Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 4959–4966

polymer

www.elsevier.com/locate/polymer

The influence of monomer types on the colloidal stability in the miniemulsion copolymerization involving alkoxysilane monomer

Yingwu Luo *, Huajun Xu, Bin Zhu

Polymer Reaction Engineering Division, The Union State Key Laboratory of Chemical Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 9 January 2006; received in revised form 4 April 2006; accepted 10 May 2006
Available online 30 May 2006

Abstract

Unlike conventional emulsion polymerization, monomer droplet nucleation becomes dominant in miniemulsion polymerization, offering the miniemulsion polymerization a great advantage over conventional emulsion polymerization when incorporating alkoxysilane monomer, which can easily undergo premature hydrolysis and condensation reactions, into polymer latex. The extensive premature hydrolysis and condensation can lead to the issue of the colloidal instability. In this article, the influence of monomer types on the colloidal stability in the miniemulsion co-(or ter-)polymerization was investigated when incorporating alkoxysilane monomer into styrene or acrylate latex. In the cases of butyl acrylate (BA)/γ-methacryoxypropytrimethoxysilane (MPMS), BA/methyl methyacrlate (MMA)/MPMS, and BA/styrene (St)/MPMS miniemulsion polymerization, nearly no coagulum was observed. The obtained latex had a long shelf life. However, the coagulum was formed in the late stage of MMA/MPMS and St/MPMS miniemulsion copolymerization. The shelf life of the corresponding latex was short. The selection of the main monomer, which can fast consume alkoxysilane comonomer, was critical to obtain the stable latex. In this way, the alkoxysilane groups were completely buried in particles thus the coagulation caused by condensation reactions derived from the alkoxysilane hydrolysis among particles was suppressed.

Keywords: Miniemulsion polymerization; Colloidal stability; Alkoxysilane

1. Introduction

Due to its benign environmental and safety characteristics, emulsion polymer latex is rapidly used as coating materials for an increasing number of industrial and consumption applications in replace of traditional solvent coatings. Over last 20 years, the performance gap between conventional solvent-based and water-borne (heterogeneous) coatings has progressively narrowed. However, the challenge of reconciling the conflicts between high mechanical properties and further decrease of volatile organic compounds (VOCs) in designing emulsion polymer is still remained [1]. A typical approach to solve this issue is to post-crosslink polymer chains after the film formation [2], [3]. In this way, film-formation additives with low molecular weight, which are the major parts of VOCs and have negative influence on environment and human health, could be removed during coating formulation.

One attempt of implementing post-crosslinking is to incorporate alkoxysilane groups into polymer chains via emulsion copolymerization. The hydrolysis and condensation reactions of alkoxysilane groups at room temperature would lead to the post-crosslinking after film formation [4]; the mechanism is shown in Fig. 1. However, alkoxysilanes are inherently susceptible to premature hydrolysis and condensation reactions in the aqueous phase during polymerization and storage. In conventional emulsion polymerization, the main loci of polymerization are the particles instead of monomer droplets. The particles are formed via the micellar nucleation or the homogeneous nucleation [5]. In the process of polymerization, monomer molecules in monomer droplets, which serve as monomer reservoirs, gradually transport to particles through water [5]. In such a situation, it is unavoidable for the alkoxysilane monomer to contact water, leading to the premature hydrolysis and condensation.

The premature hydrolysis and condensation reactions should be avoided, because the extensive hydrolysis and condensation could lead to condensation reactions between particles demonstrated by Fig. 2 [6] and thus the formation of coagulum during the emulsion polymerization. On the other

---

* Corresponding author. Tel.: +86 571 87951832; fax: +86 571 87951612.
E-mail address: yingwu.luo@cmsce.zju.edu.cn (Y. Luo).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.05.020

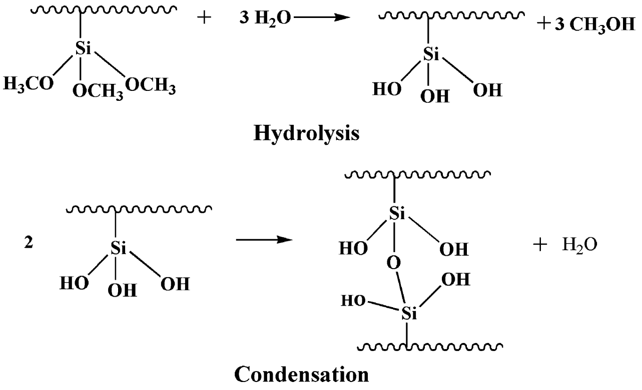


Fig. 1. Hydrolysis and condensation reactions of alkoxysilanes.

hand, such a reaction also results in a poor shelf stability of the latex.

A great number of patents and literatures in preparing stable silicone-modified self-crosslinkable latexes by conventional emulsion polymerization had been published in past decades, from which some solutions were offered to avoid premature crosslinking of organic alkoxysilane. Since, the hydrolysis of alkoxysilane is both acid and base catalyzed and the minimum hydrolysis rate occurs at about pH 7 for most systems [6–8], good control of pH value is helpful to minimize premature condensation. In order to avoid prolonged contact with water when preparing silicon-modified self-crosslinkable latexes, alkoxysilane monomers were often continuously added to a seed latex [9–11]. Novel alkoxysilanes with larger steric hindrance, which means a lower hydrolysis rate, were used to obtain stable emulsion copolymer [12–14] and a stable emulsion copolymer latex could also be obtained by a concurrent free radical and cationic initiated emulsion polymerization [15].

