Particle Size Control in Emulsion Copolymerization of Styrene with Poly(ethylene oxide) Macromonomers

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SUMMARY: This paper presents a successful application of hydrophobically enhanced poly(ethylene oxide) (PEO) macromonomers (**1**) to emulsion copolymerization of styrene using potassium persulfate (KPS) or 2, 2'-azobisisobutyronitrile(AIBN) as an initiator at 65 °C. This copolymerization yields in a batch process monodisperse, or nearly monodisperse, latex particles with 70400nm in diameters. Factors which affect the particle size and distribution include the structure and molecular weight of the macromonomers, initiator species, initiator and macromonomer concentrations. The power law exponents under the several conditions were determined and rationalized. The number of latex particles appears to be controlled by the fates of the graft copolymers formed in monomer-swollen macromonomer micelles and in continuous phase.

Introduction

One of the promising applications of amphiphilic macromonomers is in the fields of heterogeneous polymerization such as emulsion and dispersion systems1). Among a variety of methods of preparing polymeric latex particles, the macromonomer technique is unique and flexible in that the macromonomers act as not only comonomer but also reactive emulsifiers or dispersants, i. e., as polymerizable, reactive surfactant (*«surfmer»*) without any conventional surfactants2,3). The macromonomers are *in-situ* copolymerized with hydrophobic monomers in monomer-swollen micelles and in continuous phase to afford surface active graft copolymers. They form inter- and/or intramolecular micelles in a selective solvent as in the case described here, and eventually they are attached to the particle surface. The resulting core-shell type latex particles, therefore, are effectively sterically stabilized against flocculation. Several research groups4-11) have reported the synthesis and properties of latex particles prepared by emulsion polymerization in semi-batch process, using poly(ethylene oxide) macromonomers. However, the particle size control in the emulsion copolymerization using macromonomers is still poorly understood compared to that using non-reactive surfactants. Nucleation mechanisms may be a key point to be cleared12).

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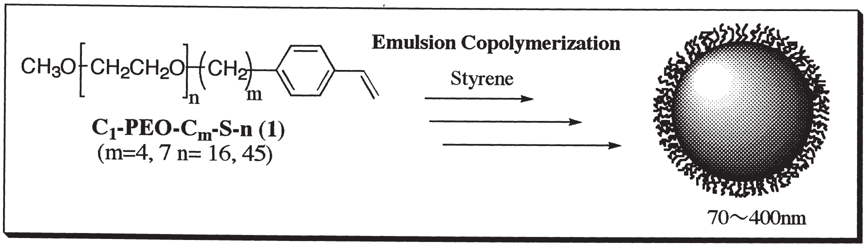
In the present study, we investigated emulsion copolymerization of styrene with hydrophobically enhanced PEO macromonomers (**1**) (C_1-PEO-C_m-S-n where m=4, 7 and n=16 and 45). Factors which affect the latex particle size and distribution include the structure and molecular weight of the macromonomers (**1**), initiator species, initiator and macromonomer concentrations. The power law exponents under the several experimental conditions are determined and rationalized. The emulsion copolymerization behavior is discussed from the viewpoint of the structure of the macromonomer, together with the particle nucleation processes.



C_1-PEO-C_m-S-n (1)
(m=4, 7 n= 16, 45)

Experimental

The macromonomers (**1**) were prepared by the method reported in the previous paper$^{13)}$. The degree of polymerization of the PEO chains (n) determined by size exclusion chromatography (SEC) is 16 and 45. The M_w/M_n(SEC) is less than 1.2 and the functionality of the double bonds determined by ^{1}H NMR is also satisfactory (> 90%). The critical micelle concentration (cmc) was determined from surface tension measurements (CBV-A3, Kyowa Interface Science Co., Ltd.) at 22 °C and static light scattering (ELS-8000, Otsuka Electronics Co., Ltd.) at 25 °C. Emulsion copolymerization was carried out at 65 °C with a 100mL three-neck reactor fitted with a condenser and a mechanical stirrer (350 ppm) under nitrogen. A half-moon-type impeller was used. After purging with nitrogen for 20 min, the polymerization was commenced by immersing the reactor in an oil bath at 65 °C. All the copolymerizations were conducted at the macromonomer concentration higher than the cmc. The conversion of styrene and macromonomer was determined from gravimetry and ^{1}H NMR measurement of the copolymers. The latex particles diameter and distribution were characterized by transmission electron microscope (TEM)(Hitachi, H-800), dynamic light scattering (ELS-8000), and field-flow fractionation-multiangle laser light scattering (FFF-MALLS). Number- and weight-average diameters of the particles were calculated by $D_n=n_iD_i/n_i$ and $D_w=n_iD_i^4/n_i D_i^3$, respectively, where n_i is the number of the particles with diameter D_i.

