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Semicontinuous Emulsion Polymerization of Vinyl Acetate. Part I. Homopolymerization with Poly-(Vinyl Alcohol) and Nonionic Coemulsifier

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ABSTRACT

The semicontinuous emulsion polymerization of vinyl acetate has been studied. Poly(vinyl alcohol) as a protective colloid and ethoxylated cetyl alcohol as a coemulsifier were used. The conversion and particle diameter were affected by the stirring speed and the coemulsifier distribution between initial reactor charge and continuously introduced monomer. The amount of unreacted monomer oscillates with time.

INTRODUCTION

In previous papers [1-5] we have studied the emulsion polymerization of vinyl acetate (VAc) in the presence of macromolecular protective colloids of poly(vinyl alcohol) (PVA), ethylene oxide-propylene oxide block-copolymers, and hydroxyethylcellulose. The results

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pointed out that during emulsion polymerization, graft copolymers of poly(vinyl acetate)-protective colloid are obtained. The level of the grafting reaction is affected by the reaction conditions; by the concentrations of the initiator, the protective colloid, and the monomer; and by the presence of chain transfer agents [1-6]. Small molecule coemulsifiers used in the presence of the protective colloids act as chain transfer agents [6]. In all these studies we used batch techniques for emulsion polymerization. In addition to frequently studied batch emulsion processes, there are semicontinuous and continuous processes. Continuous and semicontinuous reactors have advantages for large-scale commercial production [7, 8]. Papers on the continuous polymerization of vinyl acetate are not numerous [9-11]. Cyclic variation in the number of polymer particles, monomer conversion, and degree of polymerization of the resulting poly(vinyl acetate) (PAcV) were observed. In the semicontinuous emulsion polymerization of VAc, the total surface area of the particles and the feed rates of the reactants are important factors [12-14]. Snuparek studied the semicontinuous emulsion polymerization of acrylic monomers. He concluded that the distribution of the emulsifier between initial reactor charge (R) and the continuously introduced monomer (M) is another factor affecting the semicontinuous emulsion polymerization [8].

In the present paper the authors discuss some experimental data on the characteristic behavior of the semicontinuous emulsion polymerization of VAc. Polyvinyl alcohol and cetyl alcohol ethoxylated with ethylene oxide (20 mol) were used as the protective colloid and coemulsifier, respectively. This system was also used in another paper [15].

EXPERIMENTAL

Materials

Vinyl acetate was purified by distillation.

Polyvinyl alcohol, a commercial product, was used without further purification. The polymer had an 88% saponification degree and a viscosity in a 4% water solution of 15 cP (20°C).

Potassium persulfate, Austranal grade, was used as supplied.

Ethoxylated cetyl alcohol, a commercial product, was a fatty alcohol ethoxylated with 20 mol of ethylene oxide.

Procedure

Polymerizations were carried out in a 1-L glass reactor (Figs. 1, 2, 4, 5, 7, 8) and a 2-L reactor (Fig. 3). Total reactor charge (g) was VAc = 300, PVA = 9, coemulsifier = 9, potassium persulfate = 1.4, water = 300. At the beginning of the polymerization, 190-230 g water, all the PVA, and some amount of the coemulsifier were fed to the reactor. After the reactor charge was heated to 65°C, 30 g VAc and 0.7 g persulfate dissolved in 35 g water were added (Portion I). After 30 min, 270 g VAc, 0.7 g potassium persulfate dissolved in 35 g water, and the remaining coemulsifier dissolved in water (20% concentration) (Portion II) were fed for 4 h at 70°C. For Fig. 3, twofold reactants and double time for Portion I were used. Emulsion films were obtained by drying at room temperature and were subjected to successive extractions in water and benzene at boiling for 8 h each. The amounts of the polymer soluble in water, soluble in benzene, and insoluble were established gravimetrically.

