

Morphologies and Dynamic Mechanical Properties of Core-Shell Emulsifier-Free Latexes and Their Copolymers for P(BA/MMA)/P(MMA/BA) and P(BA/MMA)/PSt Systems in the Presence of AHPS

Tian-Ying Guo, Guang-Liang Tang, Guang-Jie Hao, Moud-Dao Song, Bang-Hua Zhang

Institute of Polymer Chemistry, State Key Laboratory of Functional Polymer Materials for Adsorption and Separation, Nankai University, Tianjin 300071, People's Republic of China

Received 24 May 2001; revised 12 April 2002; accepted 12 April 2002

ABSTRACT: Different poly(methyl methacrylate/*n*-butyl acrylate)/poly(*n*-butyl acrylate/methyl methacrylate) [P(BA/MMA)/P(MMA/BA)] and poly(*n*-butyl acrylate/methyl methacrylate)/polystyrene [P(BA/MMA)/PSt] core-shell structured latexes were prepared by emulsifier-free emulsion polymerization in the presence of hydrophilic monomer 3-allyloxy-2-hydroxyl-propanesulfonic salt (AHPS). The particle morphologies of the final latexes and dynamic mechanical properties of the copolymers from final latexes were investigated in detail. With the addition of AHPS, a latex of stable and

high-solid content (60 wt %) was prepared. The diameters of the latex particles are $\sim 0.26 \mu\text{m}$ for the P(BA/MMA)/P(MMA/BA) system and $0.22\text{--}0.24 \mu\text{m}$ for the P(BA/MMA)/PSt system. All copolymers from the final latexes are two-phase structure polymers, shown as two glass transition temperatures (T_g s) on dynamic mechanical analysis spectra. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3078–3084, 2002

Key words: core-shell polymers; latex; emulsifier-free emulsion polymerization; acrylates; styrene

INTRODUCTION

Because there is some grafting, interpenetrating interactions between core and shell polymers of the core-shell structured latex,^{1–3} the copolymers from core-shell latex are different from common copolymers in many properties, such as water resistance, weather resistance, spoil resistance, radiation resistance, tensile strength, impact strength, and adhesive strength. These properties can be improved by carrying out core-shell structured emulsion polymerization. Therefore, copolymers from core-shell structured latex can be of great use in the fields of plastics, coatings, biotechnology, and so on.^{4–6} Core-shell structured polymers are of particularly great commercial potentiality in the field of toughening thermoplastics for impact resistance.

Morphology structures of the final latex can be influenced by the hydrophilicity of monomers and their polymers,^{7–9} viscosity of the latex,¹⁰ molecular weight of polymer,¹ combining extent of core and shell polymers,^{2,3} diffusing speed of monomers and radical oligomers,^{11–14} interfacial energy of the systems,^{15,16} etc. In general, the morphology of core-shell structured latex is not only determined by the chemical structure

of the copolymer but also depends on the conditions of the emulsion polymerization process used; for examples, the reacting temperature, the feeding way of the comonomers, types of the initiation, and the rate of initiation.¹⁷ To date, core-shell structural latex with emulsifiers has been used successfully in coatings^{5,6} and modification of plastics.^{18–21}

The method of emulsifier-free polymerization can obviously improve the water resistance and tensile strength of the copolymer.²⁵ And core-shell structural latex can further improve the film forming properties and high–low temperature resistance. Combining these two methods can result in more excellent copolymers. In recent years, there have been some reports on core-shell structured emulsifier-free emulsion polymerization.^{22–24} However, the solid contents of the final latex was lowered by 30 wt % in almost all reports. Therefore, obtaining high solid content, stable core-shell structured latex has both very important academic and practical significance.

Our previous work mainly investigated the synthesis of high solid content, emulsifier-free copolymerization of acrylates with the addition of 3-allyloxy-2-hydroxyl-propanesulfonic salt (AHPS). The stable properties of the final latex and the properties of the copolymer cast from the final latex were investigated in detail.

