Studies on the Preparation of Stable and High Solid Content Emulsifier-Free Latexes and Characterization of the Obtained Copolymers for MMA/BA System with the Addition of AHPS

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ABSTRACT: 3-Allyloxy-2-hydroxyl-propanesulfonic (AHPS) salt was synthesized and used as a hydrophilic comonomer for the methyl methacrylate (MMA) and *n*-butyl acrylate (BA) emulsifier-free emulsion copolymerization system to obtain latices of stable and high-solid content. Properties of the latices, such as flow behavior, stability, and final diameter of the latex particles were studied. In addition, physical properties of the obtained copolymers, such as glass transition temperature (T_g), stress–strain behavior, and water resistance were investigated. With the addition of AHPS, the latices of stable and high-solid content (as high as 60%) were prepared. Flow of the latices follows the law of the Bingham body. The final diameter of the latex particles is 0.3–0.5 μm in diameter, which is larger than that of the conventional latex particles and decreases with the increase of AHPS and potassium persulfate (KPS) concentration. All the copolymers are atactic polymers, showed as single T_g on dynamic mechanical analysis spectrum. Compared with the copolymers that were prepared by surfactant emulsion polymerization, tensile strength, as well as water resistance is greatly improved. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 21–28, 2001

Key words: emulsifier-free; emulsion polymerization; acrylate; water resistance; 3-allyloxy-2-hydroxyl-propanesulfonic salt (AHPS)

INTRODUCTION

Much attention has paid to emulsifier-free emulsion polymerization due to its academic and practical interests.[1–2] Emulsifier-free emulsion polymerization has been carried out with or without ionic comonomers. For the case with ionic comonomers, used are carboxylic monomers,[3–4] polymeric organic sodium salt,[5–7] and cationic comonomers,[8] etc. For the case without ionic comonomers,[9] the fragments from the decomposition of water-soluble initiator behave as surface-active components. The essential role of the ionic comonomers in the emulsifier-free emulsion polymerization is that it can be chemically bonded onto the particle surfaces during two periods.[3] One is the nucleation period: it participates in the nucleation and is located on the particle surface. The other is after the nucleation: it can copolymerize with the comonomers to form cooligomers of its radicals in the aqueous phase which then diffuse to the particle surface to polymerize with the monomer and orient on the particle surface. Different comonomers will provide different reactivity and hydrophilic property, leading to different polymerization behaviors in

Table I   Recipes for the Polymerization

No.	MMA (g)	BA (g)	AHPS (g)	Water (g)	KPS (g)
0[a]	94	106	(SDS 2.4 g)	200	0.6
1	143	57	2.4	140	0.6
2	132	68	2.4	140	0.6
3	120	80	2.4	140	0.6
4	108	92	2.4	140	0.6
5	94	106	2.4	140	0.6
6	80	120	2.4	140	0.6
7	64	136	2.4	140	0.6

[a] As for the conventional emulsion polymerization, SDS replaces AHPS.

aqueous phase and therefore the nucleation behaviors.

Up to date, a lot of detailed particle nucleation mechanisms have been proposed for the emulsifier-free emulsion polymerization. Fitch et al.[10] proposed the homogeneous nucleation mechanism, in which a growing oligomeric free radical precipitates from the aqueous phase when it reaches a critical chain length ($n*$) to form a primary particle. Arai et al.[11] proposed that particles could be formed through coagulation of the terminated growing free radicals. In addition, growing free radicals as achieve a size and concentration at which they become surface active will undergo micellization as proposed by Van der Hoff.[12] Cox et al.,[13] Chen and Piirma,[14] and Vanderhoff.[15]

Therefore, the major purpose of this work does not focus on discussing the polymerization mechanisms. Instead, 3-allyloxy-2-hydroxyl-propane-sulfonic salt (AHPS) was synthesized and applied to the methyl methacrylate/n-butyl acrylate (MMA/BA) emulsifier-free emulsion polymerization system to obtain stable latices with perfect coating properties. With the addition of AHPS, emulsifier-free latices of stable and high-solid content (as high as 60%) were obtained. In addition, factors influencing properties of the latices and physical properties of the copolymers were discussed.

