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SHORT COMMUNICATION

Fluorinated monomer–styrene copolymer latex particles: I. kinetic studies in a soap-free aqueous medium

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Abstract Soap-free emulsion copolymerization of 2, 2, 2-trifluoroethyl acrylate (3FEA) with styrene was carried out by using potassium persulfate as an initiator, and the effects of the weight fraction of 3FEA in the monomer feed on the kinetics and the particle size were investigated. Monomer conversions were followed by a gravimetric method, revealing that the overall polymerization rate increased exponentially with an increase in the weight fraction of 3FEA. According to dynamic light scattering measurement, the final particle size was found to decrease with an increase in the weight fraction of 3FEA. The number of particles for 3FEA homopolymerization was roughly twice as large as that at the fraction of 0.9, although both fractions had the almost same polymerization rates. These results indicate that soap-free emulsion homopolymerization of 3FEA would proceed not only inside the polymer particles but also in the aqueous phase throughout the polymerization.

Keywords Soap-free emulsion polymerization · Emulsion polymerization · Fluorinated polymer · Polymeric microsphere · 2, 2, 2-Trifluoroethyl acrylate

Introduction

Fluorinated polymers have attracted much attention in a wide variety of fields because of their unique properties [1, 2]. The largest application of fluoropolymers is as wire and cable insulation, where advantage is taken of the remarkable electrical insulation properties and low flammability of the polymers. The outstanding resistance to most chemicals is well-recognized in the textile and carpet industries. These polymers have also been industrially used as highly sensitive resist polymers for microlithography [3], clad materials for optical fibers [4], cookware, and so on.

Our focus is on the colloidal dispersions of fluorinated polymers in water. These particles have been used as water-based coatings [5], optical switching devices [6, 7], and model colloids to study the structure and dynamics of concentrated colloidal systems [8]. Fluorinated particles with a diameter below 1,000 nm can be prepared by using classical emulsion polymerization [9, 10], miniemulsion polymerization [11], and microemulsion polymerization [12–14]. These polymerizations require the use of emulsifiers and co-stabilizers, whose removal could lead to a loss of particle stability. On the other hand, it is well-known that soap-free emulsion polymerization provides a stable particle without adding surface-active agents. These contaminant-free particles are desirable in the biomedical and catalytic support applications.

In the present study, fluorinated latex particles were prepared by soap-free emulsion copolymerization of 2, 2, 2-trifluoroethyl acrylate (3FEA) and styrene (St). A preliminary kinetic study was performed on the polymerization between 3FEA and St with special attention to the effect of the weight fraction of 3FEA in the monomer feed on the polymerization rate. We also measured a hydrodynamic size with dynamic light scattering (DLS) and then investigated the effects of the weight fraction of 3FEA on the size and the number of the particles obtained.

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Experimental

Materials

Styrene (St; Kanto Chemical) and 2, 2, 2-trifluoroethyl acrylate (3FEA; Daikin Industries) were distilled at 50 °C/10 mmHg and 50 °C/100 mmHg, respectively. Potassium persulfate (KPS; Kanto Chemical) was recrystallized from the distilled water.

Preparation of fluorinated latex particles

Soap-free emulsion copolymerization was carried out in a 200-ml four-necked round-bottom flask equipped with a stirrer, a nitrogen inlet, and a reflux condenser. A standard recipe for the copolymerization is as follows: (St+3FEA) 5 g, distilled water 95 g, and KPS 0.06 g. Nitrogen gas was bubbled into the mixture to purge oxygen. The reaction temperature was controlled at 70 °C in an oil bath. The overall conversion was determined gravimetrically. The polymerization rates (R_p in moles per liter per second) were deduced from the conversion–time curves. Particle number (N_p, per liter) was estimated by the following equation:

$$N_p = \frac{6S_c}{\rho\pi D_h^3} \quad (1)$$

where S_c is the solid content (grams per liter), ρ is the polymer density (grams per cubic meter), and D_h is the average particle diameter (in centimeter), which was measured with DLS.

Light scattering

Particle size was analyzed at 30 °C by using a homemade light scattering apparatus equipped with a multi-τ digital time correlator (ALV-5000) and a He–Ne laser (λ=632.8 nm). The measurement angle was fixed at 90 °. Correlation functions of the scattered intensity are analyzed by using a second-order cumulant expansion. The hydrodynamic diameter, D_h, was evaluated from the diffusion coefficient D, with the Stokes–Einstein relation:

$$D_h = \frac{kT}{3\pi\eta D} \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the medium.

