Polymer Bulletin 61, 27–34 (2008)
DOI 10.1007/s00289-008-0923-9

Polymer Bulletin

One-stage Preparation of PSt/PNVP Core/Shell Nanoparticles via Interfacial-initiated Microemulsion Copolymerization

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Received: 6 September 2007 / Revised version: 26 February 2008 / Accepted: 3 March 2008

Summary

Interfacial-initiated microemulsion copolymerizations of Styrene (St) and N-vinylpyrrilidone (NVP) by the redox initiation couple of cumene hydroperoxide (CHPO) and the presence of the base tetraethylenepentamine (TEPA) were carried out using Tween-80 and n-butanol as the surfactant and co-surfactant, respectively. Fourier Transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were recorded to analyze the chemical composition of latex particles. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) were used to observe the particle morphology and dynamic light scattering (DLS) to determine the particle size. The results demonstrated that interfacial-initiated microemulsion polymerization prompted the copolymerization of water-soluble NVP monomer with oil-soluble St monomer to form core-shell nanoparticles by one-stage.

Keywords

Core-shell polymers, Interfaces, Micro-emulsion polymerization, Nanoparticles, Redox initiation

Introduction

Microemulsions are multi-component transparent/translucent liquids that exhibit long term stability, have a low viscosity and are optically transparent and isotropic [1-2], which appear to be excellent media for facilitating chemical reactions. Polymerization in microemulsion is an evolved polymerization technique which allows the preparation of ultrafine polymer particles within in the size range 20nm ~ 200nm and can be used as a potential way to produce large molecular-weight polymers with narrow molecular-weight distribution [3-5]. Many applications have been found in a variety of areas, such as oil recovery, micro-reactors, controlled release of drugs and so on [6-9]. A lot of efforts have been devoted to reveal the characteristics of microemulsion polymerizations, including the kinetics, nucleation and initiation loci [10-13].

Redox initiation pairs have been used extensively in the microemulsion and normal emulsion polymerization of vinyl monomers [14-23]. Radicals can be produced rapidly compared with thermal initiators such as persulfate. Among them, some attentions have been paid on the two-component redox initiator system (one water soluble, the other oil soluble) in the emulsion copolymerization of hydrophobic and hydrophilic monomers. It was proposed that the primary radicals would be produced mainly at the oil-water interface, where the hydrophobic oxidant meets the hydrophilic reducing agent and both of the hydrophobic and hydrophilic monomers are present [24-25]. In our previous works, we took advantage of this interfacial-initiated (micro-) emulsion polymerization to synthesize different polymer particles [26-28]. There have several other pairs of such redox initiators: tert-butyl hydroperoxide with different water-soluble reducing agents [29-30], CHPO/tetraethylene pentamine [31-33], CHPO/ferrous sulfate heptahydrate [34-35]. In this paper, we described the preparation of one-stage polymerization to prepare hydrophobic PSt core/hydrophilic PNVP shell nanoparticles microspheres via an interfacial polymerization approach under mild reaction.

Experimental

Materials

N-vinyl pyrrolidone (NVP, Tokyo Kasei Kogyo) was distillated under vacuum before use. Styrene (St) was washed with NaOH (10 wt %) aqueous solution and then with distillated water until PH equaled = 7. After dried with anhydrous $MgSO_4$, St was distillated under vacuum before use. Cumene hydroperoxide (CHPO) and tetraethylenepentamine (TEPA), Polyoxyethylene (n=20) sorbitan monooleate (Tween-80) and n-butanol are analytical reagents and were used as received.

Interfacial-initiated microemulsion polymerization

The typical procedure for the fabrication of PSt/PNVP nanoparticles is as follows: CHPO (60.0 mg) and St (2.0 g) were dissolved in hexane (1 ml) and the resulted solution was emulsified in the aqueous solution of Tween-80 (4.012 g) 30ml and n-butanol (0.40 g) to form a clear or translucent microemulsion. After being heated to 35°C while being purged with nitrogen, the microemulsion was charged with the aqueous solution (5.0 ml) of NVP (2 g) and TEPA (50 mg) in batch. The reaction lasted for another 12 h to result in the composite latex of PSt/PNVP. PSt/PNVP solid particles were obtained by de-emulsification with ethanol, washing with ethanol and dried under vacuum.

