Grafting Mechanism in SBR–St–MMA Core–Shell Emulsion Copolymerization

JIANQING ZHAO,[1,*] HUIGEN YUAN,[2] and ZUREN PAN[2]

[1]Polymer Science and Engineering Department, South China University of Technology, Guangzhou 510641, People's Republic of China; [2]Polymer Science and Engineering Department, Zhejiang University, Hangzhou 310027, People's Republic of China

SYNOPSIS

The graft copolymerization of styrene and methyl methacrylate on SBR latex particles in the core–shell emulsion process was conducted in a 600 mL glass stirred vessel with the $BPO - Fe^{2+}$ redox initiator. The effects of the principal factors such as the polymerization temperature, monomer-to-polymer ratio, the frequency of monomer addition and conversion on the grafting degree, and the grafting efficiency were studied. The surface-controlled process model was proposed to describe the grafting mechanism. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The core–shell emulsion copolymerization is a well-known process used to control latex particle morphology. According to the polymer particle morphology, there are two main kinds of core–shell copolymers: soft core–hard shell and hard core–soft shell. Usually, polymers such as polybutadiene (PB), styrene–butadiene rubber (SBR), and poly(butyl acrylate) (PBA) are chosen as the soft components, whereas the polymers of methyl methacrylate (MMA), styrene (St), acrylonitrile (AN), vinyl chloride (VC), vinyl acrylate (VAc) and so on are chosen as the hard components. There exist graft polymers on the interface between the core and the shell. Polymers with a soft core and a hard shell are used as impact modifiers, toughened plastics, and damped oscillation materials, whereas polymers with a hard core and a soft shell are usually applied in the coating and adhesive fields.

The influences of the main process parameters such as initiator concentration, polymerization temperature, mercaptan amount, shell-to-core ratio, mode of monomer addition, and conversion on the grafting degree and the grafting efficiency are investigated and the mechanism of graft copolymerization is studied using SBR as the core and St and MMA as the shell monomers in this article. It will provide the synthetic method of polymers with a soft core and a hard shell with the theoretical foundation.

EXPERIMENTAL

Materials and Operation Conditions

The SBR latexes used were SBL-10 (St concentration is 10% by weight, from the Gaoqiao Chemical Plant) and SBL-30 (30% St of SBL composition, synthesized). The particle size of SBR latexes was controlled in the range of 0.04 to 0.12 μm and the gel content was more than 50%. Monomers, St (Gaoqiao Chemical Plant) and MMA (Ningbo Chemical Plant), were freshly distilled. The reagents such as benzoyl peroxide (BPO), ferrous salt (Fe^{2+}), and mercaptan are of CP or AR grade. A basic recipe used in the polymerization is listed in Table I.

The polymerization reaction conditions were as follows: The stirring speed of the three-curved blade impeller was 400 rpm; polymerization temperature, 70°C; pH value of the system, 10.3; and reaction time during the first graft polymerization of St, 5 h, and during the second graft polymerization of MMA, 6 h.

Table I   Basic Experimental Recipe

	First Grafting		Second Grafting	
	SBL-10	SBL-30	SBL-10	SBL-30
H_2O	6.40	3.40	3.30	2.60
SBL (solid)	1.00	1.00		
St	1.00	0.60		
MMA			0.58	0.46
BPO/M (%)	0.50	0.50	0.50	0.50
Fe^{2+}/M (%)	0.01	0.01	0.01	0.01
RSH/M (%)	0.30	0.30	0.30	0.30

M stands for monomer, and RSH, for mercaptan. Weight ratio was employed.

Polymerization Apparatus and Operation Process

The graft polymerization was conducted in a reactor as shown in Figure 1. The reactor was a cylindrical glass vessel with a dished bottom. A three-curved blade impeller was employed. SBR latex and an aqueous solution of additives were fed to the reactor and the dissolved oxygen in these materials was removed by bubbling nitrigen gas through the mixture before polymerization. The monomer St with BPO and mercaptan dissolved was charged to the reactor and the polymerization reaction was started at 400 rpm and 70°C. The stirring speed was controlled by a transformer and the polymerization temperature was maintained using a constant-temperature water bath.

The aqueous solution of additives and the monomer MMA with BPO and mercaptan dissolved were fed into the reactor after 5 h graft polymerization of St. The second graft polymerization of MMA was for 6 h.

The posttreatment included the coagulation of polymer latex, washing by distilled deionized water, and drying to the constant weight under a high vacuum at 50°C.

