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Semicontinuous Emulsion Polymerization of Vinyl Acetate. Part II. Copolymerization with Dibutyl Maleate

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ABSTRACT

The semicontinuous emulsion copolymerization of vinyl acetate: dibutyl maleate (60:40, vol/vol) was carried out at different coemulsifier distributions between initial reactor charge and continuously introduced monomer. The overall conversion, the copolymer particle size, and the properties of films obtained from emulsions were determined experimentally. Polyvinyl alcohol and cetyl alcohol ethoxylated with ethylene oxide (20 mol) were used as protective colloid and coemulsifier, respectively. Experimental investigations have shown that the unreacted monomer con-

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centration and the copolymer particle size oscillate with time. These oscillations are related to a tendency for limited particle flocculation.

INTRODUCTION

In a previous paper [1] we studied the semicontinuous polymerization of vinyl acetate (VAc). It was demonstrated that during this process the stirring rate and the distribution of the coemulsifier between the initial reactor charge and the continuously introduced monomer had a pronounced effect upon the monomer conversion and polymer particle diameters. The concentration of unreacted monomer oscillates with time.

Due to the practical importance of the copolymers of vinyl acetate, we consider it of interest to expand the area of our investigations to the copolymerization of VAc with dibutyl maleate (DBM). Reaction conditions are the same as in the homopolymerization of VAc [1].

EXPERIMENTAL

Materials

Vinyl acetate was purified by distillation.

Dibutyl maleate was purified by distillation under reduced pressure.

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

Potassium persulfate (KPS), Austranal grade, was used as supplied.

Ethoxylated cetyl alcohol (RO), 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. 6-10) and a 2-L reactor (Figs. 3, 4).

Total reaction charge (g): VAc = 185, DBM = 137, PVA = 9, RO = 9, potassium persulfate = 1.4, water = 350. At the beginning of the polymerizations, 270-315 g water, all the PVA and some amount of RO were fed to the reactor. The reactor charge was heated to 65°C. 33 g of the monomer mixture and 0.7 g KPS dissolved in 35 g water were added (Portion I). After 30 min, 289 g of the monomer mixture, 0.7 g KPS dissolved in 35 g water, and the remained RO dissolved in water (20% concentration) (Portion II) were fed for 4 h at 70°C. For Figs. 3 and 4, twofold reactants were used.

Films were obtained from the copolymer emulsions by drying at room temperature. The films were subjected to successive extractions in water and benzene by boiling for 8 h each. The amount of the polymer soluble in water and in benzene was established gravimetrically.

Measurements of interfacial tensions were made by the ring method using a du Nouy tensiometer at 25°C.

Emulsion stability was estimated by shaking 15 cm^3 water solution of 1 wt% (PVA + RO) with 10 cm^3 of the monomer mixture for 2 min. The water separated by creaming of the emulsions was measured after 2 h at 25°C.

Particle diameters were measured by electron microscopy with a JEOL 200 CX instrument.

Glass transition temperatures were measured by DSC with a Du Pont 990 instrument.

RESULTS AND DISCUSSION

Analysis of Reaction Conditions

It is well known that PVA reduces the interfacial tension between water and other substances [2, 3]. A much greater stability of emulsion of organic substances resulted when PVA was used in combination with a coemulsifier more effective in lowering interfacial tension [2].

We studied the stability of emulsions resulting from the reaction reagents. Cetyl alcohol ethoxylated with 20 mol ethylene oxide and the monomer mixture from the polymerization recipe were used as the coemulsifier and organic phase, respectively (Fig. 1).

The lowest interfacial tension was obtained at a 1:1 weight ratio of PVA:RO. A higher stability toward creaming of emulsions was obtained with this aqueous phase composition. All polymerizations were performed at this ratio of protective colloid over coemulsifier.

The splitting reaction of KPS in the presence of PVA and RO is affected (Fig. 2).

