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EFFECTS OF MONOMER POLARITY ON MMA/BA/NaMA EMULSIFIER-FREE EMULSION COPOLYMERIZATION

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Abstract—The emulsifier-free emulsion copolymerizations of methyl methacrylate (MMA) and n-butyl acrylate (BA) in the presence of a small amount of sodium methacrylate (NaMA) with potassium persulfate as initiator at 70°C were investigated. Increasing BA feed fraction causes the decrease of particle diameter, surface tension and viscosity of the latices, and the increase of particle number, polymerization rate, surface charge density of the latices and average molecular weight of copolymers. The DSC thermograms of MMA/NaMA emulsifier-free latex copolymer (EFLC) shows one glass transition temperature (T_g), that of BA/NaMA EFLC shows two T_gs, and those of MMA/BA/ NaMA EFLCs with the weight ratio of MMA to BA within 2:1–1:2 show 4 T_gs. The heterogeneity of copolymer composition for multiple T_gs is ascribed to the composition difference and phase separation, since the dissolved water in the sublayer surrounding the particle, enriched with $-OSO_3^-$ and $-COO^-$ groups, causes the diffusion of BA toward the particle core and that of MMA outward the core. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Much attention has been paid to emulsifier-free emulsion polymerization (EFEP) because of its useful merits such as high purity of the products and the monodispersity of the latex particles [1–3]. Many investigations have been made on the EFEP of polar and nonpolar monomers in the absence and presence of various functional monomers [4–7]. However, few works are concerned with acrylic-based emulsifier-free latices (EFL) which have such commercial applications as coatings and adhesives. Pan *et al.* studied the EFEP of MMA/BA [8], MMA/BA/MAA (or MMA/BA/NaMA) [9] system, but they have not studied the effects of monomer polarity on the kinetics of copolymerizations and the properties of the latices. MMA and BA are typical polar and nonpolar monomers, respectively. The effects of monomer polarity and other factors on the stability of MMA/BA EFL in the presence of small amount of NaMA had been investigated [10]. In this paper the effects of monomer polarity on the kinetics of MMA/BA/NaMA EFEP and the properties of the latices and copolymers were investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA) are of chemical pure grade and purified by distillation under reduced pressure. Sodium methacrylate (NaMA) was prepared by the neutralization of methacrylic acid and sodium hydroxide aqueous solution. Potassium persulfate (KPS, AR grade) used as initiator was recrystallized.

Polymerization

The MMA/BA/NaMA emulsifier-free emulsion copolymerization was carried out in the batch process at 70°C. The reactor was a 500 ml, double wall, four-neck glass flask equipped with a stirrer, condenser, nitrogen inlet and thermometer. The whole monomers, comonomer solution and deionized water was added into the flask at the beginning, then the KPS solution was added to start the polymerization.

After the polymerization was started, 1–2 ml of the reaction mixture was sampled at a definite time interval for the conversion measurement. The sample was placed in a tared weighed dish along with three drops of a short-stop solution (5% phenol in water–alcohol solution) and dried. The solid percentage and conversion were determined gravimetrically from the dried sample weights based on the total amount of the monomer mixture used.

Characterization

The average particle diameter D_p was measured by Malvern II submicron particle analyzer. The number density of latex particles N_p was calculated as follows [11]:

$$W X_p = \pi D_p^3 N_p \rho V/6$$

wherein W is the weight of monomers (g), X_p the conversion, ρ the density of polymer and V the volume of water (ml). The concentration of surface groups was determined by conductimetric titration after cleaning the latexes by ion-exchanging using a mixed bed (1/1 weight) of anionic and cationic resins [007 × 7 (H^+ form)–201 × 7(OH^- form)] [12, 13]. The average molecular weight of the copolymers was characterized by specific viscosity, determined with an Ubbelodhe viscometer at 25°C in acetone and calculated by one point method. The viscosity of latex was measured with a NDJ-1 rotational viscometer (Shanghai Balance Instrument Factory), similar to Brookfield Synchro Lectric Viscometer in principle. The surface tension of latex was measured with a JZHY1-180 surface tensiometer, based on the principle of cycle removing method, similar to Du Nouy surface tensiometer. The sur-

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Table 1. The properties of MMA–BA copolymer latices with different ratios of MMA to BA*

MMA:BA	1:0	2:1	1:1	1:2	0:1
D_p/nm	313	280	263	226	208
lg N_p	12.96	13.15	13.22	13.42	13.55
surface tension (22.2°C)/(mN m^{-1})	58.4	54.0	46.3	45.5	43.7
viscosity/mPa·s (14°C)	7.65	1.99	1.84	1.77	1.75

