

Encapsulation of Magnetic Particles Via Miniemulsion Polymerization of Styrene. II. Effect of Some Parameters on the Polymerization of Styrene

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ABSTRACT: Effects of some parameters on the polymerization of Styrene (St) during encapsulation of iron oxide particles via miniemulsion polymerization have been investigated. At the early stage of reaction, polymerization rate increased slightly with the increase of sonicating time, and then it leveled off. The polymerization rate increased with the increase of KPS at the early stage of polymerization, which tendency is analogous to the result of polymerization of St in miniemulsion without the presence of iron oxide particles. The increase of iron oxide not only decreased the polymerization rate but also resulted in poorer monodis-

perse of the particles when keeping the amount of dispersant constant. The dispersant played an important role in the encapsulation of magnetic particles via miniemulsion polymerization of St. It not only made the iron oxide disperse well in monomer droplets but also led to a much faster polymerization than that of no dispersant in system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3525–3530, 2007

Key words: magnetic polymers; degree of polymerization; emulsion polymerization; core-shell polymers; kinetics (polym.)

INTRODUCTION

In recent years, magnetic polymeric particles have found wide use in biomedical and bioengineering such as cell separation,^{1,2} immunoassay,³ and nucleic acids concentration.⁴ In addition, some potential applications have also been expected in several areas such as detoxification of biological fluid and magnetic guidance of particle systems for specific drug-delivery process.⁵

Over the past 10 years, great effort has been made in the preparation and characterization of magnetic polymeric microspheres. Several approaches within the context of emulsion polymerization have been attempted for the encapsulation of magnetic particles, such as conventional emulsion polymerization,^{6–9} suspension polymerization,^{10–13} dispersion polymerization,¹⁴ and microemulsion polymerization.^{15,16} So far, much progress has been made via these methods. However, the complexity of the particle nucleation mechanism and the difficulties in controlling the dispersion stability of inorganic particles in the continuous or disperse phase during

emulsification and encapsulation polymerizations appear to be the major obstacle to prepare magnetic polymeric microspheres with high encapsulation efficiency and high magnetic response. For example, for the conventional emulsion polymerization, the principle locus for particle nucleation is either in the aqueous phase or in the monomer-swollen micelles.¹⁷ In the presence of inorganic magnetic particles dispersed in the aqueous phase, an additional site can be the surface of the particles. Therefore, the competition between these mechanisms can lead to both polymer particles containing magnetic particles and unencapsulated ones.

The characteristic features of the miniemulsion polymerization such as the ability to nucleate all of the droplets containing the inorganic particles, and a good control of the drop size and size distribution plus the direct dispersion of the inorganic particles into the oil phase can provide potential advantages for the encapsulation of the inorganic particles.

Miniemulsions are relatively stable submicron oil-in-water dispersions.^{18,19} The monomer droplets can range in size from 50–500 nm, and are typically obtained by shearing a system containing oil, water, surfactant, and a costabilizer. Because of the small droplets size, the overall surface area of the droplets can compete effectively for radical capture. As a result, the monomer droplets in a miniemulsion become the dominant sites for particles nucleation. The stability of these droplets arises from the use of an ionic surfactant coupled with a low molecule

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weight, highly water insoluble costabilizer. The costabilizer, such as hexadecane, substantially retards diffusion of monomer out of the miniemulsion droplets. Miniemulsions had been used to encapsulate of titanium dioxide in the past few years by Erdem et al.,^{20–22} and they have achieved a good result.

However, the research works of our group indicated that the conversions of monomer in miniemulsion system that are used to prepare magnetic polymer spheres show different normal miniemulsion polymerization.²³ It seems that the amount of iron oxide, dispersant, etc., influences the conversion and polymerization rate of monomer during capsulation. In this work, miniemulsions have been used to prepare PSt/iron oxide microspheres, the effects of the amount of iron oxide, dispersant, initiator, and the time of sonication on the polymerization rate, and the morphology of particles have been investigated in detail.