The major purposes of this work focus on the synthesis of high-solid content (60 wt %) core-shell structured emulsifier-free poly(methyl methacrylate/*n*-bu-

Correspondence to: T.-Y. Guo (gtying@eyou.com).

tyl acrylate)/poly(*n*-butyl acrylate/methyl methacrylate) [P(BA/MMA)/P(MMA/BA)] and poly(*n*-butyl acrylate/methyl methacrylate)/polystyrene [P(BA/MMA)/PSt] latexes, the characterization of morphology of the final latex, and determination of the dynamic mechanical behavior of the copolymers.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), *n*-butyl acrylate (BA), and styrene (St) from Tianjin No.1 Chemical Reagent Plant were analytical reagents that were purified by distillation under reduced pressure and then stored at -20°C before use. Potassium persulfate (PSP, $\text{K}_2\text{S}_2\text{O}_8$) from China No. 3 Chemical Reagent Plant was recrystallized in absolute methyl alcohol. 3-Allyloxy-2-hydroxypropanesulfonic salt (AHPS) was synthesized by us.²⁵ Triallyl isocyanurate (TAIC; $\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}_3$), with a density of 1.1133 (30°C), m.p. of 27°C , and b.p. of $144^{\circ}\text{C}/3\text{ mmHg}$, was used. Deionized water was used in all polymerizations.

Polymerization was carried out in a 0.5-L glass reactor equipped with a microfeeder, an anchor-type glass stirrer, an N_2 inlet, and a reflux condenser.

Preparation of latexes

The core-shell structured latex was produced by a semicontinuous emulsifier-free emulsion polymerization procedure. The copolymerization was carried out in a 0.5-L four-necked kettle equipped with stirrer, thermometer, reflux condenser, inlet system of inert gas, and dropping funnel. The polymerization kettle was placed in a water bath of 70°C . The stirring speed was controlled at 350 rpm. First, water and AHPS were added to the kettle that was purged with nitrogen and heated to 70°C , then PSP was added, and then the core monomers (BA/MMA, 9/1 by weight) were added in a dropwise manner into the reactor. The shell monomers were fed into the reactor in succession when the core monomers were fed out. Throughout the polymerization process, the feeding rate was fixed at $\sim 20\text{ g/h}$. Recipes for three emulsifier-free emulsion polymerization used are shown in Table I.

Characterization

The diameters of final latex particles were determined by transmission electron microscopy (TEM; Hitachi-600, Japan). The sample was prepared by dropping 0.1 mL of diluted latexes (0.5–1 wt %) on a copper grid coated with PVB [poly(vinyl butyrate)] and allowed the latexes to dry in a desiccator. The morphologies of core-shell particles were also studied by transmission electron microscopy (TEM), with the particles stained

TABLE I
Recipes for the Core-Shell Structured Emulsifier-Free Emulsion Polymerizations for the P(BA/MMA)/P(MMA/BA) System and Average Diameters of Final Latex Particles^a

Polymer	Core (g)		Shell (g)		Diameter (μm)
	BA	MMA	MMA	BA	
A	18	2	38	42	0.26
B	36	4	43	17	0.25
C	36	4	30	30	0.26
D	36	4	50	10	0.25
E	36	4	35	25	0.27
F	63	7	25	5	0.24
G	54	6	34	6	0.26

^a Deionized water (70 g), AHPS (1.2 g), potassium persulfate (PSP, 0.5 g), sodium bicarbonate (NaHCO_3 ; 0.5 g), temperature, (70°C), and stirring speed (350 rpm).

negatively with phosphotungstic acid (PTA) for the background. Glass transition temperature (T_g), determined from peaks of the $\tan \delta$ -temperature curve, was investigated by dynamic mechanical analysis (DMA; Rheovibron DDV-II-EA, Japan) at 3.5 Hz, at a heating rate of $2^{\circ}\text{C}/\text{min}$, and sample size of $2 \times 0.2 \times 0.020\text{ cm}^3$. Copolymers subjected to the physical property tests were cast at room temperature, then vacuum dried at 50°C for 72 h and kept at room temperature for 24 h.

RESULTS AND DISCUSSION

Morphology of the core-shell structured emulsifier-free latex particles

TEM micrographs of the final core-shell emulsifier-free latex particles for the P(BA/MMA)/P(MMA/BA) system prepared by the semicontinuous procedure are shown in Figure 1. The particles have the morphology of a solid sphere as on the copper grid was dried in a desiccator. To enhance the contrast behavior of the phase components of particles, the latex particles were dyed with PTA. The size distribution of the final latex particles is very narrow, and the average diameter is $\sim 0.26\ \mu\text{m}$ (see Table I). Therefore, in this situation, the core and shell structures of latex particles can not be seen clearly in TEM micrographs. This result is similar to that reported by Lin et al.,²² although they prepared the acrylate latex by a two-stage emulsion polymerization procedure. These observations indicate that neither the particles with a uniform monomer distribution nor those with BA and MMA as the core and shell materials are similar in structure and physical properties. Furthermore, TEM is not an efficient measure to confirm the core-shell structure when the core and shell monomers are similar in structure and physical properties.