Analysis and Measurement

The polymer powder sample was dispersed in the mixture solvent of acetone and methyl ethyl ketone (MEK) (1 : 1 by volume) at 1 wt % concentration and extracted for 5 h at 80°C in a constant-temperature bath. The dispersion of polymer powder in the solvent mixture was separated into the real solution and deposited, adhering to the bottom of the cell by ultracentrifuging.

There are the possible following components in the polymer sample:

SBR, MS, PSt, PMMA   (nongrafts)

SBR-g-MS, SBR-g-PSt,

   SBR-g-PMMA   (grafts)

where MS is a copolymer of MMA and St. MS, PSt, and PMMA are dissolved in the solvent mixture. It is then easy to determine Wn', wt % content of the precipitate (which is not dissolved in the solvent mixture) in the sample; Gd, the grafting degree, wt % of St–MMA grafts bound to the SBR chain; and Ge, the grafting efficiency, wt % of St–MMA grafts per total polymer produced from the monomers:

$$Wn'(\%) = Wn/(Wn + Ws) \times 100 \qquad (1)$$

$$Gd(\%) = (Wn' \times Wo - W_{SB})/W_{SB} \times 100 \qquad (2)$$

$$Ge(\%) = (Wn' \times Wo - W_{SB})/$$
$$(Wo - W_{SB}) \times 100 \qquad (3)$$

where Wn (g) is the weight of the precipitate; Ws (g), the weight of the extract (which is dissolved in the solvent mixture); Wo (g), the weight of the total polymer; and W_{SB} (g), the SBR content of the polymer.

RESULTS AND DISCUSSION

Initiator System

The $BPO–Fe^{2+}$ redox system is used as the initiator. The BPO content is changed while Fe^{2+} concentration is kept constant. Then, the amount of BPO and Fe^{2+} is changed under the condition of the ratio of 55 by weight between BPO and Fe^{2+}. The variations of Gd and Ge are shown in Figure 2. Gd and Ge in-
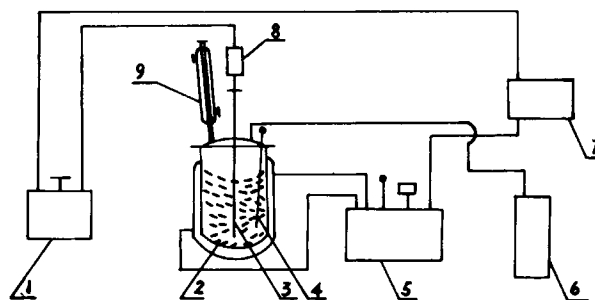

Figure 1   Schematic diagram of the experimental apparatus: (1) voltage regulator; (2) reaction vessel; (3) three-curved blade impeller; (4) thermometer; (5) thermostatic water bath; (6) N_2 gas cylinder; (7) stabilized voltage supply; (8) motor; (9) reflux condenser.
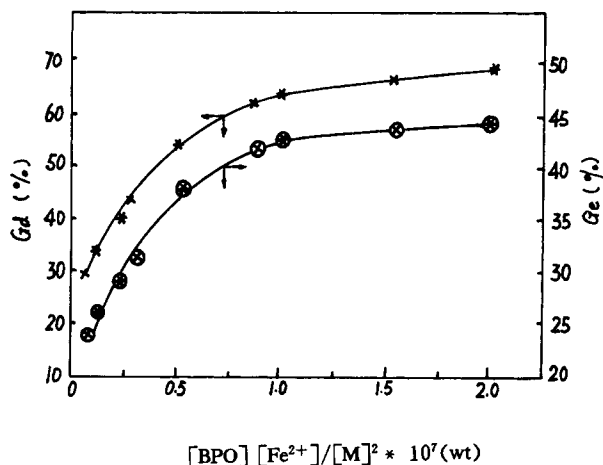
Figure 2 Gd and Ge vs. product of [BPO] and [Fe^{2+}]: (∗) only changing BPO; (×) changing BPO–Fe^{2+}.

T(°C)

Figure 3 Effect of reaction temperature on Gd and Ge: (∗) experimental data for Gd; (○) experimental data for the Ge.

crease with increase of the initiator amount in the range of a low amount of initiator and hardly vary with the change of initiator amount in the range of a high amount of initiator.

