

Grafting Behavior of *n*-Butyl Acrylate onto Poly(butadiene-*co*-styrene) Latexes

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ABSTRACT: The radical-induced grafting of *n*-butyl acrylate (BA) onto poly(butadiene-*co*-styrene) [P(Bd-S)] latexes during seeded emulsion polymerization was studied. This P(Bd-S)/PBA rubber/rubber core/shell latex system exhibited unique grafting behavior as compared to other extensively studied rubber/glass core/shell latex systems, such as poly(butadiene-*co*-styrene)/poly(methyl methacrylate) [P(Bd-S)/PMMA], poly(butadiene-*co*-styrene)/polystyrene [P(Bd-S)/PS] and poly(butadiene-*co*-styrene)/poly(acrylonitrile) [P(Bd-S)/PAN]. These composite latexes were characterized by the formation of a highly grafted/crosslinked P(Bd-S)/PBA interphase zone generated during the seeded emulsion polymerization process. Although both of the individual core and shell polymers studied were "soft" themselves, the resulting P(Bd-S)/PBA composite latex particles were found to be rather "hard." The formation of the interphase zone was studied by using techniques such as solvent extraction, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 511–523, 1997

Key words: latex particles; SBR latex; grafting; crosslinking; *n*-Butyl acrylate

INTRODUCTION

Grafting in polybutadiene (PBd)-based seeded emulsion polymerization systems has been extensively studied. However, because a rubber/glass core/shell composite latex system is of general industrial interest, almost all of these studies used methyl methacrylate (MMA),¹ styrene (S),² styrene/acrylonitrile (S/AN),³ or S/MMA⁴ as the second stage monomers. In these applications, PBd-based latex particles are usually used as impact modifiers or toughening agents which are dispersed in a plastic matrix. The degree of grafting of the shell polymer onto the poly(butadiene-*co*-styrene)[P(Bd-S)] core latex particles has proven to be very important in obtaining the maximum benefit from the rubber phase in these applications.⁵

On the other hand, glass/rubber^{6,7} or rubber/rubber^{8,9} structured latexes have been found to be very useful in the production of self-supported rubbery materials. However, the rubbery polymers used in all of these studies, for either the core or the shell materials, were usually acrylic polymers. A rubber/rubber core/shell latex system involving PBd-based elastomers, such as a poly(butadiene-*co*-styrene)/poly(butyl acrylate)-[P(Bd-S)/PBA] latex system, has rarely been reported.

P(Bd-S) (so-called SBR rubber) is a widely used elastomer. The most common method used to process P(Bd-S) latex is a coagulation-vulcanization process, where the crosslinking process for the P(Bd-S) polymer is carried out during the shaping stage of the coagulated P(Bd-S) latex. This procedure requires a very low degree of crosslinking of the original P(Bd-S) latex before coagulation, and the vulcanization temperature is usually quite high. These kinds of conditions are not suitable in circumstances where P(Bd-S) is used

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in the form of an elastomeric film cast directly from the latex under mild temperature conditions. In these applications, a certain degree of pre-crosslinking within the latex particles (i.e., intraparticle crosslinking) is required to form an elastomeric film. However, crosslinking within the latex particles would hinder the interdiffusion of polymer chains between adjacent particles during the film formation process. A P(Bd-S) latex with a high degree of crosslinking in the latex particles usually cannot form a strong elastomeric film by simply casting the latex. The properties of the latex film might be improved through the modification of the pre-crosslinked P(Bd-S) latex particles using another linear or lightly crosslinked rubbery polymer to form a core/shell structured latex particle. Obviously, the grafting behavior of the second-stage rubbery polymer onto the P(Bd-S) core latex particles would be important in influencing the properties of the final latex polymer film.

In this study, it was found that the grafting behavior of the second stage PBA polymer onto the P(Bd-S) seed particle turned out to be crucially important in determining film properties. The resulting P(Bd-S)/PBA composite latex particles, at certain core/shell ratios, exhibited an unexpected degree of hardness, although both polymers involved are soft by themselves. A series of studies indicated that a highly grafted/crosslinked P(Bd-S)/PBA core/shell interphase zone was developed during the second stage polymerization of butyl acrylate using P(Bd-S) as the seed. The thickness of the interphase zone and/or the amount of the second stage PBA polymer used to form this interphase zone was primarily dependent on the gel fraction of the P(Bd-S) seed particles. The lower the gel fraction of the seed particles, the higher was the relative amount of PBA which would be used to form this interphase zone. It appeared that no pure PBA phase could be formed in the composite latex particles during the formation of the interphase zone. The films cast from the latexes at this stage, i.e., before the formation of the interphase zone was completed, were noncontinuous and brittle due to the tremendously increased degree of crosslinking in the core/shell interphase zone, which is present at the surface layer of the latex particles. Only after this "Soft polymer + Soft polymer = Hard polymer" stage (i.e., the development of the core/shell interphase zone) was complete, could a pure PBA shell be formed on the outer surface of the compos-

Table I Recipe Used for the Preparation of the P(BD-S) Seed Latex

Component	Weight (g)
Butadiene	45.0
Styrene	5.0
Triton X-200 ^a	0.1
Triton X-45 ^b	0.3
Potassium persulfate	0.4
Potassium metabisulfite	0.5
<i>n</i> -Dodecyl mercaptan	0.1
Distilled-deionized (DDI) water	100.0

^a Sodium octyl phenoxy tetra-ethoxy sulfonate; Union Carbide.

^b Octyl phenoxy penta-ethoxy ethanol; Union Carbide.

ite latex particles. The latex film then became sticky and elastic.

EXPERIMENTAL

Materials

The monomers used, i.e., styrene (S), *n*-butyl acrylate (BA), methyl methacrylate (MMA), *iso*-butyl methacrylate (*i*-BMA) (all Fisher Scientific) and butadiene (Matheson Gas Products, Inc.) were treated by passing them through inhibitor-removal columns. Sodium octyl phenoxy tetra-ethoxy sulfonate (Triton X-200) and octyl phenoxy pentaethoxy ethanol (Triton X-45) surfactants (Union Carbide) were used as received. Potassium persulfate (KPS), ammonium persulfate (APS), potassium metabisulfite (PMBS), all analytical grade (Fisher Scientific), and three azo-type initiators, 4,4'-azobis(4-cyanopropanoic acid) (V-501), 2,2'-azobis(2-amidinopropane), dihydrochloride (V-50), and 2,2'-azobis(isobutyronitrile) (V-60) (all analytical grade, Waco Pure Chemical Industries, Ltd.), and normal dodecyl mercaptan (*n*-DDM), (commercial grade, Pennwalt Chemicals), were used as received. Distilled-deionized (DDI) water was used in all polymerization.