EXPERIMENTAL

Materials

MMA and BA were purified by distillation under reduced pressure. Allyl alcohol, sodium sulfite, epichlorohydrin, and sodium dodecyl sulfate (SDS) were analytical reagent and used as received. Water was deionized. Potassium persul-fate (KPS) was recrystallized in absolute methyl alcohol. All reagents are supplied by Beijing Chemical Reagent Co.

Synthesis of AHPS

In reference to the work of Mouzin et al.,[16] AHPS was synthesized as follows: 1 mol allyl alcohol and 1 mol epichlorohydrin were added to a 1-L reaction kettle that bubbled with nitrogen. The reaction temperature was raised to 100°C and maintained for 4 h. After that, 1 mol sodium sulfite dissolved in water was added to the kettle and maintained at 90°C for 5 h. After that, a colorless liquid solution was obtained. The total yield of AHPS is 86%.

Polymerization

Copolymerization was carried out in a 1-L five-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 rate was controlled at 400 rpm. First, water and AHPS were added to the kettle that was purged with nitrogen and heated to 70°C. Then the initiator and some monomer mixture were charged. The remaining monomer mixture was fed into the kettle for 4 h. Finally, the polymerization was kept at 90°C for 2 h. As for the conventional emulsion polymerization, it was carried out with the same conditions as above except that the AHPS was replaced by SDS. Recipes for the emulsion polymerization are presented in Table I.

Apparatus

The final diameter of the latex particles was observed by transmission electron microscopy (TEM) (Hitachi-600, Japan). The sample was pre-

Table II   Properties of the Latexes

No.	η (Pa s)	D (μm)	pH	s.c. (wt %)
0	0.0756	0.12	7.0	50
1	0.0289	0.46	7.0	60
2	0.0288	0.44	7.0	60
3	0.0284	0.50	7.0	60
4	0.0286	0.45	7.0	60
5	0.0285	0.46	7.0	60
6	0.0290	0.44	7.0	60
7	0.0292	0.45	7.0	60

η: shear viscosity at shear rate 729 s^{-1}; D: diameter of the latex particles; s.c.: solid content.

pared by dropping 0.1 mL of the diluted latices (0.5–1%) on a copper sieve coated with PVB [poly-(vinyl butyrate)] and allowed to air-dry at room temperature. Flow behavior of the latices was estimated by rotation viscometer (Rheotest-2, formerly DDR) with a sample volume of 25 mL and tested at 25°C. Glass transition temperature (T_g) was investigated by dynamic mechanical analysis (DMA) (Rheovibron DDV-II-EA, Japan) at 3.5 Hz, with a heating rate of 2°C/min, and sample size of $2 \times 0.20 \times 0.020$ cm^3. Tensile behavior of the copolymers was studied by a Testometric Materials Testing Machine (M500–25KN, England) at 23°C, with a tensile rate of 100 mm/min and a tensile load of 250N. Tensile stress is given relative to the original cross-sectional area (A_0) of the sample; the ultimate elongation is defined as $\epsilon\%$ $= (L - L_0)/L_0 \times 100$. Water resistance was characterized by soaking the copolymers at 23°C in water and weighing the amount of water absorbed at a preset time period. Sample size is 2.0 cm in length, 1.5 cm in width, and 0.60 ± 0.10 mm in thickness. Water uptake is defined as wt % $= (W - W_0)/W_0$, where W_0 is the weight before soaking and W is the weight after soaking. (Copolymers subjected to the physical properties test 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

Properties of the Latices

Shear viscosity at a shear rate of 729 s^{-1}, diameter of the final latex particles, and solid content of the latices are listed in Table II.