Chemical composition of PSt/PNVP latex nanoparticles

In order to confirm the copolymerization of St with NVP, PSt/PNVP solid particles were extracted with water for 3 days and dried under vacuum. Their FTIR spectra were recorded on Bruker Vector-22 infrared spectrometer with KBr pellets. Also X-ray photoelectron spectroscopy (XPS) measurement of PSt/PNVP extracted solid particles was performed on a VGESCALAB MKII X-ray photoelectron spectrometer with a nonmonochromatic Al Kα radiation (1486.6 eV) under high vacuum of 10^{-11} mbar.

Morphology and size of PSt/PNVP latex nanoparticles

The morphology of PSt core/PNVP shell nanoparticles can be clearly observed under transmission electron microscopy (TEM, Hitachi Model H-800) at an accelerating voltage of 200 kV. As for the morphology observation under Field-emission Scanning Electron Microscopy (FESEM, JEOL JSM-6700) with the acceleration voltage of 10 kV, the solid particles were attached to adhesive tape and coated with gold under vacuum. Dynamic laser light scattering (DLS) was performed on a modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlation and a He-Ne laser (output power = 10 mw at 632 nm) at 25°C to get the size of PSt/PNVP latex particles. Before DLS measurement, the latex was diluted with distilled water to a given concentration and a filter (0.45 μm) was used to eliminate any dust. Laplace inversion of the intensity-intensity time correlation function G(2) (t,q) in the self-beating mode resulted in a line-width distribution G(Γ). G(Γ) was directly converted to the hydrodynamic radius distribution f(Rh) by using the Stokes-Einstein equation: Rh = kBT/(6πηD) with kB, T, η and the translational diffusion coefficient being Boltzman constant, absolute temperature, the solvent viscosity and translational diffusion coefficient, respectively. Polydispersity index (PDI) of Rh was defined as Eq. 1.

$$\mathrm{PDI} = \mu_2 / \overline{\Gamma}^2 \text{ and } \mu_2 = \int (\Gamma - \overline{\Gamma})^2 G(\Gamma) d\Gamma \qquad (1)$$

Results and discussion

Chemical composition of PSt/PNVP latex nanoparticles

CHPO and St are oil-soluble and stay in the micelles and latex particles, whereas NVP and TEPA are water-soluble and exist in the aqueous medium. The redox reaction between CHPO and TEPA occurs at the interface where their encounter took place. Therefore, the primary radicals are formed mainly at the interface. This radical formation way helps the copolymerization of St and NVP near the interface. Otherwise, primary radicals are formed in the oil phase or in water phase for other microemulsion polymerizations.

PSt/PNVP solid particles were extracted with water for three days to remove homopolymer of NVP and the surfactants. FTIR analysis of the remaining solid was performed in KBr pellets. As shown in Figure 1, the typical absorption band due to PSt appear at 700, 757, 1029, 1452, 1493 and 1601 cm^{-1}. The absorption band attributed to carbonyl stretching vibration and C-N stretching vibration of NVP appears at 1670 cm^{-1} and 1290 cm^{-1}, respectively. Since homopolymer of NVP was removed by the extraction, this result confirms the occurrence of copolymerization between St and NVP.

Morphology and size of PSt/PNVP latex nanoparticles

The core-shell morphology of the composite nanpartilces can be confirmed under TEM observation. After PSt/PNVP solid particles was extracted with water for 3 days, we get the yield of core/shell particles be about 85% after we put the extracted powder into oven until constant weight. The remaining solid powder was re-dispersed

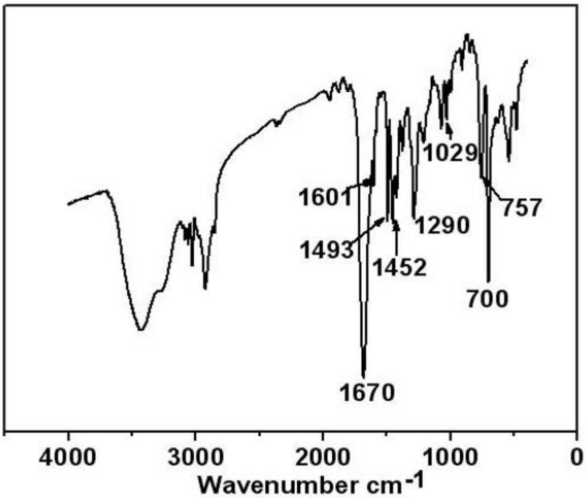


Figure 1. FTIR spectra of PSt/PNVP latex nanoparticle after the extraction with water.

