

Study of the Synthesis and Properties of PBA/PS/PMMA Latex Interpenetrating Polymer Networks

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SYNOPSIS

In this article, we use the technique of multistage emulsion polymerization to synthesize the LIPN PBA/PS/PMMA and use the gravimetric analysis method to study the apparent kinetics of the reaction process and to investigate the influence of the concentration of the initially emulsifying agent, the initiator, and the extent of the crosslinking on the distribution of the particle diameter and the dynamic mechanical properties of the products.

INTRODUCTION

Latex interpenetrating polymer networks (LIPN) is one of the most active fields of the applied technique for IPN. Some of the species have realized industrial productions. LIPN have been widely used in plastic modifications, coatings, adhesives, damping materials, high polymers for medical applications, and ion exchanging resins, etc.

Preliminary research has been carried out on the apparent kinetics of reaction process for LIPN PBA/PS/PMMA, the particle diameter and its distribution, and the dynamic mechanical properties of the products in this study.

EXPERIMENTAL

Raw Materials and Treatment

Normal butyl acrylate (BA): chemically pure, reduced pressure distillation refinement. Styrene (St): chemically pure, reduced pressure distillation refinement. Methylmethacrylate (MMA): analytically pure, reduced pressure distillation refinement. Ethylene glycol dimethacrylate (EGDMA): product of An-li Chemical in Su Zhou. Divinyl benzene (DVB): industrial product, reduced pressure distillation refinement. Sodium borate: analytically pure. Potas-

sium persulfate ($K_2S_2O_8$): chemically pure, recrystallized refinement. Sodium dodecylsulfonate: purity > 97%.

Synthesis of LIPN PBA/PS/PMMA

The polymerization was carried out in a 1000-mL tetra-neck bottle. Temperature was changed no more than $\pm 0.2^\circ\text{C}$; agitation rate was 250 ± 5 rpm.

Crosslinked PBA Seed Latex

Putting the deionized water into a tetra-neck bottle and adding the emulsifying agent (sodium dodecylsulfonate) and the pH-modifying agent (sodium borate), after being mixed and resolved thoroughly, the polymerization reaction was carried out by adding the monomer BA and the crosslinking agent EGDMA, filling with nitrogen, and then adding $K_2S_2O_8$ water solution.

Crosslinked PS Overcoating

After the preceding stage was performed, adding St and crosslinking agent DVB and initiator $K_2S_2O_8$, the polymerization reaction was carried out under constant temperature.

PMMA Overcoating

After the second stage was performed, monomer MMA and initiator were added to perform the third stage polymerization reaction to get the final product, LIPN PBA/PS/PMMA.

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To study the reaction kinetics of the polymerization process by the method of gravimetric analysis, we took a sample of 2–3 g from the reaction system and put it into the weighted bottle, which contained a little bit of hydroquinone and, after weighing it, put it into a stoving oven, stove-drying to a constant weight at 100–120°C. The conversion was

$$C \% = \frac{G_1 - G_0 W}{G_0 M} \quad (1)$$

where G_0 is the weight of sample, G_1 is the constant weight, W is the percentage content of nonvolatile component in the polymerization system, and M is the percentage content of monomer in the polymerization system.

Determination of the Distribution of Particle Diameter of the Emulsion

Instruments

Transmission electron microscope (TEM): H-600, product of Hitachi, Japan. Photograph analysis instrument: IBASI/II, product of West Germany.

Experimental Method and Data Processing

The synthesis of LIPN PBA/PS and LIPN PBA/PS/PMMA is the same as above. First, dilute the obtained emulsion with water and then brominate it for 10 min and coat it on a small copper grid with supporting wafer for observation and for taking pictures by TEM. Using the photograph analysis technique for statistical analysis of the picture, we get the size of the particle diameter and its distribution. The polydispersity index is defined as¹

$$\text{Distribution width} = \frac{dw}{dn} = \frac{\sum n_i d_i^4 / \sum n_i d_i^3}{\sum n_i d_i / \sum n_i} \quad (2)$$

where dw , dn stand for the weight average diameter and number average diameter of the particle, respectively, and n_i stands for the number of latex particle with the diameter within a range whose central value is d_i .

Determination of the Dynamic Mechanical Properties

Coagulating obtained emulsion by aluminum sulfate, filtered, and cleaned up to neutrality, and then stove-drying at 80°C, the white powder is obtained and hot pressed at 180°C. We may get the films of 0.2–

0.3 mm in thickness, and then the dynamic mechanical properties were measured using a viscoelastometer (Model DDV-II-EA, made in Japan). The measuring frequency is 110 Hz, the range of temperature is –100–150°C, and the temperature-rising rate is 2°C/min.