As seen from Table II and Figure 1, the final diameter of the emulsifier-free latex particles is much larger than that of the conventional latex, which may have contributed to the difference in latex-particle formation mechanism. Latex particles formed in conventional emulsion are chiefly by micelle nucleation mechanism as proposed by Harkins.[17] Nearly all the polymer-particle nuclei are formed by polymerization of the monomer or monomers in the oil cores inside the emulsifier micelles. Particle size is greatly influenced by the emulsifier concentration; the higher the concentration of emulsifier, the higher the number of particles formed in the system, the smaller particle size would be. In general, for latex particles prepared by surfactant emulsion, the particle size is about 100–300 nm, as observed in this study. Latex particles in acrylate emulsifier-free emulsion is formed mainly by homogeneous nucleation mechanism as proposed by Fitch,[10] in which a growing oligomeric-free radical precipitates from the aqueous phase when it reaches a critical chain length ($n*$) to form a primary particle. Then the polymerization is continued in the particles. The number of particles formed in emulsifier-free system is limited, therefore, particle size is surely larger than that of the conventional latex. In ad-
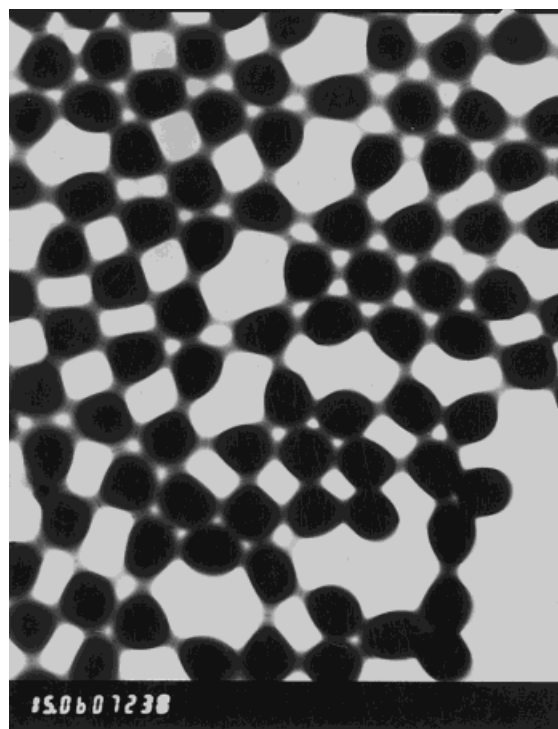

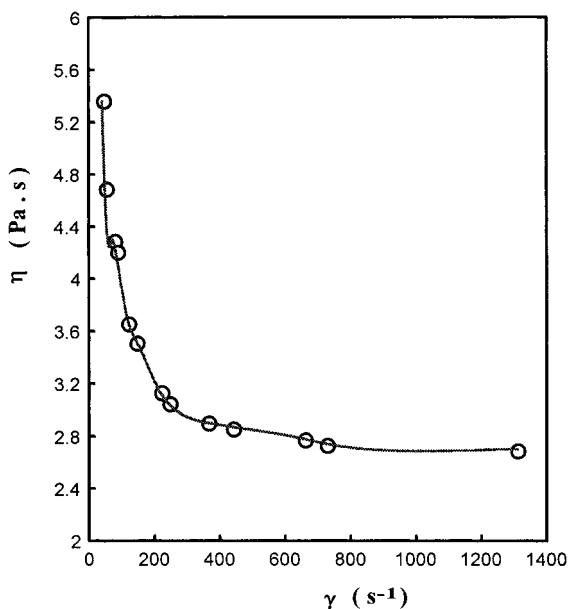**Figure 1**   TEM photograph of the emulsifier-free latex particles (Sample No. 4, magnified ×15,000).

Figure 2 Variation of shear viscosity (η) with shear rate (γ) for the emulsifier-free, high solid content latex (Sample No. 5).

dition, in the case of the hydrophilic groups such as sulfate and hydroxyl that were introduced by the addition of hydrophilic comonomers and initiators in the emulsifier-free emulsion polymerization that bonded onto the latex particles, would also lead to the increase of the diameter of latex particles.

All the latex particles are chiefly formed by the homogeneous nucleation mechanism as proposed by Fitch et al.[10] Therefore, as seen from the morphology of the emulsifier-free latex particles in Figure 1, particles are of almost the same size, that is, monodispersed. However, latex particles formed in the conventional emulsion polymerization system are polydispersed, because latex particles can be formed by micelle nucleation mechanism, homogenous mechanism, and heterogeneous mechanism as suggested by Min and Ray.[18]

It can be seen from Table II that when the amount of monomers and other ingredients is constant, the diameter of the latex particles and viscosity of the latices show little variation, even though the ratio of MMA/BA changed. Viscosity of the latices prepared by conventional emulsion polymerization is much higher than that of the emulsifier-free emulsion latices. In addition, to probe the flow behavior of the high solid content and water-borne latex, shear viscosity (η) at different shear rate (γ) was tested. As shown in Figure 2, apparent viscosity decreases sharply as

the shear rate increases (called shear thinning). There existed a stress limit to flow in Figure 3, above which, shear rate was varied almost linearly with shear stress, so the flow of the latex obeys the Bingham fluid body.[19] It is a desirable characteristic for paints because the concentrate latices would not flow until extra force is applied, which is conducive to the operation as it is used directly as paints.