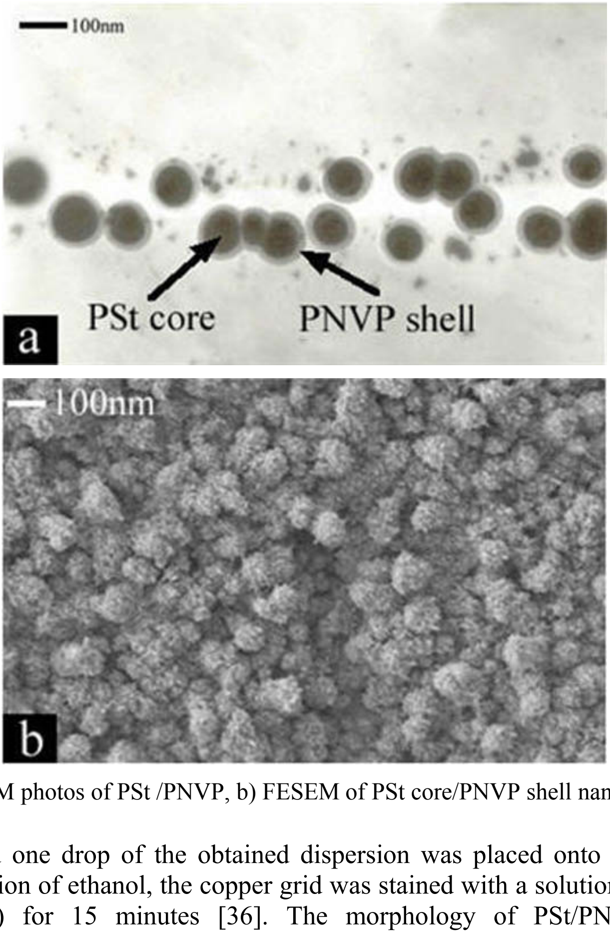


Figure 2. a) TEM photos of PSt /PNVP, b) FESEM of PSt core/PNVP shell nanoparticles.

in ethanol and one drop of the obtained dispersion was placed onto a copper grid. After evaporation of ethanol, the copper grid was stained with a solution of RuO_4 (1% mass fraction) for 15 minutes [36]. The morphology of PSt/PNVP core/shell nanoparticles was shown in Figure 2a, which demonstrates the core/shell structure with PSt (the black region) as the core and PNVP (the pale region) as the shell. The radius of PSt/PNVP nanoparticles is about 50.4 nm, the averaged shell thickness is about 8 nm, so the ratio of volumes (the core / shell regions) is about 1.45. Figure 2b shows us the FESEM image of hydrophobic core/hydrophilic shell amphiphilic nanoparticles. Those particles showed rough surface, which might be caused by NVP chains attached to the particle surface.

The hydrodynamic radius (R_h) of PSt/PNVP nanoparticles and its polydispersity index (PDI) were shown in Figure 3. The result shows us that the radius of PSt/PNVP nanoparticles is about 49.8 nm and PDI is 0.176, which is also in good accordance with TEM result as shown in Figure 2. Those results show that the idea of interfacial-initiated microemulsion polymerization to synthesize hydrophobic core/hydrophilic shell nanoparticles in one batch does work.

Figure 4 offers XPS spectrum of PSt/PNVP nanoparticles after the extraction with water and reveals the existence of the element of N at the electron binding energy of

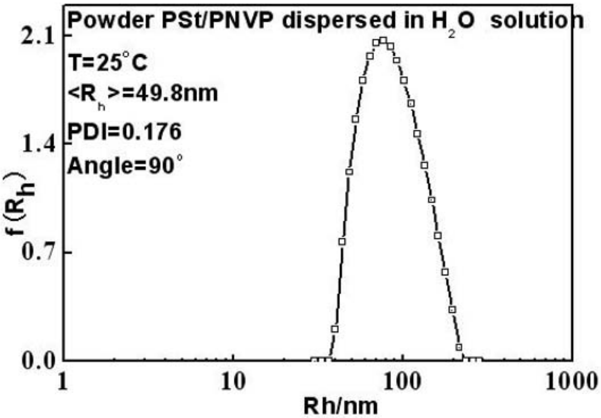


Figure 3. Hydrodynamic radius distribution (f(Rh)) and PDI of PSt/PNVP nanoparticles in water

