Polymer Bulletin 58, 371–379 (2007)
DOI 10.1007/s00289-006-0677-1

Polymer Bulletin

Synthesis and properties of branched organosilicon-acrylate copolymer latexes

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Received: 6 June 2006 / Revised version: 31 July 2006 / Accepted: 21 August 2006

Summary

Stable organosilicon-acrylate copolymer latexes with high silicon content were prepared by seeded semibatch emulsion polymerization of butyl acrylate (BA), methyl methacrylate (MMA) with a novel branched organosilicon monomer 3-methacryloxypropyl tris(trimethylsiloxy) silane (MPTS). Monomer conversion, evolution of the particle size and its distribution were monitored by dynamic light scattering. The effects of MPTS on the polymerization kinetics, the nucleation mechanism and properties of latex were investigated. The results indicated that, in addition to micellar nucleation, a coagulative nucleation step was also observed as a result of the addition of the organosilicon monomer, accordingly, the particle number of the silicon-acrylate latexes increased, the average particle diameter decreased and the polymerization rate accordingly increased compared to those of the acrylate latexes without organosilicon monomer. Moreover, the particle size distribution presented bimodal curves, which indicated that there were large particles formed at an early stage. However, the particle size distribution curves became monomodal at the later stage, and the final latex shows a narrow particle size distribution. It was found that the properties of latex and latex film were obviously influenced by MPTS content. With increasing MPTS content, latex film glass transition temperature and water absorption ratio decreased, the degradation temperature and water contact angle were increased. Hence, the resulting latex films containing MPTS showed lower glass transition temperature and excellent water-resistance, which probably due to the incorporation of the bulky branched hydrophobic group of MPTS into the copolymer chains.

Introduction

Organosilicon-acrylate copolymer latexes are hybrid materials with specific properties designed to take advantage of combining the water repellency, non-polluting and thermal stability of organosilicon component, as well as the mechanical strength and cohesiveness of the acrylic matrix, and are of high scientific and technological interests [1]. At present, there are two class of organosilicon used to modify polyacrylate latex. One is organo alkoxysilanes and its derivatives [2-8], for example, methacryloxy propyl trimethoxysilane or vinyl trimethoxysilane. The other includs polysiloxanes [9-18], such as vinyl-terminated polydimethylsiloxane macromonomer, hydrogen-containing polymethylsiloxane, octamethyl cyclo tetrasiloxane and tetravinyl tetramethyl cyclo tetrasiloxane. Since alkoxysilane in the copolymers can undergo hydrolysis/polycondensation reactions between alkoxysilyl groups to provide self-crosslinking ability to the copolymer films, alkoxysilylanes can enhance the cohesive strength, mechanical strength and integrity of the coating [2-4]. On the other hand, the introduction of unreacted residual alkoxysilyl and silanol groups into the hybrid copolymers makes it possible to produce functionalized hybrid latex particles [5-8]. However, it is difficult to obtain polymer latex with high oganosilicon content because of the excessive crosslink and coagulation during the polymerization when more alkoxysilane monomer was introduced.

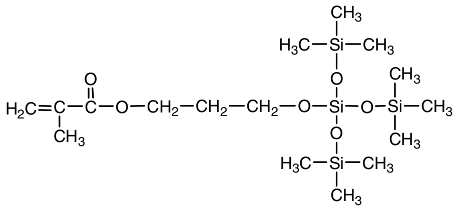
Polyorganosiloxane can be incorporated into polyacrylate to prepare high silicon-containing hybrid polymer latexes with different macromolecule chain structure and particle morphology. Kan and co-authors have reported the synthesis of comb-like polymer via emulsion copolymerization of acrylate and vinyl-terminated polydimethylsiloxane macromonomer [11]. Silicon-Polyacrylate hybrid copolymer latexes with interpenetrated networks were produced by performing the radical and the ionic ring-opening polymerization simultaneously [12-14]. Core-shell particles with a silicon core and an acrylic copolymer shell [15-20], as well as a polyacrylate core and a silicon shell [21] can be found in many works [15-21]. However, there is significant phase separation in the copolymer because of the poor compatibility between the polysiloxane and the polyacrylate [22].