Stability of the Emulsifier-Free Latex

The experimental results show that, with the addition of AHPS, latices prepared by emulsifier-free emulsion polymerization are quite stable and the solid content reaches as high as 60%. During the polymerization process, no coagulates or scraps are formed. When the latices have been stored for 10 months at room temperature, no precipitates are produced. However, the amount of AHPS added to the emulsifier-free emulsion polymerization is only 1–2% based on the total weight of monomer. So it obviously demonstrates that AHPS is an effective comonomer to obtain high solid content emulsifier-free latex.

On the one hand, the functional monomer AHPS is soluble in the water phase. As the polymerization is carried out, AHPS can be bonded onto the surface of the latex particles, provided the sulfonate groups acted as surfactant, or AHPS
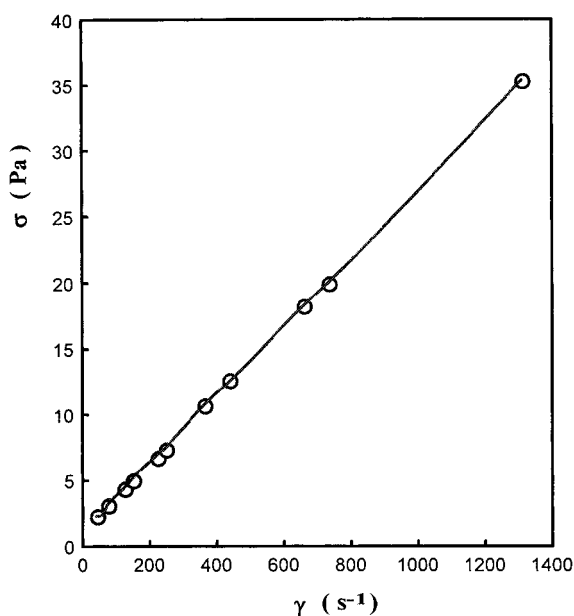

Figure 3 Variation of shear stress (σ) with shear rate (γ) for the emulsifier-free and high solid content latex (Sample No. 5).

Table III   Effect of KPS Content on the Diameter of the Latex Particles

No.	8	9	10	11
KPS (wt %)	0.3	0.5	0.8	1.0
D (μm)	0.46	0.42	0.39	0.37

Other conditions: MMA = 94 g, BA = 106 g, water = 140 g, AHPS = 2.4 g, pH = 7.0; wt % of KPS is based on total monomers.

can be polymerized in water phase acted as polyelectrolyte hydrosoluble chains. No matter what the case is, surface-charge densities of the latex particle can be greatly improved and therefore lead to the production of high solids content and stable latices.

On the other hand, KPS is also a great help to the improvement of the stability of the latices. Conductometric titrations on dialyzed samples have demonstrated the presence of sulfate, hydroxyl, and weak-acid groups on the particle surfaces.[20] The end groups on the particle surfaces act as surfactants to increase electostatic repulsion and therefore stabilize the particles and result in high-solid content.

Influence of the Content of KPS and AHPS on the Size of Latex Particles

KPS and AHPS concentrations control the size of latex particles in the emulsion polymerization system. As seen from the data listed in Tables III and IV and Figures 4 and 5, the final diameter of the latex particles decreases with the increasing amount of KPS and AHPS that was added to the emulsifier-free emulsion polymerization system. Higher initiator and AHPS concentration give smaller particle size because more particles are produced. In addition, the final diameter of the latex particles shows logarithmic variation with KPS and AHPS concentration and obeys the

Table IV   Effect of AHPS Content on the Diameter of the Latex Particles

No.	8	12	13	14
AHPS (wt %)	1.2	2.0	3.0	4.0
D (μm)	0.46	0.40	0.38	0.34

Other conditions: MMA = 94 g, BA = 106 g, water = 140 g, KPS = 0.3 g, pH = 7.0; wt % of AHPS is based on total monomers.