Recently, batch miniemulsion copolymerization of *n*-butyl acrylate (BA)/vinyltriethoxysilane (VTES) was investigated. It was concluded that miniemulsion copolymerization have potential in incorporating high amounts of vinyltriethoxysilane into butyl acrylate latex by a one-step batch process [16,17]. Miniemulsion polymerization is a modified emulsion polymerization process [18–20], in which the monomer is pre-emulsified as 30–500 nm monomer droplets by high shear, stabilized by the combination of surfactant and costabilizer. Unlike conventional emulsion polymerization, monomer droplet nucleation is dominant in a miniemulsion polymerization that means the particles directly form from monomer mini-droplets since there exists no micelles and the monomer droplets have very large interfacial area to efficiently capture the radicals born in the aqueous phase [18–20]. The dominant monomer droplet nucleation has been substantially supported by the experimental data from different groups [19]. When hexadecane is used as a co-stabilizer, it is well accepted that the most particles are directly transformed from the droplets with carefully sonification procedures [18,19]. The most compelling evidence for the dominant monomer droplet nucleation is experimental observations that the number of particles is independent of the initiator levels [19]. In a miniemulsion polymerization system, it is not necessary for monomer to diffuse from monomer droplets to growing polymer particles, which allows the incorporation of hydrophobic materials and obtains stable latexes. For siloxane comonomer, it becomes possible to suppress the premature hydrolysis and condensation of alkoxylsilane groups in a miniemulsion copolymerization. Marcu et al. [16,17] reported that for the copolymerization of BA and VTES with high amounts of VTES, the coagulum formed in miniemulsion is much less than it formed in conventional emulsion. Stumbé et al. [21] synthesized poly(methyl methacrylate-*g*-dimethylsiloxane) copolymers via a miniemulsion process. Landfester et al. synthesized polydimethylsiloxane-containing polymer latexes by polymerizing telechelic polydimethylsiloxane macromonomers wearing two terminal acrylate units in miniemulsion [22].

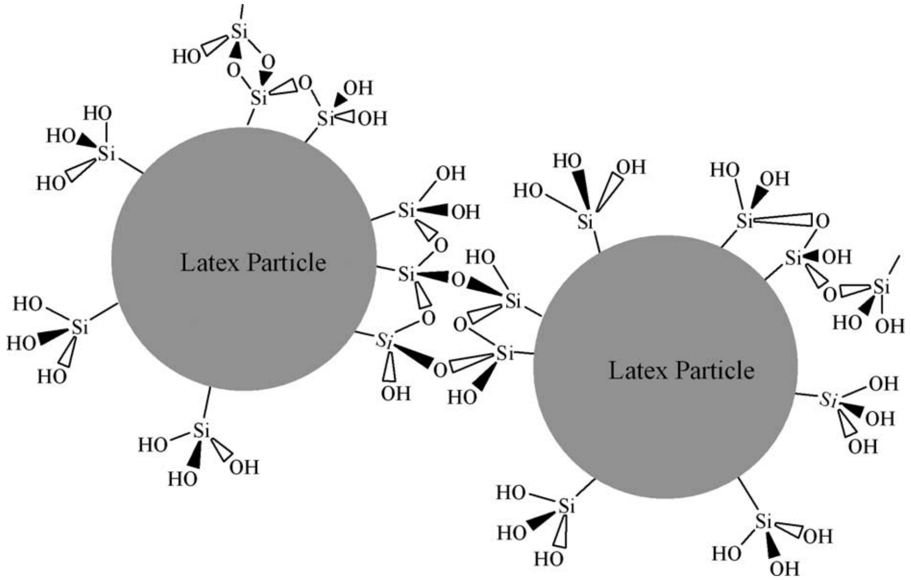


Fig. 2. Illustration of condensation reactions occurred between two adjacent latex particles, leading to coagulation (bridging flocculation).

In the present study, the miniemulsion co-(or ter-)polymerization of methyl methacrylate, styrene, and butyl acrylate, three typical types of monomer for emulsion polymerization, with alkoxysilane monomer of γ-methacryoxypropytrimethoxysilane (MPMS) and vinyltriethoxysilane (VTES) was investigated. The influence of monomer types on colloidal stability, particle size and particle size distribution was also studied.

2. The experimental

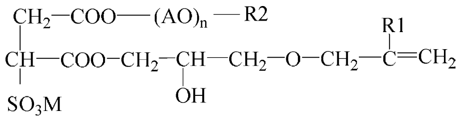
2.1. Materials

Deionized water (conductivity < 4 s/cm) was used as received. Styrene (St), methyl methacrylate (MMA), butyl acrylate (BA), and α-methacrylic acid (MAA) were purified by vacuum distillation prior to use. Ammonium persulfate (APS > 99%), sodium dodecyl sulfate (SDS, surfactant), hexadecane (HD, costabilizer; Aldrich), and Latemul S-180A (reactive surfactant, Kao Chem.) were used without further purification. Alkoxysilane monomers γ-methacryoxypropytrimethoxysilane (MPMS, Dow-corning) and vinyltriethoxysilane (VTES) were also used without further treatment.

A composite surfactant system was used. Latemul S-180A is a reactive polymeric surfactant with a structure shown in Scheme 1. The reactive surfactant was used to reduce the amount of the normal surfactant (SDS). The high amount of SDS increases water sensitivity and affect gloss of the coating film formed from the latex [23].