EXPERIMENTAL

Materials

Styrene (St), (chemical pure, Dagang Yizhong Chemical Plant of Tianjin, China), was distilled under reduced pressure prior to polymerization. Sodium persulfate (KPS), the initiator, (analytical reagent, Xi'an Chemical Plant, China), iron trichloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), (analytical reagent, the Third Chemical Plant of Tianjin, China), and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), (analytical reagent, Xi'an Chemical Plant, China), were used without further purification. Sodium dodecylsulphonate (SDS), liquid paraffine, hydroquinone, and Disperbyk-106 were used as received. All other chemicals are of analytical reagent and were used as supplied. Water used was doubly distilled.

Preparation of ferrofluid

FeCl_3 (0.5M) solution (300 mL) and 0.5M of FeSO_4 solution (150 mL) were placed in 1000-mL four-necked flask equipped with a stirrer, a condenser, a thermometer, and a N_2 inlet. The mixture was stirred at 55°C under N_2 atmosphere, and then 3M of NaOH solution (250 mL) was added. The temperature was then raised to 65°C . After 1 h, 100 mL of water solution dissolving 0.03 mol of SDS was added. And then the temperature was raised to 90°C . The reaction was allowed to proceed for 30 min and then cooled. After that, the resulting colloidal particles were washed several times with distilled water by decantation until it turned neutral. At last, a ferrofluid (10 wt %) was made with distilled water for use to prepare polymer magnetic particles.

Preparation of magnetic P(St/MAA) microspheres

St, dispersant, and liquid paraffine were mixed together as oil phase. The solution of SDS was used as water phase. The ferrofluid was decanted to remove water, then was mixed with dispersant and oil phase, and was homogenized at room temperature by ultrasound mixer before it was mixed with water phase. A pre-emulsion made by sonicating the above mixture for several minutes to the miniemulsion was obtained. Polymerization of the miniemulsion was carried out in a four-necked flask equipped with a stirrer, a condenser, a thermometer, and a N_2 inlet with constant temperature of 70°C , maintained by a water bath under N_2 atmosphere for 6 h. The addition of the water-soluble initiator (KPS) generated free radicals that enter the droplets to bring about encapsulation.

Characterization

Monomer conversion

The samples were taken out from the flask during polymerization in a 5-min interval. Then, several drops of 1% of hydroquinone solution were added in samples to terminate the polymerization. The conversion is calculated according to the following equation:

$$\text{Conversion} = \frac{m_s m_t - m_{\text{Fe}} m_l}{m_m m_l} \times 100$$

where m_l and m_s are the weight of latex taken out from flask every time and its remaining after drying, respectively, m_m is the weight of monomer in total latex, m_t is the weight of total latex, and m_{Fe} is the weight of iron oxide in whole latex.

Size and morphology

The size and morphology of magnetic polymer microspheres were investigated by HITACHI H-600 transmission electron microscopy. The particle size is calculated based on 100 particles. Number average diameter (D) and the dispersion coefficient (f) were calculated according to eqs. (1) and (2), respectively, as follows:

$$D = \frac{\sum D_i}{n} \quad (1)$$

$$f = \frac{\sqrt{\sum (D_i - D)^2 / (n - 1)}}{D} \quad (2)$$

where D_i is the diameter of individual microsphere and n is the number of calculated microspheres.

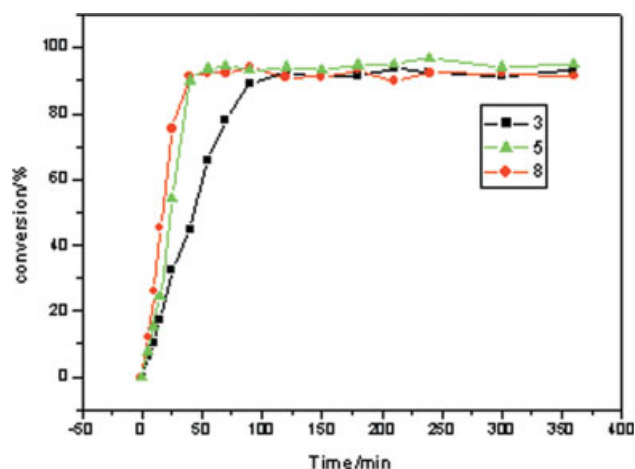


Figure 1 Conversion versus time plot of miniemulsion polymerization in the presence of magnetic nanoparticles under different ultrasonic miniemulsification time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Effect of ultrasonic miniemulsification time