A large acceleration of the rate of persulfate decomposition in the presence of PVA was observed. The initiator and macromolecular protective colloid act as a redox system, in good agreement with other results [6-8]. The coemulsifier decreases the rate of KPS decomposition. In the hydroxyethylcellulose-ethoxylated nonylphenols system this phenomenon was explained by the formation of a complex between polymer colloid and coemulsifier [9].

In a paper concerning the batch emulsion copolymerization VAc-DBM, Emirova et al. [4] studied the influence of the monomer mixture composition on the consumption rate. A higher consumption rate of DBM was obtained at molar fractions of 0.2 to 0.8. We used an initial molar fraction of 0.218 for DBM.

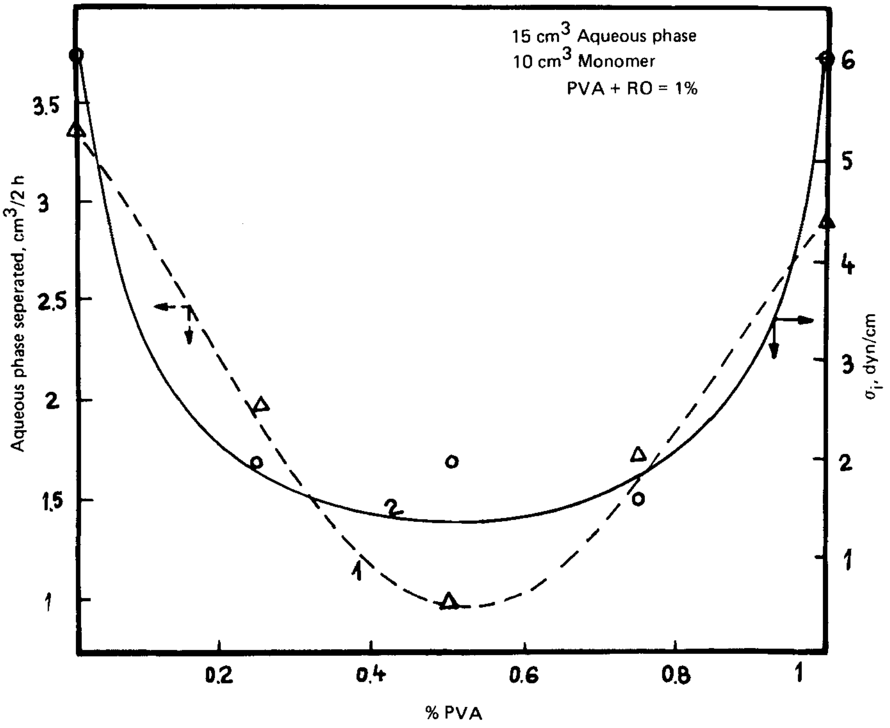

FIG. 1. Dependence of the interfacial tension and the aqueous phase separated in 2 h on PVA concentration (t = 25°C).

VAc has a high rate of polymerization at this composition. Under these conditions the composition of the copolymers in a semicontinuous process are constant over time.

Time Evolution of the Process

In a study concerning emulsion polymerization by the continuous monomer addition method, Wessling and Gibbs concluded [5] that at low feed rate of the monomer, the rate of polymerization is controlled by the rate of monomer addition. At higher rates of addition the reaction floods, the rate of polymerization is not controlled by the rate of monomer addition, and the unreacted monomer level increases with time.

The evolution of polymer formation versus the amount of monomer introduced is plotted in Fig. 3 for our experimental conditions.