EXPERIMENTAL RESULTS

Apparent Kinetics of Emulsion Polymerization of BA Containing Crosslinking Agent

The basic experimental conditions are given in Table I. Figure 1 shows the conversion-time experimental curve under various emulsifying agent concentrations. From Figure 1 we get the relationship curve of reaction velocity-conversion under various emulsifier concentrations (Fig. 2). From Figure 2, using the method of linear regressive analysis of the experimental data, the relationship between reaction velocity (R) and the emulsifier concentration ($[E]$) in the rate-constant stage was obtained as following:

$$R \propto [E]^{0.61} \quad (3)$$

The experimental results of the influence of initiator concentration on reaction rate is shown in Figure 3. Practicing linear regression for Figure 3 in rate-constant stage, the relationship between initiator concentration and reaction rate can be represented as following:

$$R \propto [I]^{0.39} \quad (4)$$

The influence of temperature on reaction rate is shown in Figure 4. A linear regressive analysis is carried out on the experimental data in the rate-constant stage, and according to the Arrhenius equation, we illustrate with $\ln(R)$ to $1/T$, and the apparent activation energy of the reaction is obtained as follows:

$$E_1 = 83 \text{ kJ/mol}$$

Table I Basic Ingredients and Experimental Conditions

Deionized water (450 mL)
Sodium borate (2.0 g)
Sodium dodecylsulfonate (1.5 g)
BA (40.0 g)
EGDMA (0.8 g)
K ₂ S ₂ O ₈ (0.15 g)
Reaction temperature (65°C)
Agitation rate (240–250 rpm)

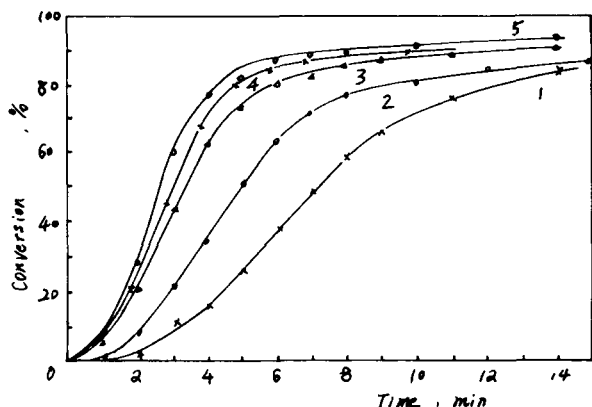


Figure 1 Influence of emulsifier concentration of the relationship between conversion and time for emulsion copolymerization of BA and EGDMA. The ingredient and conditions are as shown in Table I; $[E] \times 10^3 M$: (1) 1.48, (2) 2.80, (3) 11.99, (4) 18.38, (5) 27.97.

Apparent Polymerization Kinetics of St Containing DVB and Taking Crosslinked PBA Latex as Seed Emulsion

The ingredient and reaction conditions for cross-linked PBA seed latex is given in Table II. The experimental results of the influence of the initiator concentration and the dose of the initial emulsifier on the polymerization rate have been shown in Figures 5 and 6, respectively. Based on the linear regression, the relationship between polymerization rate (R) and initiator concentration $[I]$, surfactant concentration $[E]$ in the rate-constant stage can be obtained as follows:

$$R \propto [I]^{1.44}[E]^{0.5} \quad (5)$$

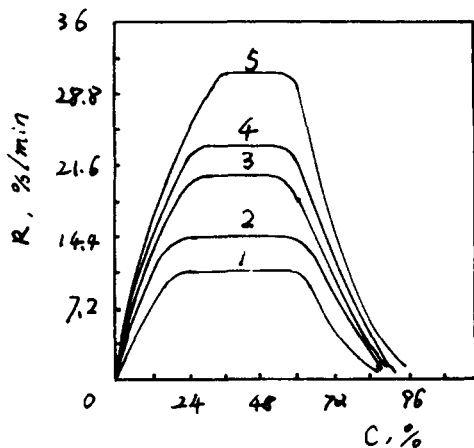


Figure 2 Reaction velocity-conversion curves under different emulsifier concentrations for crosslinked PBA. The number on the curves correspond to Figure 2.

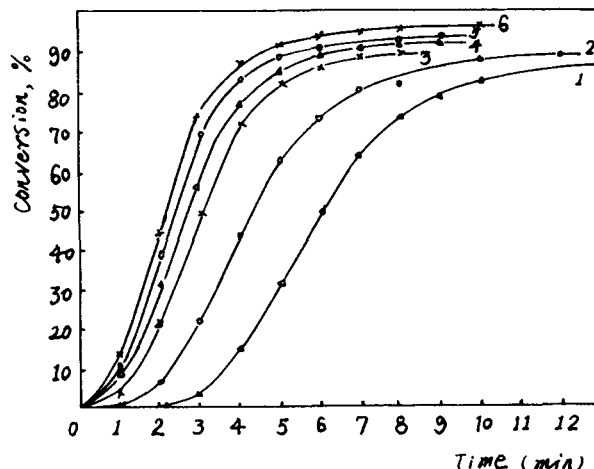


Figure 3 Influence of initiator concentration on the relationship between conversion and time. The experimental conditions are shown in Table I. Initiator concentration ($10^3 M$): (1) 0.81, (2) 1.01, (3) 1.93, (4) 2.42, (5) 2.82, (6) 3.86.