RESULTS AND DISCUSSION

Effect of Stirring Speed

The effect of stirring in emulsion polymerization is not well understood [10, 11, 14, 16, 18]. The rate of polymerization can be affected by the rate of agitation. An intense shear field increases the mechanical and surface coagulation, thereby reducing the total number of polymer particles and consequently the polymerization rate [10, 11, 16]. By studying the semicontinuous emulsion polymerization of ethyl acrylate, Eliseeva obtained a very interesting result: The minimum coagulum content and a monomodal particle diameter distribution curve were obtained at only one stirrer speed [17]. Kiparissides et al. [10] found that in the continuous emulsion polymerization of VAc, an increase in the agitation rate induces a decrease in the steady-state conversion. Unlike other authors, Daniel and co-workers [14] established that by increasing the time of stirring, an increase in the emulsion polymerization rate of VAc takes place.

The influence of stirring speed on conversion under the experimental conditions of this paper is presented in Fig. 1. A minimum conversion at one stirrer speed was obtained.

The decrease in conversion with an increase in stirrer speed is in good agreement with the above-mentioned literature data [10, 11, 16]. What happens after minimum conversion at 400 r/min? We suppose that an increase in conversion takes place because diffusion phenomena may indirectly affect the rate of polymerization in this region of stirring speed.

Conversion change follows particle diameters (Fig. 2), in good agreement with the results of Kiparisides et al. [10, 11].

The amount of unreacted monomer oscillates as in the continuous process [10, 11]. A higher amplitude of oscillation corresponds to a higher stirrer speed. These oscillations are related to the tendency of limited particle flocculation (Fig. 3).

These oscillations can lead to emulsifier levels too small to cover

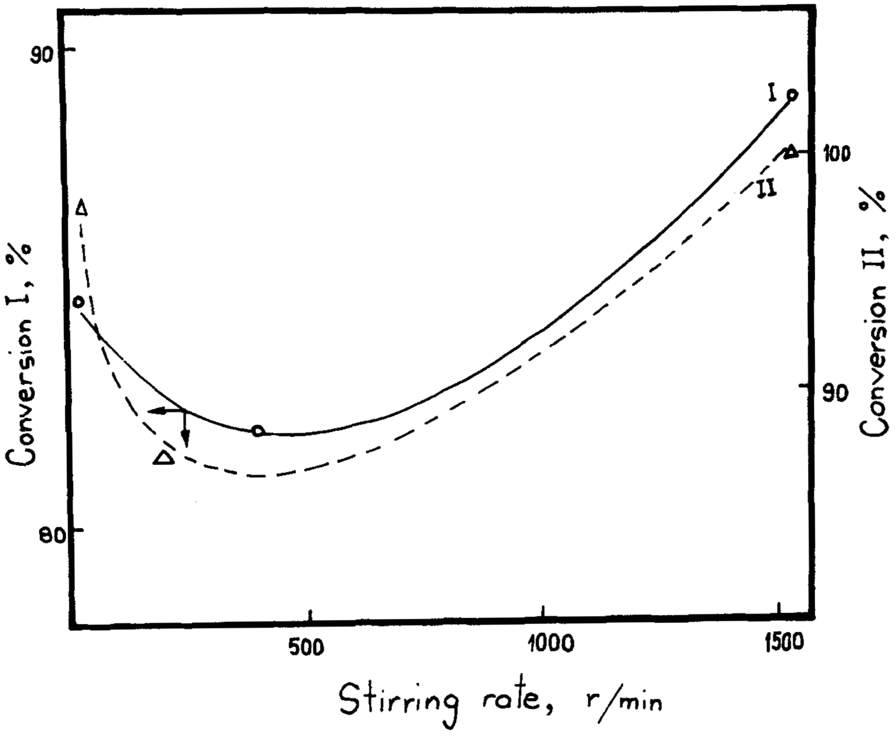

FIG. 1. Dependence of the conversion of Portion I and of the final conversion (II) on the stirring speed ($(R/M)_E = 5/0$).

the polymer particles, resulting in excessive agglomeration. Oscillations appear at low emulsifier concentration.