The grafting active point increases with increase of the initiator. Under our polymerization conditions, the chain length of grafts has hardly anything to do with the initiator amount.[1] With increase of the initiator charged, the number of grafting points increases and so do Gd and Ge. When more initiator is used, excessive radicals will react with each other and lessen the chain length of the grafts. Beyond the limit of the initiator amount, therefore, Gd and Ge do not increase but almost keep constant (shown in Fig. 2). They even go so far as to decrease if the amount of initiator is increased more, the same as the results reported by Manaresi et al.[2] and Merkel et al.[3]

Polymerization Temperature

Grafts are produced by transfer of radicals to the rubber chain. It is well known that the activation energy of the transfer reaction is greater than that of the propagation reaction. Gd and Ge increase when the polymerization temperature increases; the result is illustrated in Figure 3.

The very rapid decomposition of the initiator yields a high instantaneous radical concentration at the high temperature and the radicals then destroy each other, which results in decreasing the initiator efficiency and shortening the chain length of the grafts. The effect of temperature on Gd and Ge is reduced as it increases above a certain temperature. Only little variations of Gd and Ge occur when the
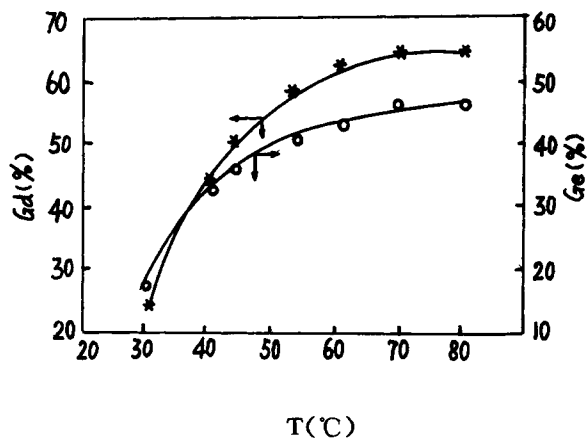
temperature increases above 50°C, due to the very low activation energy of the decomposition of the BPO–Fe^{2+} redox system used in the experiments (shown in Fig. 3). The experimental results are in agreement with those from the literature.[4]

Mercaptan Content

In the polymerization recipe, dodecyl mercaptan (RSH for short) is used as a chain-transfer agent. It is interesting to know how Gd and Ge depend on this agent. The experimental results are illustrated in Figure 4. Gd and Ge decrease with increase of the RSH content. As the RSH content increases, the transfer reaction of radicals to RSH intensifies, which shortens the chain length of the grafts and lessens the average number of grafts. Dinges and
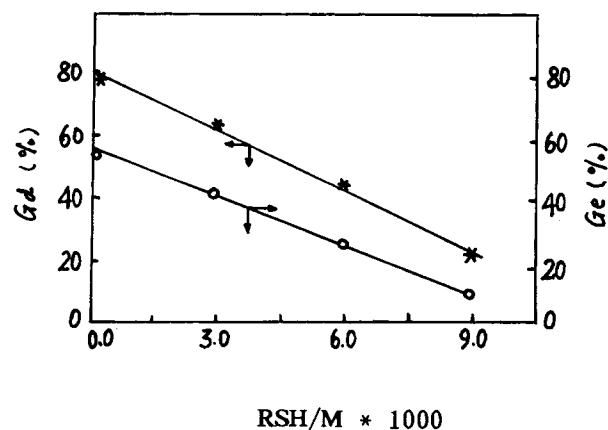

RSH/M ∗ 1000

Figure 4 Effect of mercaptan on Gd and Ge: (∗) experimental data for Gd; (○) experimental data for Ge.

Schuster[5] found similar results when they studied the graft polymerization of SBR–AN in emulsion.

Emulsifier Content

The seeding polymerization in our experimental recipes is emulsion polymerization during interval III.[6] The majority of monomers swell or reside inside the latex particles during interval III and the emulsifier charged is just sufficient to maintain colloidal stability of the particles. Above a critical surfactant concentration when more is charged, the possibility of polymerization that is free of grafting onto the SBR latex backbone increases and Gd and Ge decrease (see Fig. 5). This is the result of the formation of new micelles in the aqueous phase, which, in turn, cause the formation of a new crop of the latex particles void of SBR.

The emulsifier concentration on the seed particle surface has little effect on Gd and Ge in the absence of coagulation or renucleation of particles when the emulsifier-to-monomer weight ratio (E/M) is smaller than 2% (Fig. 5). However, Gd and Ge decrease with the increase of emulsifier when $E/M > 2\%$. It is suggested that the emulsifier charged covers mainly the SBR latex seed particles and keeps the emulsion system stable when $E/W < 2\%$ and new micelles are formed in the system that cause "homopolymerization" (free of attacking the SBR backbone) to intensify when $E/M > 2\%$.