In contrast, MPTS is a novel reactive organosilicon monomer, and materials thus obtained from the solvent copolymerization of MPTS with various monomers (such as methacrylic acid) possess good mechanical and optical properties, and have been successfully used as intraocular lenses (IOL) [23-25]. However, to the best of our knowledge, there are no report on the synthesis of latex through emulsion polymerization of MPTS. Because of MPTS has bulky branched hydrophilic group as well as stable alkyl silyl groups, which could not be hydrolyzed and could prevent the excessive crosslink and coagulation of monomer during the emulsion polymerization process, so it is possible to obtain a novel silicon-acrylate composite latex with high silicon content by emulsion polymerization of MPTS with acrylate monomers, and the copolymer may be expected to present excellent water repellency by the introduction of bulky branched hydrophobic group of MPTS. Based on the above consideration, in this paper, our objective is to report the synthesis of MPTS/BA/MMA tercopolymer latex through seeded semicontinuous emulsion polymerization. The influence of the organosilicon monomer MPTS on the emulsion polymerization and the properties of the latex films were also investigated.

Experimental Part

Materials

3-Methacryloxy propyl tris(trimethyl siloxy) silane (MPTS, the structure shown in Scheme 1) was obtained from Aldrich,; Methyl methacrylate (MMA), n-Butyl acrylate (BA) were obtained from Xi'an chemical Co., China. Disodium salt of sulfonic alkyldiphenylate(DSB) was obtained from Rhone-Poulenc Co., Ltd., France. Ammonium persulfate (APS) and Hydroquinone were from Tianjing Chemical Co., China. The monomers, BA and MMA were distilled under reduced pressure and then stored at 4°C. Unless otherwise specified, other materials were used as received. Deionized water was employed throughout the work.



$$H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}CH_2{-}O{-}Si[O{-}Si(CH_3)_3]_3$$

Scheme 1. The formula of MPTS

Emulsion Polymerization

The copolymer latexes were prepared via the seeded semibatch emulsion polymerization process. All the experiments were carried out in a 500-mL glass reactor equipped with a reflux condenser, a mechanical poly(tetrafluoroethylene) stirrer, a sampling tube, a nitrogen inlet tube and a feed inlet tube. Table 1 presented the recipe of the emulsion polymerization system. Firstly, the seed latex was prepared batchwise using 10% of the mixture of the monomers, 20% DSB, 50% APS and 60% H2O, respectively. Polymerization was carried out at 75 °C for 10 min. Subsequently, the rest monomers, emulsifier, initiator and water were preemulsified and feed in 3 h. After the feeding completed, the polymerization was continued in the batch for another 1 h. All polymerization were carried out under a nitrogen atmosphere.

Table 1. Recipe used in emulsion polymerization

Run	MPTS	MMA	BA	DSB/Co-897[a]	APS	H_2O
ACR	0	57.6	70.4	3.84	0.512	128
AS5	6.4	57.6	70.4	4.03	0.538	134.4
AS10	12.8	57.6	70.4	4.22	0.563	140.8

[a] m/m=1/1. All the data are indicated in grams

Measurements and Characterization

The conversions were determined gravimetrically. Samples withdrawn from the reactor during the polymerization were short-stopped with a solution of 1% hydroquinone in water. The overall conversion is defined as the weight ratio of polymer in the reactor to the total polymer and monomer in the recipe. The instantaneous conversion is the weight ratio of the polymer in the reactor to the monomer fed in the reactor until the sampling time.

Particle size and particle size distribution (PSD) was measured by dynamic light scattering using a Zetasizer Nano-ZS (Malvern). For the DLS analysis, samples were diluted to low concentrations ($<10^3$ g/L), so that one could safely assume that there is no monomer present in the polymer particles, and only unswollen particle sizes are measured. The results obtained by this technique were used to calculate the total number of particles of the latex at time *t*. The polydispersity index (*U*) of the latex particles was calculated by the follow formula: *U*=Dv/Dn, where Dv is the volume-average diameter and Dn is the number-average diameter.

The number of the polymer particles of the latex (Np) can be calculated from the following equation:

$$Np = (6WX / \rho \pi Dv^3) \times 10^{21} \qquad \textbf{(1)}$$

where W is the total weight of the monomers (g), X is the overall conversion (%), ρ is the density of the latex particle (g/cm^3).

Differential scanning calorimetry (DSC) studies were conducted on a TA MDSC instrument under a dry nitrogen atmosphere at constant heating rate of 10K/min in a temperature range from –20°C to 100°C.

Thermogravimetric analysis (TGA) was carried out on a TA Q100 thermogravimetric analyzer running at constant heating rate of 10K/min under a dry nitrogen atmosphere.

Contact angle measurements were performed on a Chende JY-82 contact angle goniometer; and the static contact angle was obtained from a droplet (ca. 5 μL) on the surface.