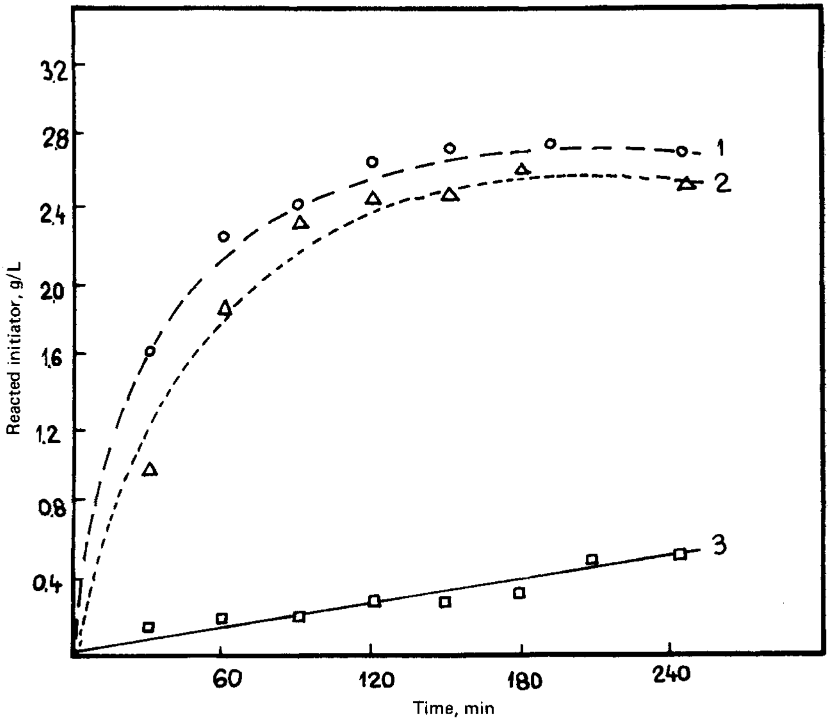

FIG. 2. Influence of aqueous phase composition on the decomposition reaction of KPS ($[KPS]_0$ = 3 g/L, t = 65°C): 1) KPS + APV; 2) KPS + APV + RO; 3) KPS in water.

In the first stage of the process the evolution of conversion is similar to a flooded system. Due to the increase of polymer concentration, the surface of the polymer particle increases enough to offer an available locus for polymerization [5]. The process passes through an apparently linear region and then the conversion rises rapidly. By following the variation of the unreacted monomer, oscillations appear which depend on the amount of monomer introduced (Fig. 4).

Particle diameters increase with the evolution of the process. In the first moments of the process (Samples 4, 6) a narrow particle size distribution curve is obtained. Then, due to limited flocculation, the particle size distribution curve becomes broad (Samples 7-9). The first increase in unreacted monomer concentration is related to this flocculation (Fig. 5).

The final decrease in unreacted monomer is related to a decrease in the average diameter of the particles (Samples 10, 11). The dis-

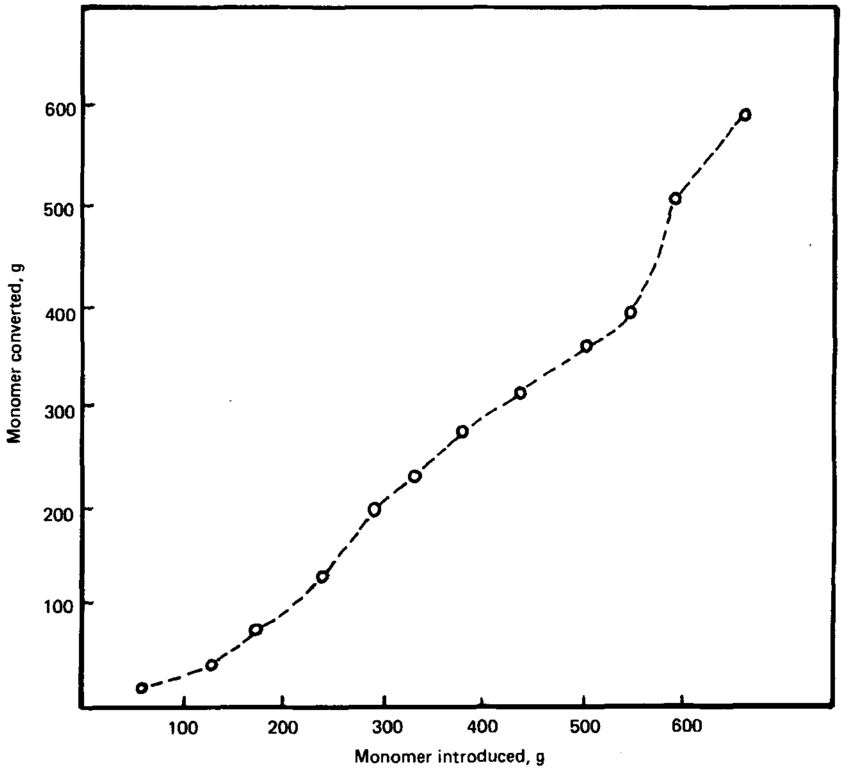

FIG. 3. Correlation converted polymer and monomer introduced.