Styrene was washed with aq sodium thiosulfate, aq sodium hydroxide, and distilled over calcium hydride under reduced pressure just before use. Water was purified by a Millipore Milli Q purification system. 2, 2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization three times from methanol. Potassium persulfate(KPS) was purified by recrystallization from water.

Results and Discussion

Semi-logarithmic plots of surface tension as a function of macromonomer concentration [macromonomer] are shown in Figure 1. With increasing [macromonomer], the surface tension decreases and becomes to be constant above a certain concentration. The value of cmc was determined as an inflection point to be 0.03_0 wt%($2._8$x10^{-4} mol/L) for C_1-PEO-C_7-S-16 and 0.1_3wt%($5._6$x10^{-4}mol/L) for C_1-PEO-S_7-S-45. The weight-average aggregation number of C_1-PEO-S_7-S-16 micelle was determined at 25 °C to be 46 by static light scattering14), and the number-average aggregation number of C_1-PEO-C_7-S-45 and C_1-PEO-C_4-S-45 micelle at 22 °C was determined to be 38 and 27, respectively, by time-resolved fluorescence technique using pyrene as a probe15).

A typical TEM photograph given in Figure 2 shows that the resulting particles are essentially monodisperse in size. The polystyrene latex particles with 70-400 nm and nearly monodisperse ($D_w/D_n=1.00_3$-1.0_8) in diameter were prepared by the present emulsion copolymerizations. Figure 3 presents the evolution of conversions of styrene and C_1-PEO-C_7-S-16 in the emulsion copolymerization with KPS as an initiator at 65°C. The S-shaped time-conversion curve was obtained, which is typical in the conventional emulsion polymerization with a non-reactive surfactant. It should be emphasized that the conversions of styrene are nearly equal to those of macromonomer over all copolymerization time. In addition, the macromonomer composition of the final copolymers was found to be equal to that in the feed over the whole experiment, showing that the copolymerization proceeds azeotropically in the present emulsion system.

Figure 4 plots the number-average particle diameter (D_n) and its distribution (D_w/D_n) as a function of styrene conversion. With increasing the conversion of styrene, the diameter of particles increased, but its distribution decreased and became almost constant above 30 % conversion. This results imply that each particle grows in size without coagulation between

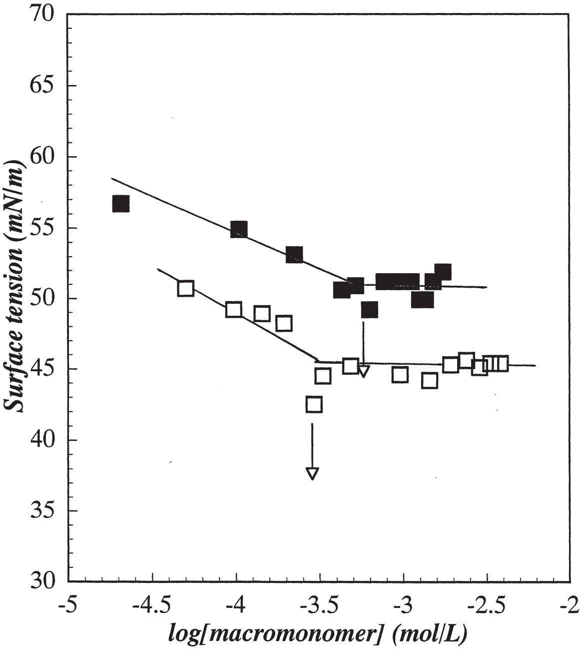


Figure 1. Semi-logarithmic plots of surface tension vs. macromonomer concentration; (□)C_1-PEO-C_7-S-16 and (■)C_1-PEO-C_7-S-45. The arrow indicates cmc.