Monomer–Polymer Ratio

The effect of the monomer–polymer weight ratio (M/P) on Gd and Ge is listed in Table II. Gd in-
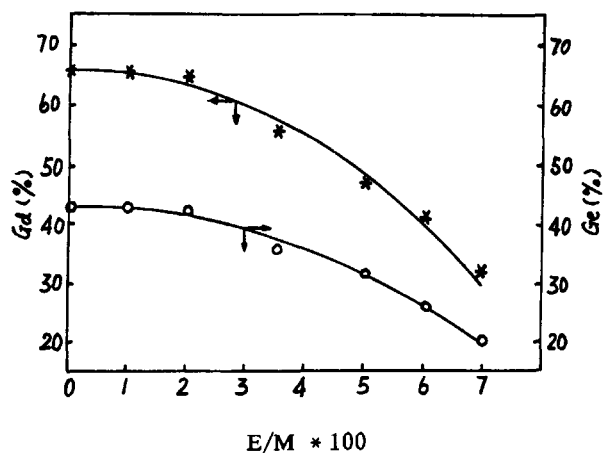

E/M * 100

Figure 5   Effect of emulsifier content (disproportional abietitate) on Gd and Ge: (*) experimental data for Gd; (○) experimental data for Ge.

Table II   Effect of the Ratio of Monomer to Polymer on Gd and Ge

	M/P				
	1.033	1.058	2.138	3.049	4.262
Gd (%)	40.74	60.86	82.21	100.25	122.05
Ge (%)	54.54	50.27	46.52	41.31	37.48

creases with increase of the M/P value. On the other hand, the opposite is observed for the effect of M/P on Ge; Ge decreases with increase of the M/P value. It is easy to accept the former result from the Gd definition and the later result may be explained on the basis of the mechanism of the surface-controlled process.

The physical model of the surface-controlled process is illustrated in Figure 6. One of the principal features of this model is that there are reaction loci on the surface of the latex particles. There is less monomer on the outerface of the SBR core at the low M/P value, so it is easier for the monomer to graft onto the rubber chains and Ge is larger. With increase of the M/P value and the development of graft polymerization, the graft layer gets thicker and thicker and the distance between the monomer and the SBR chain becomes greater and greater. Therefore, it is more difficult for graft polymerization to occur through diffusion of the monomer to the SBR chain or segment to the monomer, compared to the "homopolymerization" of monomers. This inevitably results in less and less Ge. The whole process is frequently controlled by diffusion owing to the large viscosity on the particle surface.

To verify the model, the following analytical method is used: The graft copolymer is separated into two parts in the mixture solvent of acetone and MEK. The composition of the soluble part in the solvent mixture is quantitatively determined by the IR spectrum and the analytical results are presented in Table III. The weight ratios of St to MMA (St/MMA, for short) of the soluble part are smaller than 1.8, which is the ratio of charge, except for sample no. 6-1-2, where the charge ratio is 3.0. Sample no. 3-22-2 was synthesized by a different graft order, where St was added to the polymerization system after the graft polymerization of MMA onto the SBR backbone almost comes to an end. The result is that St/MMA of the soluble part is larger than the St/MMA ratio of the charge for sample no. 3-22-2 (respectively, 3.1 and 1.8).

The experimental results demonstrate that it is easier for first-step graft polymerization than for
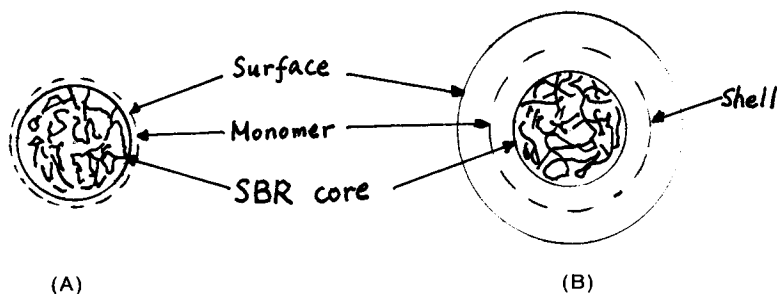
(A)   (B)

Figure 6 Physical model of the surface-controlled process: (A) small M/P value, thin shell; (B) large M/P value, thick shell.

second-step. The greater the distance between the reaction loci and the SBR chain, the more difficult is the graft polymerization through diffusion. The process of graft polymerization is a surface-diffusion-controlled process.