Figure 7 shows the experimental results of the influence of temperature on the reaction rate. According to the Arrhenius equation, the apparent activation energy in the rate-constant period was obtained:

$$E_2 = 130 \text{ kJ/mol} \quad (6)$$

Apparent Polymerization Kinetics of MMA Taking LIPN PBA/PS as Seed Emulsion

The ingredient and reaction conditions of seed latex LIPN PBA/PS are shown in Table III. The experimental results of the relationship between conversion and time is shown in Figure 8. The relationship

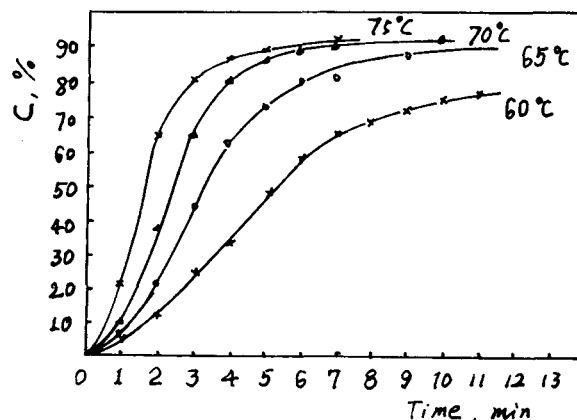


Figure 4 Relation curve of conversion-time under various polymerization temperatures.

Table II Ingredient and Reaction Conditions for Crosslinked PBA Seed Latex

Deionized water (450 mL)
Sodium borate (2.0 g)
Sodium dodecylsulfonate (2–5 g)
BA (40.0 g)
EGDMA (0.8 g)
K ₂ S ₂ O ₈ (0.15 g)
Reaction temperature (75°C)
Agitation rate (240–250 rpm)

curve of reaction rate-conversion being obtained from Figure 8 was shown in Figure 9. Figure 10 represents the influence of the initiator's concentration on the reaction. Figure 11 is the relationship curve among conversion-time under various temperatures. Using the data of the relation of conversion-time at the initial stage ($C < 20\%$) for Figure 10, to practice the linear regression, we get

$$R_{\text{initial}} \propto [I]^{1.90} \quad (7)$$

Similarly, to practice linear regression on experimental data at the middle period reaction, we get

$$R_{\text{middle}} \propto [I]^{1.79} \quad (8)$$

The influence of $[E]$ on the reaction rate is small.

From the experimental data shown in Figure 11, the apparent activation energy corresponding to the initial and middle stage of reaction was calculated as follows:

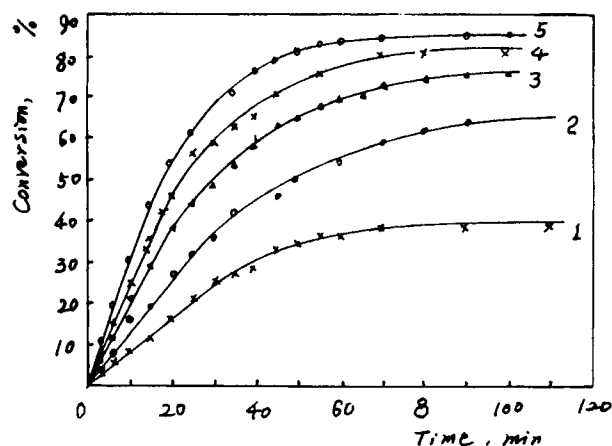


Figure 5 Influence of the initiator concentration on the conversion for seeded emulsion copolymerization of St and DVB, 60°C; $[K_2S_2O_8] \times 10^3 M$: (1) 1.58, (2) 2.13, (3) 2.68, (4) 3.23, (5) 3.94.

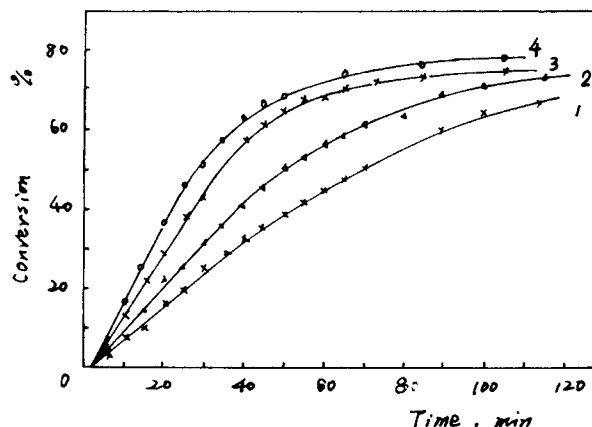


Figure 6 Influence of the concentration of initial emulsifying agent on the conversion. Seed emulsion reacted for 1.5 h, 60°C, $K_2S_2O_8$: 0.3 g, $[E] \times 10^3 M$: (1) 5.48, (2) 10.17, (3) 19.55, (4) 31.29.

$$E_{\text{initial}} = 232 \text{ kJ/mol} \quad (9)$$

$$E_{\text{middle}} = 170 \text{ kJ/mol} \quad (10)$$

Experimental Results of Particle Diameter and Its Distribution

Table IV shows the influence of the feeding method on the two-stage LIPN PBA/PS latex particle diameter and its distribution. Table V shows the influence of the MMA feeding method on LIPN/PBA/PS/PMMA latex particle diameter and its distribution. Table VI shows the influence of concentration of $K_2S_2O_8$ on LIPN PBA/PS latex particle diameter and its distribution at the second-stage reaction. Table VII shows the influence of concentration of $K_2S_2O_8$ on LIPN PBA/PS/PMMA latex particle diameter and its distribution