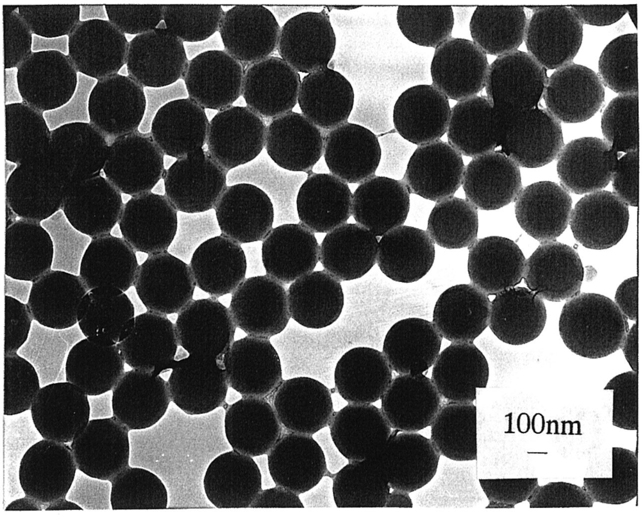


Figure 2. TEM photograph of polystyrene latex particles prepared by emulsion copolymerization of styrene with C_1-PEO-C_7-S-45 at 65 °C: [Styrene]=100g/L, [C_1-PEO-C_7-S-45]= 8.0g/L, and [AIBN]=1.0g/L.

similar sized particles, or secondary nucleation at least after certain critical conversion for the nucleation.

Double logarithmic plots of the diameter (D_n) of the latex particles as a function of [macromonomer] are shown in Figure 5, where AIBN was used as an initiator. With increasing [macromonomer], the latex size decreases, as expected. The following scaling behavior is obtained.

$D_n\ [macromonomer]^{-0.2_4}$ for C_1-PEO-C_7-S-16 (1)

$D_n\ [macromonomer]^{-0.6_9}$ for C_1-PEO-C_7-S-45 (2)

The value of the exponent, 0.2_4 for more hydrophobic macromonomer, C_1-PEO-C_7-S-16 is only slightly larger than that (0.20) predicted from Smith-Ewart theory$^{16)}$. In remarkable contrast, when one uses the macromonomer with longer PEO chain length (n=45), a less hydrophobic macromonomer, the exponent value remarkably increased up to 0.6_9. In addition, with KPS as a water soluble initiator, D_n was proportional to $[C_1\text{-PEO-}C_7\text{-S-45}]^{-0.8_6}$. The high exponent value may not be simply interpreted in terms of the micellar entry model. It can be likely explained by the homogeneous coagulative nucleation model as in the case of the dispersion copolymerizations$^{17-19)}$. In the model, D_n should be proportional to $[macromonomer]^{-0.50}$. One key to explain the present experimental data is thought to be due to high water solubility of the graft copolymers formed in the monomer-swollen macromonomer micelles and in continuous phase.

To characterize the present systems more deeply, two control experiments were carried out. First, to examine the influence of *in-situ* graft copolymers in both micelles and water on the particle nucleation, we synthesized the macromonomer model (C_1-PEO-C_7-EB-45, EB: ethylbenzene) and used it as a non-polymerizable emulsifier. One obtained a scaling behavior, $D_n[C_1\text{-PEO-}C_7\text{-EB-45}]^{-0.4_0}$ with AIBN as an initiator. The exponent value(0.40) seems to be significantly smaller than that in Eq.(2), indicating the important contribution of *in-situ* graft copolymers to the particle formation. Another experiment is a homogeneous, micellar copolymerization of C_1-PEO-C_7-S-16 micelles with a limited amount of styrene solubilized therein. The copolymerization of (**1**)(n=16, m=7) with equimolar styrene was carried out with 4,4'-azobis(4-cyanovaleric acid) (AVA) at 60 °C. The copolymerization was found to proceed very rapidly, apparently transparently and azeotropically to give 15 nm