The water absorption ratio of latex films was determined according to ASTMD570-8. The water absorption ratio of the films was calculated by the following formula:

Water absorption ratio (wt %) $= (W_1 - W_0)/W_0 \times 100\%$, where W_0 is the weight of dry film, and W_1 is the weight of film absorb water, respectively.

Results and discussion

Variation of monomer conversion during the seeded semi-batch emulsion polymerization

Figure 1 presents the effect of the MPTS content on the overall conversion and instantaneous conversion of the seeded semi-batch emulsion polymerization. It can be observed that reactions AS5 and AS10 reached higher overall conversion and instantaneous conversion than reaction ACR in the same reaction time, the polymerization rate increase with an increasing in the content of MPTS.

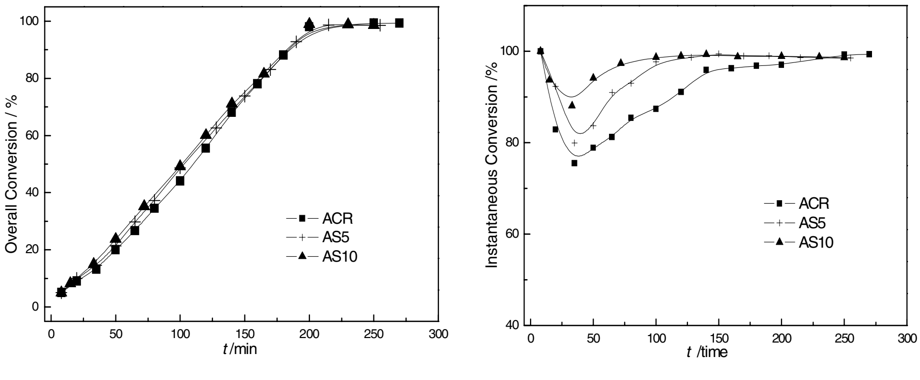


Figure 1. Variations of conversion with reaction time (left: Overall conversion versus time; right: Instantaneous conversion versus time)

For an emulsion polymerization system, the reaction occur predominantly in the polymer particles, and the rate of polymerization can be analyzed by the follow formula:

$$R_p = \frac{k_p[M]_p \bar{n} N_p}{M_0 N_A} \qquad (\mathbf{2})$$

where K_p (dm^{3}mol^{-1}s^{-1}) is the propagation rate constant, $[M]_p$ (mol/dm^3) the concentration of monomer in the polymer particles, $\bar{n}$ the average number of free radicals per particle, Np (dm^{-3}) the number of particles per unit volume of water, and N_A Avogadro's number. As shown in Table 1, in the recipes of the three reaction systems, the monomer, emulsifier and initiator concentrations are the same, so the emulsion polymerization rate depended mainly on the number of the polymer particle where the polymerization reaction performed. Compared with reaction ACR, the polymerization rate of reaction AS5 and AS10 increase, this is because there are more polymer particles in the polymerization systems, which can be further confirmed by the data of total particle number described in Figure 3.

Variation of the particle size and number in the course of the emulsion polymerization

Variation of the volume-average diameter (Dv) of latexes particles during the semi-batch emulsion polymerization is shown in Figure 2. It was noted that the latexes particles continuously grew with the feeding of the monomers, and after feeding, the particle size remained almost constant though essential increase of the monomer conversion was observed. The MPTS content in the emulsion polymerization systems had obvious effects on both the growth of the process and the final size of the latexes particles. Dv of the final latexes decreases as the concentration of MPTS increases.