Emulsion Polymerization

Preparation of P(Bd-S) Seed Latexes

Emulsion polymerizations to prepare P(Bd-S) seed latexes were carried out in 250-mL pressure bottles at 60, 65, and 70°C, which were rotated end-over-end at 40 rpm in a bottle polymerizer unit according to the recipe shown in Table I. The

Table II Recipes for the Second Stage Polymerization Using P(Bd-S) as Seed Latexes

Component	Weight (g)					
	Run 1	Run 2 ^b	Run 3	Run 4	Run 5	Run 6
P(Bd-S) seed (20 % solids) ^a	50.0	50.0	50.0	50.0	50.0	50.0
<i>n</i> -Butyl acrylate	10.0	10.0 : 50.0	10.0	—	—	—
<i>iso</i> -Butyl methacrylate	—	—	—	10.0	—	—
Methyl methacrylate	—	—	—	—	10.0	—
Styrene	—	—	—	—	—	10.0
Ammonium persulfate	0.10	0.1 : 0.5	—	—	—	—
Potassium metabisulfite	0.10	0.1 : 0.5	—	—	—	—
Thermal initiator ^c	—	—	0.07	0.07	0.07	0.07
Distilled-deionized water	30.0	30 : 150	30.0	30.0	30.0	30.0

^a Gel fractions of P(Bd-S) seed latexes: run 1, 2% and 47%; run 2, 6% and 87%; runs 3–6, 57%.

^b Second stage BA monomer: 10 g for 87% gel-fraction P(Bd-S) seed; 50 g for 6% gel-fraction seed. The same amount of initiators and DDI water were also used.

^c Runs 3–6 were carried out at 70°C using the thermal initiators, potassium persulfate (KPS), 4,4'-azobis(4-cyanopropanoic acid) (V-501), 2,2'-azobis(2-amidinopropane)dihydrochloride (V-50), and 2,2'-azobis(isobutyronitrile) (V-60), respectively.

gel fraction of the P(Bd-S) latex was controlled by terminating the polymerization at desired conversions. The remaining monomers in the latexes were removed immediately after the termination of the polymerization by flash evaporation, which was repeated at least three times. Distilled-deionized (DDI) water was added to the latexes between the evaporation processes.

P(Bd-S) Latex Seeded Emulsion Polymerization

Using P(Bd-S) as seed latex, a series of second-stage polymerizations were carried out in a four-neck 250-mL flask by using recipes run 1 to 6 in Table II. Runs 1 and 2 were carried out at 40°C using a redox initiator system comprised of ammonium persulfate/potassium metabisulfite (APS/PMBS). Runs 3 to 6 were carried out at 70°C using the thermal initiators potassium persulfate (KPS), V-501, V-50, and V-60, respectively. All of the initiators used were water-soluble except for the V-60. Two modes of addition of the second stage monomers to the seed latexes were used: 1) an equilibrium-swelling process was employed for all runs except run 2, in which the monomer was allowed to swell the seed particles with tumbling for 24 h at room temperature before the seeded emulsion polymerization was started; and 2) a semi-continuous process was utilized for run 2, in which 5 wt % of the monomer and initiator were added at the beginning of the second stage polymerization, with the remaining monomer and initiator being added continuously to the reaction flask at a constant rate of 0.028 mL/min.

Measurement of the Gel Fraction and Grafting Efficiency using a Solvent Extraction Method

The gel fractions (GF) of the seed latexes were determined by a solvent extraction method. This method involved adding 0.2 g of polymer film, which was cast at room temperature and dried under vacuum for 10 h, to 25 mL toluene and mixing for 24 h with end-over-end tumbling at room temperature. The weight of dissolved polymer, *W*, was determined gravimetrically from the solids content in the supernatant after centrifugation at 5,000 rpm for 30 min at ambient temperature. The gel fraction (GF) is calculated by

$$\text{GF (\%)} = \frac{0.2 - W}{0.2} \times 100 \quad (1)$$

The grafting efficiency (GE) of the second stage polymer, i.e., PBA, onto the P(Bd-S) seed latex particles, represents the fraction of grafted PBA compared to the total amount of PBA in the P(Bd-S)/PBA seed particle. Specifically, for the P(Bd-S)/PBA composite latex with a 1 : 1 (w/w) core/shell ratio, 0.2 g of polymer film sample was added in acetone [a good solvent for the linear part of PBA and a nonsolvent for P(Bd-S)] and treated in the same manner as described previously for the determination of gel fraction. The total amount of PBA was 0.1 g in this system. The grafting efficiency (GE) is given by

$$\text{GE (\%)} = \frac{0.1 - W_1}{0.1} \times 100 \quad (2)$$

where W_1 is the amount of the PBA dissolved in the supernatant. Acetone was used for the GE measurements for all of the composite films except for the polystyrene-based system, in which methyl ethyl ketone was used.

In order to determine the gel fraction of the P(Bd-S) seed particles after the second stage polymerization (GF'), a 0.2 g sample of a 1 : 1 P(Bd-S)/PBA core/shell latex film was extracted with toluene (a good solvent for the linear part of both P(Bd-S) and PBA). The soluble amount (W') of both P(Bd-S) and PBA obtained from toluene extraction was used along with results obtained from the acetone extraction experiment in order to estimate GF' using the following equation:

$$GF' (\%) = \frac{(0.2 - W') - (0.1 - W_1)}{0.1} \times 100 \quad (3a)$$

which simplifies to:

$$GF' (\%) = \frac{0.1 - W' + W_1}{0.1} \times 100 \quad (3b)$$

The first term in eq. (3a) represents the insoluble amount after the toluene extraction [which includes both grafted PBA and crosslinked P(Bd-S)]; whereas the second term represents the amount of PBA involved in the grafting reaction with the seed. The weights of core polymer and shell polymer in the 0.2 g sample are 0.1 g each.

RESULTS AND DISCUSSION

P(Bd-S) Seed Latex

The P(Bd-S) seed latexes were prepared by emulsion polymerization. The polymerizations were carried out at 60, 65, and 70°C using the recipe shown in Table I. The gravimetric conversion versus time curves for each reaction temperature are shown in Figure 1. As expected, the overall polymerization rate increased with increasing temperature. The extent of the crosslinking of the P(Bd-S) latexes was controlled by terminating the polymerization at certain conversions.

Appearance of Latex Films

Films were cast on glass plates at ambient temperature. P(Bd-S) latexes (GF, 6% and 57%) and a PBA homopolymer control latex were able to form continuous elastomeric films. Both P(Bd-S)

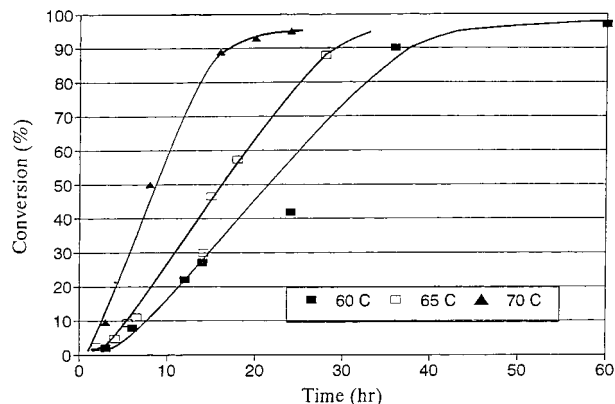


Figure 1 Overall percentage of monomers converted versus reaction time for SBR latexes prepared at 60, 65, and 70°C.