* MMA + BA = 25 g, monomer:water (wt) = 1:5; 0.1 M KPS 7.4 ml, [KPS] = 0.8 wt% (based on monomers); 1 M NaMA 3 ml, [NaMA] = 1.3 wt% (based on monomers); T = 70°C.

face tensiometer was calibrated with distilled water. Glass transition temperature (T_g) of copolymers were determined by a PE DSC-7 differential scanning calorimeter (DSC) with a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Particle diameter and number

The solubility of MMA in water is 0.15 mol L^{-1} (45°C) [3], the critical nucleation degree of polymerization (n_{cr}) of a PMMA oligomeric radical is up to 65–75 [9]. The n_{cr} is so big that the nucleation mechanism of MMA homopolymerization is believed to be homogeneous nucleation. The n_{cr} of MMA/NaMA oligomeric radical will be bigger than that of PMMA. Thus, the nucleation rate of MMA/NaMA oligomeric radical will be slower, particle diameter bigger, number density of the latex particles lower. The solubility of styrene (St) in water is 0.0038 mol L^{-1} (30°C) [3], the n_{cr} of PSt oligomeric radical is 3–4 [9]. From the solubility of BA in water (0.01 mol L^{-1}, 45°C) [3], it can be believed that the n_{cr} of PBA oligomeric radical will be much smaller than that of PMMA, but bigger than that of PSt. Therefore, the nucleation rate of BA/NaMA EFEP is faster than that of MMA/NaMA EFEP, particle diameter smaller, number density higher (Table 1). The particle diameter and number density of the EFL with various ratios of MMA to BA are between these two limiting cases, that is, an increase of the content of BA monomer feed or the units of BA in copolymer results in the decreases of the polarity and hydrophilicity of latex copolymer, n_{cr} of surface active oligomer and particle diameter, but enhancement of number density.

Polymerization rate

As shown in Fig. 1, the polymerization rate of BA/NaMA EFL is much faster than that of MMA/NaMA, while those of MMA/BA/NaMA with various ratios of MMA to BA are between these two cases with changing the ratios. It is first ascribed to the difference of distribution coefficient of monomers in polymer particle/water phase. In the case of BA, the distribution coefficient value is bigger, so once the polymer particles are formed, they absorb monomers faster. Second, the n_{cr} of oligomeric radicals with higher BA contents are smaller, hence the nucleation faster, D_p smaller, N_p higher, the number of loci of polymerization increased. After nucleation, the polymerization mainly takes place in the monomer-swollen particles, the radicals in particles were separated, so the termination of radicals is difficult, their lifetime is prolonged, and the concentration of them is increased. As a result the polymerization rate of MMA/BA/NaMA EFL increases with increasing contents of BA in the monomer feed.

Surface charge density

The surface charge density (SCD) of primary particles in the earlier stage formed from homogeneous nucleation in emulsifier-free emulsion polymerization system is usually low, therefore the primary particles are not sufficiently colloidally stable and easy to coagulate. The size of particles formed by coagulation is bigger, while SCD and the stability increase.

An increase of BA content in the monomer feed in MMA/BA/NaMA EFEP results in the reduction of n_{cr} of oligomer radicals and particle diameter of primary particles, the growth of SCD of primary particles and final latex particles (Table 2).

In the emulsifier-free emulsion polymerization initiated by persulfate, the number of SO_4^- located on particle surface is an important factor influencing the stability of the particles. The results as shown in Table 2 indicate that the number of SO_4^- located on particle surface is only 20%–30% based on the assumption that the initiators are completely

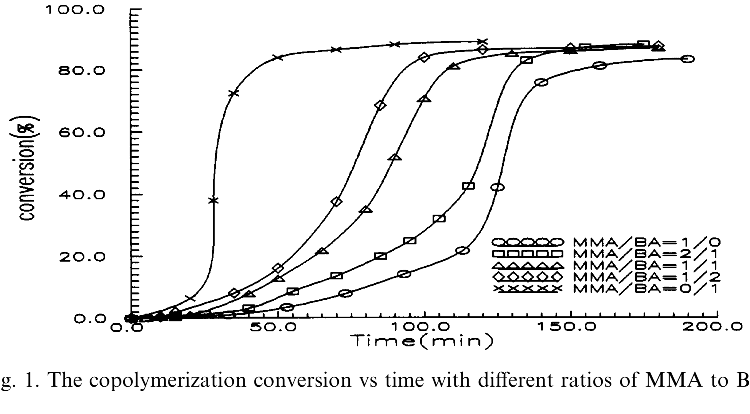

Fig. 1. The copolymerization conversion vs time with different ratios of MMA to BA.