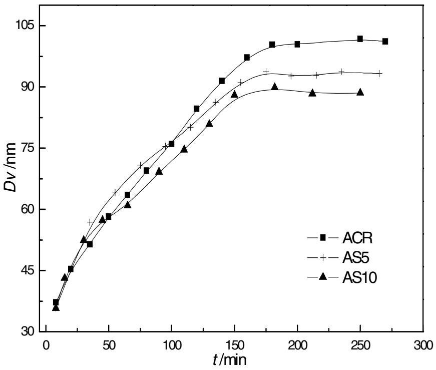


Figure 2. Variations of Dv with reaction time

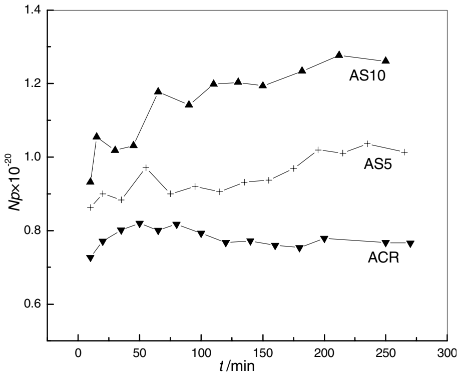


Figure 3. The total number of particles during the emulsion polymerization

There are two main facts that affect the particle number in emulsion polymerization system. One is the new nucleation process which increases the particle number, and the other is the aggregation between the particles which decreases the particle number. Figure 3 shows the variation of the particle number during the course of the emulsion polymerization. One can see that in emulsion system ACR which has no MPTS, the total particle number of the latex increased slightly at the initial stage of the monomer addition, then decreased gradually, and remained almost constant at the middle and later stage. However, in the polymerization systems, for run AS5 and AS10 with 5% and 10% MPTS, respectively, the total particle number of the final latexes increased significantly compared to that of the seed latexes, and much more than the particle number of ACR system. The results may be caused by the following possible nucleation mechanism, namely, in the AS5 and AS10 systems, there probably are certain coagulative nucleation [26] other than the normal micellar nucleation. Initially, free radicals would react with BA, MMA and MPTS in the aqueous phase to form oligomeric radicals. Presumably, there are also some MPTS chain units with bulky branched Si-O-Si groups formed among these oligomeric radicals, which had poor compatibility with polyacrylate [27]. They are not easily stabilized by normal emulsifier, so these oligomeric radicals aggregated together quickly and coagulated to form new primary polymer particles. As a result of the coexistence of two kinds of nucleation processes, the particles number in AS5 and AS10 systems increased more than that of ACR system, at the same time, there are more polymerization loci, thus the reaction rate increased accordingly.

Evolution of the particle size distribution during the emulsion polymerization

Figure 4 shows the variation of the polydispersity index (*U*) of the latex particles from reaction ACR, AS5 and AS10 during the process of semi-batch emulsion polymerization. One can see that the polydispersity index of run ACR is near-constant at about 1.2 throughout the course of copolymerization, at the same time, the final latex particle number of run ACR is almost equal to that of the seed latex (Figure 3). These results indicate that, for run ACR, the particles in the seed latex served as seeds for monomer adsorption and growth, nucleation of new particles appears to be a less important event. For runs AS5 and AS10, the polydispersity indexes increased rapidly at the beginning of the reaction, and then decreased gradually with the performing of the polymerization, the polydispersity indexes of the final latexes was less than run ACR which indicates the particle size distribution became narrow.

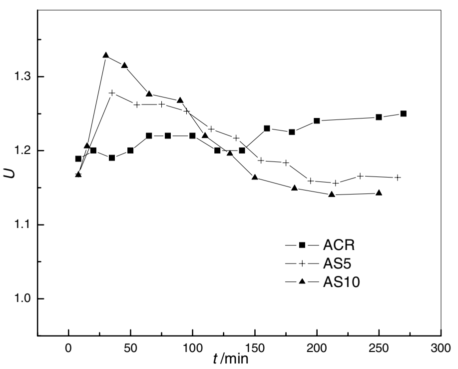


Figure 4. Variation of polydispersity index distribution with reaction time

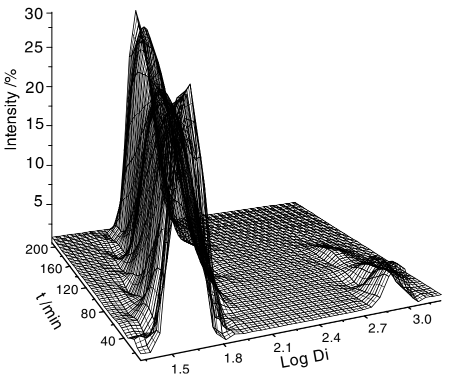


Figure 5. Evolution of particle size during the polymerization of AS10

Figure 5 shows the evolution of particle size distribution during the semi-batch emulsion polymerization of AS10. Bimodal PSD curves can be observed at the early stage of the polymerization, in which the small particle peak is located between 30nm-120nm and the large particle peak between 600nm-1200nm. The large particle peak decreased gradually and disappeared at last. It was found that the PSD curves of run

AS5 showed similar evolution trends to that of AS10, however, the PSD curves of run ACR presented unimodal throughout the course of polymerization. These results confirmed further that, in run AS5 and AS10, there are two kinds of nucleation mechanisms as mentioned above. Since the stability of the primary polymer particles formed from coagulative nucleation is poor, some of them will grow via polymerizing monomers to form stable polymer particles; on the other hand, some of the primary particles will aggregate with one another as a result of agitation and grow up to form large particles of micron scale, so the PSD curves is bimodal and the polydispersity index is greater than run ACR. The size of the large particles increased continuously and eventually precipitated via coagulation from the emulsion system. Therefore, the PSD curves of the resulting latex showed unimodal, the polydispersity index decreased and the particle size distribution became narrow.