The conversions of St versus time of polymerization in the presence of magnetic nanoparticles under different ultrasonication time were shown in Figure 1. During the early stage of reaction, polymerization rate increased slightly with the increase of sonication time. About 50 min later, no obvious difference was found for polymerization systems with different sonication time and conversions achieved up to 90% and leveled off. This result is similar to the miniemulsion polymerizations of pure monomers without

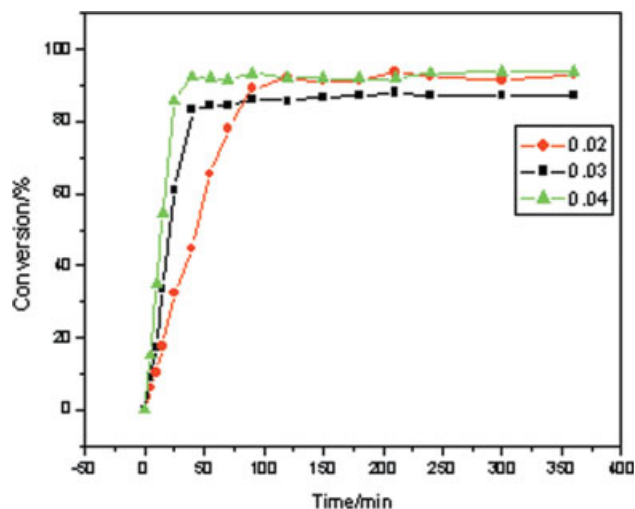


Figure 2 Conversion versus time plot of miniemulsion polymerization in the presence of magnetic nanoparticles with different initiator content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

inorganic particles that the rate of the polymerization increased with the ultrasonication time because longer ultrasonication time is benefited for the dispersion of monomer and the formation of more monomer drops where the locations of polymerization in miniemulsion are, at last, lead to the rapid polymerization¹⁸ with the amount of monomer drops increased. So, it can be deduced that influence of ultrasonication time on the miniemulsion polymerization in the presence of magnetic nanoparticles is similar to that of miniemulsion polymerization system of pure St.

Effect of initiator

With the increase of KPS content from 0.02 to 0.04 g, as shown in Figure 2, polymerization rate increased during the early stage of polymerization when the amount of iron oxide and the dispersant were kept constant of 0.4 and 0.2 g, respectively, and then leveled off. Although this kinetics tendency was analogous to the kinetic behavior of miniemulsion polymerization of St without the presence of iron oxide particles, which has been reported in literature,²⁴ the difference still existed. First, the increase amplitude of polymerization rate was small with the increase of KPS; second, the polymerization rate of St was fast compared to the case where no iron oxide particles were used. It seems that, besides KPS, there should be other factors affecting the kinetic behavior of St.

Effect of the amount of iron oxide particles

To examine the effect of a varying amount of iron oxide on the polymerization of St, a series of miniemulsions had been prepared. The costabilizer level

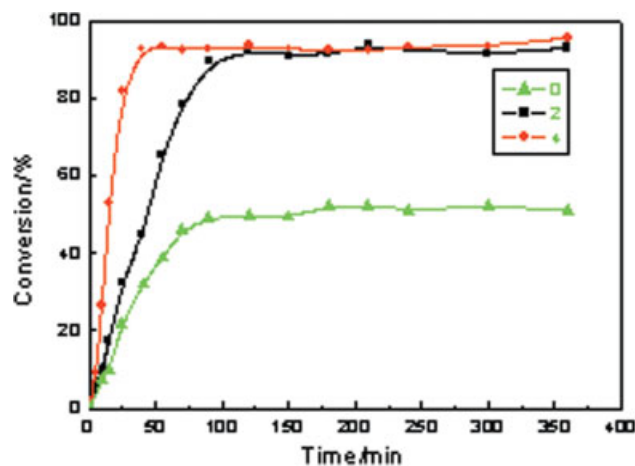


Figure 3 Conversion versus time plot of miniemulsion polymerization in the presence of different magnetic nanoparticles content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was maintained constant at 4 wt % based on monomer while the amount of iron oxide was varied (0, 2, and 4 g), and the ratio of iron oxide/dispersant was kept constant. The results were shown in Figure 3.