2.2. Miniemulsion polymerization

Firstly, emulsifiers (SDS and Latemul S-180A) and MAA were dissolved in water and the main monomer was mixed with MPMS (or VETS) and hexadecane. The recipe was listed in Table 1. Then, the organic mixture was added to the emulsifier aqueous solution to form a coarse emulsion with magnetic stirring for 2 min. The coarse emulsion was ultrasonified by a KS-600 Sonifier (amplitude 70%, 600 W) for 15 min under magnetic stirring in an ice–water bath. The resultant miniemulsion was then transferred into a 250 mL five-necked flask reactor equipped with a reflux condenser, a thermometer, a nitrogen inlet, and a mechanical stirrer. The miniemulsion was stirred at room temperature for 15 min while purging with nitrogen and then the reactor was immersed in a water bath at 60 °C. Finally, the addition of APS dissolved in 5 g of water gave the zero time of the miniemulsion polymerization. The time of polymerization was 210 min. The final total conversion was around 91%. There has been extensive evidence to show that the droplet nucleation is dominant with the above sonication and polymerization procedure [19].



$$\underset{\displaystyle \mathrm{SO_3M}}{\overset{\displaystyle \mathrm{CH_2{-}COO{-}(AO)_n{-}R2}}{\mathrm{CH}}}\mathrm{{-}COO{-}CH_2{-}}\underset{\displaystyle \mathrm{OH}}{\mathrm{CH}}\mathrm{{-}CH_2{-}O{-}CH_2{-}}\overset{\displaystyle \mathrm{R1}}{\mathrm{C}}\mathrm{{=}CH_2}$$

Scheme 1. The structure of Latemul S-180A, where R1 represents a hydrogen atom or a methyl group; R2 represents C_2–C_4 alkylene group; *n* represents an integer from 0 to 200; and M represents an ammonium group, a sodium atom or a potassium atom.

Table 1
Miniemulsion co(or ter)-polymerization recipe

Ingredients	Amounts
Deionized water	80 g
Main monomer (St, MMA or BA)	20 g
Methacrylic acid (MAA)	1 wt% on main monomer
MPMS or VTES	10 wt% on main monomer
Sodium dodecyl sulfate (SDS, surfactant)	2 wt% on main monomer
Latemul S-180A (polymeric surfactant)	4.5 wt% on main monomer
Ammonium persulfate (APS)	0.38 wt% on water
Hexadecane	2 wt% on main monomer

Considering that in most commercial emulsion polymerization a small fraction of MAA or AA was used to improve the mechanical properties of the coating film, 1% MAA on main monomer was also used in current studies. Santos et al. [24] investigated the batch emulsion copolymerization of styrene with butyl acrylate in the presence of metharcrylic acid. The distribution of the carboxyl groups at different positions with the emulsion system (surface and core of particles, and in the aqueous phase) was found to be pH dependent. At acidic pH, most methacrylic acid groups are located in the interior of particles. In the current study, the pH values of systems were about 4.6 before polymerization and about 2.6 after polymerization. The acidic pH is helpful to suppress the possible homogeneous nucleation caused by the addition of MAA.

2.3. Coagulum percentage

The amounts of coagulum formed during miniemulsion copolymerization were evaluated by gravimetry. After the polymerization was completed, the coagulum was collected by filtration through 200 mesh stainless steel wire cloth. The coagulum percentage was calculated by

$$C_P = W_C/W_M \times 100\%$$

where C_P, W_C, and W_M are coagulum percentage (%), the amount of coagulum(g), and the amount of the total input monomer(g) (Note: monomer conversion close to 100%), respectively.

2.4. Particle size and particle size distribution of latex

The particle size and particle size distribution (PSD) of the final latex were measured by dynamic light scattering (Zetasizer3000 HAS Zeta, Malvern Co., UK) at 25 °C. The ratio of weight average diameters to number average diameters was used to characterize PSD. The latex was diluted with deionized water before measuring in order to adjust suitable light strength to the measurement conditions.

2.5. Transmission electron microscopy

Transmission electron microscopy (TEM) analysis was performed with a JEM-1230 (Jeol Electron Microscope).

The synthesized latexes were diluted with deionized water to about 1000:1. One drop of latexes was placed on the coated side of a 200-mesh copper grid in a Petri dish. After 18–24 h of drying, the samples were ready to be analyzed.

3. Results and discussion

3.1. Copolymerization of MMA/MPMS, St/MPMS, and BA/MPMS

MMA, St, and BA were, respectively, copolymerized with MPMS (Runs 4–6). Fig. 3 shows the total conversion versus the reaction time for various monomer combinations. It is clear that all the polymerization proceeds very fast. Within 50 min, the conversion reaches 91%. In the meanwhile, the coagulum percentage was monitored during the polymerization. It is surprisingly found that the types of the main monomer dramatically influenced the colloidal stability during the copolymerization. In the BA/MPMS copolymerization system, nearly no coagulum was formed in the entire polymerization course, indicating that the colloidal system was stable. However, for the MMA/MPMS copolymerization, the coagulum percentage was as high as 21.6% in the end of polymerization. The St/MPMS miniemulsion copolymerization has a moderate stability with a coagulum percentage of 5.5% in the end of polymerization. The changing trends of coagulum percentage with polymerization time and conversion for MMA/ MPMS and St/MPMS copolymerization are presented in Figs. 4 and 5, respectively. From Fig. 4, it is found that in the first 30 min of the polymerization, there is no coagulum formed in both systems. Since then, the coagulum percentage increases dramatically with time in the case of MMA/MPMS but more moderate in the case of St/MPMS. Fig. 5 indicates that the coagulum is formed after 85% conversion. Before that, no coagulum was observed. As a comparison, no coagulum was observed in the homopolymerization of each main monomer without alkoxysilane monomer (Runs 1–3). For the BA/MPMS copolymerization system, the particle size and PSD is as same as those without MPMS (Table 2). But the particle sizes of MMA/MPMS and St/MPMS copolymerization systems, in which PSDs are bi-modal, are larger than those of their corresponding homopolymerization systems. These observations clearly show that premature hydrolysis and condensation of MPMS could not be avoided merely by using miniemulsion polymerization technique. The colloidal stability is highly dependent on main monomer types.