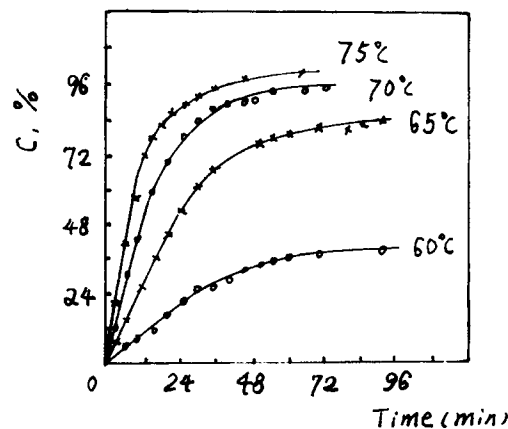


Figure 7 Influence of temperature on the conversion.

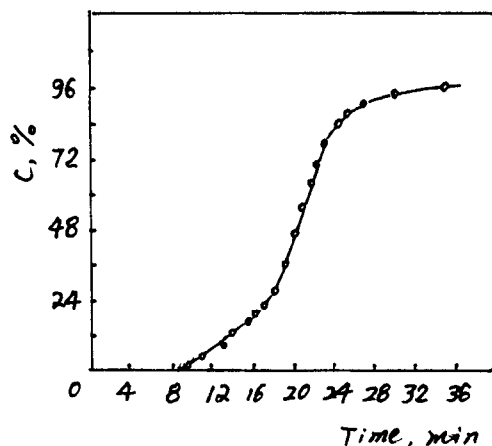


Figure 8 Relation curve of the conversion-time for MMA-seeded emulsion polymerization MMA: 40.0 g, $K_2S_2O_8$: $1.85 \times 10^3 M$; reaction temperature: $70^\circ C$.

at the third-stage reaction. The influence of the dose of emulsifying agent in a first-stage reaction on particle diameter and its distribution are shown in Figures 12 and 13, respectively. Figures 12 and 13 show that increasing the dose of initially added emulsifying agent will make LIPN PBA/PS particle diameter smaller and the distribution wider; as for LIPN PBA/PS/PMMA, the decreasing of particle diameter goes along with the increasing of the dose of emulsifying agent but has no obvious influence on the width of its distribution.

Determination of Dynamic Mechanical Properties

Figure 14 is the dynamic mechanical spectrum of LIPN PBA/PS. There are two distinct spectral peaks corresponding to the glass transition of PBA and PS, respectively. The obtained values of T_g are higher than that found in the literature. It may be caused by the higher crosslinkages and testing frequencies.

Table III Ingredient and Reaction Conditions of Seed Latex LIPN PBA/PS

Crosslinked PBA	Crosslinked PS
Deionized water (450 mL)	$K_2S_2O_8$ (0.25 g)
Sodium borate (2.0 g)	St (40.0 g)
Sodium dodecylsulfonate (1.5 g)	DVB (0.4 g)
BA (40.0 g)	
EGDMA (0.8 g)	
$K_2S_2O_8$ (0.15 g)	
Reaction temperature ($75^\circ C$)	

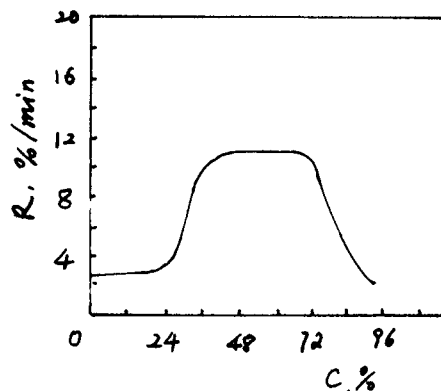


Figure 9 Relation curve of reaction rate-conversion for MMA-seeded emulsion polymerization (obtained from Fig. 8).

Figure 15 is the dynamic mechanical spectrum of LIPN PBA/PS/PMMA. The two distinct transition peaks correspond to the glass transition of BA and the glass transition of PS/PMMA. In addition, there is a wide transition region at about $50^\circ C$ that corresponds to the secondary transition of PMMA.³

DISCUSSION

1. According to the Smith-Ewart theory, the relationship between polymerization rate, the concentration of the emulsifying agent $[E]$, and the initiator concentration $[I]$ in the rate-constant stage as follows:

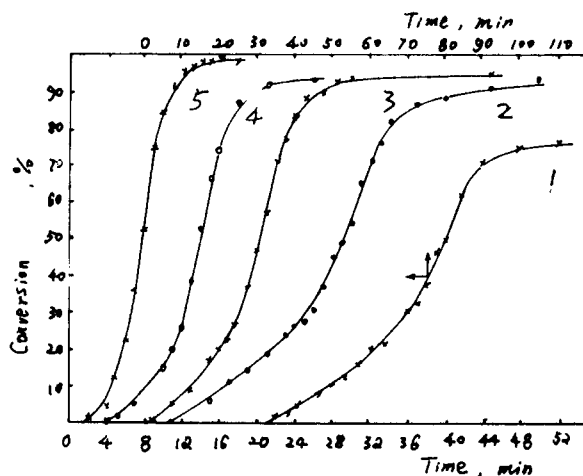


Figure 10 Influence of initiator's concentration $[I]$ on the curve of conversion-time for seeded emulsion polymerization of MMA. Reaction temperature: $70^\circ C$; $[K_2S_2O_8] \times 10^3 M$: (1) 1.16, (2) 2.19, (3) 2.34, (4) 2.70, (5) 3.70.