Figure 3 indicates that the conversion of St increased with the amount of iron oxide, which is controversial to the normal result that the magnetite is an inhibitor with the adsorption of free radicals. The reason of this may attribute to the dispersant. Since the ratio of iron oxide to the dispersant is kept constant, the varying amount of iron oxide also leads to the increase of the dispersant content. So, further experiments were performed to investigate the effects of the iron oxide and dispersant, respectively. The conversion of St versus time of miniemulsion polymerization under the same amount of dispersant was measured. The result was shown in Figure 4.

Figure 4 indicates that the conversion of St decreases with the increase of the amount of iron oxide if the amount of dispersant was kept constant. The difference between Figures 3 and 4 implies that the dispersant in the polymerization system play an important role.

Effect of the dispersant

Furthermore, two miniemulsion systems without iron oxide particles present were prepared, and the conversion of St versus time with and without dispersant incorporated were measured. The results were shown in Figure 5, which showed that using dispersant could lead to a much faster polymerization of St indeed.

According to the theory of miniemulsion, several possible reasons have been suggested here for the

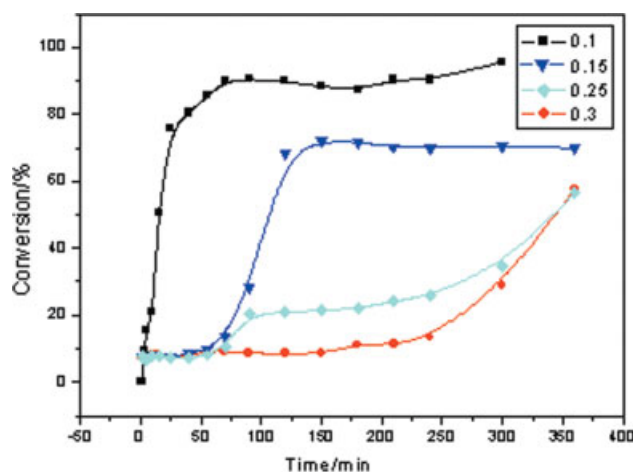


Figure 4 Conversion versus time plot of miniemulsion polymerization in the presence of different iron oxides content and the same amount of dispersant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

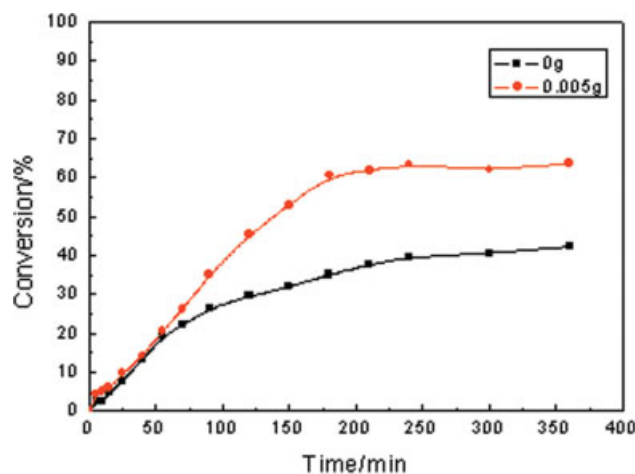


Figure 5 Conversion versus time plot of miniemulsion polymerization in the absence of magnetic nanoparticles with different Disperbyk-106 content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increased rate of polymerization of St. First, the Disperbyk-106 is a water insoluble substance, the presence of it increases the viscosity of monomer droplets, and thus reduce the diffusion of oligomer radicals out from the droplets. In general, miniemulsion droplets act as the main reaction site in miniemulsion polymerization, so the higher probability of propagation could occur in more viscous droplets, and the higher polymerization rate is achieved. Second, according to the investigation results of Miller et al. about the effect of polystyrene on the miniemulsion polymerization,^{25,26} the presence of polymer dispersant may change the interface of monomer and continues phase by disrupt a SLS/liquid paraffine interfacial barrier to radical entry, make the entry of oligomeric radicals from continues phase to the monomer droplets easily. Third, the fast polymerization of St may relate to the interaction of amine group of Disperbyk-106 (organic amine salt composed by the phosphate partly esterified and organic amine) with the KPS. This assumption was supported by the report of Feng et al.,²⁷ who have found that aliphatic amine were benefited for the polymerization of acrylamide because of the amine groups interacting with KPS and promoting the polymerization of St.