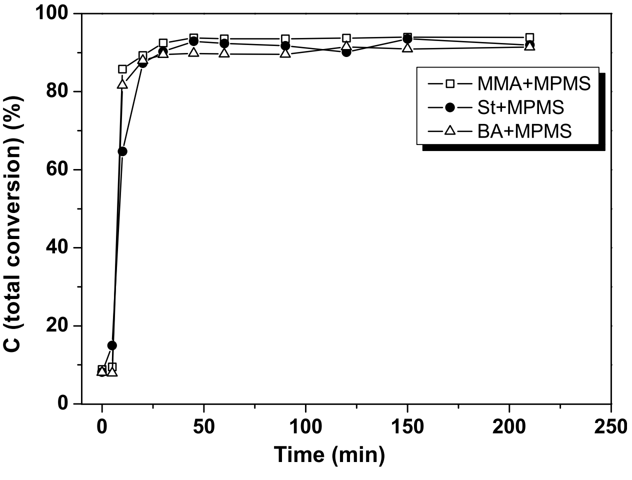


Fig. 3. The total conversion versus the reaction time for various monomer combinations.

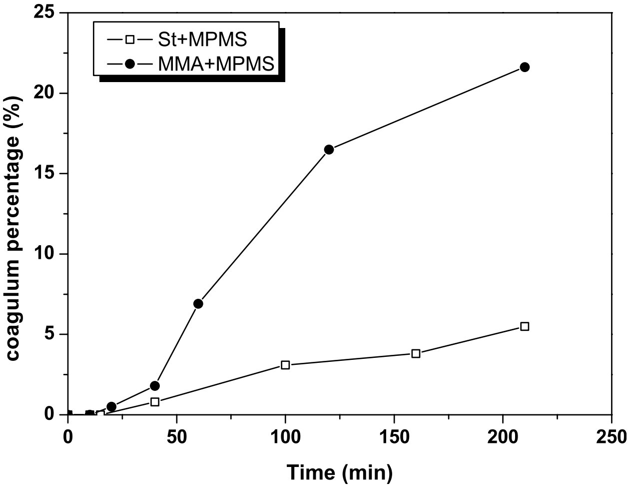


Fig. 4. The coagulum percentage versus the reaction time in St/MPMS and MMA/MPMS binary copolymerization systems.

Besides, the main monomer types, the alkoxysilane monomer types also play a role in the colloidal stability during the miniemulsion copolymerization. In Run 7, MPMS was replaced by VTES, considering that ethoxysilane groups in VTES have larger steric hindrance than methoxysilane groups in MPMS in the view of molecular structures. Thus, it is supposed that VTES should be less susceptible to hydrolysis than MPMS. However, it was found that the coagulum percentage of the BA/VTES miniemulsion copolymerization system was larger than that of the BA/MPMS copolymerization system, as described in Table 2. In the meanwhile, the particle size of the BA/VTES copolymerization system was also larger

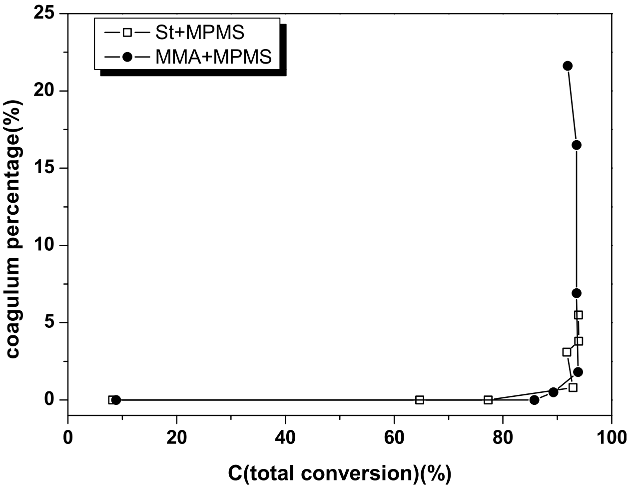


Fig. 5. The coagulum percentage versus the total conversion in St/MPMS and MMA/MPMS binary copolymerization systems.

Table 2
The colloidal stability during miniemulsion co-(or homo-)polymerization

Run	Monomers	Coagulum (wt%)[a]	Particle size (nm)	PSD
1	MMA	0	74.6	1.08
2	St	0	85.8	1.13
3	BA	0	85.1	1.09
4	MMA/MPMS	21.6	166.9/767.8	Bi-modal
5	St/MPMS	5.5	103.3/373	Bi-modal
6	BA/MPMS	0.02	85.4	1.10
7	BA/VTES	2.21	96.4	1.06

[a] The coagulum in the end of polymerization.

than that of the BA/MPMS copolymerization system. Both of these data suggest that the BA/VTES copolymerization system is less stable than the BA/MPMS copolymerization system, which is in conflict with the inference of the molecular structures of these alkoxysilanes.