(GF = 6%) and PBA latex films exhibited a significant degree of tackiness, as expected. Because both components, i.e., P(Bd-S) and PBA, were originally soft, a P(Bd-S)/PBA core/shell latex was also expected to be able to form a soft elastomeric film. However, contrary to this expectation, in spite of varying the conditions of the second stage polymerization of BA using P(Bd-S) seed, e.g., polymerization temperature, mode of addition of the second stage BA monomer, and the addition of chain transfer agent, the films formed from these latexes were cracked and brittle, and did not exhibit any elasticity. Obviously, the resulting composite latex particles do not have a simple P(Bd-S)PBA core/shell structure since a continuous, soft elastomeric film should be formed otherwise. A possible reason, if not the only one, for the hardening of an originally soft polymer by itself is the formation of a highly crosslinked network in the polymer structure. One of the methods that is usually used to evaluate the extent of crosslinking is the gel fraction measurement.

Gel Fraction Measurements During the Second-Stage Polymerization

Figure 2 shows the changes in the gel fraction of the latexes obtained during the second stage polymerization along with the conversion of the BA monomer using the run 1 recipe shown in Table I. At the beginning of the reaction, the gel fractions shown in Figure 2 (at time = 0) are those for the P(Bd-S) seed latex. For both the low and high gel fraction P(Bd-S) seeds (i.e., LG and HG), the gel fraction increased rapidly immedi-

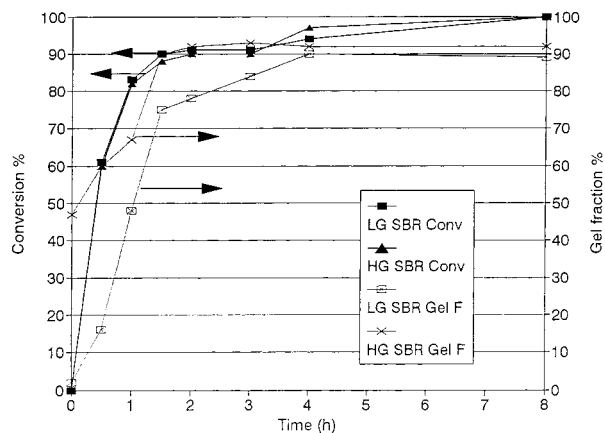


Figure 2 Percentage of second-stage BA monomer converted and total gel fraction of the latex versus reaction time using the P(Bd-S) seed latex polymerized to 27% (LG SBR, 2% gel-fraction) and 57% (HG SBR, 47% gel-fraction) conversions.

ately after starting the reactions, and again increased quickly after the conversion of BA reached 70 to 80%. The final gel fractions were $\sim 90\%$ when the reaction was finished. The increase in the gel fraction occurred during the polymerization of the second stage BA monomer. The gel fraction for PBA homopolymer obtained in a parallel experiment via the emulsion polymerization of BA under the same conditions used for the second stage polymerization was 16%. The gel obtained from the homopolymerization of butyl acrylate was a result of chain transfer reactions at the α -hydrogens in the PBA polymer chains during the polymerization. When P(Bd-S) latex was used as the seed latex, large amounts of double bonds and allylic hydrogens were present in the P(Bd-S) copolymer chains. These moieties are very active in the radical reactions which occur during the second stage polymerization of BA. Any of these reactions, e.g., chain transfer reactions to the allylic hydrogens and direct attack on the vinyl double bonds in P(Bd-S), could lead to crosslinks or grafts on the P(Bd-S) copolymer chains. These two kinds of reactions compete with the propagation reaction of BA monomer during the entire polymerization process. In the region up to 60% conversion (time: 0–0.5 h), the gel fraction for both the LG and HG P(Bd-S) seed systems increased 17 and 14%, respectively. In sharp contrast, in the region from 70 to 90% conversion (time: 0.8–1.5 h), which represents only a 20% increase in conversion, the gel fractions increased 50 and 20% for the LG and HG P(Bd-S) seed

systems, respectively. The rapid increase in gel fraction in this high conversion region was due to the much lower BA monomer concentration and/or the higher concentration of polymers, which makes the grafting/crosslinking reactions resulting from the chain transfer reactions to the existing polymer chains more competitive compared to propagation reactions.

Influence of the Type of the Second Stage Monomer and Initiator on the Extent of Grafting/Crosslinking

By comparing the results for the P(Bd-S)/PBA latex system obtained in this article with results from P(Bd-S)/PMMA and P(Bd-S)/PS systems in the papers published by other researchers,^{1–3} it was found that the BA system exhibited a higher grafting efficiency than those determined for the MMA or S systems. Furthermore, contradictory results on the influence of the type of the initiator on the grafting have been reported in some studies, for example, whether an azo-type initiator, such as AIBN (V-60), will induce any grafting reaction or not.^{10–12} Since the methods used to measure the grafting efficiency and the reaction systems employed for each of the above-mentioned studies were not completely the same, it was necessary to carry out the polymerizations under the same conditions to compare these different systems.

Comparable second-stage polymerizations were carried out according to the recipes in runs 3–6 shown in Table I using the equilibrium swelling process described in the Experimental section. Figure 3 shows the results for the grafting effi-

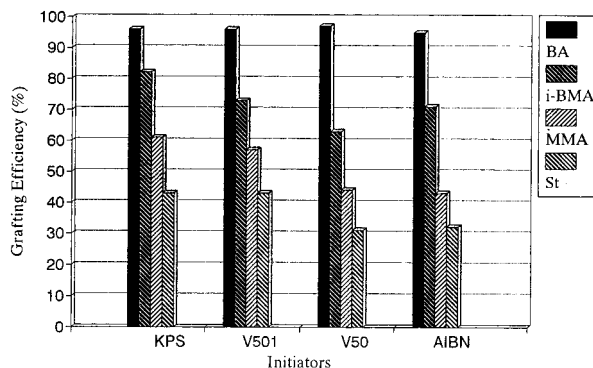


Figure 3 Grafting efficiency (GE) for a variety of second stage polymers onto P(Bd-S) latex seed particles after seeded latex emulsion polymerization using a variety of initiators.

ciencies of each system obtained from acetone extraction experiments (methyl ethyl ketone for the S system since acetone is a nonsolvent for PS). It is quite clear that BA does exhibit a higher GE value than any of the other systems, regardless of the type of initiator used. Three types of free radicals can be formed from S, MMA, *iso*-BMA, and BA monomers and the stabilities of the radicals are in the order of: $S^{\bullet} > MMA^{\bullet} \sim iso\text{-BMA}^{\bullet} > BA^{\bullet}$.¹³ This order also reflects the reverse order of chain transfer reactions, i.e., S monomer has the highest tendency to be initiated to form an S radical, while BA radicals have the highest tendency to transfer to existing polymer chains to form grafting sites. This is understandable from the large difference in the chain transfer constants to polymer for these three types of radicals.¹⁴ As mentioned before, a gel fraction of 16% was found for a PBA homopolymer system prepared by batch polymerization. In the presence of the pre-formed P(Bd-S) crosslinking network, the chain transfer reactions of BA radicals to the α -hydrogens in the PBA polymer chains could also lead to the formation of an interpenetrating polymer network (IPN), i.e., P(Bd-S)-*ipn*-PBA, a special form of grafting in which there might not be direct chemical bonding between P(Bd-S) and PBA. It is difficult to distinguish between these three structures, i.e., chemically grafted PBA, IPN PBA, and an independent PBA crosslinked network, using the solvent extraction technique because none of these structures are soluble in the solvent. Nonetheless, considering the presence of large amounts of allylic hydrogens and residual double bonds in the P(Bd-S) seed particle, the probability of forming a completely independent PBA crosslinked network should be small. This suggests that the high GE for the BA system is indeed caused by either chemical grafting or physical chain entanglements instead of an independent PBA crosslinked network.