Results and discussion

Polymerization kinetics

Figure 1 shows conversion–time curves of the soap-free emulsion copolymerization of St with 3FEA at various monomer ratios. All curves were concave upward until about 90%, and then leveled off. It also can be found from Fig. 1 that the polymerization rate was significantly dependent on the weight fraction of 3FEA in the monomer feed. It requires 90 min to get a final conversion for 3FEA homopolymerization instead of 350 min for styrene homopolymerization.

Figure 2 shows the polymerization rate as a function of conversion (for all runs). The polymerization rates were deduced from Fig. 1. Relation between the rate and the conversion was a trapezoid shape except for the 3FEA fraction of 0.3 and 0.5; that is, the rate of polymerization (R_p) at first increased up to the maximum value ($R_{p,max}$), then kept an almost constant value, and finally decreased. At the 3FEA fraction of 0.3 and 0.5, polymerization rate increased sharply in the beginning of polymerization, then increased gradually up to about 80% conversion and dropped. In this way, the process of the polymerization can be divided into three stages. According to the classical theory [15], these stages would correspond to the particle formation stages, termed Interval I, and particle growth stages, Intervals II and III.

Figure 2 also shows that the relationship between the polymerization rate and the conversion was affected by the weight fraction of 3FEA in the monomer feed. A period of a constant rate was shorter by copolymerizing 3FEA with St. Moreover, a conversion at which a polymerization rate started to decrease was lower as the weight fraction of 3FEA increased.

Figure 3 summarized the maximal rate of polymerization ($R_{p,max}$) as a function of the weight fraction of 3FEA. The rate of polymerization sharply increased with an increase in the 3FEA fraction. The polymerization rate of soap-free

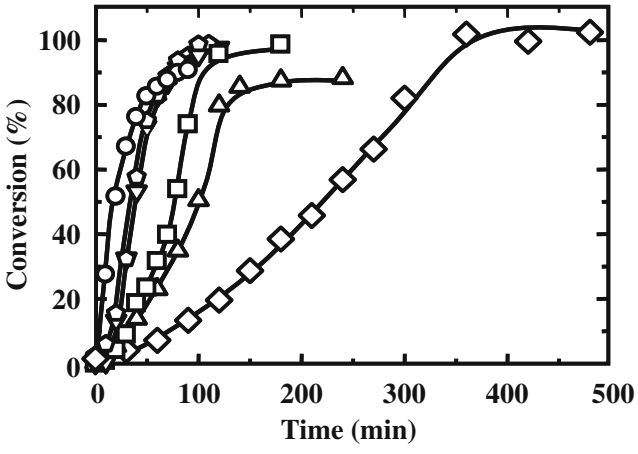

Fig. 1 Time–conversion curves for soap-free emulsion copolymerization of styrene with 3FEA. Weight fraction of 3FEA in the monomer feed: *diamond* 0, *triangle* 0.3, *square* 0.5, *inverted triangle* 0.7, *pentagon* 0.9, *circle* 1.0