The TEM micrographs of the final P(BA/MMA)/PSt core-shell structured latex particles are shown in

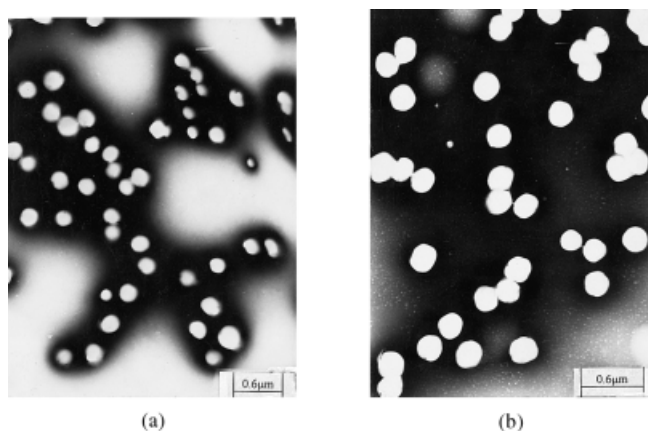


Figure 1 TEM micrographs of the P(BA/MMA)/P(MMA/BA) core-shell emulsifier-free latex particles after dyed with PTA: (a) magnification, 18,000 \times ; (b) magnification, 23,000 \times .

Figures 2 and 3. It is obvious that each particle is spherical and has uniform size, as shown in Figures 2 and 3 and in Table II, and the average diameter is $\sim 0.22\text{--}0.24\ \mu\text{m}$. There are light gray circle shell layers around the dark cores (see Figure 2). Clear core (dark region) and shell (gray region) structures can be seen at magnification of 100,000 times (as seen in Figure 2b).

Figure 3 is the TEM micrographs of dyed latex particles at different magnifications. The core-shell structure is still not obvious at low magnification (Figure 3a). But when the magnification is increased to 57,000, the core-shell structure can be seen clearly. There is a dark gray core region inside the white particle, which indicates that there are large differences in structure and physical properties between acrylates and styrene. Therefore, there is a big contrast in TEM photographs, especially when the latex particles are dyed.

The formation of core-shell structured latex could be attributed to the semicontinuous feeding method in

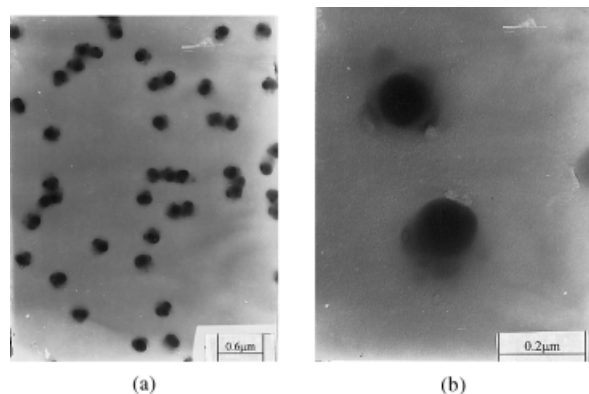


Figure 2 TEM micrographs of the P(BA/MMA)/PSt core-shell emulsifier-free latex particles: (a) magnification, 18,000 \times ; (b) magnification, 100,000 \times .

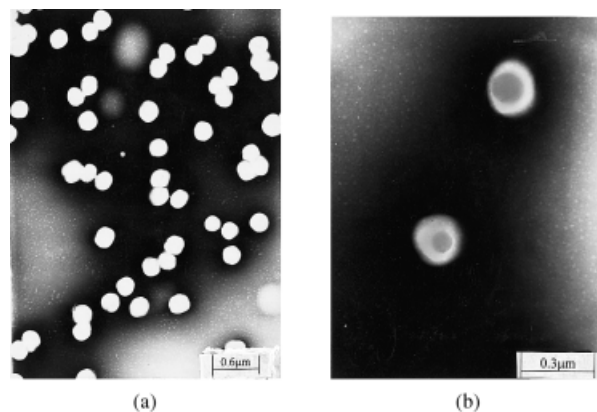


Figure 3 TEM micrographs of the P(BA/MMA)/PSt core-shell emulsifier-free latex particles after dyed with PTA: (a) magnification, 18,000 \times ; (b) magnification, 57,000 \times .

which the core and shell monomers were fed slowly into the reactor in succession. Thus, the shell monomers MMA/BA or St were polymerized out the surface of BA/MMA (9/1 by weight) core latex particles because the concentration of monomers in the polymerization systems was kept very low from beginning to end. Therefore, the latex particles with core-shell structure were obtained by this procedure.