By comparing *i*-BMA with the MMA monomer system, it is evident that systems including *i*-BMA exhibited higher GE values than those for the MMA systems, although the chain transfer tendencies for the radicals generated from both kinds of monomers are similar to each other. This suggests that the mobility of the second stage polymer chains could also play a role in influencing the grafting reaction. It has been shown in Figure 2 that the gel fractions of the seeded emulsion polymerization system increased rapidly in the high monomer conversion region, where the polymer concentration in the latex particles is

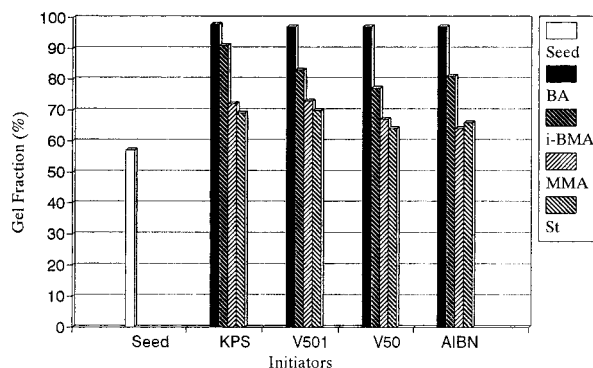


Figure 4 Gel fraction (GF) of composite latex particles prepared via a P(Bd-S) seeded emulsion polymerization with different second stage monomers.

high. In this instance, the mobility of a polymer chain is correlated to its glass transition temperatures (T_g). P(*i*-BMA) has a T_g of 53°C, which is lower than the polymerization temperature (70°C). On the other hand, PMMA has a T_g of $\sim 105^\circ\text{C}$, which is much higher than the polymerization temperature. Although the actual T_g of the polymer in a monomer-swollen particle is lower than that for the pure polymer, a big difference in the mobilities of these two types of polymer chains would be expected in the high conversion region of the polymerization, where the polymer/monomer ratio in the monomer-swollen particles is high.

Figure 4 shows the change in the gel fraction (GF) of the composite latex system after the second stage polymerization as determined by the toluene extraction method. The results were similar to those seen in Figure 3 for GE. The BA system showed the greatest increase in the GF of the composite latex system, from the original 57% GF for the P(Bd-S) seed to a value $> 95\%$. The other three monomer systems also exhibited an increase in the GF of the composite latex system compared with the seed latex. Because these results obtained from the toluene extraction experiment reflect the GF for the entire composite latex particles, it would be interesting to investigate the changes in the GF for only the P(Bd-S) seed latex after the second stage polymerization for each system. In most of the previous grafting studies carried out by other researchers, high gel fraction ($> 90\%$) PBd-based seed latexes have been used. In those cases, the change in the GF of the seed latexes after the seeded emulsion polymerization could not be observed.

Figure 5 shows the increase in the gel fraction

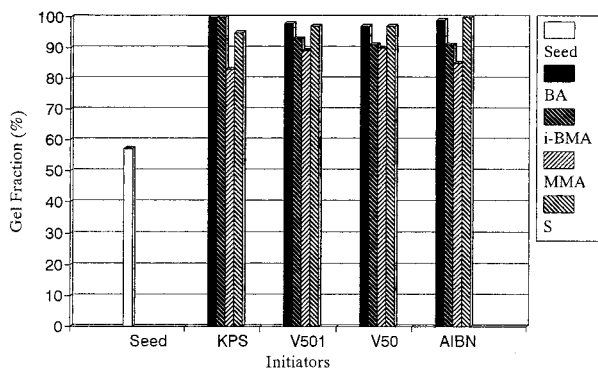


Figure 5 Changes in the gel fraction (GF) of P(Bd-S) seed latexes after the second stage seeded emulsion polymerization was complete for different monomer and initiator systems.

of the P(Bd-S) seed latex itself (GF') after the seeded emulsion polymerization was complete, calculated from the results obtained from both acetone (methyl ethyl ketone for S system) and toluene extraction experiments according to eq. (3b) shown in the experimental section. The gel fraction of the P(Bd-S) seed latexes increased from the original 57% to > 97% for the BA monomer system regardless of the type of initiator used. The other two acrylate monomer (*i*-BMA and MMA) systems exhibited increases in the gel fraction of the P(Bd-S) seed latex to ~ 85–93%. S monomer also showed significant increases to > 95%.

As mentioned previously, controversial results concerning the influence of the type of initiator on grafting has been described in the literature. It was claimed that azo-type initiators, e.g., AIBN, could not initiate any grafting reactions in solution polymerization systems. The results shown in Figures 3 and 4 demonstrate that the P(Bd-S)/PBA system exhibited almost the same high value of GE and GF, regardless of the initiator type. For the other three polymer pairs, the persulfate (KPS) initiator did show notably higher values of GE and GF than did the other three azo-type initiators. Nonetheless, there were significant increases in either GE or GF for all of the azo-type initiators. These results suggested that the grafting/crosslinking reactions could be initiated not only by the primary radicals, but also by chain transfer or direct attack from the propagating polymer radicals to those allylic hydrogens and vinyl double bonds present in the P(Bd-S) seed latex. In the case of the BA second-stage monomer system, the high chain transfer to polymer concealed the influence of the type of initia-

tor. For the other three systems with lower chain transfer tendencies, the influence of the type of initiator could be observed.

Figure 6 shows the relationship between GE and the PBA/P(Bd-S) shell/core ratio. Two types of P(Bd-S) seed latexes with high and low gel fractions, i.e., HG SBR with 87% GF and LG SBR with 6% GF, were used. In both cases, the GE remained at values between 80% to 90% before the shell/core ratio reached ~ 1.0 for the HG SBR seed series, and 1.5 for the LG SBR seed series. Note that in this figure, the units for the X-axis are expressed as a shell/core ratio (not a core/shell ratio as is normally used) for convenience. The GE values decreased after these two values of the shell/core ratio are reached, i.e., 1.0 and 1.5 for the HG and LG SBR series, respectively. These two ranges could indicate the beginning of the formation of separate PBA phases in the composite particles. In these PBA phases, the post-formed PBA chains were not grafted to any great extent to the P(Bd-S) chains.