Table 2. The surface charge density (SCD) of MMA/BA/NaMA latices with different ratios of MMA to BA*

MMA:BA (wt)	1:0	2:1	1:1	1:2	0:1
Calcd. SO_4^- charge/μeq (g polymer)$^{-1}$	58.6	58.6	58.6	58.6	58.6
SO_4^- SCD Q_{SO4^-}/μeq (g polymer)$^{-1}$	11.98	12.59	13.42	14.99	17.30
SO_4^- surface distribution*/%	20.44	21.48	22.90	25.58	29.52
Calc. COO^- charge/μeq (g polymer)$^{-1}$	118.7	118.7	118.7	118.7	118.7
COO^- SCD Q_{COO^-}/μeq (g polymer)$^{-1}$	30.97	41.68	44.61	49.50	55.42
COO^- surface distribution/%	26.09	35.11	37.58	41.70	46.69

* Calculated on the assumption that KPS was completely decomposed.

decomposed, because only some of SO_4^- anion radicals formed from decomposition of KPS initiated the polymerization and bonded to macromolecular chain ends, the others will create surface active substances in water, form $NaHSO_4$, or be left undecomposed [14].

The surface distribution of carboxyl groups is also an important factor influencing the stability of the particles. As shown in Table 2, the surface distribution of COO^- groups depends upon the monomer polarity, within the range of 26%–47%. The other COO^- groups are buried and form NaMA homopolymers or COO^- containing surface active substances in water. When the polarity of monomers is larger, carboxyl groups are easier to be buried, their surface distribution is smaller. In the case of smaller polarity of monomers, the highly hydrophilic carboxyl groups favor diffusion to the outside of the particle to cause a higher surface distribution.

Surface tension

The surface tensions of latices decrease with increasing BA content in the monomer feed (Fig. 2). The fact that the combination of oligomeric radicals produced by the initiation and polymerization in water can give surface active substances (SAS) is well known [14]. The polymer particles containing more MMA have lower SCD, they need absorb more SAS for stabilization, therefore the free SAS in latex is less, and the surface tension of latex is higher. On the other hand, the polymer particles containing more BA, have higher SCD and need less SAS for stabilization. In addition, the n_{cr} and solubility of surface active oligomer (SAO) are smaller, the SAS in latex is easier to reach critical micelle concentration (CMC). Thus the free SAS in latex is more and the surface tension of latex is lower.

Viscosity of latex

As shown in Table 1, the viscosities of various MMA/BA/NaMA EFL decrease with increasing the contents of BA in monomer feed. This is imputed to be related with SAO in water. When the contents of MMA in monomer feed is high, the n_{cr} of growing oligomer radicals is large, the molecular weight of SAS in water produced by termination of oligoradicals before they reaching n_{cr} is large, so the viscosity of latex is high. When the contents of BA in monomer feed is higher, the n_{cr} of growing oligomer radicals and the molecular weight of SAS in water is smaller, accordingly the viscosity of latex is lower.

Molecular weight of copolymer

The average molecular weight (MW) of copolymers is characterized by specific viscosity. As shown in Table 3, the molecular weight of the copolymers of MMA/BA/NaMA EFL increases with increasing the contents of BA in monomer feed. As the polymerization of the system containing more BA monomers reaches Trommsdorff effect earlier (Fig. 1), the increase of viscosity in particle results in remarkable decrement of k_t caused by difficult termination of radicals, wherein the termination is controlled by diffusion. But the viscosity is not high enough to hinder the diffusion of monomers and the change of k_p is little. As a result, $k_p/k_t^{1/2}$ and molecular weight are significantly increased. On that account, the MW of copolymers containing more BA monomers is larger, while the polymerization system containing more MMA reaches gel effect later and MW of copolymers is smaller.

Glass transition temperature

The glass transition temperatures determined by DSC are shown in Table 4. MMA/BA/NaMA

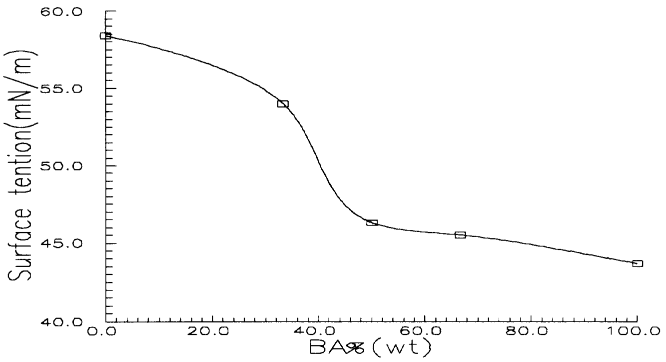

Fig. 2. The surface tension of MMA/BA/NaMA latices vs BA weight fraction in monomers.