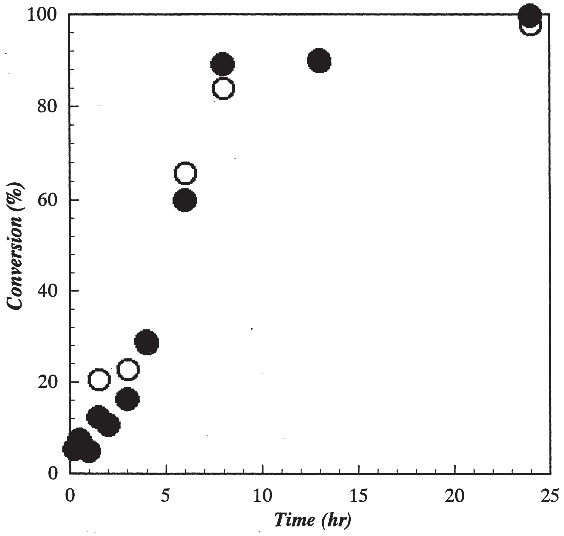


Figure 3. Time-conversion plots of styrene and macromonomer in emulsion copolymerization; (●)styrene and (○)macromonomer. [Styrene]=100g/L, [C_1-PEO-C_7-S-16]= 8.0g/L, and [KPS]=1.0g/L, Temp.=65°C.

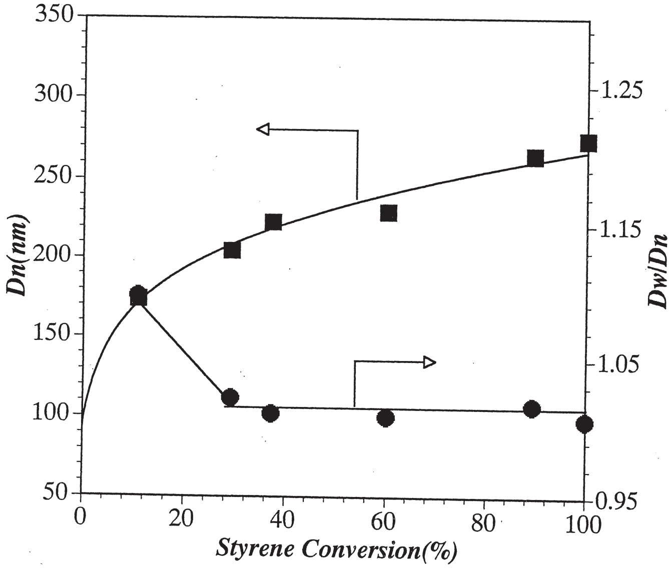


Figure 4. Plots of latex diameter (D_n) and its distribution (D_w/D_n) with styrene conversion; [Styrene]=100g/L, [C_1-PEO-C_7-S-16]= 8.0g/L, [KPS]=1.0g/L, and Temp.=65°C.

sized microparticles (as estimated by DLS) in quantitative yields[14]. The apparent weight-average molecular weight and z-average radius of gyration, $<S^2>_z{}^{1/2}$ of the graft copolymers were estimated by SEC-MALLS measurements in DMF to be 7.44x 10^6 and 94 nm, respectively[14]. This suggests interestingly that the microparticle in water consists of one graft copolymer, i. e., supposedly «*unimolecular particle*», which can become to be a candidate for the particle nucleation. A conclusion drawn from the present experimental results is that the number of latex particles is controlled by the fates of the graft copolymers formed both in micelles and in continuous phase. Therefore, the compositions of hydrophobic monomer and macromonomer in micelle and continuous phases play a crucial role in the particle nucleation. Mathematical formulations are now in progress and will be reported in future.