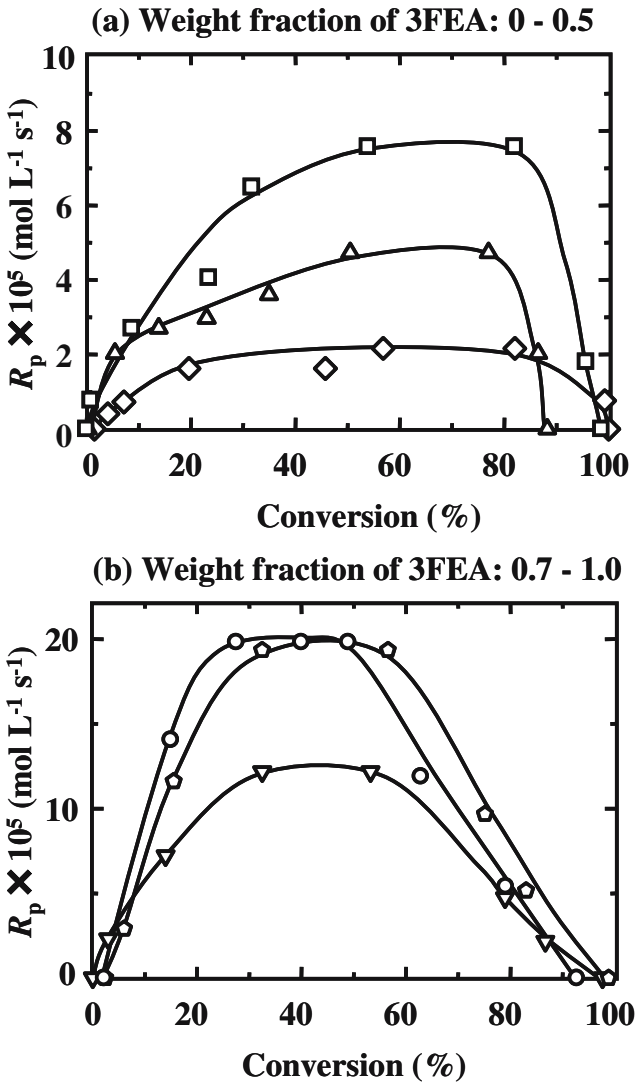

Fig. 2 Polymerization rate as a function of conversion. Weight fraction of 3FEA in the monomer feed: *diamond* 0, *triangle* 0.3, *square* 0.5, *inverted triangle* 0.7, *pentagon* 0.9, *circle* 1.0

emulsion polymerization can be expressed by the following equation [16]:

$$R_p = \overline{n} \times \frac{N_p}{N_A} \times k_{pp} \times [Mp] + k_{pw} \times [M_w] \times [R_w] \qquad (3)$$

The first and second terms on the right side of the above equation represent the polymerization rates in the particle phase and in the aqueous phase, respectively. k_{pp} and k_{pw} are the propagation rate coefficients of the monomer at the appropriate temperature for the particle phase and the aqueous phase, respectively (in liters per mole per second). $[M_p]$ and $[M_w]$ are the monomer concentrations in the latex particles and in the aqueous phase, respectively (in moles per liter). N_A is the Avogadro number, $\overline{n}$ is the average radical number in the particles, and N_p is the particle number per volume unit of latex (per liter). $[R_w]$ is the

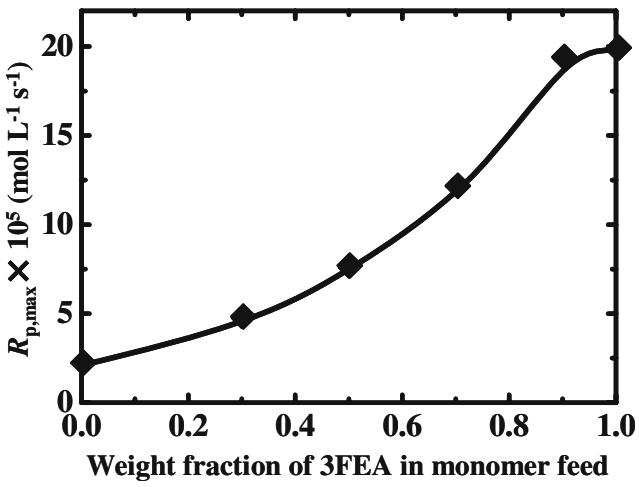

Fig. 3 Effect of weight fraction of 3FEA on maximal polymerization rate

oligomeric radical concentration in the aqueous phase. It has been reported that propagation rate coefficient of 3FEA is about ten times larger than that of St [17]. We will then make an attempt at determining the particle number experimentally in the next section.

Effect of weight fraction of 3FEA on particle number

The size of the particles prepared by soap-free emulsion polymerization of St with 3FEA was measured with dynamic light scattering (DLS). The dependence of the final particle size and number on the weight fraction of 3FEA is shown in Fig. 4. As the 3FEA fraction increased, the final particle size decreased and the particle number increased. For all fractions, the particle number remained almost constant except for the early stage of the polymerization. In addition, the polydispersity index was evaluated by transmission electron microscopy observations (data not

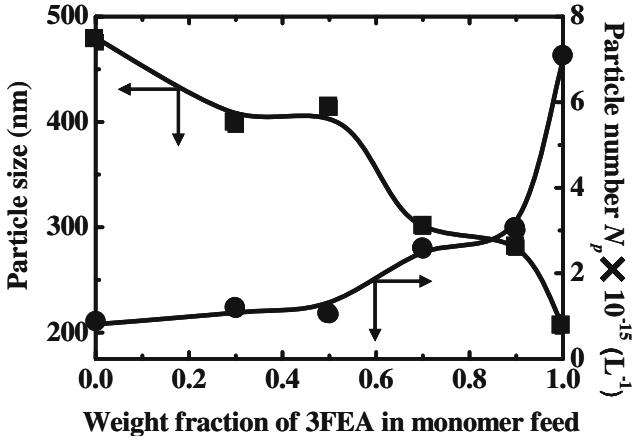

Fig. 4 Effect of weight fraction of 3FEA on particle size (*shaded square*) and number (*shaded circle*)