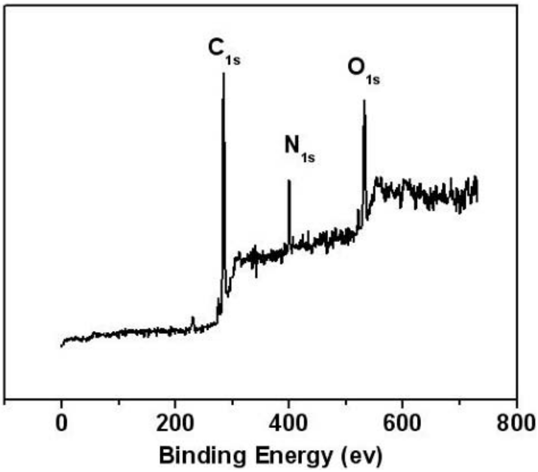
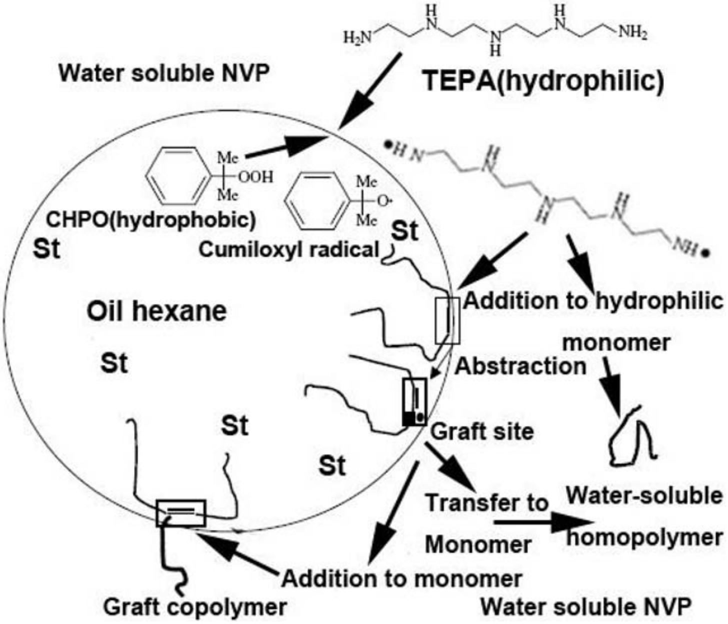


Figure 4. XPS spectrum of PSt/PNVP nanoparticles after the extraction with water

423 eV, indicating that PNVP was incorporated onto the surface of latex particles. The above results including FTIR spectra and TEM image confirmed the formation of core/shell structure in interfacial-initiated microemulsion polymerization.

Mechanism for the formation of core/shell nanoparticles by one-step

PSt/PNVP core-shell nanoparticles were prepared through one-stage interfacial-initiated polymerization in emulsion and the probable mechanism was suggested as followed.



Scheme 1. Schematic preparation of PSt/PNVP core/shell nanoparticles through interfacial-initiated microemulsion polymerization

In this polymerization initiated by the redox couple, the oil-soluble oxidant component of CHPO stayed in the micelles and latex particles while the reductive water-soluble component of TEPA existed in the water phase. Primary cumene hydroperoxide (hydrophobic) and TEPA (hydrophilic) radicals would be produced only at the oil water interface where both of them encountered. The primary cumene hydroperoxide radicals initiated the polymerization of St monomers near the interface to form PSt propagating chains. PSt propagating chains might be anchored to the interface by initiate NVP polymerization or coupling with water-soluble PNVP radicals at the interface. At the same time, the TEPA radicals initiated the polymerization of NVP monomers near the interface of oil/water to form the shell layer, as demonstrated in Scheme 1. Also, PNVP propagating chains might be anchored to the interface by initiate St polymerization or coupling with oil-soluble PSt radicals. Thus copolymer of St and NVP was formed.