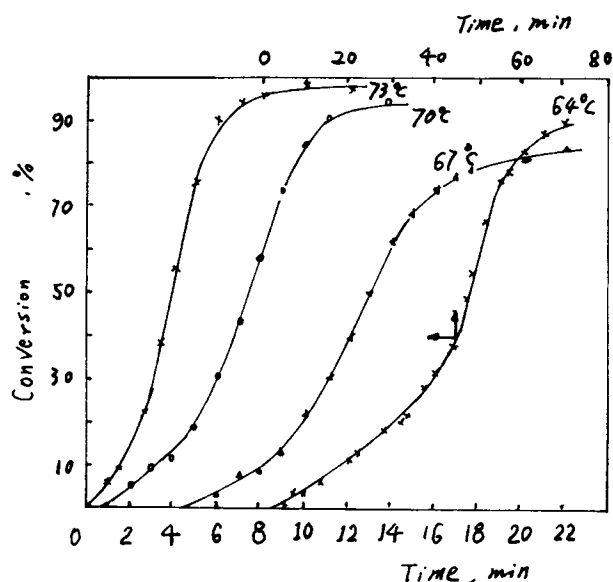


Figure 11 Relationship curve of conversion-time under various temperatures.

$$R \propto [E]^{0.6}[I]^{0.4} \quad (11)$$

The polymerization rate is in proportion to the number of latex particles. In 1968, Medvedev proposed that the deciding factor for reaction rate was the total surface area of micelle and latex particles, then

$$R \propto [E]^{0.5}[I]^{0.5} \quad (12)$$

On the basis of kinetics of acrylate emulsion polymerization, Piirma² proposed the following formula for strong polarity monomers:

$$R \propto [E]^x [I]^{0.5} \quad (13)$$

where the value of x is determined by the absorbed feature of the emulsifying agent on interface.

According to the experimental data of the first-stage reaction in this study,

Table IV Influence of Feeding Method Monomer 2 on Particle Diameter and Its Distribution (conversion > 97%)

Feeding Method	dn (μm)	dw (μm)	dw/dn
Batch process	0.0670	0.0722	1.078
Dropfeeding for 0.5 h	0.0792	0.0851	1.075

$$R \propto [E]^{0.61}[I]^{0.39} \quad (14)$$

is fundamentally in agreement with Smith-Ewart theory, but having some difference, it may be caused by the existence of the crosslinking agent and small amount of polymerization in the water phase.^{4,5}

When taking crosslinked PBA as a seed emulsion and on the existence of crosslinking agent DVB during the polymerization of St, it can be seen from Figure 5 that the polymerization rate at initial stage is rather high, until conversion up to 30%; then the reaction rate decreases gradually. It shows that owing to the existence of seed emulsion, the reaction is fundamentally carried out on the seed latex particles. Thus, from the beginning, the reaction already has higher constant reaction velocity. With the increasing of conversion, the diffusion factor gradually becomes the deciding factor, thus resulting in the gradual decrease of reaction velocity.

Bataille⁶ investigated the emulsion polymeriza-

Table V Influence of MMA Feeding Method on Product Particle Diameter and Its Distribution (conversion > 97%)

Feeding Method	dn (μm)	dw (μm)	dw/dn
Batch process	0.0657	0.0848	1.292
Dropfeeding for 0.5 h	0.0838	0.0879	1.047

Table VI Influence of $\text{K}_2\text{S}_2\text{O}_8$ Concentration on LIPN PBA/PS Particle Diameter and Its Distribution

$[\text{K}_2\text{S}_2\text{O}_8] \times 10^3 \text{ M}$	dn (μm)	dw (μm)	dw/dn
2.13	0.0556	0.0625	1.124
3.94	0.0543	0.0600	1.105

Table VII Influence of $\text{K}_2\text{S}_2\text{O}_8$ Concentration on LIPN PBA/PS/PMMA Particle Diameter and Its Distribution

$[\text{K}_2\text{S}_2\text{O}_8] \times 10^3 \text{ M}$	dn (μm)	dw (μm)	dw/dn
1.85	0.0845	0.0892	1.055
2.70	0.0795	0.0831	1.045
3.90	0.0717	0.0762	1.062