On the basis of the earlier discussion of dispersant, it is not difficult to explain the results exhibited in Figure 3. In fact, because of the ratio of the iron oxide to the dispersant was kept constant, the change of amount of the iron oxide also led to the increase of the dispersant. Therefore, the two factors to determine the overall polymerization rate of St under the amount of KPS, temperature, and other parameters were kept constant. One is a promoting action of the

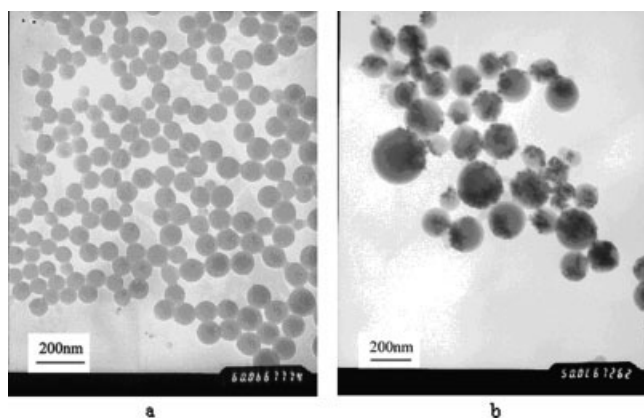


Figure 6 TEM photographs of microspheres prepared via miniemulsion: (a) pure PSt, (b) PSt/iron oxide.

dispersant, and the other is a retardant action of iron oxides. It can be speculated that just because the promoting action of dispersant is stronger than that of the latter, the overall polymerization rate of St increases with the increase of iron oxide and the dispersant.

It can be concluded from the earlier results that the dispersant play a very important role in the system. The dispersant not only make the iron oxide disperse well in monomer droplets but also lead to a much faster polymerization.

Effect of the magnetic particles on the morphology of PSt

Undoubtedly, the presence of the iron oxide particles makes the polymerization complicated from the discussion mentioned earlier. Figure 6 and Table I show the TEM photographs and the particle size of magnetic composite microspheres prepared with and without iron oxide, respectively. They indicate that the addition of iron oxide particles makes the particle size and particle size distribution increase. The mean diameter of composite particles is 156 nm, nearly twice as large as it prepared via pure St system, and the monodisperse of particles becomes poorer.

According to the theory of miniemulsion, the particle nucleation takes place by direct oligoradical entry into monomer droplets relative to particle nucleation by homogeneous and/or micellar nuclea-

TABLE I
Effect of Iron Oxides on the Particle Size and Dispersion Coefficient

Miniemulsion systems	Mean particle diameter (nm)	Dispersion coefficient (%)
Pure PSt	88	14.8
PSt/iron oxide particles	156	24.4

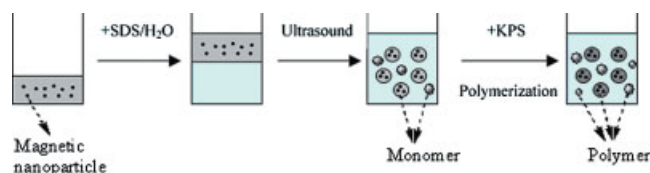


Figure 7 Schematic illustrations of preparation of magnetic composite microspheres by miniemulsion polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion, the monomer droplets are the main locus of polymerization in miniemulsion (as well as in microemulsion) polymerization. When the iron oxide particles are dispersed in the monomer droplets, there is a high probability of them are capsulated in polymer, and at last, forming somewhat large composite particles comparing pure St polymerization process. The possible capsulation process was illustrated as shown in Figure 7, which can show the effect of magnetic particles on the morphology of PSt intuitively.