Log D = 0.371 - 0.169Log [KPS] + C
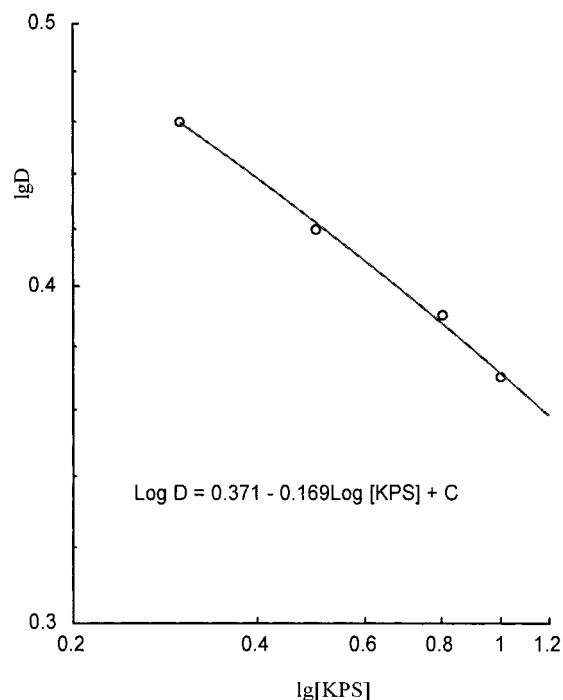
Figure 4   Logarithmic plot of particle diameter, D (μm), versus KPS concentration (wt %).

equations: Log D = 0.371 − 0.169 log[KPS] + C, and Log D = 0.46 − 0.196 log[AHPS] + C for initiator KPS and comonomer AHPS, respectively.
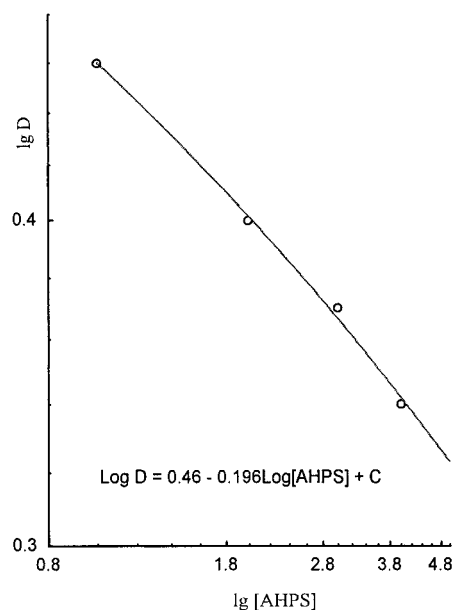

Log D = 0.46 - 0.196Log[AHPS] + C

Figure 5   Logarithmic plot of particle diameter, D (μm), versus AHPS concentration (wt %).

Table V   Data of T_g from Theory Calculation and DMA Measurement

No.	0	1	2	3	4	5	6	7
Theoretical T_g (K)	273	313	303	293	283	273	263	253
Observed T_g (K)	301	346	337	324	312	302	292	283

Physical Properties of the Copolymers

Glass Transition Temperature

Because the lowest film formation temperature is near T_g, T_g's of the copolymer had to be decreased to about 298 K to prepare latices that can be film-formed at room temperature. As we know, T_g of PMMA is 378 K and T_g of PBA is 219 K, so T_g's of the copolymers can be adjusted according to Fox equation, $1/T_g = w_1/T_{g,1} + w_2/T_{g,2}$ ($w_1 + w_2 = 1$). To find the optimum T_g, a series of experiments was carried out with different recipes of MMA and BA. Data of T_g for the copolymers are listed in Table V.

The results show that the observed T_g is about 28 K higher than that of the theory calculation according to the Fox equation. Because latex No. 5 can film-form at room temperature without extra heating and T_g of its copolymer is 302 K, therefore, it is the preferable recipe for preparing latex that can be film-formed at room temperature. In addition, T_g of the copolymer that was prepared by emulsifier-free emulsion polymerization (No.5) is equal to that of the copolymer that was prepared by conventional emulsion polymerization (No. 0), evidently showing that polymerization methods have no influence on T_g.