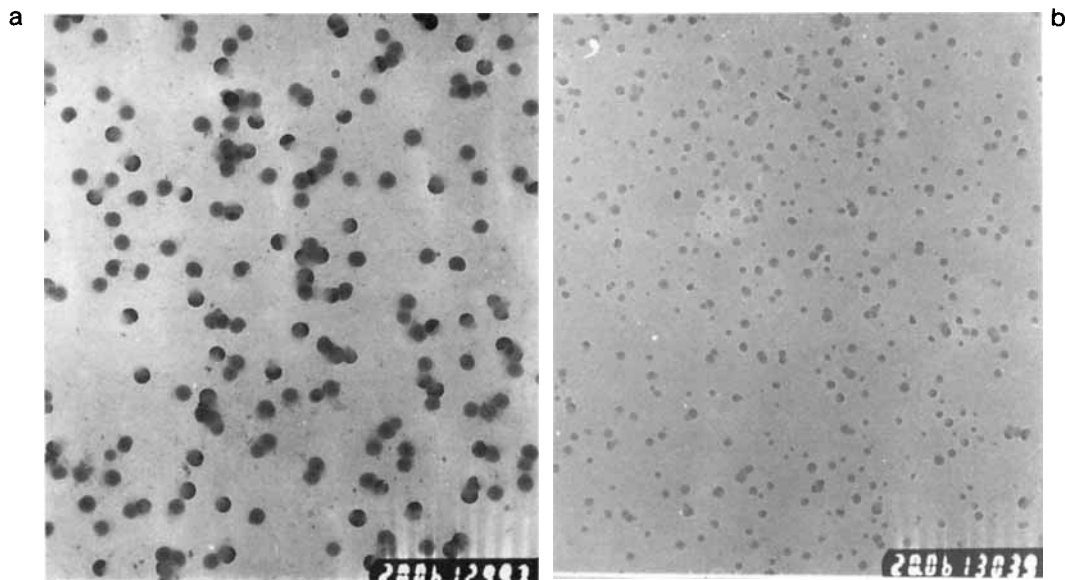


Figure 12 Electron microscope photograph of LIPN PBA/PS latex particle under various doses of emulsifier. Dose of emulsifier: a. 1.0 g; b. 4.0 g.

tion of styrene, and Hasan¹ studied the seeded emulsion polymerization of styrene. The experimental results of Hasan show that the polymerization rate increases with initiator concentration in the low concentration range. Sundberg⁷ studied the kinetics of the diffusion-controlled seeded emulsion polymerization of styrene. The experimental results have shown that at initial stage the reaction is rather stable, but an accelerated phenomenon emerges as the conversion reaches 70%.

Hasan¹ in his study of polymerization of St-seeded emulsion polymerization obtained the apparent activation energy of 43 kJ/mol. Okamura⁸ studied the polymerization of St-DVB under the existence of Hypalon-20 (a kind of elastomer), and the apparent activation energy of 87 kJ/mol was obtained. In this study, with the crosslinked PBA latex as seed emulsion, the apparent activation energy of St-DVB-seeded emulsion polymerization was 130 kJ/mol. We consider that the difference is

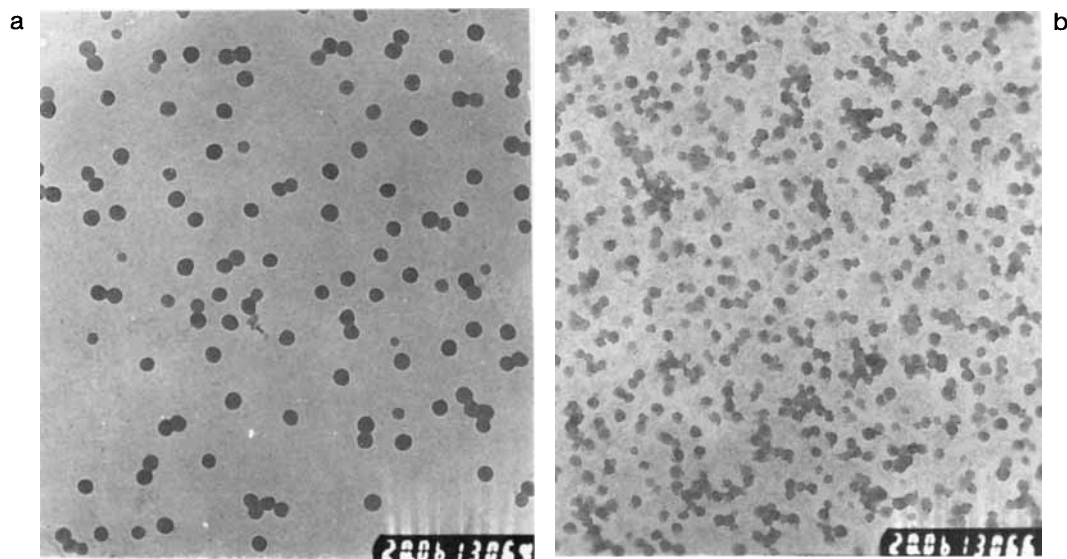


Figure 13 Electron microscope photograph of LIPN PBA/PS/PMMA latex particle under different dose of emulsifier. Dose of emulsifier: a. 1.0 g; b. 3.5 g.

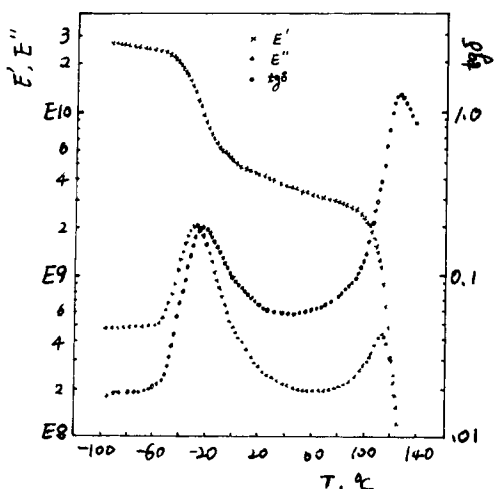


Figure 14 Dynamic mechanical spectrum of LIPN PBA/PS.

caused by using a different seed emulsion and the existence of the crosslinking agent in our work.