Monomer Addition Frequency

The effect of the monomer addition frequency on Gd and Ge is shown in Table IV. Both Gd and Ge increase with increase of the addition times of the monomer for graft polymerization of a certain monomer onto a certain SBR latex under the same conditions (comparing sample nos. 12-28-1 and 12-28-2 and sample nos. 1-11-1 and 1-11-2, respectively, under similar conversion).

The experimental phenomena can well be explained by the model of the surface-controlled process. The initial monomer concentration on the latex particle surface is higher when all the monomer is charged at the outset. The monomer concentration on the surface decreases continually and the vis-

cosity at the surface increases in steps during the reaction process, which leads to more difficult graft polymerization, because the influence of a diffusion on graft polymerization of the monomer onto SBR chains becomes more important. More uniform monomer concentration at the latex particle surface and the surface viscosity is less and changes more slowly when the monomer addition is done in successive steps, which is favorable for graft polymerization through diffusion.

Conversion

The higher the conversion of the monomer, the more the absolute grafts of the monomer on the rubber chain and the larger the Gd; however, the opposite result was found for Ge, under the same number of monomer addition steps (see Table IV). Although the changes of Ge are not obvious in the range of high conversion, it is still seen that Ge decreases with increase of the conversion.

The increasing of the conversion may lead to thickening of the latex particle shell. It is more difficult for graft polymerization through the diffusion of the monomer to SBR chains according to the model of the surface-controlled process. The pos-

Table III   Composition of Soluble Part in Acetone and MEK Determined by IR

Sample No.	St (%)	Bd (%)	MMA (%)	St/MMA
3-22-2[a]	70.1	7.5	22.5	3.12
3-22-1	53.2	6.7	40.2	1.32
4-22-1	42.5	6.9	50.7	0.84
4-22-3	37.1	5.5	57.5	0.65
4-28-2	21.2	5.1	63.9	0.49
5-6-1	49.3	4.1	46.7	1.06
5-6-3	48.1	7.7	44.1	1.09
5-20-3	53.7	7.9	38.3	1.40
6-1-2	58.6	8.1	33.3	1.76
6-8-2	47.7	15.3	36.9	1.29

[a] Different graft order: first MMA, second St.

Table IV   Effect of Frequency on Monomer Addition and Conversion on Grafting

Sample No.	No. Times	Conversion (%)	Gd (%)	Ge (%)
12-28-1	1	54.4	33.7	38.0
1-11-1	1	86.4	48.7	34.6
12-28-2	3[a]	59.4	46.0	47.7
1-11-2	3[a]	85.0	63.4	45.7

[a] The amount of monomer, initiator, and other additives was divided into equal parts three times.

sibility of "homopolymerization" of the monomer, comparatively speaking, becomes larger, so Ge will decrease. It is difficult to coagulate polymer latex and to determine the Gd and Ge of terpolymers exactly at low conversion under our polymerization conditions; the changes of Gd and Ge are not obtained in the range of low conversion. However, it may be predicted that the change of Ge is very striking in the range of low conversion in accordance with the model of the surface-controlled process suggested above. The experimental results of the literature,[2] presented in Table V, verify this prediction.

CONCLUSION

The process of graft copolymerization of SBR–St–MMA in the core–shell emulsion process is very complicated and there are many effective factors. The influences of the principal factors on the grafting degree (Gd) and the grafting efficiency (Ge) are listed in Table VI. The local viscosity at the surface

Table V   Effect of Conversion on Grafting[a]

Conversion (%)	Gd (%)	Ge (%)
2.43	17.1	84.0
4.07	24.0	76.7
5.25	20.3	48.0
8.09	19.9	30.4
12.92	24.9	25.4
16.69	34.3	30.9
21.88	30.3	19.7
24.88	37.5	23.9

[a] Data from the literature[2] on grafting St to PB.

Table VI   Qualitative Effect of Various Factors on Grafting

Factors	Gd	Ge
Initiator content[a] ↑	↑	↑
Reaction temperature ↑	↑	↑
Mercaptan content ↑	↓	↓
Emulsifier content[b] ↑	↓	↓
Monomer-to-polymer ratio ↑	↑	↓
No. times of monomer addition ↑	↑	↑
Conversion ↑	↑	↓

[a] $I/M < 0.074\%$; I/M for initiator-to-monomer weight ratio.
[b] $E/M > 2.0\%$; E/M for emulsion-to-monomer weight ratio.

of the latex particles is quite large and the graft polymerization is a surface-controlled process.

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