All the latex particles prepared by emulsifier-free emulsion polymerization in this work are assumed chiefly to be formed by the homogeneous nucleation mechanism proposed by Fitch et al.²⁶ in which a growing oligomeric free radical precipitated from the aqueous phase when it reaches a critical chain length to form a primary particle. Then the polymerization is continuous in the particles. The particles are firstly stabilized by the end groups from the decomposition of PSP, which attached to the surfaces of the particles acts as a surfactant to increase electrostatic repulsion. As the polymerization is being carried out, the functional monomer AHPS, which is soluble in the water phase, tends to copolymerize with other monomers in the water–oil interface and then bonds onto the surface of the latex particles, provides the sulfonate and

TABLE II
Recipes of the P(BA/MMA)/PSt Core-Shell Structured Emulsifier-Free Emulsion Polymerizations and Average Diameters of the Final Latex Particles^a

Polymer	Core (g)		Shell (g)	Diameter (μm)
	BA	MMA	St	
I	45	5	50	0.22
II	54	6	40	0.23
III	63	7	30	0.21
IV	72	8	20	0.22
V	81	9	10	0.24

^a Deionized water, 70 g; AHPS, 1.2 g; potassium persulfate (PSP), 0.5 g; sodium bicarbonate (NaHCO_3) 0.5 g; temperature, 70 $^\circ\text{C}$; stirring speed, 350 rpm.

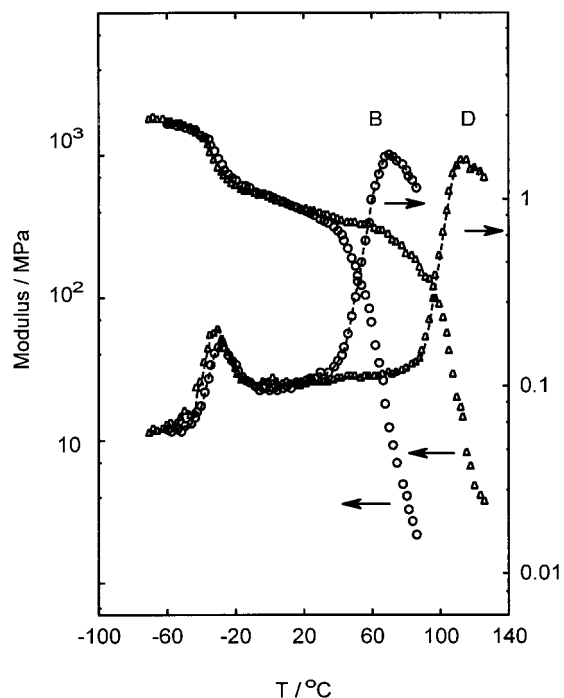


Figure 4 DMA spectra of copolymers B and D (see Table I).

hydroxyl groups to act as a surfactant, and can be partially polymerized in water phase to act as polyelectrolyte hydrosoluble chains. Thus, the stability of the latex particles can be greatly improved, leading to high solids content and stable latexes.

Dynamic mechanical behaviors of the copolymers from core-shell structured emulsifier-free latexes

Copolymers subjected to the dynamic mechanical analysis were cast at room temperature, then vacuum dried at 60°C for 72 h and kept in a desiccator at room temperature before the test.

The DMA spectra of copolymers for samples B, D, and E from the emulsifier-free P(BA/MMA)/P(MMA/BA) latex are shown in Figures 4 and 5. The T_g data for the copolymers are shown in Table III.

The DMA spectra show that there are two T_g s in each copolymer, one is the low temperature peak attributed to the copolymer of core component and the other corresponds to the high temperature peak of the shell component. These results are decidedly different from the results of our previous work²⁵ on semicontinuous emulsifier-free latex of acrylates, which displayed only single T_g peaks on the DMA spectrum.