3.2. Terpolymerization of MMA/BA/MPMS and St/BA/MPMS

In many application fields of emulsion polymer coatings, the glass transition temperature is a critical parameter for film formation. MMA and St are considered to be 'hard' monomer for PMMA and PSt have T_gs around 100 °C. BA is 'soft' monomer with PBA's T_g at -54 °C. Emulsion homopolymer of MMA or St is seldom used in commercial applications. In most commercial applications, BA is often used to adjust the T_g of the emulsion copolymer. Considering these reasons, MMA/BA/MPMS and St/BA/MPMS miniemulsion terpolymerization were investigated (MMA(or St)/BA = 51/49 based on weight). It was found that the colloidal stability of miniemulsion terpolymerization systems was excellent and nearly no coagulum was observed in both systems. Particle sizes were almost as the same as those of homopolymerization of St and BA. The data are listed in Table 3. Comparing to data of binary copolymerization systems, it was obvious that monomer BA played a critical role in improving the colloidal stability.

3.3. Storage stability

For Runs 4 (MMA/MPMS copolymerization) and 5 (St/MPMS copolymerization), it was found that the final latex became totally coagulated within 2 days. On the other hand, for all the other runs, the final latex remained stable over 6 months.

Table 3
The colloidal stability during miniemulsion terpolymerization course of MMA/BA/MPMS and St/BA/MPMS

Run	Monomer	Coagulum (wt%)[a]	Particle size (nm)	PSD
8	MMA/BA/MPMS	0.25	87.0	1.10
9	St/BA/MPMS	0.08	85.2	1.09

[a] The coagulum in the end of polymerization

3.4. TEM images

The latexes of poly(MMA-*co*-MPMS), poly(MMA-*co*-BA-*co*-MPMS), poly(St-*co*-MPMS), and poly(St-*co*-BA-*co*-MPMS), whose glass transition temperatures are higher than room temperature, were characterized by TEM as soon as the polymerization ended. The typical TEM images are shown in Fig. 6. For poly(MMA-*co*-MPMS) latex, two kinds of TEM images were observed. One kind of TEM images ((a)-2) looks similar to other systems. The other kind of TEM images ((a)-1) clearly shows that particles are 'bridged' by hydrolysis and condensation products of MPMS. The bridged coagulation would lead to a unique coarse and irregular dark region (the condensation product), as seen in Fig. 6(a)-1. Surprisingly, the particles are not covered homogeneously by condensed products of MPMS. For the other copolymerization systems, TEM images look homogeneous. However, it should be cautious to draw a conclusion that the MPMS units are totally buried within the particles, considering that the gelation occurred within 2 days for the latex of poly(St-*co*-MPMS). In the cases of terpolymerization (b) and (d), TEM images show that the fused boundary of the particles looks dark due to the lower T_gs, the terpolymer particles are easier to fuse than poly(St-*co*-MPMS) and poly(MMA-*co*-MPMS). It is probable that when the particles were packed and deformed during drying of the samples, the alkoxysilane groups became to be exposed to air and hydrolysis and condensation reactions occurred in the boundary, just as we expect happened during the film formation of these emulsion coating. This argument is supported by the excellent agreement between the particle sizes derived form TEM images and those measured from dynamic light scattering in the case of terpolymerization systems (refer to Table 3). Such an agreement means that the particles are well dispersed in the water in the measurement of dynamic light scattering (no 'bridged' particles). On the other hand, the particles sizes measured from dynamic light scattering are much larger than those obtained from TEM observations in the cases of MMA/MPMS and St/MPMS (refer to Table 2). This can be ascribed to the existence of a small fraction of 'bridged' particles formed by coagulation as a result of hydrolytic condensation of alkoxysilane groups, which leads to a much higher intensity of scattering light.

4. Discussion

In the miniemulsion copolymerization, alkoxysilane molecules do not need to transport from droplets to particles through water, which suppress the premature hydrolysis and condensation of alkoxysilanes. This is the reason to use miniemulsion copolymerization to solve the colloidal instability issues observed in the conventional emulsion copolymerization, which involves alkoxysilane monomers. Because alkoxysilane monomers are more hydrophobic than most monomers such as MMA and St, it was argued that alkoxysilanes might have less chance to contact water and be protected against the hydrolysis by more hydrophilic monomer by assuming that more hydrophilic monomer would prefer to locate in the interface of