The crosslinking PBA latex particles are a system with higher viscosity; the polymerization of St, at the very beginning, is in such a high-viscosity condition. Owing to the lack of compatibility between PBA and PS, microphase separation occurs on the latex particles at the very beginning. It is thought that in a single particle there are several separated regions. Therefore, the average number of free radicals on every latex particle will greatly exceed 0.5, and the reaction-loci number may be proportional to the number of free radicals produced by initiator. Thus $R \propto [I]^{1.44}$ may result. But the reason is not clear yet. Meanwhile, owing to the existence of a DVB crosslinking agent, the viscosity of every polymerization zone of styrene will increase rapidly, resulting in a decrease in reaction velocity in the middle and final stages, thus enhancing the apparent activation energy of the reaction.

The emulsion and seeded emulsion polymerization of acrylate monomers has been studied by many authors, such as Banerjee,⁹ Fitch,¹⁰ Goldwasser,¹¹ and Dimonie.¹² The experimental results of all these authors are rather different from our work. The reason may stem from the fact that the seed latex is LIPN PBA/PS in this study. Why the initiator order (1.9 and 1.79) is so high in our study is not clear yet.

2. Concerning the particle diameter and its distribution, it can be seen from Table IV that the distribution width corresponding to the batch process is slightly wider than that of the semibatch process and the average particle diameter is a little smaller.

Using Fluid-dynamic chromatography to determine the particle diameter and its distribution of the product of two-stage emulsion polymerization of PBA/PS (in every stage adding no crosslinking agent), Min¹³ obtained the distribution width for the semibatch process of 1.022, average particle diameter of 0.105 μm , the distribution width for batch process of 1.037, and the average diameter of 0.106 μm . This result is similar to our study, but the regularity of average particle diameter is different.

From Table V it is obvious that for LIPN PBA/PS/PMMA, the influence of feeding method is more distinct. Using drop-feeding (semibatch process) for MMA, the average particle diameter is rather large, but the distribution is narrow. It is probably due to the greater solubility of MMA in water, and the homogeneous nucleation cannot be neglected, and the probability of homogeneous nucleation is greater for the batch process.

From Tables 6 and 7, there is no distinct influence of the dose of initiator on the width of distribution, but it has some effect on particle diameter for LIPB PBA/PS/PMMA. It may be related to the greater solubility of MNA in water.

3. In careful observation of Figures 14 and 16 we find out that the temperature corresponding to the low-temperature transition peak of LIPN PBA/PS is a little higher than that of LIPN PBA/PS/PMMA. We believe it may be related to some MMA monomer diffused in to the crosslinked PBA phase during the third-stage polymerization. MMA has compatibility with PBA, and because PBA is crosslinked with high viscosity and with the protection

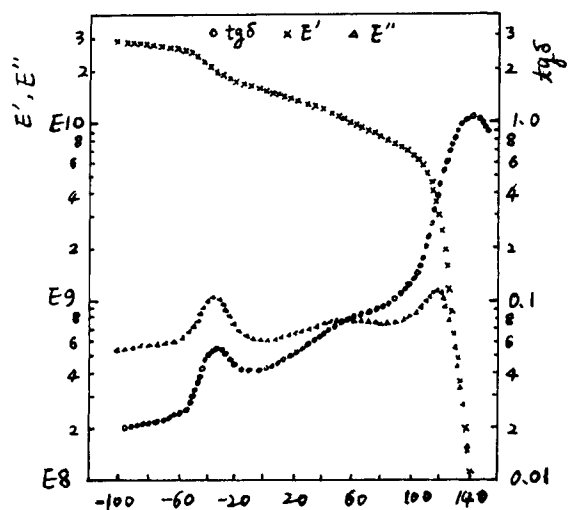


Figure 15 Dynamical mechanical spectrum of LIPN PBA/PS/PMMA.

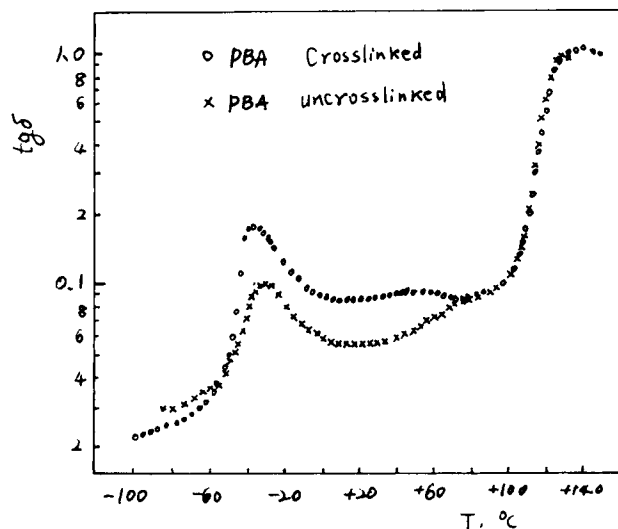


Figure 16 Influence of the dose of crosslinking agent for PBA on the dynamic mechanical spectrum of LIPN PBA/PS/PMMA.

of PMMA at the outer layer, the small amount of MMA monomer can hardly be eliminated from PBA even after the film being made is stove-dried. It can be seen from Figure 16 that the temperature corresponding to the transition peak of the crosslinked PBA is lower than that of the uncrosslinked one. This fact may follow the same reasoning.