Conclusions

With CHPO and TEPA as the redox initiation couple, the interfacial-initiated microemulsion copolymerizations of St and NVP were carried out and resulted in core/shell latex particles in one stage. FTIR, XPS and TEM results demonstrate that interfacial-initiated microemulsion copolymerization facilitate the copolymerization of the oil-soluble St monomer with the water-soluble NVP monomer and the formation of core-shell morphology of latex particles. The core-shell structure of PSt/PNVP latex particles can be built in one-stage polymerization via interfacial-initiation.

Acknowledgements. We thank Natural Science Foundation of Zhejiang Province for the financial support and the Center Analysis & Structure Research Laboratory of University of Science and Technology of China (USTC). We also thank professors Zhicheng Zhang and Wedong He of the Department of Polymer Science and Engineering of USTC.

References

1. Hoar JP, Schulman JH (1943) Nature 152:102
2. Gandau F, in Paleos CM(ed) (1992) Polymerization in Organized Media, Gordan Science Publications, Philadelphia
3. Zhou QF, Hun HJ (2001) Polymer Science Series: Polymer Chemistry (Chapter 16), Chemistry Industry Press, Beijing
4. Batra U, Russel WB, Mays JW, Huang JS (1997) Macromolecules 30(20):6120
5. Co CC, Cotts P, Kaler EW (2001) Macromolecules 34(10):3245
6. Eriksson S, Nylen U, Rojas S (2004) Appl Catal A-Gen 265(2):207
7. Date AA, Patravale VB. (2004) Curr Opin Colloid Interface Sci 9(3-4):222
8. Tojo C, Blanco MC, Leis JR. (2004) Curr Opin Colloid Interface Sci 9(3-4):264
9. Hansen SH (2003) Electrophoresis 24 (22-23):3900
10. Capek I (2001) Adv Colloid Interface Sci 91:295
11. Capek I (2001) Adv Colloid Interface Sci 92:195
12. Chow PY, Gan LM (2005) Adv Polym Sci 175:257
13. Lopez-Quintela MA (2003) Curr Opin Colloid Interface Sci 8:137
14. Radenkov M, Topliyska A, Radenkov P (2004) Polym Bull 52:275
15. Badran AS, Ayoub MMH, Naser HE, El-hakim AA (1997) Eur Polym J 33:537
16. Candan E, Yalcın Y, Nurseli U (2000) Polym Int 49:795
17. Tang LG, Weng ZX, Pan ZR (1996) Eur Polym J 32:1139
18. Murugan R, Panduranga K (2003) Polym Bull 49:395
19. Shaffei KA, Ayoub MMH, Ismail MN, Badran AS (1998) Eur Polym J 34:553
20. Zhang XJ, Baker WE (1998) J Appl Polym Sci 67:427
21. Emine KG, Candan E (2003) Polym Bull 50:175
22. Vladimir ILozinsk, Irina AS, Valentina KK, Elena AK (2003) Macromolecules 36:7308
23. Cho SH, Ryu JH, Suh KD (2005) Eur Polym J 41:2209
24. Luo YW, Joseph Schork F (2001) J Polym Sci Polym Chem, 39:2696
25. Yun Y, Li HQ, Ruckenstein E (2001) J Colloid Interface Sci 238(2):414
26. He WD, Wang YM, Wang D, Zhang ZC (2005) Polymer 46:8366
27. He WD, Ye FM, Wang YM, Li LF (2004) Appl Polym Sci 92(4):2334
28. He WD, Wang YM, Wang D, Zhang ZC (2006) Polym Int 55:520
29. David JL, Gilbert RG (2005) Polymer 46:7874
30. Radenkov M, Kyulanov AP, Radenkov P (2004) Polym Bull 52:275
31. Pedro CO, Cavaille JY, Chazeau L, Gilbert RG, Amilton MS (2005) Polymer 46:1105
32. David JL, James FA, Christopher MF, Michael JM, Gilbert RG (2001) Biomacromolecules 2:518

33. Pedro CO, Adriana G (2005) Eur Polym J 41:1883
34. Delphine LT, Peter MF, Oren R, Cor EK (2005) Polymer 46:7094
35. Geurts FLS, German AL (2001) J Microencapsul 18:533
36. Joan ST (1983) Macromolecules 16:589