Table 3. The specific viscosity of MMA/BA/NaMA copolymer with different ratios of MMA to BA

MMA:BA	1:0	2:1	1:1	1:2	0:1
[η]*	61.62	134.52	141.08	157.22	293.78
Mn	3.71×10^5				1.50×10^6

* Calculated by one point method. The viscosity was determined at 25°C in acetone.

emulsifier-free emulsion copolymers exhibit one or more glass transition temperature (T_g) dependent on the monomer compositions. The MMA/NaMA EFL copolymer exhibits only one T_g. It may be explained by the fact that T_gs of PMMA and PNaMA homopolymers are similar and the composition distributions of MMA/NaMA latex particles are more homogeneous which can be known from the low surface distribution of carboxyl groups on MMA/NaMA EFL particles (Table 2). On account of the much different T_gs of PBA and PNaMA homopolymers, BA/NaMA EFL copolymer exhibits two T_gs, indicating the heterogeneous composition distributions of BA/NaMA EFL particles, enriched with carboxyl groups on particle surface (Table 2), with BA in particle core. The MMA/BA/NaMA copolymers with the ratios of MMA to BA 2:1–1:2 exhibit 4 T_gs. It reveals that the distribution of monomers in particles are not homogeneous, and phase separation has occurred. The multiple T_gs are not caused by either the molecular weight heterogeneity or the shifts in compositions due to the differences of reactivity ratios of MMA and BA [8]. A sublayer consisting of relatively rich SO_4^- and COO^- group polymers was built around particles. These hydrophilic groups may cause more water dissolved in the sublayer. The dissolved water in the sublayer can induce the diffusion of BA toward the particle core and that of MMA toward the shell, since the solubility of MMA in water is larger than that of BA. Consequently, this results in the heterogeneous composition of monomers and copolymers in the latex particles, and causes phase separation [8, 9]. The T_gs of MMA/BA copolymers prepared by bulk radical polymerization closely obey the Fox equation, so the Fox equation may be used to estimate the copolymer and feed compositions (F_1s and f_1s) [9]. The results indicate that calculated f_1s corresponding to those T_gs obtained are different from monomer feeds. It reveals that the distribution of monomers in particles are not homogeneous. The differences of F_1s for two neighboring T_gs are larger than 15%, which is beyond the critical composition difference for phase separation in the MMA–BA copolymers [15].

Table 4. The T_g of MMA/BA/NaMA copolymers with different ratios of MMA to BA

MMA:BA	1:0	2:1	1:1	1:2	0:1
T_g/°C	105.2	−8.3	−23.9	−33.1	−47.7
		−0.4	−7.4	−7.7	−8.5
		25.4	27.3	19.1	
		67.5	59.4	53.2	

CONCLUSION

Monomer polarity has an important influence on the kinetics of MMA/BA emulsifier-free emulsion copolymerizations in the presence of small amount of sodium methacrylate; the properties of the lattices are also affected. Increasing the hydrophobicity of monomers and polymers will lead to the reduction of the critical nucleation degree of polymerization of oligomeric radicals. Hence, an increase of BA feed fraction results in the decrease of particle diameter, the increase of particle number and polymerization rate. The increase of the hydrophobicity of monomers and polymers results in the increase of surface distribution of hydrophilic SO_4^- and COO^- groups so as to increase the surface charge density of particles, these particles need less surface active oligomers for stabilization so that the free surface active oligomers in water are more and the surface tension of latex is lower. The decrease of n_{cr} of oligomeric radicals will lead to the decrease of molecular weight of surface active oligomers in water so as to decrease viscosity of the latices. The system containing higher contents of BA is faster in polymerization rate and reaches to gel effect earlier, causing the enlargement of average molecular weight of copolymers. The DSC thermograms of MMA/NaMA emulsifier-free latex copolymer (EFLC) shows one glass transition temperature (T_g), that of BA/NaMA EFLC shows two T_gs, and those of MMA/BA/ NaMA EFLCs with the ratio of MMA to BA within 2:1–1:2 show 4 T_gs. The heterogeneity of copolymer composition for multiple T_gs is ascribed to the composition difference and phase separation, since the dissolved water in the sublayer surrounding the particle enriched with $-OSO_3^-$ and $-COO^-$ groups, causes the diffusion of BA toward the particle core and that of MMA outward the core.

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