Because the rate of emulsion polymerization of VAc is proportional to the surface of the particles [12, 19, 20], we conclude that coagulation of the particles occurs. It is possible that, toward the end of the process, new nucleation takes place. This phenomenon was observed in the copolymerization of VAc with dibutyl maleate [20].

If the diameters of particles in respect to the total surface of particles are variable with the reaction conditions, then chain transfer reactions with the colloid and coemulsifier will be affected. To study the modification of the chain transfer reaction, we subjected the polymer films to extractions in water and in benzene. In water, small quantities of ungrafted colloid and coemulsifier and graft copolymers with a very small amount of poly(vinyl acetate) were extracted, while in benzene, graft copolymer with a high content of poly(vinyl acetate) and ungrafted polymer were extracted. Insoluble fractions are poly(vinyl acetate) crosslinked with poly(vinyl alcohol). This means that

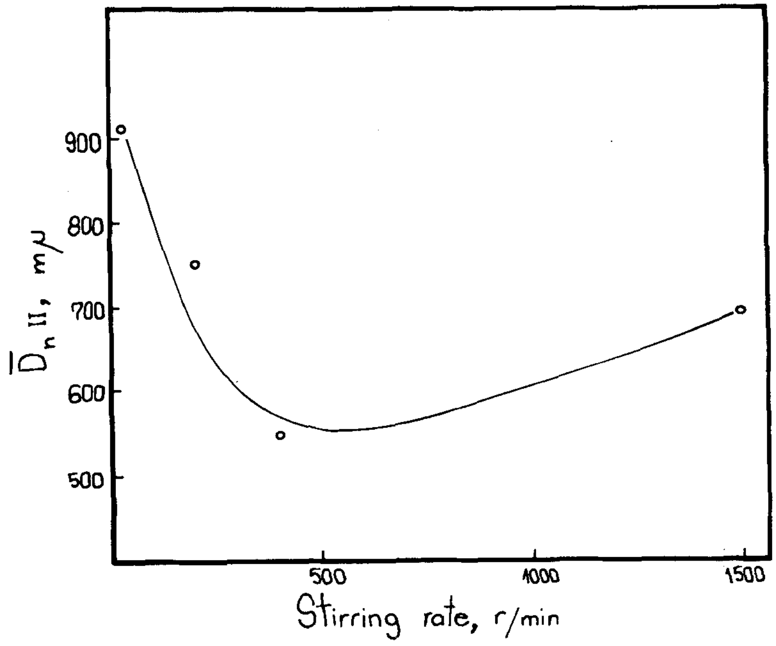

FIG. 2. Influence of stirring speed on particle diameters ($(R/M)_E = 5/0$).

the polymers finally obtained are semi-interpenetrating poly(vinyl acetate) networks. Due to the network structure, films with a higher degree of crosslinking, and with a higher content of insoluble fractions, have higher glass transition temperatures (Fig. 4).

Influence of the Distribution of the Coemulsifier

An important factor affecting the semicontinuous emulsion polymerization is the distribution of emulsifier between the initial charge (R) and the continuously introduced monomer (M) [8, 21]. Snuparek established that if the amount of emulsifier fed continuously with monomer is high, the final surface tension of the emulsions is low and the final particle diameters are large.

We studied the influence of the distribution ratio of a constant amount of the coemulsifier between initial charge and the monomer fed continuously on the conversion and on the particle diameters (Fig. 5).

In good agreement with the results of Snuparek [21] at higher $(R/M)_E$ values, smaller particle diameters were obtained.