Morphological Observations of the Development of the Grafting/Crosslinking Interphase Zone Using Transmission Electron Microscopy (TEM)

In order to investigate the development of the core/shell interphase zones, the second stage polymerizations of BA using P(Bd-S) as seed were carried out according to the run 2 recipe shown in Table II. The addition rate of BA monomer was controlled to maintain monomer-starved conditions, i.e., the instantaneous conversion of BA monomer as detected by gas chromatography

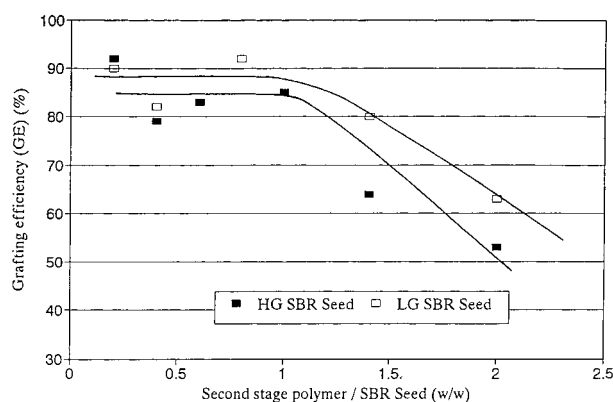


Figure 6 The grafting efficiency (GE) of butyl acrylate grafted on P(Bd-S) seed latexes (HG or LG SBR seed) versus shell/core ratios as determined by solvent extraction measurements.

(GC) reached 100% during the entire addition period. In order to investigate the influence of the gel fraction of the P(Bd-S) seed latex particles on the development of the core/shell interphase zone, two series of second stage polymerizations were carried out with different gel fractions (6% and 87%) of the P(Bd-S) seed latexes, which are referred to as LG SBR and HG SBR, respectively. Latex samples were taken from the reactor at various times (i.e., varying P(Bd-S)/PBA ratios) during the addition process of BA monomer.

Figure 7 shows transmission electron micrographs obtained for both the LG (left) and HG (right) series. These particles were stained with osmium tetroxide (OsO_4). Phosphotungstic acid (PTA) was used as a background stain in some cases. From the LG SBR series shown in the left half of Figure 7, it was noted that as the second stage polymerization progressed, some nonuniform domains with different contrast [Fig. 7(B-L)] were developed around the original spherical seed particles [Fig. 7(A-L)]. Because OsO_4 can only stain the polybutadiene regions through reactions with the residual double bonds present in polybutadiene (shown as the dark regions within the particles), the presence of lighter domains suggests that there were lower concentrations of double bonds in these regions. With the further progression of the second stage polymerization, as shown in Figure 7(C-L), a third light domain could be observed. These domains are believed to represent pure PBA phases. Through these observations, it is believed that the gray domains shown in Figures 7(B-L) and 7(C-L) actually represent the core/shell interphase zones. These interphase zones are comprised of PBA grafted onto crosslinked P(Bd-S) networks. Because the double bonds in these domains were "diluted" by the incorporated PBA, the color in these regions was found to be gray instead of dark black, as was seen in the center regions of the particles. The image of the 1/0.8 core/shell ratio latex particles shown in Figure 7(B-L), where the pure PBA phase can not be observed yet, indicates that the amount of PBA consumed to form these core/shell PBA-graft-P(Bd-S) interphase zones could represent almost the same weight as the LG-SBR seed particles. It seems that only after the formation of these highly grafted interphase zones could it be possible to form some separated PBA domains, as shown in Figure 7(C-L) in which the core/shell ratio was 1/1.5. Figure 7(D-L) shows complete coverage of the P(Bd-S) seed by the PBA shell. Here, the core/shell ratio was 1/3 and the

shell is so thick that the P(Bd-S) core could not be stained by OsO_4 within the treatment period (6 h).

A similar situation could also be observed in the case of the HG SBR seed latex [Fig. 7(A-R)]. Compared to the LG SBR latex shown in Figure 7(B-L), the deformation of the HG SBR latex particles shown in Figure 7(B-R), caused by the formation of the interphase zones, was not that obvious. In this case, only a thin gray ring around the seed particles could be observed. Another difference was that the core/shell ratio [Fig. 7(C-R)] at which the visible PBA phases started to form was lower than that for the case shown in Figure 7(C-L). The core/shell values shown in Figure 7(B-R) (1/0.5) and Figure 7(C-R) (1/0.7) indicate that the amount of PBA consumed in forming the interphase zones for this higher gel fraction seed was about half the weight of the HG SBR seed latex particles.

The results shown in Figure 7 suggested that the extent of the formation of the core/shell interphase zone was very much influenced by the gel fraction of the P(Bd-S) seed particles. The lower was the gel fraction of the seed particles, the higher was the mobility of both the P(Bd-S) and the PBA chains, and the higher was the probability for both types of chains to interact with each other, which led to the formation of a relatively thicker interphase zone. It is also observed that the interphase zone is developed non-uniformly, especially in the low gel fraction P(Bd-S) seed system. This observation suggests that the entering oligomeric free radicals, and hence the grafting sites, do not distribute uniformly within the particle.¹⁵

P(Bd-S)/PBA Core/Shell Interphase Zone Hardening Process—Comparison with P(Bd-S)/PMMA Core/Shell Systems via Platinum Shadowing TEM Studies

The high degree of crosslinking in the interphase zone could greatly harden the particle surfaces, which makes film formation from these particles very difficult. Platinum (Pt)-shadowing TEM studies are useful in evaluating the hardness of individual latex particles. In this technique, latex samples were first dried on a carbon-coated TEM grid. A very thin layer of Pt was then coated onto these particles in a vacuum chamber at a certain angle, as shown schematically in Figure 8. The shadows of the particles that are coated by the Pt would appear as a white shadow in a TEM photograph. In this way, soft particles that would