CONCLUSIONS

Encapsulation of magnetic particles via miniemulsion polymerization of St has been carried out. Studies on the effect of ultrasonication and KPS on the polymerization of St revealed that the polymerization behavior of St in the presence of iron oxide particles was similar to that of polymerization of St without magnetic particles. The ultrasonication treatment of sample leads to the well dispersion of monomer and the rapid polymerization. The polymerization rate increases with the increase of KPS. However, the presence of iron oxide particles leads to the conversion of St decreasing with increase of the amount of iron oxide if the amount of dispersant is kept constant. Moreover, it also reduces the monodispersity of the composite particles. The dispersant plays an important role in the encapsulation of magnetic particles via miniemulsion polymerization of St. It not only makes the iron oxide disperse well in monomer droplets but also leads to a much faster polymerization.

References

- Haik, Y.; Pai, V.; Che, C. J. *J Magn Magn Mater* 1999, 194, 254.
- Sugibayashi, K.; Morimoto, Y.; Nadai, T.; Kato. *Chem Pharm Bull* 1977, 25, 3433.
- Mary, M. In *Scientific and Clinical Applications of Magnetic Carriers*; Hafeli, U.; Schutt, W.; Zborowski, M., Eds.; Plenum: New York, 1997; p 303.
- Elaissari, A.; Rodrigue, M.; Meunier, F.; Herve, C. *J Magn Magn Mater* 2001, 225, 127.
- Gupta, P. K.; Hung, C. T. *Life Sci* 1989, 44, 175.
- Yanase, N.; Noguchi, H.; Asakura, H.; Suzuta, T. *J Appl Polym Sci* 1993, 50, 765.

7. Noguchi, H.; Yanase, N.; Uchida, Y.; Suzuta, T. *J Appl Polym Sci* 1993, 48, 1539.
8. Kondo, A.; Kamura, H.; Higashitani, K. *Appl Microbiol Biotechnol* 1994, 41, 99.
9. Khng, H. P.; Cunliffe, D.; Davies, S.; Turner, N. A.; Vulfson, E. N. *Biotechnol Bioeng* 1998, 60, 419.
10. Margel; Shlomo, B. U.S. Pat. 4,783,366 (1988).
11. Meiji, T. *Jpn. Pat.* 62,204,501 (1987).
12. Daniel; Jean-Claude, S.; Jean-zur, T. D. U.S. Pat. 4,358,388 (1982).
13. Charmot; Dominique, V. U.S. Pat. 5,356,713 (1994).
14. Richard, J. V. U.S. Pat. 5,976,426 (1999).
15. Deng, Y.; Wang, L.; Yang, W.; Fu, S.; Elaýssari, A. *J Magn Magn Mater* 2003, 257, 60.
16. Liu, Z. L.; Ding, Z. H.; Yao, K. L.; Tao, J.; Du, G. H.; Lu, Q. H.; Wang, X.; Gong, F. L.; Chen, X. *J Magn Magn Mater* 2003, 265, 98.
17. EL-Aasser, M. S. In *An Introduction to Polymer Colloids*; Candau, F., Ottewill, R. H., Eds.; Kluwer: The Netherlands, 1990; p 1.
18. Sudol, E. D.; EL-Aasser, M. S. In *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A.; EL-Aasser, M. S., Eds.; Wiley: New York, 1997; p 699.
19. Ugelstad, J.; EL-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Polym Lett Ed* 1973, 111, 503.
20. Erdem, B.; Sudol, E. D.; Dimonie, V. L.; EL-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 2000, 38, 4419.
21. Erdem, B.; Sudol, E. D.; Dimonie, V. L.; EL-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 2000, 38, 4431.
22. Erdem, B.; Sudol, E. D.; Dimonie, V. L.; EL-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 2000, 38, 4441.
23. Zhang, Q.; Xie, G. Encapsulation of Iron Oxide Particles Via Miniemulsion Polymerization of Styrene. I. Dispersion of Iron Oxide, Preparation and Characterization of PS Coating Iron Oxide, to appear.
24. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; EL-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1995, 33, 1391.
25. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; EL-Aasser, M. S. *Macromolecules* 1995, 28, 2765.
26. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; EL-Aasser, M. S. *Macromolecules* 1995, 28, 2772.
27. Guo, X. Q.; Qiu, K. Y.; Feng, X. D. *Macromol Chem* 1990, 191, 577.