Typical DMA spectrum is shown in Figure 6; only single T_g appears on DMA spectrum and the modulus drops sharply near T_g, indicating that the obtained copolymers are of atactic polymers. It is a little different from the results reported by Chen and coworkers[21] that heterogeneous structure is displayed. Although water solubility of MMA is 14 times that of BA, starve copolymerization was carried out in this copolymerization system; that is, no excess monomers are left in the water, so MMA had to copolymerize with BA and form the homogenous copolymers.

Tensile Behavior

Typical stress–strain curves are shown in Figure 7. Stress–strain curves for both the copolymers that were prepared by emulsifier-free or conventional emulsion polymerization exhibit the elastic stress–strain behavior, showing increasingly strong stress with increasing strain until broken. However, tensile strength of the emulsifier-free copolymer is much higher than that of the conventional copolymer, which is the advantage of the emulsifier-free emulsion polymerization, because no extra emulsifier is left in the copolymer. Emulsifiers that were left in the copolymer for conventional emulsion polymerization system would lead to weakening of interaction between molecular chains and result in lowering of the tensile strength.

Water Resistance

Water uptakes of the copolymers are shown in Figures 8 and 9. Water uptakes of the copolymers that are prepared by emulsifier-free emulsion polymerization are much lower than that of the
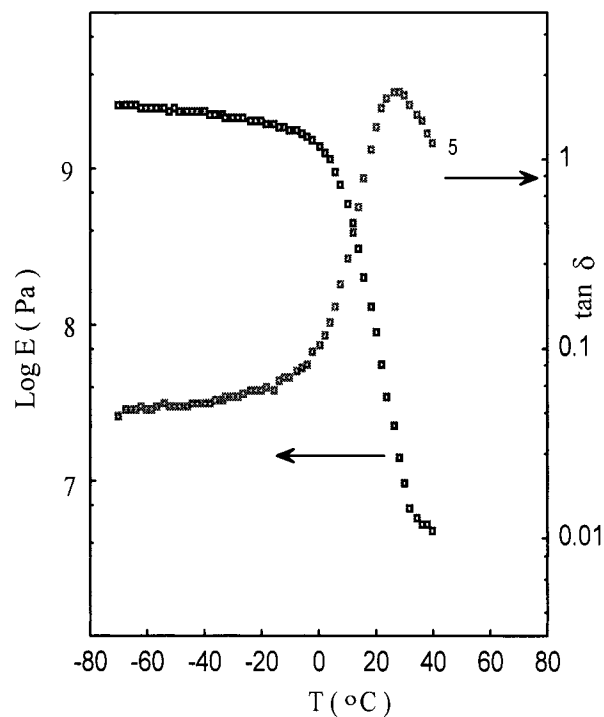

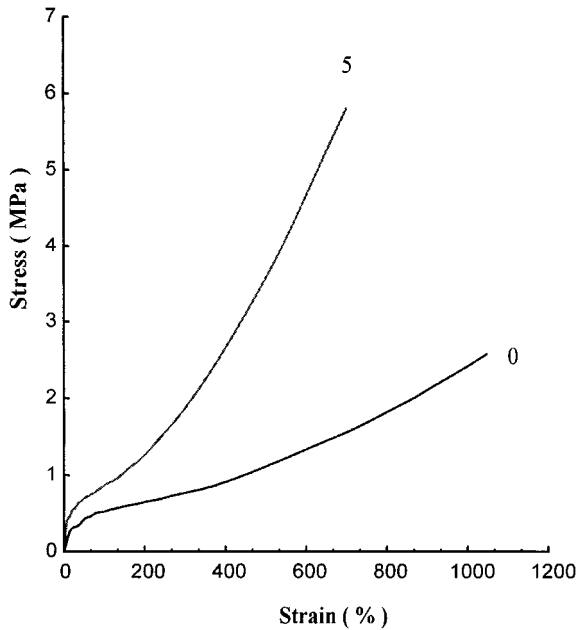**Figure 6**   Typical DMA spectrum of the emulsifier-free copolymer (Sample No. 5).