DSC analysis

DSC curves of the copolymers with different MPTS content are given in Figure 6. As shown in Figure 6, the glass transition temperatures (Tg) of the copolymers decrease with the increasing of the MPTS content. This is probably due to the low Tg of homopolymer of MPTS itself, at about 27.1°C. In the case of MPTS/BA/MMA copolymer, on the other hand, there are certain branched Si-O-Si side group in the polymer molecular chain, which weaken the van der Waals' force of the polymer molecules because of the poor compatibility between MPTS segment and polyacrylate. This leads to the fact that the segmental motion become easier, and the Tg decreases.

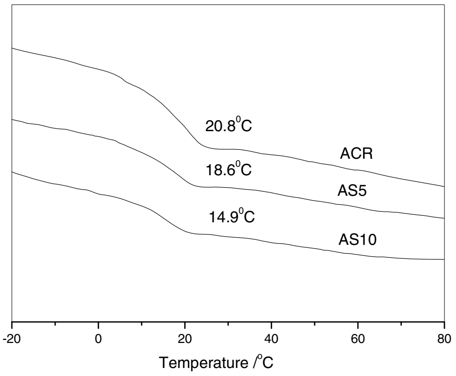


Figure 6. DSC thermograms of films for latexes with different MATS content

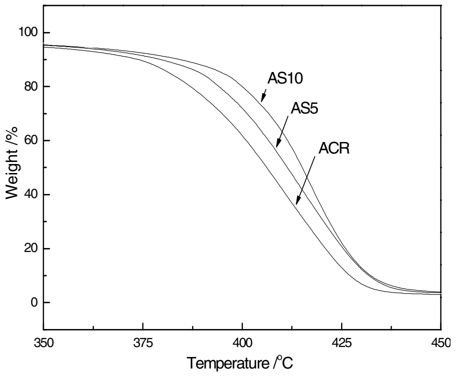


Figure 7. TGA curves of copolymers with different MATS content

Thermal stability

Figure 7 shows the thermogravimetric curves of copolymers with different MPTS content. The initial thermal degradation temperature of the copolymers ACR, AS5 and AS10 were 384.7°C, 389.6°C and 399.4°C, respectively. Obviously, the thermal stability of the copolymers increased with the increase of the MPTS content. This phenomenon may be understood based on the fact that the Si-O-Si bond in MPTS has high bond energy, and at the same time, the large branched groups of MPTS can sufficiently shield and protect the main chains of the copolymer, and thus improves the copolymers' thermal stability.

Water-resistance of the copolymer films

The water contact angles of the copolymer films from latexes ACR, AS5 and AS10 were 51°, 66° and 72°, respectively, indicating the fact that the wetting-resistant property of the copolymer films were significantly enhanced by incorporation of MPTS into copolymer chains. Figure 8 shows the water absorption ratio of the copolymer films with different MPTS content. It was found that the water absorption ratio decreased obviously with the increase of MPTS content. As expected, the bulky branched hydrophobic groups of MPTS prevented water molecules into the film, and provided the copolymer film with excellent water-resistance.

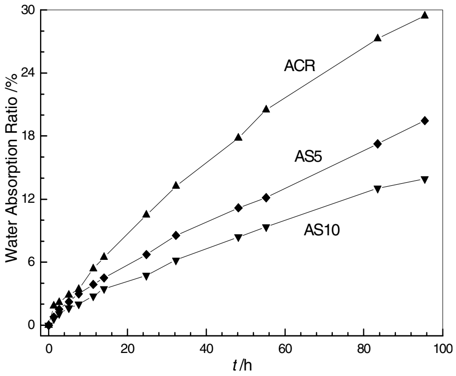


Figure 8. Hydroscopicity versus time for films of copolymers

Conclusions

(1) Stable organosilicon-acrylate copolymer latexes with high silicon content can be prepared by emulsion copolymerization of MPTS with BA and MMA, respectively. With increasing MPTS content, the particle size decreased and the particle size distribution became narrow.

(2) Beside the normal micellar nucleation, a coagulative nucleation was also observed during the emulsion polymerization of MPTS, BA and MMA, and as a result, the number of the polymer particle increased and the polymerization rate improved.

(3) The hydrophobic branched groups of MPTS can improve effectively the hydrophobic nature of the film surface and reduce effectively the hydroscopicity of the copolymer film, and provide materials with excellent water repellency.

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