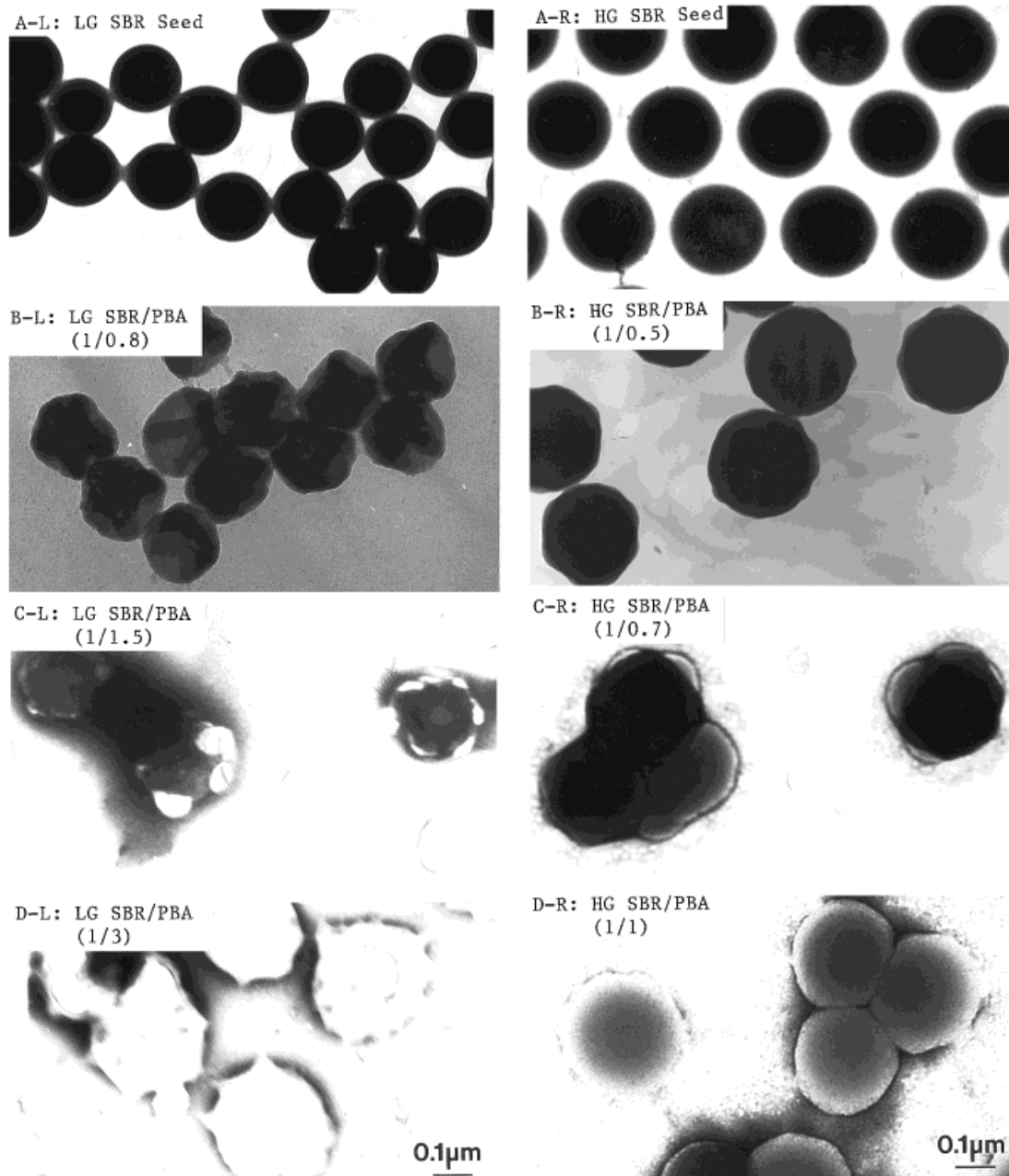


Figure 7 TEM micrographs (cold stage) of LG-SBR/PBA (left) and HG-SBR/PBA (right) composite particles with different core/shell ratios obtained during the second stage semi-continuous polymerization.

collapse during the sample preparation drying process would display a small shadow, as shown in Figure 8(A). In contrast, a hard particle would retain its spherical shape during drying and would exhibit a large shadow, as shown in Figure 8(B). The distance between the bottom of the particle and the intersection of the particle center line with the shadow line (H), can be calculated by the shadow length (L) and the Pt coating angle

(θ), which was 27° in this experiment. At this small shadowing angle, the difference between the H value and the real particle height is very small (H is slightly larger than the real particle height); thus, H is used to represent the particle height in this study. The diameter of the particle (R) on the grid can be measured directly from the micrograph. The H/R ratio can be used to represent the hardness of the particle. A hard particle

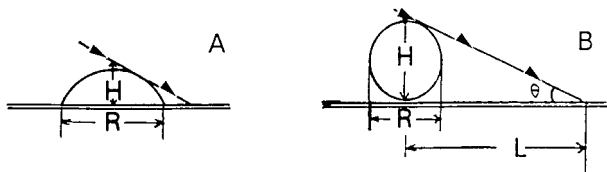


Figure 8 Schematic illustration of Pt-shadowed transmission electron micrograph (TEM) for: (A) soft and (B) hard latex particles.

would give a H/R value of one (or slightly higher than one for a hard spherical particle), while a soft particle would exhibit a small H/R value. For comparison, two series of latex samples were investigated in parallel by the semicontinuous emulsion polymerization of BA or MMA monomers onto a low GF (27%) P(Bd-S) seed latex. Because the polymerizations were carried out under monomer-starved conditions, latex samples with different core/shell ratios could be obtained by taking latex samples from the reactor during the second stage polymerization.

As shown at the top of Figure 9, the soft P(Bd-S) seed latex particle exhibits a very small shadow that can barely be seen. The H/R ratio is only 0.33. Starting from this soft seed particle, the left half of Figure 9 shows an increase in the shadow length with increasing amounts of the second-stage PMMA polymer. H/R reaches 1 at a P(Bd-S)/PMMA ratio of 1 : 0.6. This phenomenon had been demonstrated in some previous studies by other researchers and was considered to be caused by the complete coverage by a hard PMMA shell around the soft P(Bd-S) core. Following this reasoning, a soft PBA shell, if formed on the soft P(Bd-S) core, should not lead to an increase in H/R because both polymers are soft. However, the results shown in the right half of Figure 9 for the P(Bd-S)/PBA system were quite similar to those of the P(Bd-S)/PMMA system. H/R reached 0.95 at a P(Bd-S)/PBA ratio of 1 : 0.8. This tendency could be seen more clearly by plotting the H/R ratio as a function of the shell/core ratio (the shell/core ratio, instead of the core/shell ratio, was used for convenience), as shown in Figure 10. It was observed that the H/R ratio increased with an increasing shell/core ratio for both systems. The increase in the H/R values for the P(Bd-S)/PBA system was only slightly slower than that found for the P(Bd-S)/PMMA system before the shell/core ratio reached 1 : 1. For the P(Bd-S)/PMMA system, the H/R ratios remained at 1.1 after the shell/core ratio reached 0.6 : 1.

Interestingly, for the P(Bd-S)/PBA system, the H/R ratio approached 1 at a 1 : 1 shell/core ratio, and then dropped down at higher shell/core ratios. This indicates that the increase in H/R before reaching a 1 : 1 shell/core ratio was due to the formation of the highly grafted/crosslinked core/shell interphase zone. The increase in the crosslinking density in the interphase zone resulted in a hardening of the originally soft P(Bd-S) particle. A PBA phase with much less grafting/crosslinking began to form as polymerization was continued to higher shell/core ratios. The PBA phase formed at this stage was soft and would collapse during the drying process when the TEM sample was prepared, which consequently led to a decrease in the H/R ratio. The onset of this decrease in H/R at about a 1 : 1 shell/core ratio indicates that the formation of the interphase zone was almost complete, after which a pure PBA shell will start to form. This result is in good agreement with the results obtained by the morphological observations shown in Figure 7. Comparing these results with those shown in Figure 6 for the LG SBR seed system, it can be found that the GE is still very high in the shell/core ratio range of 1 : 1, where pure PBA phases start to be seen from TEM observations. This comparison suggests that the GE is still very high at the point where the pure PBA phase starts to form.