There are two transitions in the $\tan \delta$ and storage modulus (E') of the copolymers cast from the final latex. The T_g data from Figures 4 and 5 and Table III indicate that the low temperature peaks do not change when the composition of core component is fixed. Also, the T_g values are 15–16°C above the theory

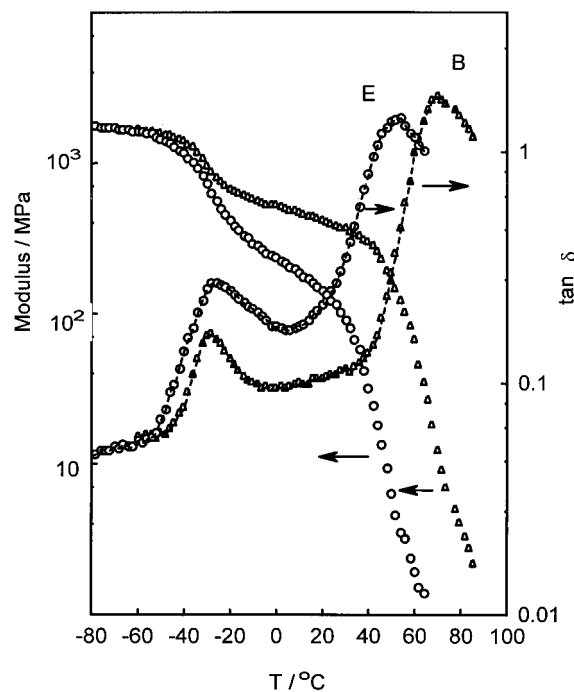


Figure 5 DMA spectra of copolymers B and E (see Table I).

calculation values in which random copolymers are assumed to be formed.

As the proportion of the hard monomers in shell component increases, the T_g values in the high-temperature region increase. Furthermore, the higher the hard monomer content in the shell component, the larger is the difference between the observed T_g values and those calculated on the basis of theory.

As we know, the rubbery cores can provide resistance to impact, whereas the grafted glassy shell provides rigidity and compatibility with the polymer matrix. Therefore, the T_g values of low and high temperature are very important when the copolymers are used as toughening modifiers in a polymer blending system. The Fox experimental equation, $1/T_g = W_1/T_{g1} + W_2/T_{g2}$, can be used to determine the T_g values of the final copolymers. Thus, to find the optimum T_g value, the composition of core and shell copolymers

TABLE III
Data of the T_g s from Experimental Observation and Theoretical Calculations

Polymer	T_{g1} (°C)		T_{g2} (°C)	
	Calculation	Observed	Calculation	Observed
A	-45	-28	0	24
B	-45	-29	40	70
C	-45	-27	4	28
D	-45	-30	63	112
E	-45	-29	16	54
F	-45	-30	64	—
G	-45	-30	68	—

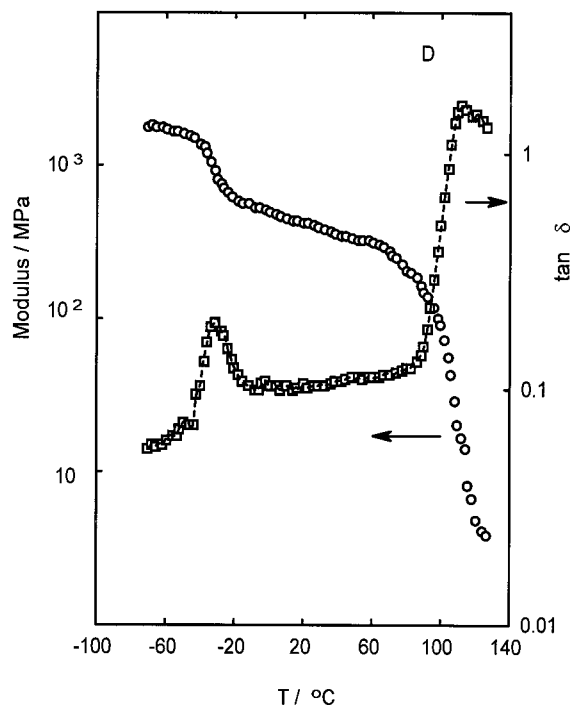


Figure 6 DMA spectra of copolymer D (see Table I).

can be designed in advance. In our present work, we found that the low and high T_g values are greater than the theoretically calculated values by ~ 15 and $24\text{--}49^\circ\text{C}$, respectively. This result can be partly attributed to the difference in the solubility in water phase of these two monomers [MMA (1.5 g/100 mL water) and BA (0.2 g/100 mL water)].