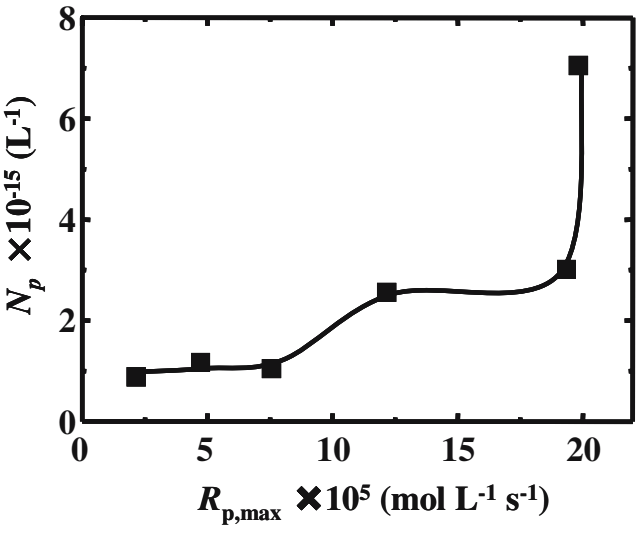

Fig. 5 Relationship between maximal polymerization rate and particle number

shown). The index was defined by the uniformity ratio U:

$$U = D_W/D_n \quad (4)$$

where D_w is the weight average diameter and D_n is the number average diameter. As a result, the index was below 1.01 for all fractions; thus, the particle size distributions were found to be narrow.

Let us now consider the mechanism of soap-free emulsion polymerization [18]. Polymerization starts in the aqueous phase by the reaction of a monomer in the aqueous phase with a water-soluble initiator, followed by the formation of water-soluble oligomers. Once they reach a critical chain length, the oligomeric radicals would precipitate to form primary particles. This homogeneous nucleation mechanism indicates that monomers in the aqueous phase largely involve the particle nucleation process [19]. The solubility of 3FEA in the aqueous phase was about 0.5 wt%, while that of St was about 0.05 wt%. These results suggest that 3FEA is more easily partitioned in the aqueous phase than St. As a result, 3FEA would preferentially react with a water-soluble initiator to produce many oligomeric radicals. The radicals are precursors for primary particles; thus, an increase in the weight fraction of 3FEA would lead to an increase in the number of primary particles and final particles.

Moreover, the solubility of monomers in the aqueous phase also would affect the tendency of desorption of free radicals from particles. As solubility increases, free radicals are prone to desorb and return to the aqueous phase. This process would be expected to increase the number of particles formed because the desorbed radicals participate in particle formation. This desorption process may be associated with the increase in the particle number as the weight fraction of 3FEA increases. Such an increase in the particle number has been previously reported when less hydrophobic monomers than St were used such as vinyl acetate, methyl methacrylate, and vinyl chloride [20, 21].

Figure 5 illustrated the relationship between the maximal polymerization rate and the particle number. The number of particles appears to increase stepwise with an increase in the polymerization rate. Particularly in the case of 3FEA homopolymerization, an increased particle number scarcely affected the polymerization rate. From Eq. 3, this is probably because polymerization, not only inside the particles but also in the aqueous phase, would proceed even in the particle growth stages. These oligomeric radicals formed in the aqueous phase were considered to be captured by primary particles because few secondary particles were produced.

According to ^{1}H NMR analysis, the copolymer composition varied only a little during the polymerization and was almost the same as the composition in the feed. These results suggest that the density of fluorinated sites was controlled by varying the weight fraction of 3FEA. Further work will be devoted to the unique surface properties of fluorinated particles. The results will be described elsewhere.

Conclusions

Soap-free emulsion copolymerization of St with 3FEA at various monomer ratios leads to the following conclusions:

1. The overall polymerization rate increased exponentially with an increase in the weight fraction of 3FEA.
2. The final particle size drastically changed from 475 to 205 nm by increasing the weight fraction of 3FEA from 0 to 1. This is due to the increase in the particle number with an increase in the 3FEA fraction.

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