Mechanism and Grafting Reactions in Seeded Emulsion Polymerization with Emulsified Monomer Feeding

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ABSTRACT: The seeded emulsion polymerization of styrene with emulsified monomer feeding was performed by polyethyl acrylate (PEA) latex as seed emulsion. It was shown that the grafting reactions occurred between two components on the composite latex particles. The loci of seeded polymerization were studied by the kinetics of grafting reaction. The highest grafting efficiency in the initial period of seeded emulsion polymerization supported the fact that the surfaces of PEA particles are the sites of polymerization of styrene. The grafting efficiency decreased with increasing monomer-to-polymer ratio and initiator concentration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1495–1499, 1999

Key words: styrene; ethyl acrylate; emulsion polymerization; composite particles; grafting

INTRODUCTION

Multiphase composite polymer emulsions can be prepared by seeded emulsion polymerization. The polymer emulsion with core-shell morphology of latex particles is one of them. Their properties depend on the structures of latex particles. It is very important to know the polymerization mechanism to make particle design and to control the morphology of latex particles.^{1,2} Grafting reactions often occur during the course of core-shell composite particles' production. Many factors can affect the grafting reaction between the core and shell of the particles. The authors in this field report different results about the efficiency of grafting.^{3–5} From study on microstructure and morphology of latex particles, not only can much be learned about the mechanism of emulsion polymerization, but also much information can be gained about micromixing between multiphase polymer composites. The multiphase composite latex particles are, furthermore, an ideal model system for studying the properties of polymer blends and composite materials.

EXPERIMENTAL

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To obtain core-shell composite polymer emulsion, two-stage polymerization is often performed by seeded emulsion polymerization without any emulsifier postfeeding to prevent the production of new homopolymer particles.^{6,7} However, it is difficult to change the core-shell phase ratio as well as to get composite polymer emulsion. Thus, it is the purpose of this paper to show that polyethyl acrylate-polystyrene composite polymers emulsion, which are two incompatible polymers, can be prepared by seeded emulsion polymerization with emulsified monomer feeding, and grafting copolymerization also occurs. The reaction sites of the emulsified monomers in the system were investigated by determination of grafting efficiency. This is useful for understanding the mechanism of the seeded emulsion polymerization with emulsified monomer feeding. The effects of some polymerization variables on the grafting efficiency were also studied.

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The monomers of ethyl acrylate (EA) and styrene (St) were chemical grade and were both distilled under vacuum conditions prior to use. The initi-

No.	PEA Emulsion (g)	EA (g)	St (g)	KPS (g)	SDBS (g)	$H_2O\left(g ight)$	Feeding Time (h)
1	_	100	_	0.4	2.0	400	
2	100		5.0	0.1	0.1	20	0.75
3	100		8.6	0.114	0.13	34.3	1.3
4	100		13.3	0.133	0.16	53.2	2.0
5	100		20.0	0.16	0.21	80	3.0
6	100		30.0	0.2	0.27	120	4.5
7	100		13.3	0.186	0.16	53.2	2.0
8	100		13.3	0.16	0.16	53.2	2.0
9	100	—	13.3	0.08	0.16	53.2	2.0

 Table I
 Recipes of Seed and Seeded Emulsion Polymerization

ator potassium persulfate (KPS) and emulsifier sodium dodecyl benzyl sulfonate (SDBS) were both analytical grade and were used as received. Analytical grade acetonitrile and cyclohexane were used for extracting homopolymers.

The emulsion polymerization of EA was run in a four-necked flask, equipped with stir, condenser, thermometer, and feeding funnel, which was placed in a water bath at the desired temperature. The flask was charged with distilled water, emulsifier, and a fraction of monomers, purged with nitrogen, and heated until 70°C; then at nitrogen atmosphere initiator, KPS was added and the other fraction of monomers was added continuously to the flask in 2.5 h. The recipe was shown as No. 1 in Table I. The total reaction time was 10 h. The conversion of EA was above 99.8%. The average particle size of the seed emulsion was 0.076–0.078 μ m.