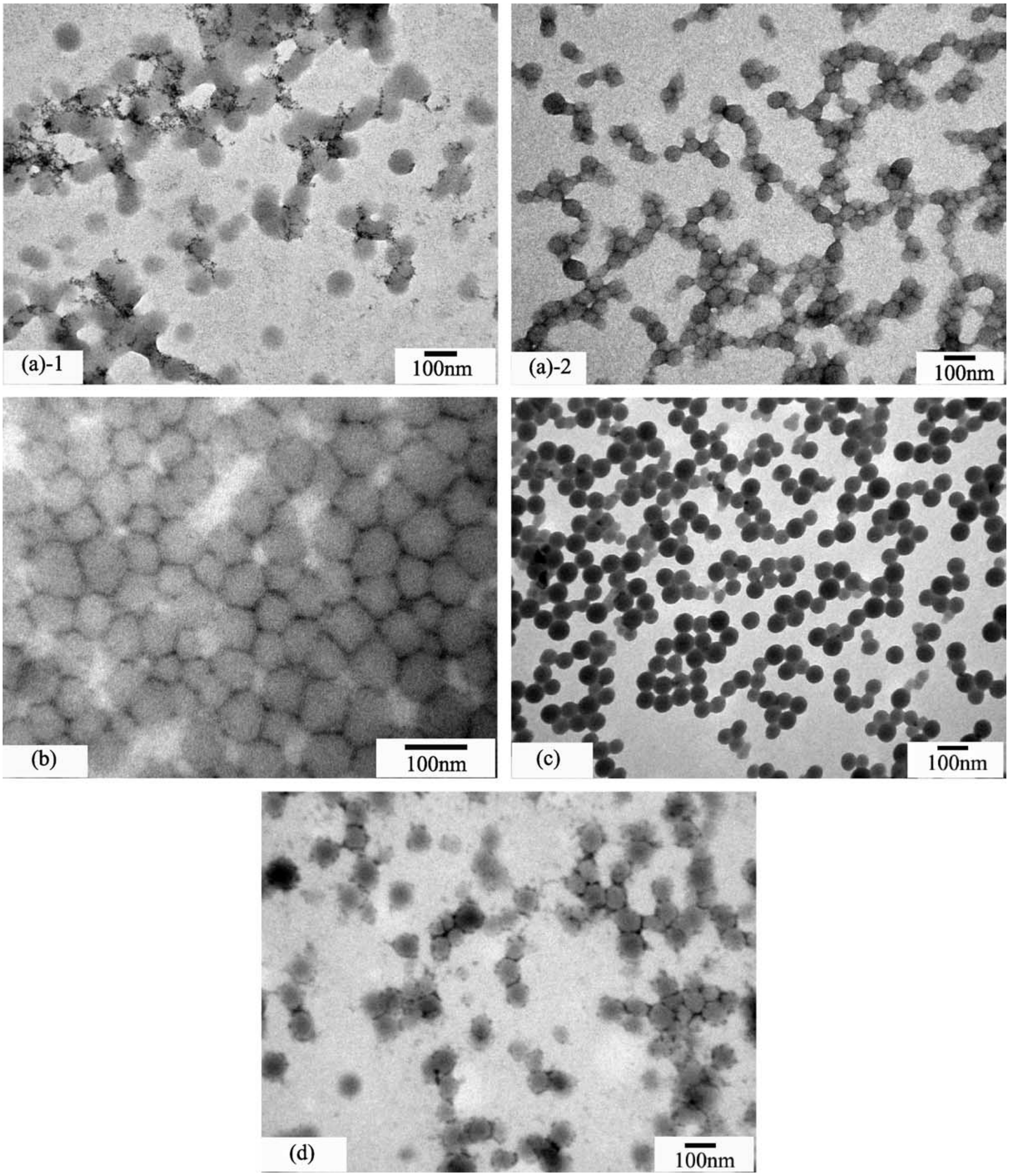


Fig. 6. TEM images of the latex of (a) poly(MMA-*co*-MPMS), (b) poly(MMA-*co*-BA-*co*-MPMS), (c) poly(St-*co*-MPMS), and (d) poly(St-*co*-BA-*co*-MPMS).

droplet (or particle)/water [16,17]. However, the experimental results mentioned above clearly show that merely using miniemulsion polymerization is insufficient to obtain stable silicone-modified polymer latex in some cases. The selection of the main monomer seems to play an important role in obtaining stable latex. Actually, using the most hydrophilic monomer MMA as the main monomer leads to the highest amount of coagulum. In fact, no evidence supports the argument that more hydrophilic monomer like MMA would preferably locate in the interface of oil/water. It was reported that the very hydrophobic hexadecane is randomly distributed within St/HD mini-droplets [25]. It is derived that the alkoxysilane monomer (very hydrophobic compounds like hexadecane) is also randomly distributed with the monomer droplets. Thus, even using miniemulsion polymerization technique, the alkoxysilane monomers still have a chance to contact water via the interface of droplets or particles/water. TEM images of poly(MMA–MPMS) latex (Fig. 6), from which the condensed product is clearly observed on the surface of particles, indicate that there are many alkoxysilane monomer units locating in the interface of polymer/water.

In order to explain the dependence of the colloidal stability on the monomer pairs, the reactivity ratios of all studied monomer pairs are collected in Table 4.

Table 4
The data of reactivity ratios [6,17,26]

r_1	r_2
$r_{MMA}=0.74$	$r_{MPMS}=1.33$
$r_{St}=0.45$	$r_{MPMS}=0.9$
$r_{BA}=0.005$	$r_{MPMS}=0.007$
$r_{BA}=8.51$	$r_{VTES}=0.086$

For binary copolymerization systems, the monomer consumption rate is determined by four propagation reactions shown in Scheme 2, where M_1 and M_2 represent the main monomer (monomer 1) and alkoxysilane monomer (monomer 2), respectively, $\sim\!\sim M_1\cdot$ and $\sim\!\sim M_2\cdot$ represent free radicals with terminal monomers 1 and 2.