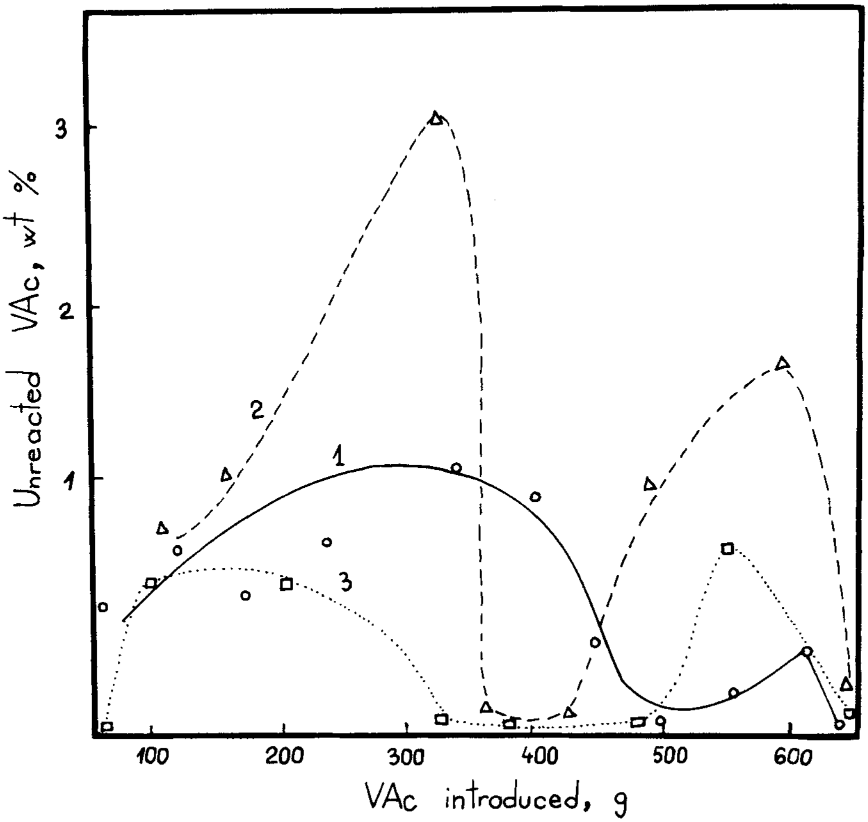

FIG. 3. Unreacted monomer versus VAc introduced. 1: $(R/M)_E$ = 5/0, 400 r/min. 2: $(R/M)_E$ = 5/0, 1500 r/min. 3: $(R/M)_E$ = 0/5, 400 r/min.

The conversion is unchanged at small $(R/M)_E$ values. At higher $(R/M)_E$ values the conversion is lower. As in the case of the other coemulsifiers, the rate of polymerization decreases when the concentration of the surfactant increases [22]. This can be explained by the existence of a strong chain transfer reaction of the growing radicals to the coemulsifier. Active radicals which appear in this reaction have a lower activity. When a large amount of the coemulsifier is introduced in the initial charge, the ratio of coemulsifier over growing radicals is high and the probability of chain transfer is higher. Due to this reaction, the level of unreacted monomer is higher during the process