In addition, as seen from Figure 6, a small T_g can be seen slightly between the T_g s of low and high temperature. This small T_g can be an indication that the copolymers from the latex particles contained the third domain in which the monomers are grafted or interpenetrated together; that is, there is interfacial layer of core and shell.

The experimental data presented indicate that there is a soft-core phase with the low T_g at about -30°C and a shell phase with a high T_g of $\sim 24\text{--}112^\circ\text{C}$ for the P(BA/MMA)/P(MMA/BA) system. These results indicate that a core-shell structured latex is formed, although it is not evident in the TEM micrographs for this system.

Effect of cross-linking agent on the dynamic mechanical properties of the copolymers from core-shell structured emulsifier-free latexes

To investigate the effect of the core structure on the dynamic mechanical behavior of the copolymer, the cross-linking agent TAIC was added to the reactor on the core forming stage.

The recipes for the core-shell emulsifier-free emulsion polymerization with cross-linking agent are

shown in Table IV and the DMA spectra are shown in Figures 7 and 8. It can be shown from the discussion just presented that there are two T_g s attributed to the core component and shell component, respectively, for the copolymers without cross-linking agent. With the addition of TAIC (see Figure 7) the T_g peaks of the core component in the low-temperature region obviously shifts to higher temperature and that of the shell component in the high-temperature region shifts somewhat to a lower temperature. When the amount of TAIC is increased to 0.4 g, the T_g value in the high-temperature region decreases and the T_g peak in the low-temperature region changed into a shoulder peak. The curves of $\tan \delta$ versus temperature for the copolymers are shown in Figure 8. The results indicate that the cross-linking agent has a large effect on the dynamic mechanical behavior of the copolymer. This large effect can be explained by dynamics of polymerization.²⁷ The morphology of the core-shell structured latex particles is related to the diffusing rate of each component in the polymerization system, which contains core monomers, polymers from core latex particles, shell monomers, and their oligomers. All the inner structure and surface properties of the core latex particles were changed when the cross-linking agent was added. Therefore, the behaviors of diffusing into the latex particles for other monomers, monomer or oligomer radicals, etc. were also influenced, thus resulting in the change of dynamic mechanical behaviors of the final copolymers.

CONCLUSION

High solid content (as high as 60 wt %) core-shell structured emulsifier-free latexes for (BA/MMA)/(MMA/BA) and (BA/MMA)/St monomers were prepared by a semicontinuous polymerization procedure with adjustment of the composition of fed monomers. The latex particles are uniform, and the diameter of the latex particles is $\sim 0.26 \mu\text{m}$ for the P(BA/MMA)/P(MMA/BA) system and 0.22–0.24 for the P(BA/MMA)/PSt system. The characters of core-shell structured latex particles could not be seen in the TEM

TABLE IV
Recipes for the P(BA/MMA)/P(MMA/BA) Core-Shell Emulsifier-Free Emulsion Polymerizations Added with Cross-Linking Agent TAIC^a

Polymer	Core (g)			Shell (g)	
	BA	MMA	TAIC	BA	MMA
H	32	8	0	30	30
I	32	8	0.2	30	28
J	32	8	0.4	30	28

^a Deionized water, 70 g; AHPS, 1.2 g; potassium persulfate (PSP), 0.5 g; sodium bicarbonate (NaHCO₃), 0.5 g; temperature, 70 °C; stirring speed, 350 rpm.

micrographs for acrylate emulsifier-free emulsion polymerization systems because their monomers are similar in physical features in this work.

In contrast, for the P(BA/MMA)/PSt system, the core-shell structure was very clear in TEM micrographs, especially when the latex particles were stained negatively with PTA. The emulsifier-free latex