DSC Study of the Development of the Core/Shell Interphase Zone

It is clear that a highly crosslinked P(Bd-S)/PBA interphase zone is formed during the emulsion polymerization of BA using P(Bd-S) as seed. Notable deformation in the shapes of the particle surface layer could also be observed in Figure 7. This indicates that a nonuniform structure for the crosslinking networks might be present in the P(Bd-S) seed particle, which caused a nonuniform development of the core/shell interphase zone during the second stage polymerization. Electron microscopy has proven to be a powerful tool to investigate the appearance of the morphology of these particles. However, it could not provide much information related to the configuration of the polymer chains, i.e., the extent and distribution of grafting and crosslinking in the composite particles. To investigate the evolution of grafting and crosslinking in the composite P(Bd-S)/PBA particle, differential scanning calorimetry (DSC) was used to study the development of crosslinking and the phase separation process

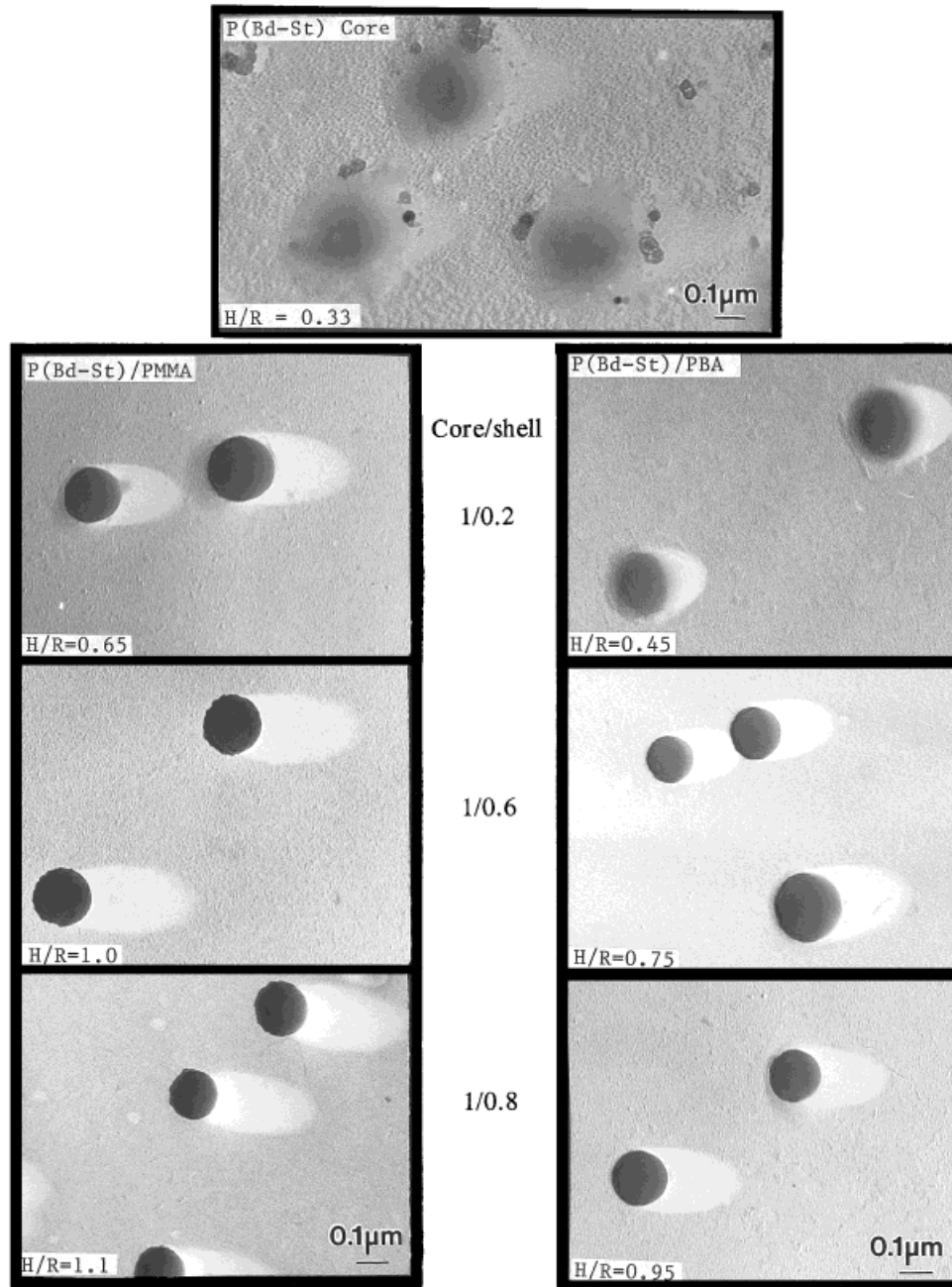


Figure 9 Hardening process for the original soft P(Bd-S) seed latex particle (top) during the seeded emulsion polymerization of MMA (left) and BA (right) as observed by Pt-shadowed TEM micrographs.

during the second stage polymerization according to the recipe and procedure shown as run 2 in Table II. The 6% gel-fraction P(Bd-S) seed was used in this study.

Figure 11 presents the DSC results. Curve 1 represents the transition for the P(Bd-S) seed latex; curves 2–6 show the transitions for the P(Bd-S)/PBA composite latexes with core/shell ratios

from 1 : 0.2 to 1 : 1.5, respectively. It was noted that when moving from curve 1 to curve 4, which corresponds to the samples with core/shell ratios from 1 : 0.0 to 1 : 0.4, the starting temperatures for the DSC transition did not change significantly, while the ending temperature rose from -66.5 to -55.1°C , a change of 11.4°C . According to the glass transition theory based on the free-volume

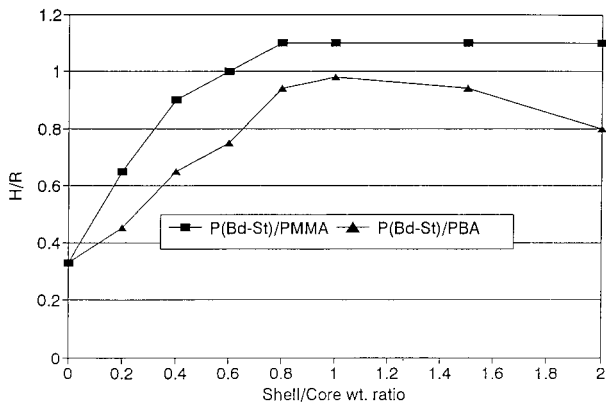


Figure 10 Changes in the H/R ratio of composite latex particles as determined by Pt-shadowing TEM studies with different shell/core ratios prepared by the P(Bd-S) seeded emulsion polymerization with MMA or BA.