Under steady-state assumptions, the ratio of consumption rates of two monomers can be derived as [27]:

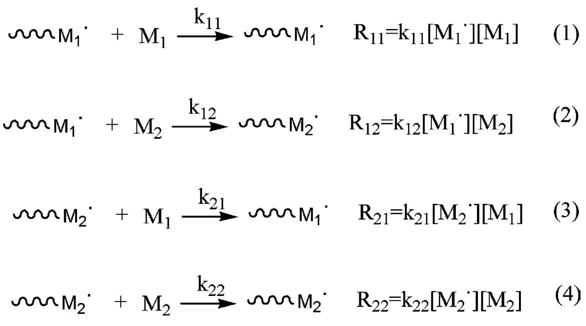
$$\frac{d[M_1]}{d[M_2]}=\frac{[M_1]}{[M_2]}\frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \tag{5}$$

After integrating [28], we have

$$C=1-\frac{M}{M_0}=1-\left[\frac{1-f_2}{(f_1)_0}\right]^{\alpha}\left[\frac{f_2}{(f_2)_0}\right]^{\beta}\left[\frac{(f_1)_0-\delta}{1-f_2-\delta}\right]^{\gamma} \tag{6}$$

where M and M_0 represent the instant total molar and initial total molar of monomers; f_1 and $(f_1)_0$ represent the instant molar fraction and the initial molar fraction of main monomer; f_2 and $(f_2)_0$ represent those of alkoxysilane monomer, and $\alpha=\frac{r_2}{1-r_2}$, $\beta=\frac{r_1}{1-r_1}$, $\gamma=\frac{1-r_1r_2}{(1-r_1)(1-r_2)}$, $\delta=\frac{1-r_2}{2-r_1-r_2}$.

According to Eq. (6), we can get Fig. 7, in which f_2 is plotted against C for four monomer pairs of MMA/MPMS, St/MPMS, BA/MPMS, and BA/VTES. It is clearly seen from Fig. 7 that MPMS is consumed faster than the main monomer. So, f_2 decreases with the total monomer conversion. However, the consumption rates in terms of the total conversion are dependent on main monomer type. For BA/MPMS copolymerization system, MPMS is almost completely consumed within 10% conversion. For those systems using MPMS as an alkoxysilane comonomer, MPMS is consumed slowest in the copolymerization of MMA/MPMS. At 90% conversion, f_2 values for MMA/MPMS, St/MPMS and BA/MPMS copolymerization systems are about 0.017, 0.002, and 0, respectively. According to Eq. (6), the polymer compositions (F_2, molar fraction) are calculated to be 0.024, 0.007, and 0, respectively.



Scheme 2. Propagation reactions in the copolymerization.

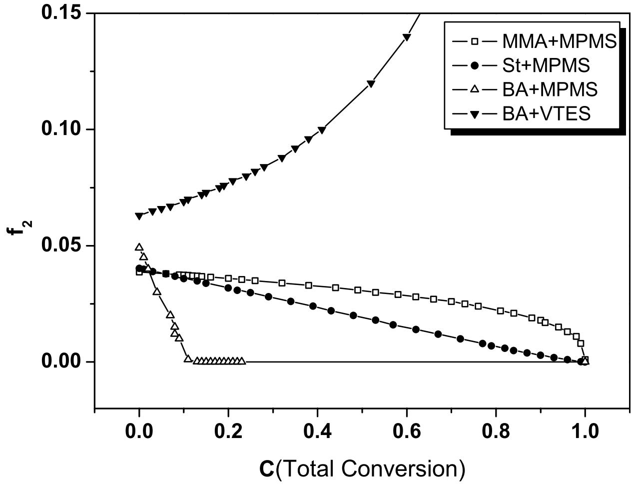


Fig. 7. The instant molar fraction of alkoxysilane monomer f_2 versus the total conversion of main monomer and alkoxysilane monomer for various monomer combinations.

On the other hand, it has been reported that particles are not homogeneous in the late stage of emulsion polymerization [29]. Because of the entropic repulsion of polymer chains, the polymer chains tend to stay away from the confined region of particle/water interface (as illustrated in Fig. 8) in the monomer swollen polymer particles. As a result, the monomer-swollen particles have a polymer-rich core surrounded by a monomer-rich shell. The polymerization in the late stage mainly occurs in the monomer-rich shell, which means that the surface composition of particles is determined by the monomer composition in the late stage of miniemulsion copolymerization. Combing with the data shown in Fig. 7, it is derived that the surface of the final poly(BA–MPMS) particles would have no MPMS units. However, there exist the most MPMS units on the surface of poly(MMA–MPMS) particles. The poly(St–MPMS) particles have a much less MPMS units on the surface than those of poly(MMA–MPMS). Since, the coagulation is caused by the hydrolysis and condensation of MPMS units located on the surface of particles (as demonstrated in Fig. 2), the dependence of the colloidal stability on the main monomer type becomes understandable. Because no MPMS units present on the particle surface, no coagulum is formed during the BA/MPMS miniemulsion copolymerization. The resultant latex shows a long shelf life. Due to the existence of MPMS units on

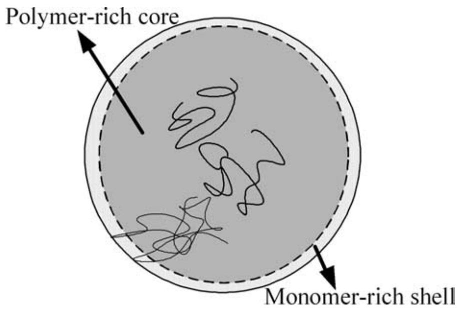


Fig. 8. Graphical illustration of the 'repulsive-wall' effect, whereby polymer chains stay away from the boundary of the particle containing both polymer and monomer.

the surface of particles, the coagulum is formed during the MMA/MPMS and St/MPMS miniemulsion polymerization. The resulted latex of both systems has a very short shelf life. There are more MPMS units located on the poly(MMA–MPMS) particle surface than those of poly(St–MPMS), so the amount of the coagulum is higher for the copolymerization of MMA/MPMS.