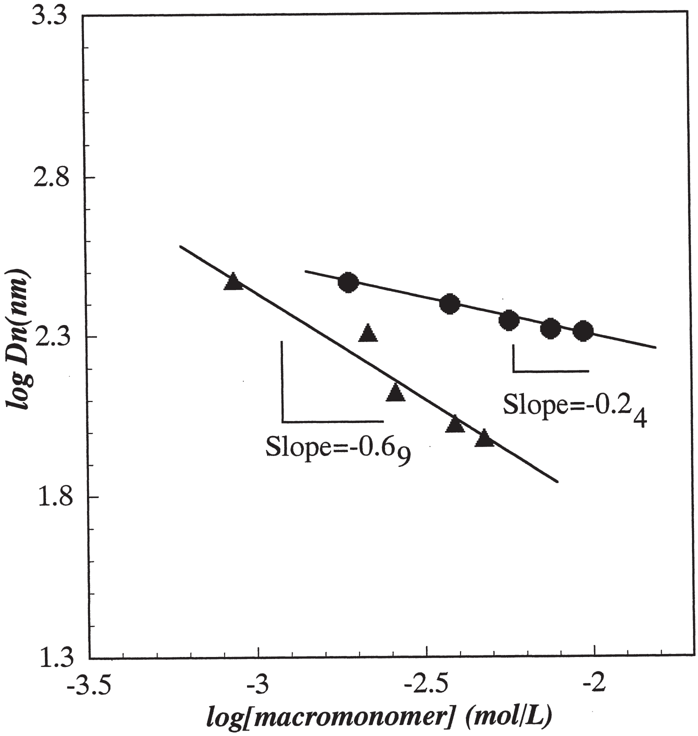


Figure 5. Double logarithmic plots of latex diameter (D_n) vs. [Macromonomer]: (●)C_1-PEO-C_7-S-16 and (▲)C_1-PEO-C_7-S-45; [Styrene]=100g/L, [AIBN]=2 g/L, and Temp.=65°C.

Conclusions

We have examined emulsion copolymerization behavior of styrene with hydrophobically enhanced PEO macromonomers as a reactive emulsifier. The copolymerization was found to proceed azeotropically to afford monodisperse or nearly monodisperse core-shell polystyrene particles, ranging in size from 70 to 400 nm in diameter. The power law exponent between latex diameter and macromonomer concentration was found to strongly depend on the structure of macromonomers. The composition of styrene and macromonomer in micelles and in continuous phase is a key factor to understand the present copolymerization.

Acknowledgment

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References

1) K. Ito, S. Kawaguchi, *Adv. Polym. Sci.* **142**, 129(1999).
2) J. M. Asua, H. A. Schoonbrood, *Acta Polym.* **49,** 671(1998).
3) A. Guyot, K. Tauer, *Adv. Polym. Sci.* **111**, 43(1994).
4) K. Ito, S. Yokoyama, F. Arakawa, *Polym. Bull.* **16**, 345(1986).
5) F. Hoshino, M. Sakai, H. Kawaguchi, *Polym. J.* **19**, 383(1987).
6) R. H. Ottewill, R. Satgurunathan, *Coll. Polym. Sci.* **265**, 845(1987).
7) G. Levesque, V. Moitie, B. Bacle, P. Deraetere, *Polymer* **29**, 2271(1988).
8) D. Chao, K. Ito, *34th IUPAC Symp. Macromol. Prepr.* 1(1992)
9) R. Brown, Stutzel B., T. Sauer, *Macromo. Chem. Phys.* **196**, 2047(1995).
10) J. Liu, C.H. Chew, L.M. Gan, W.K. Teo, L.H. Gan, *Langmuir* **13**, 4988(1997).
11) A. Búcsi, J. Forcada, S. Gibanel, V. Heréguez, M. Fontanille, Y. Gnanou *Macromolecules*, **31**, 2087(1998).
12) R. G. Gilbert, *Emulsion Polymerization*, Academic Press, New York, 1995.
13) D. Chao, S. Itsuno, K. Ito, *Polym. J.* **23**, 1045(1991).
14) M. Maniruzzaman, S. Kawaguchi, K. Ito, to be submitted for publication.
15) S. Kawaguchi, A. Yekta, J. Duhamel, M.A. Winnik, K. Ito, *J. Phys. Chem.* **98**, 7891(1994).
16) W. V. Smith, R. H. Ewart, *J. Chem. Phys.* **16**, 592(1948).
17) A. J. Paine, *Macromolecules* **23**, 3109(1990).
18) M.B. Nugroho, S. Kawaguchi, K. Ito, M.A. Winnik, *Macromol. Reports* **A32**, 593(1995).
19) S. Kawaguchi, M. A. Winnik, K. Ito, *Macromolecules* **28**, 1159(1995).