Figure 7 Stress–strain curves for the copolymers (Sample No. 5 and No. 0).

emulsifier-contained sample when soaked for 1 week. Extra emulsifiers that were added to conventional emulsion polymerization system to sta-
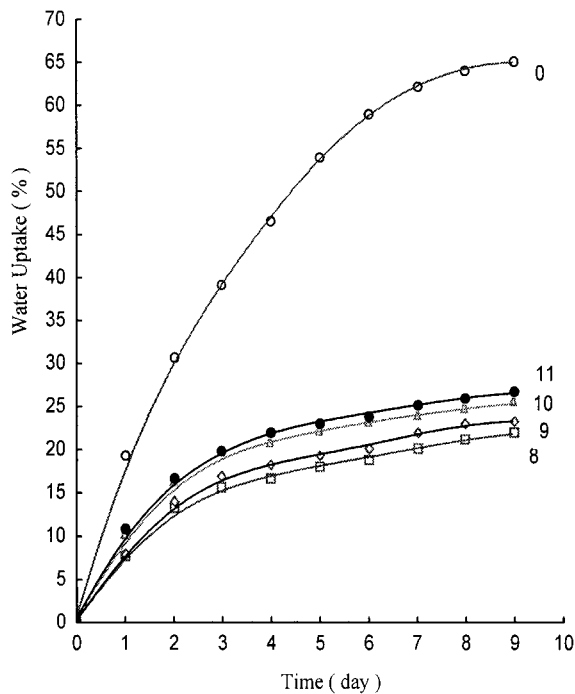

Figure 8 Influence of KPS concentration on water resistance of the copolymers and a comparison with conventional emulsion copolymer.
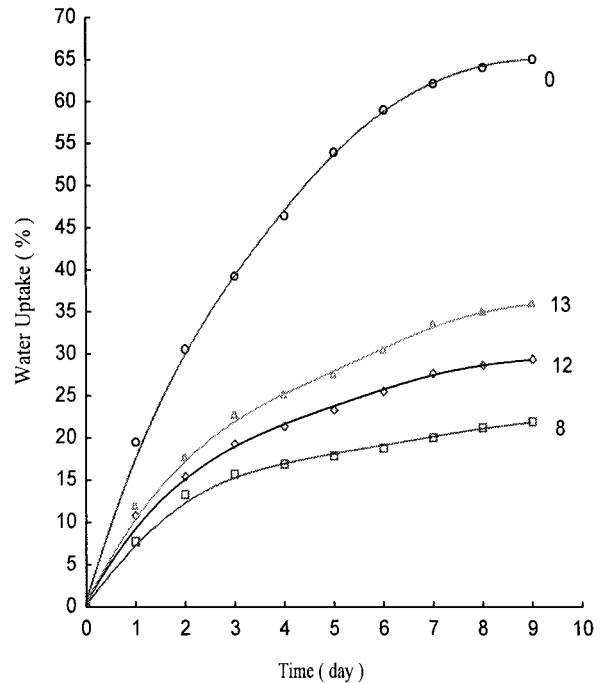

Figure 9 Influence of AHPS concentration on water resistance of the copolymers and a comparison with conventional emulsion copolymer.

bilize the latex are only physically absorbed on latex surface, leading to the high amount of water uptake. Water uptakes of the copolymers increase with the increase of KPS and AHPS concentration because the more the KPS and AHPS added to the emulsifier-free emulsion polymerization system, the more the hydrophilic groups would be introduced to the copolymer. That is to say, the improvement of the latex stability always accompanies a sacrifice of water resistance, so the amount of initiator and ionic comonomers added to the emulsifier-free emulsion polymerization system should be thoroughly considered when preparing materials of high water resistant.

CONCLUSION

AHPS is a kind of effective comonomer for the preparation of stable and high solid content and water-borne emulsifier-free latices. With the addition of AHPS, stable and high solid content (as high as 60%) latices were prepared. Flow of the latices follows the law of the Bingham body. The obtained particles are 0.3–0.5 μm in diameter, monodispersed, and larger than that of the conventional latex particles. Particle sizes decrease

with the increase in AHPS and KPS concentration in the emulsifier-free system. All the copolymers are atactic polymers, showing single T_g on DMA spectrum. Compared with the copolymer prepared by conventional emulsion polymerization, tensile strength, as well as water resistance of the copolymers, is obviously improved.

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