From Figure 16, we see that crosslinking makes the value of $t_g \delta$ between the two transition peaks increase, showing that the compatibility between phases is increased.

Figure 17 shows the $t_g \delta$ temperature curve of LIPN PBA/PS/PMMA for the crosslinking and uncrosslinking of PS. It can be seen that the crosslinking brings two transition peaks closer to each other, showing that the crosslinking of the PS phase makes the interpenetrating extent between each phase increase and the intermixing degree increase.

SUMMARY

1. Taking EGDMA as a crosslinking agent, the apparent activation energy of the emulsion polymerization reaction of BA is 83 kJ/mol and conforms to the following law:

$$R \propto [E]^{0.61} [K_2S_2O_8]^{0.39}$$

At the second stage, taking DVB as crosslinking agent and taking crosslinked PBA as seed emulsion, the apparent activation energy of St-seeded emul-

sion polymerization is 130 kJ/mol, and the polymerization rate conforms:

$$R \propto [E]^{0.5} [K_2S_2O_8]^{1.44}$$

At the third stage, under the existence of the obtained LIPN PBA/PS seed emulsion, the reaction velocity of MMA-seeded emulsion polymerization has little relation to $[E]$. The two constant reaction rates in initial and middle period are $R_{in} \propto [K_2S_2O_8]^{1.9}$ and $R_{mid} \propto [K_2S_2O_8]^{1.79}$, respectively. The corresponding apparent energies are 232 and 173 kJ/mol, respectively.

According to experimental data and a comparison of the related literature, it can be seen that the law of apparent kinetics of seeded emulsion polymerization is closely related with the kind of seed emulsion and the crosslinking condition.

2. The particle diameter and its distribution of LIPN PBA/PS and LIPN PBA/PS/PMMA have been determined. The influence of feeding method on the monomer and the dose of initiator in the second stage on the distribution width of LIPN PBA/PS are small, but the influence of the method of feeding MMA on the particle distribution of LIPN PBA/PS/PMMA is obvious. Using the drop-feeding method can decrease the distribution width. There is no obvious influence of the dose of initial emulsifying agent and the dose of initiator during the third stage on the particle diameter within this investigated range.

3. The investigation of dynamic mechanical properties shows the phase separation morphology

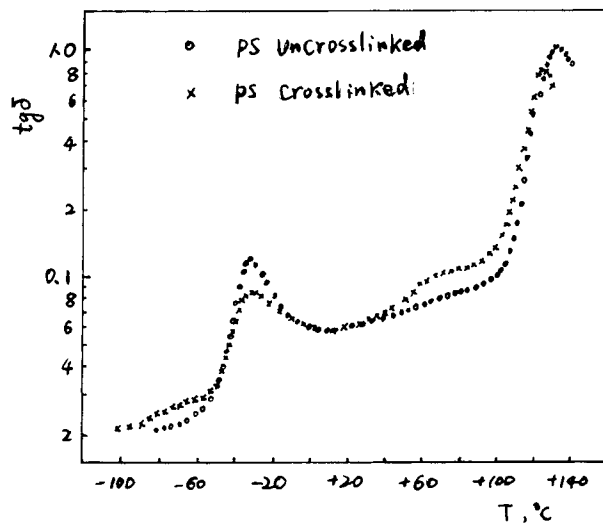


Figure 17 Influence of PS crosslinking on the dynamic mechanical properties of LIPN PBA/PS/PMMA.

structure of the LIPN PBA/PS/PMMA and LIPN PBA/PS. The crosslinking can increase the extent of intermixing degree between phases.

REFERENCES

1. S. M. Hasan, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 3031 (1982).
2. I. Piirma, *Emulsion Polymerization*, New York, 1981, Chapter 7.
3. Heijboer, *J. Polym. Mater.*, **6**, 11-37 (1977).
4. M. Banerjee et al., *Polymer*, **22**, 1729 (1981).
5. D. Zersberg, *Polymer*, **27**, 147-157 (1986).
6. P. Bataille et al., *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 795 (1982).
7. D. C. Sundberg, *ACS*, **165**, 327 (1981).
8. K. Okamura, *J. Appl. Polym. Sci.*, **22**, 267 (1978).
9. M. Banerjee and R. S. Konar, *Polymer*, **27**, 147 (1986).
10. R. M. Fitch et al., *J. Polym. Sci., Polym. Symp.*, **72**, 221-224 (1985).
11. J. M. Goldwasser et al., *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1993-2006 (1982).
12. V. Dimonie et al., *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2197-2215 (1984).
13. T. I. Min et al., *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2845 (1983).

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