The seeded emulsion polymerizations of St were carried out with runs 2–9 in Table I. The flask was first charged with the polyethyl acrylate (PEA) seed emulsion, heated, and purged with nitrogen, then the KPS was added at 70°C. The St, distilled water, and emulsifier were pre-emulsified in a hopper and drop-fed into the flask during the various periods. The total reaction times were 7–10 h.

The conversions of monomers were determined by gravimetry. The seeded emulsion polymers were resolved into graft copolymer and two homopolymers by extraction method using Soxhlet Thimble. Cyclohexane and acetonitrile were used for extracting polystyrene (PSt) and PEA homopolymers for 72 h, respectively, but not for the graft copolymers.⁵ The grafting efficiency of styrene is defined as follows:

$$GE = \frac{\text{amount of PSt into the graft copolymer}}{\text{amount of St consumed}}$$

The IR spectrum was run on a Nicolet 5DX-FTIR spectrometer.

RESULTS AND DISCUSSION

Mechanism and Characterization of Graft Copolymerization

In the previous publication,⁸ we have shown that the seeded emulsion polymerization with emulsified monomer feeding in the presence of seeds can prevent new particle generation. The experimental conditions must be such that the feeding rate of the monomer is slower than that of the polymerization, and the total emulsifier contents to the power of 3/2 are proportional to the amounts of feeding monomer. They comply to the following two equations:

$$W_E(\max)^{3/2} = K_1^{3/2}(Kt + dp_1^3)$$
(1)

$$W_E(\min)^{3/2} = K_2^{3/2}(Kt + dp_1^3)$$
(2)

where K_1 , K_2 , and K are the specific constants related to the seeded emulsion polymerization system, W_E is the total emulsifier amount in the system, t is the time for emulsified monomer feeding, and dp_1 is the size of the seed latex particles. For this reason, the core-shell composite polymer emulsion can be prepared according to recipes in Table I.

During the formation of the composite polymer particles, the surfaces of seeded latex particles became the loci of polymerization. Because the α -hydrogen atoms connected to tertiary carbon atom in the PEA macromolecules are more active, it is possible for them to become the sites of graft copolymerization, so that not only the initial radicals can attack the α -hydrogen atoms to produce



Figure 1 IR spectra of polymers. (a) Grafted copolymer, (b) PEA, (c) PSt.

macromolecule radicals PEA*, which initiate St to form the graft copolymers, but also the radicals can initiate St to form macromolecule radicals PSt*, which combine with PEA* to terminate or transfer to PEA macromolecules to form graft copolymers. Certainly, there are still PSt homopolymers formed on the surfaces of seed latex particles.

To demonstrate the presence of the graft copolymers, the products of two-stage emulsion polymerizations were extracted by acetonitrile and cyclohexane, respectively. There are some insoluble residues. This is the evidence that the graft copolymers were formed during the seeded emulsion polymerization. Figure 1 shows the IR spectrum for the residues (the graft copolymer), homopolymer PEA, and homopolymer PSt. In Figure 1(a), there are several characteristic peaks attributed to PEA and PSt at wavenumbers of 1730, 3060, 698, and 757 cm^{-1} . It demonstrates reversely that the St was grafted during emulsified monomer feeding.

Kinetics of Grafting Copolymerization and Locus of Seeded Polymerization

Figure 2 shows the plot for the efficiency of graft versus the emulsified monomer feeding time. The curve indicates that the efficiency of graft decreases gradually from 81–63% and then tends to remain constant during emulsified monomer feeding.

Under the condition of the emulsified monomer feeding, the emulsified liquor contains a number of monomer-solubilized micelle and monomer



Figure 2 Fraction of PSt grafted as a function of time. St/PEA = 40/60, St = 13.3 g.

