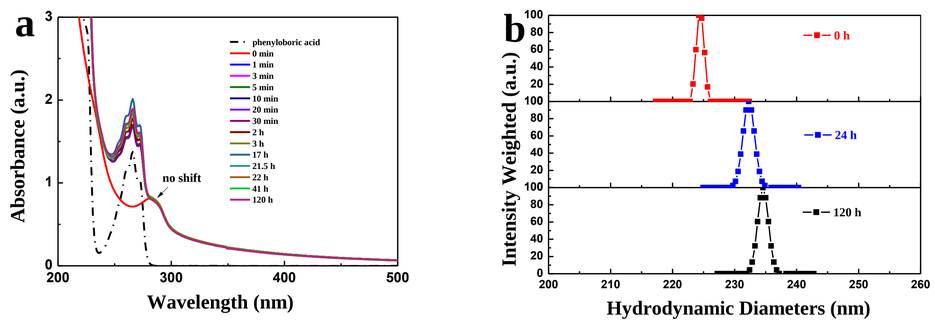


Figure 9. UV-visible spectra (a) and hydrodynamic diameter (b) of poly(NIPAM-*co*-DMA)-1/10 microgel aqueous suspension with addition of sodium borate as a function of observation times.

向微凝胶中加入硼酸钠没有引起微凝胶解交联，机理(ii)可排除，机理(iii)被认为是DMA基微凝胶交联的主要方式

结果与讨论

• DMA基微凝胶的形貌

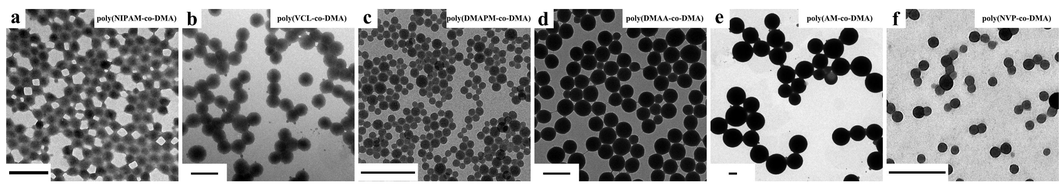


Figure 1. Representative TEM images of the obtained DMA-based microgels. The scale bar is 500 nm.

• DMA基微凝胶在水中的尺寸分布

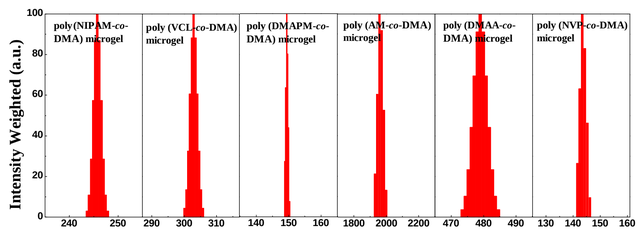


Figure 2. Particle size distributions of the obtained DMA-based microgels measured by DLS at 25 ℃.

• DMA基微凝胶的结构表征

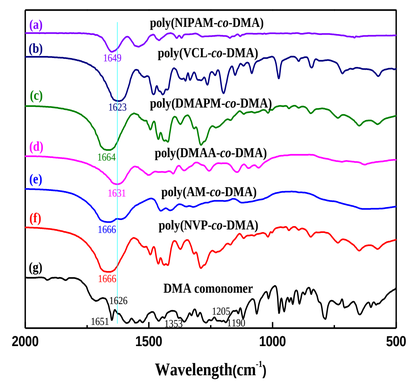


Figure 3. FT-IR spectra of the obtained DMA-based microgels and DMA comonomer.

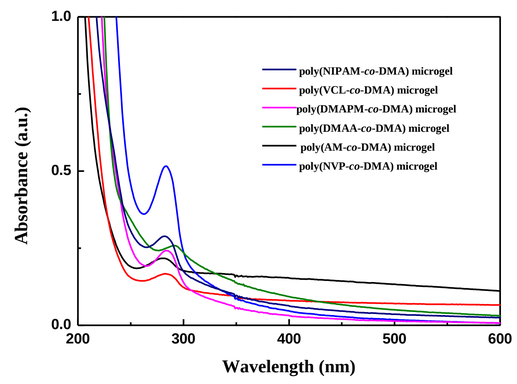


Figure 4. UV-visible spectra of the obtained microgel aqueous suspensions.

• DMA基微凝胶的性能表征

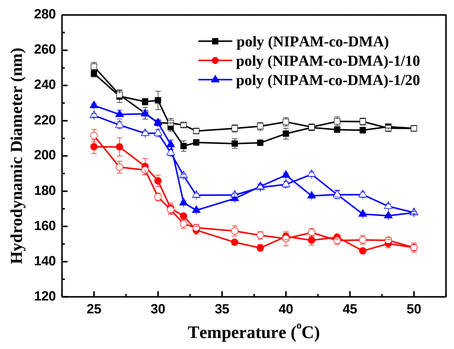


Figure 5. Hydrodynamic diameters of poly(NIPAM-*co*-DMA) series of microgels measured by DLS as a function of measuring temperature. Solid symbols: heating process, Open symbols: cooling process.

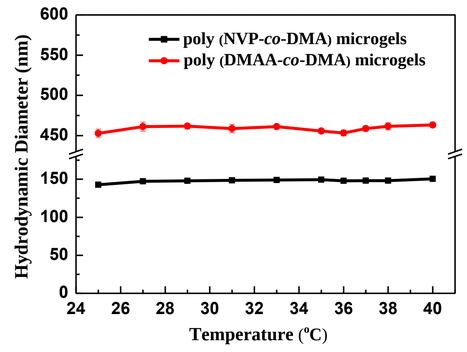


Figure 6. Hydrodynamic diameters of poly(DMAA-*co*-DMA) and poly(NVP-*co*-DMA) microgels dispersed in PBS solution measured by DLS as a function of measuring time.

小结

- 无需外加交联剂，通过SFEP方法以含有儿茶酚基团的DMA为共聚单体，在70°C水溶液中分别成功制备了六种以不同丙烯酰胺类主单体聚合物为骨架的微凝胶；
- 验证了DMA基微凝胶的交联是由儿茶酚基团捕捉增长链上自由基导致；
- 利用儿茶酚基团与自由基的反应可大大拓宽适用于SFEP方法的微凝胶骨架单体类型。

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