model,^{16,17} the starting temperature in a DSC transition curve reflects polymer chains with lower molecular weights for linear chains, or lower degrees of crosslinking for crosslinked chains. The ending temperature, on the other hand, reflects polymer chains with higher molecular weights or higher degrees of crosslinking. The small shift in the starting temperatures from curve 1 for the P(Bd-S) seed latex polymer to curve 4 for the P(Bd-S)/PBA composite latex polymer with a core/shell ratio of 1 : 0.4 indicates that some domains of P(Bd-S) polymer are not in contact with the second stage PBA polymer and still remain in their original state, i.e., they maintain their original compositions and crosslinking level. The large shift in the ending temperatures corresponds to the domains which consist of the grafted/crosslinked P(Bd-S)/PBA interphase zone. As the second stage polymerization proceeds, and the core/shell ratio reaches 1 : 0.8 as shown in curve 5, both the starting and ending temperatures shifted significantly to higher temperatures and the curve becomes much broader. This suggests that the degree of crosslinking has increased throughout the entire composite particles while a gradient of composition and crosslinking level may be present, i.e., higher PBA composition and crosslinking levels in the outer surface and lower crosslinking levels within the particles. However, the transition for the PBA polymer, which is supposed to appear at $\sim -45^{\circ}\text{C}$, still cannot be detected until a core/shell ratio of 1 : 0.8 was reached. In other words, the composite latex particle formed at this stage still consists of P(Bd-S) mixed with PBA polymer through crosslinking

and grafting, instead of a P(Bd-S)/PBA core/shell structure with a sharp core/shell interface. When the core/shell ratio reached 1 : 1.5 (curve 6), only one transition at $\sim -45^{\circ}\text{C}$, which corresponded to the PBA phase, could be seen. The disappearance of the transitions at lower temperatures indicates that the degree of crosslinking in the mixed P(Bd-S)-PBA domains was too high to exhibit any DSC thermal transition. The high degree of crosslinking would greatly restrict the diffusion of newly formed PBA polymer chains as well as pre-formed P(Bd-S) and P(Bd-S)-PBA composite polymer chains. At the same time, the number of grafting sites in the surface layer of this composite particle has also decreased as a result of the formation of the highly crosslinked/grafted interphase zone. Only at this stage can a PBA phase be formed on the composite particles. These results are in good agreement with those discussed previously in describing the morphological observations obtained by using TEM.

CONCLUSIONS

A schematic illustration of the phase development in these systems is given in Figure 12, which sums up the results on the grafting/crosslinking behavior for a P(Bd-S)/PBA core/shell system. The structures of polymers in the interphase zone, considering the nature of both kinds of polymer species, could consist of P(Bd-S)-graft-PBA, P(Bd-S)-cross-

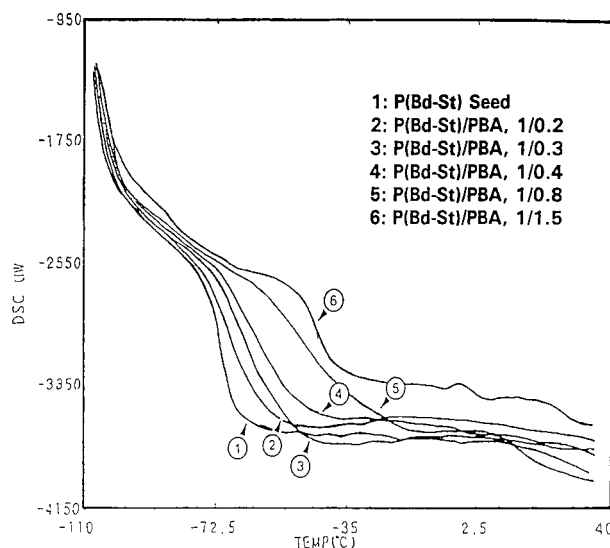


Figure 11 DSC curves for the core/shell LG-SBR/PBA latexes prepared with different core/shell ratios; the arrows show the end points of the transitions.

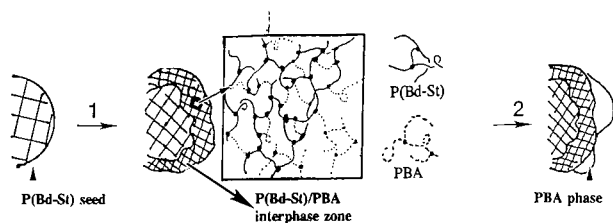


Figure 12 Schematic illustration of the development of the core/shell SBR/PBA interphase zone and the formation of PBA phase during the second stage semi-continuous polymerization.

PBA, P(Bd-S)-*ipn*-PBA, and a very small amount of linear PBA. A pure PBA phase would be formed only after the completion of the formation of the interphase zone. The formation of a gradient in the grafting and crosslinking density, i.e., high to low grafting/crosslinking level from the surface to the center of the P(Bd-S)/PBA composite particles, could be hypothesized. The development of these grafted composite particles would be followed by the formation of a much lower grafted PBA phase with further polymerization of BA.

REFERENCES

1. M. P. Merkel, V. L. Dimonie, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1219 (1987).
2. D. C. Sundberg, J. Arndt, and M. Y. Tang, *J. Dispers. Sci. Techn.*, **5**, 433 (1984).
3. J. Schellenberg and B. Hamann, *J. Appl. Polym. Sci.*, **45**, 1425 (1992).
4. M. A. Aerdt, Ph.D. Dissertation, Techn. Univ. Eindhoven, 1993.
5. S. L. Rosen, *Polymer. Eng. Sci.*, **7**, 115 (1967).
6. H. G. Hoffmann, U.S. Pat. 4,180,529 (to E. I. duPont Co.) (1979).
7. C. J. Falk, S. Mylonakis, and V. Beek, U.S. Pat. 4,473,679 (to Borg-Warner Chem. Inc.) (1984).
8. V. Stanislawczyk, U.S. Pat. 4,879,364 (to The BF Goodrich Co.) (1989).
9. M. Fryd, U.S. Pat. 4,956,252 (to E. I. duPont Co.) (1990).
10. G. Ayrey and C. G. Moore, *J. Polym. Sci.*, **36**, 41 (1959).
11. D. J. Honrston and J. Romaine, *J. Appl. Polym. Sci.*, **43**, 1207 (1991).
12. M. Sacak, N. Bastug, and M. Talu, *J. Appl. Polym. Sci.*, **50**, 1123 (1993).
13. H. G. Elias, *Macromolecules II*, Plenum Press Inc., New York, 1977.
14. K. C. Berger and G. Meyerhoff, in *Polymer Handbook*, 3rd ed., J. Brandrup and E. H. Immergut, Eds., John Wiley & Sons, New York, 1989.
15. C. S. Chern and G. W. Poehlein, *J. Polym. Sci., Part A*, **28**, 3073 (1990).
16. T. G. Fox and P. J. Flory, *J. Polymer Sci.*, **14**, 315 (1954).
17. D. H. Kaelble, in *Rheology—Theory and Applications*, R. Frederick, Ed., Academic Press, New York, 1969.