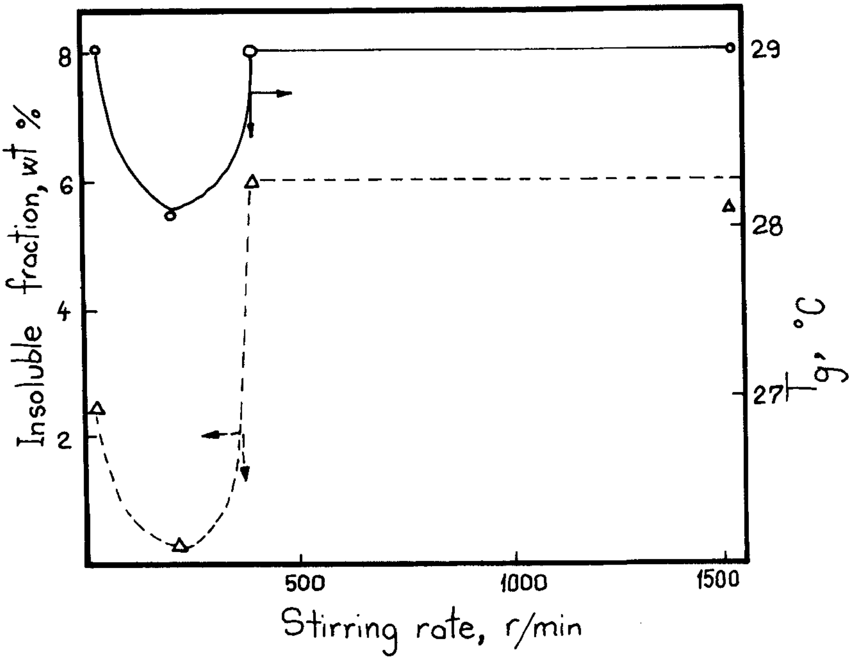

FIG. 4. Influence of agitation rate on the insoluble fractions and on the glass transition temperature of the films ($(R/M)_E$ = 5/0).

at high $(R/M)_E$ (Fig. 3). In the presence of the coemulsifier, the rate of splitting of the initiator is reduced [20].

If a large amount of coemulsifier is present in the first moment of the polymerization process at high $(R/M)_E$, the decomposition reaction of persulfate is smaller. Under these conditions, the probability of initiation may be smaller, thus reducing the polymerization rate.

The correlation between the distribution of the coemulsifier and the insoluble fraction is plotted in Fig. 6.

The decrease in the amount of insoluble fraction with $(R/M)_E$ is proof of the coemulsifier being a chain transfer agent. Due to the higher level of transfer reaction to coemulsifier at higher $(R/M)_E$ = (5/0) values, the water-soluble fraction is minimum (Fig. 7). Under these reaction conditions the polymer obtained had a higher benzene-soluble fraction content. The benzene-soluble fraction at $(R/M)_E$ = 5/0 includes a large amount of coemulsifier in the macromolecular chain.

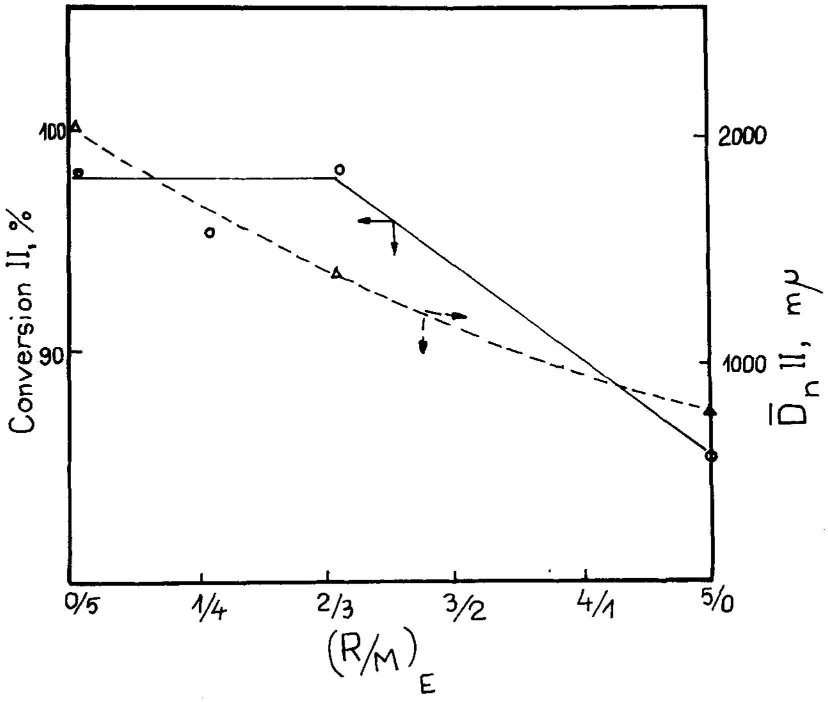

FIG. 5. Final conversion and particle diameters in relation to $(R/M)_E$ (200 r/min).