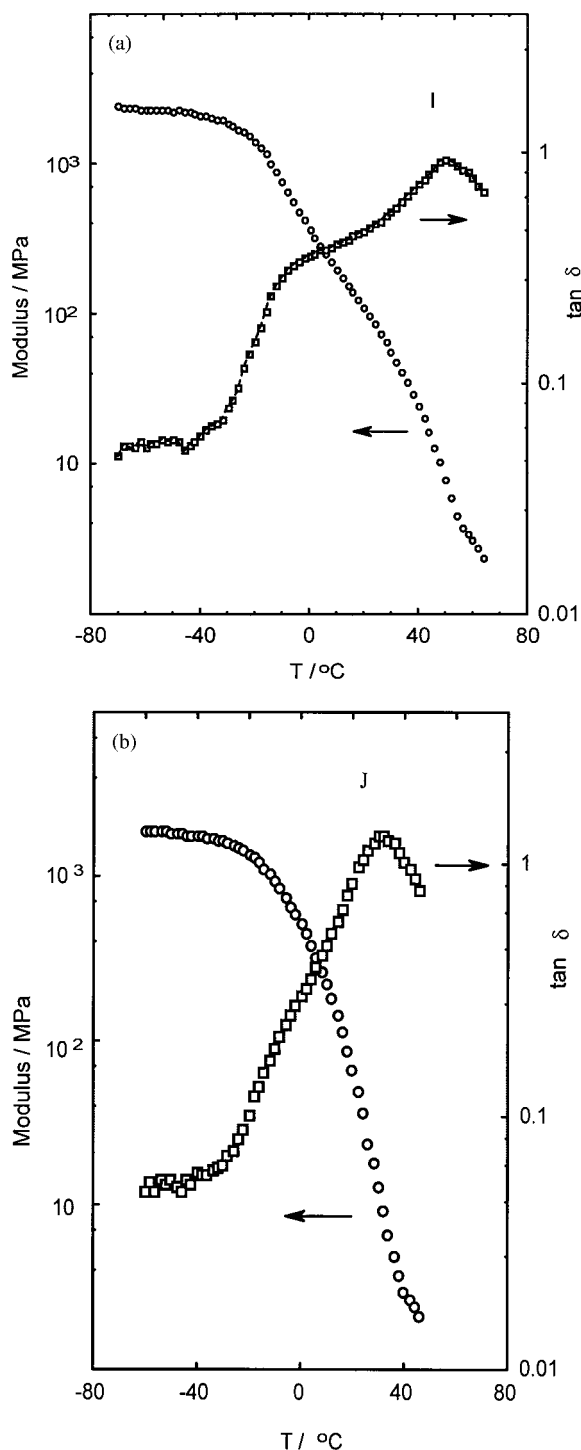


Figure 7 DMA spectra of copolymers (a) I and (b) J (See Table IV).

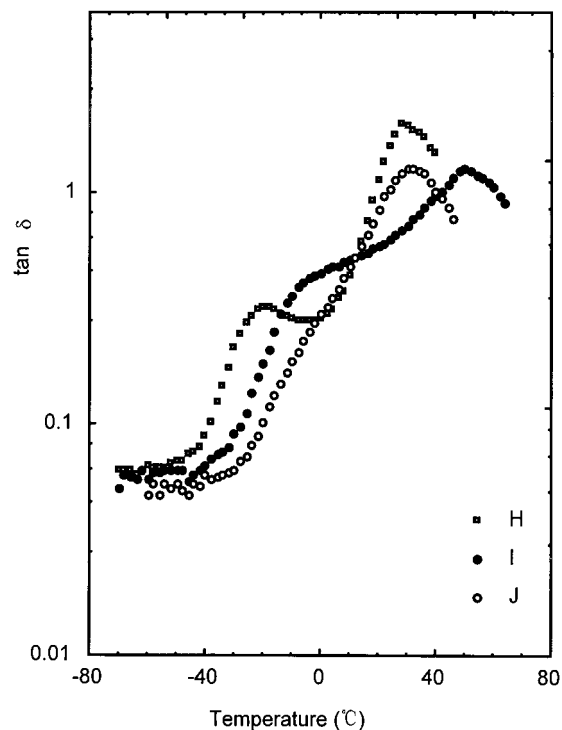


Figure 8 Tan δ versus temperature curves of copolymers (see Table IV).

particles were very stable both during the polymerization process and in storage.

There are two T_g s in the DMA spectra of the copolymers from the final latex; the lower one represents the chain relaxation and transition of the core component of the copolymers, and the higher one represents that of shell component.

When the composition of core component was fixed, its T_g location was not changed. As the proportion of hard monomer MMA in shell component increased, its T_g shifted accordingly to a higher temperature.

The dynamic mechanical behavior was obviously changed when the cross-linking agent TAIC was added to the core component. As the amount of added TAIC was increased, the T_g peak for core component shifted to a higher temperature. This result demonstrates that the addition of a cross-linking agent has a large effect on the copolymerization.

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