droplets. There are two ways for St polymerization, namely, the polymerization on the seed latex particles or the polymerization in aqueous phase to form new particles. For a vast amount of seed latex particles present in the system, the concentration of St in the system is small enough with starved feeding that the emulsified monomer would disperse rapidly to seed latex particles and polymerize on its surface. Therefore, the new particle formation can be avoided. The surface of seed latex particles becomes the loci of graft copolymerization. The graft efficiency decreasing monotonously with the time of monomer feeding well supports the fact that the loci of polymerization are on the seed latex particles. If there are some new homopolymer particles formed in the initial interval, the graft efficiency would be very low. It is known from the slope of the curve that the instantaneous graft efficiency has a maximum value in the initial and the tendency to homopolymerization was very small. Furthermore, in the presence of new particles, the mixing free-energy of monomer dispersed onto new PSt particles is much less than that of dispersing onto seed latex particles. This would result in the possibility of the grafting reaction decreasing. On the other hand, the relationship of graft efficiency decreasing with feeding time shows that the graft efficiency varies with the areas of contacting two components. If it was independent of the contacting area, the graft efficiency, which represents the ratio of graft copolymerization to homopolymerization, would be almost constant with feeding time. Clearly, the surface of PEA latex particles is recovered increasingly by graft copolymer along with the feeding time. The interface of the two components decreases with time and results in the graft efficiency decreasing.



Figure 3 Percent of PSt grafted versus M/P ratio.

Effect of Monomer-to-Polymer Ratio on Grafting

To demonstrate further that the graft efficiency depends on the interface, a group of experiments for various ratios of monomer-to-polymer (M/P) are carried out. Figure 3 shows the relationship between the graft efficiency and M/P ratio in PEA/ PSt two-stage emulsion polymerization. The graft efficiency decreases with increasing M/P ratio. This means that the graft reactions occur mainly on the surface of the latex particles but not inside the latex particles under continuous feeding conditions. Because a higher equilibrium conversion is achieved in the reaction system, the concentration of monomer inside the seed latex particles is very low. The polymerization occurs mainly in the shell of the particles. When the M/P ratio increases, the amounts of PSt grafted and PSt homopolymers on the particle surface increases gradually. The contact area between monomer St and PEA decreases gradually. As a result, the graft efficiency decreases with increasing M/P ratio.

Figure 4 shows the plot of the total amounts of PSt grafted versus that of the PSt charged under



Figure 4 Dependence of PSt grafted on styrene charged under different M/P ratio.



Figure 5 Effect of initiator concentrations on grafting coefficients.

different M/P ratios. It was clear that the percentage of the PSt grafted decreases with increasing St charged, although the total amount of PSt grafted increases, and thus, the slope of the curve decreases. When the M/P ratio goes beyond 1.0, the slope of the curve is almost zero. Further increasing the M/P ratio will not increase the amount of the graft copolymers.

The tested properties of film formed for PEA(I)/ PSt(II) composite polymer emulsion indicates that the emulsion can form a clear film at ambient temperature when PSt(II) content is less than 50%. But when PSt(II) content is over 60%, the emulsion will not form a continuous film. This may be due to more homopolystyrene produced on the surface of the particles.

Effect of the Concentration of Initiator on the Graft Efficiency

The experiment was performed under an M/P ratio of 40/60. The effect of the concentration of initiator on the graft efficiency is shown in Figure 5. The graft efficiency decreases with increasing concentrations of the initiator in this range of initiator.

As explained previously, graft copolymerization contains both macromolecule radicals PEA* to initiate St to graft and active macromolecule radicals PSt* to transfer to PEA or terminate with PEA* to graft. When the concentrations of initiator used in the seeded emulsion polymerization are lower, they reduce both PEA* grafting copolymerization and PSt* homopolymerization simultaneously, but the radical PSt*, which are longer lived, prefer to transfer to PEA, increasing the fraction of graft copolymers, and therefore, reducing homopolymerization. On the other hand, the increase in concentration of initiator increases the tendency for PSt* to terminate to form homopolymers, but the tendency for PSt* to carry out grafting copolymerization is decreased. We propose that this is why the graft efficiency drops.

CONCLUSIONS

The composite polymer emulsion can be prepared by the seeded emulsion polymerization of St with emulsified monomer feeding in the presence of PEA seed latex. The graft copolymers were produced between two phases in the composite particles. The fact that simultaneous graft efficiency is the highest in the initial period of the seeded polymerization demonstrates that the loci of polymerization are on the surface of the seed latex particles, rather than producing the new particles.

The graft efficiency decreases with increasing monomer-to-polymer ratio. This suggests that the graft reaction occurs mainly on the surface of the seed latex particles, but not inside the particles. In addition, the graft efficiency decreases with increasing initiator concentration.

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