As in Fig. 4, the insoluble fraction content is correlated to the glass transition temperature of the films. A polymer with a smaller degree of crosslinking has a lower glass transition temperature (Fig. 6).

CONCLUSIONS

In the semicontinuous emulsion polymerization of vinyl acetate, the stirring rate and the distribution of the coemulsifier between the initial reactor charge and the continuously introduced monomer affect the monomer conversion and the polymer particle diameter. The amount of the unreacted monomer oscillates with time. The coemulsifier acts as a chain transfer agent.

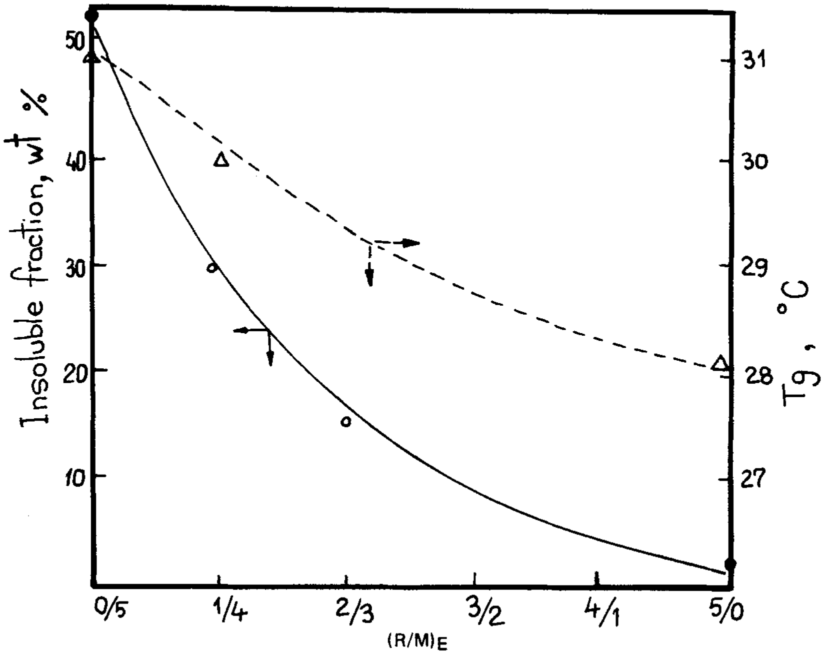

FIG. 6. Insoluble fractions and T_g in relation to $(R/M)_E$ (200 r/min).

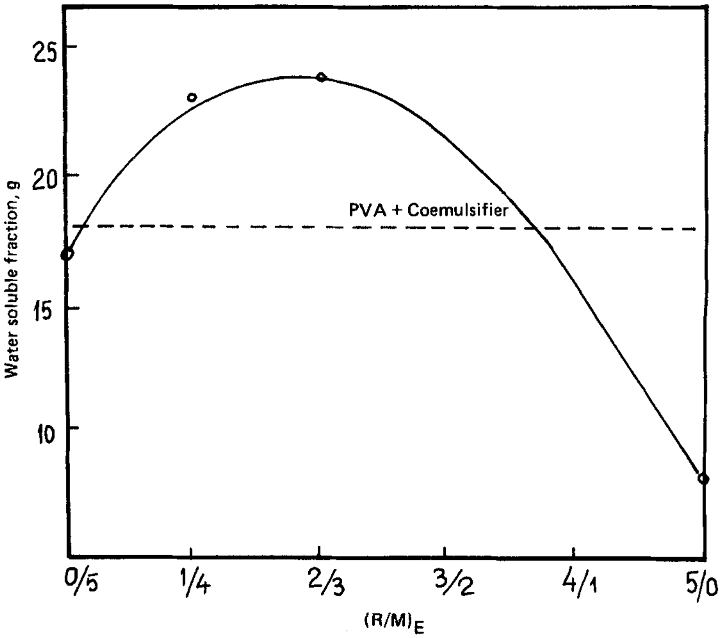

FIG. 7. Variation of water-soluble fraction on $(R/M)_E$.

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