In the cases of terpolymerization of MMA/BA/MPMS and St/BA/MPMS, the consumption rate of MPMS should be much faster than those of copolymerization of St/MPMS and MMA/MPMS due to the presence of BA monomer (Note: BA and MPMS molecules are incorporated into polymer chains in an alternative way, suggested by the reactivity ratios). Thus, the colloidal stability is also very good.

On the other hand, when we replace alkoxysilane monomer by VTES, it can be seen from Fig. 7 that VTES is consumed slower than BA. f_2 increases with the total conversion. According to Eq. (6), the copolymer composition at 90% (F_2) is around 0.103. Thus, a great larger number of alkoxysilane groups are located on the particle surface in the case of VETS than that of MPMS. So, even VTES is more stable against hydrolysis than MPMS is, some coagulum formed during the copolymerization was still observed.

In summary, fast consumption of alkoxysilane comonomer seems to be critical to obtain the stable latex in the miniemulsion copolymerization involving alkoxysilane comonomer. In this way, the alkoxysilane groups are completely buried in the particles so that the coagulation caused by condensation reactions derived from the alkoxysilane hydrolysis among particles is suppressed. It needs to point out that even though the alkoxysilane groups are completely buried in the particles in the resulted latex, they still can be used to crosslink the polymer chains in the film formation. During the film formation, the particles will be deformed by the capillary pressure and polymer chains can be free to move to form a coherent film [30]. During this film formation process, the alkoxysilane groups will prefer to transport to the film surface driving by the lower surface energy of silicone compounds. By exposing to air, the hydrolytic and condensation crosslinking reactions are triggered.

5. Conclusion

The influence of types of monomer on the colloidal stability in the miniemulsion co-(or ter-)polymerization was investigated when incorporating alkoxysilane monomer into the styrene or acrylate latex. It was found that merely using miniemulsion polymerization technique is insufficient to obtain colloid stable silicone modified latex. In the case of BA/MPMS, BA/MMA/MPMS, and BA/St/MPMS miniemulsion polymerization, nearly no coagulum was observed. The obtained latex has a long shelf life. However, the coagulum was formed in the late stage of MMA/MPMS and St/MPMS miniemulsion copolymerization. The shelf life of the corresponding latex is short. The selection of the main monomer, which can fast consume alkoxysilane comonomer, is critical to obtain the stable latex. In this way, the alkoxysilane groups are completely buried in the particles thus the coagulation caused by condensation reactions derived from the alkoxysilane hydrolysis among particles is suppressed.

Acknowledgements

This work is financially supported by Program for New Century Excellent Talent in University from Education Ministry of China.

References

[1] Matheson R. Science 2002;297:976–9.
[2] Gebhard MS. Macromol Symp 2002;187:771–81.
[3] Castelvetro V, Vita CD, Giannini G, Malvaldi M. Macromol Symp 2005;226:289–302.
[4] Witucki GL. J Coat Tech 1993;65(822):57–60.
[5] Gilbert RG. Emulsion polymerization. A mechanistic approach. San Diego: Academic Press; 1995 p. 292.
[6] Bourgeat-Lami E, Tissot I, Lefebvre F. Macromolecules 2002;35:6185–91.
[7] Plesich M. Zavaglia E. US patent 3729438, 1970.
[8] Bourne TR, Bufkin BG, Wildman GC, Grawe JR. J Coat Tech 1982;54(684):69–82.
[9] Liles DT, Murray DL. EP 0818497, 1997.
[10] Masuda T, Hatano T, Ando N. EP 0578229 A2, 1993.
[11] Ladika M, Rose GD. WO 0043427, 2000.
[12] Chen MJ, Chaves A, Guillet A, Johnston RR, Osterholtz FD, Ramdatt PE, et al. J Coat Tech 1997;69(870):43–51.
[13] Hashimoto T, Takeshi K. EP 0810243, 1997.
[14] Chang WH. US patent 4043953, 1977.
[15] Lavoie AC. US patent 5214095, 1993.
[16] Marcu I, Daniels EC, Dimonie VL, Roberts JE, El-Aasser MS. Prog Colloid Polym Sci 2004;124:31–6.
[17] Marcu I, Daniels EC, Dimonie VL, Hagiopol C, Roberts JE, El-Aasser MS. Macromolecules 2003;36:328–32.
[18] Landfester K. Macromol Rapid Commun 2001;22(12):896–936.
[19] Schork FJ, Luo YW, Smulders W, Russum JP, Butte A, Fontenot K. Adv Polym Sci 2005;175:19–145.
[20] Asua JM. Prog Polym Sci 2002;27:1283–346.
[21] Stumbé JF, Calderara F, Riess G. Polym Bull 2001;47:277–82.
[22] Landfest K, Pawelzik U, Antonietti M. Polymer 2005;9892–8.
[23] Unzue MJ, Schoonbrood HAS, Asua JM, Gohi AM, Sherrington DC, Stähler K, et al. J Appl Polm Sci 1997;66:1803–20.
[24] Santos AMD, Mckenna TF, Guillot J. J Appl Polym Sci 1997;65:2343–55.
[25] Landfeste K, Bechthold N, Forster S, Antonietti M. Macromol Rapid Commun 1999;20:81–4.
[26] Rao VL, Babu GN. Eur Polym J 1989;25:605–9.
[27] Mayo FR, Lewis FM. J Am Chem Soc 1944;66:1594–601.
[28] Meyer VE, Lowry GG. J Polym Sci 1965;3:2843–51.
[29] Gilbert RG. Emulsion polymerization. A mechanistic approach. San Diego: Academic Press; 1995 p. 71.
[30] Keddie JL. Mater Sci Eng 1997;21:101–70.