tribution curves of polymer particle diameters and the variation in the average diameter at different moments of the process indicate that new, small particles appear toward the end of polymerization.

Oscillations in conversion and in the number of particles are also related in other systems [1, 10, 14]. These oscillations can lead to an emulsifier level too small to cover the polymer particles, with the result that excessive agglomeration occurs. The degree of emulsifier saturation of the particle surfaces passes through a minimum at the maximum of the number of particles.

Our experimental results (Figs. 4 and 5) are in good agreement with the results of Kiparissides et al. [10, 11] and of Sütterlin and Markert [14]. They concluded that agglomeration occurred during a relatively short period of time and with the generation of a second class of particles. The final number of particle is a result of successive processes of particle nucleation and agglomeration.

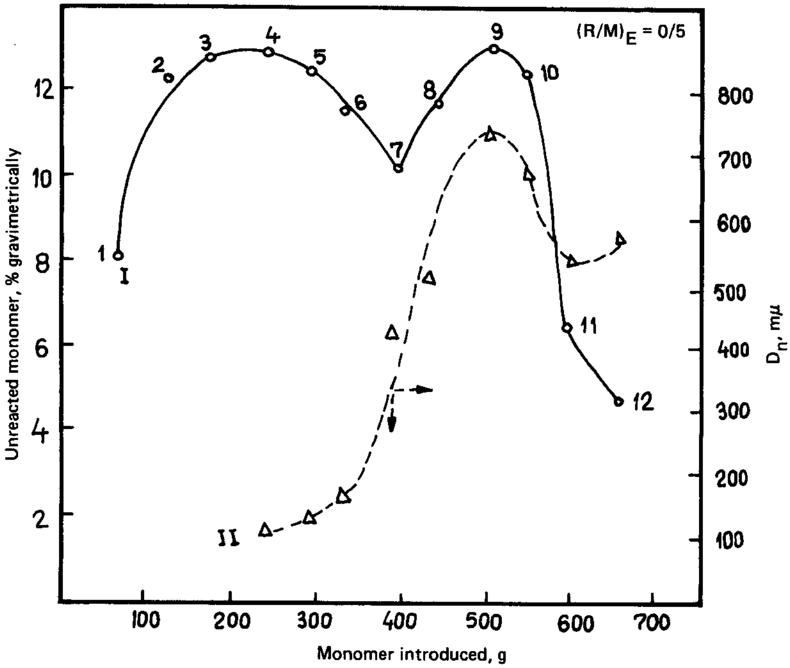

FIG. 4. Unreacted monomer (I) and particle diameter (II) versus monomer introduced.

Effect of Stirring Speed

Our previous paper [1] showed that the semicontinuous emulsion polymerization of VAc is affected by the stirring speed. Minimum conversion and smaller polymer particle diameters were obtained at a certain stirrer speed.

The effect of stirring speed on conversion in the copolymerization VAc-DBM is plotted in Fig. 6.

Under the same reaction conditions, a minimum conversion was obtained at the same stirrer speed as for the homopolymerization of VAc. This means that the hydrodynamic phenomena may exert a double effect on conversion.

The results of Nomura et al. [15] and of Kiparissides et al. [10, 11] demonstrated that intense agitation reduced the polymerization rate. Daniel and co-workers [16] established that by increasing the stirrer speed, an increase of the emulsion polymerization rate of VAc was obtained.

Our experiments were performed over a large range of stirrer

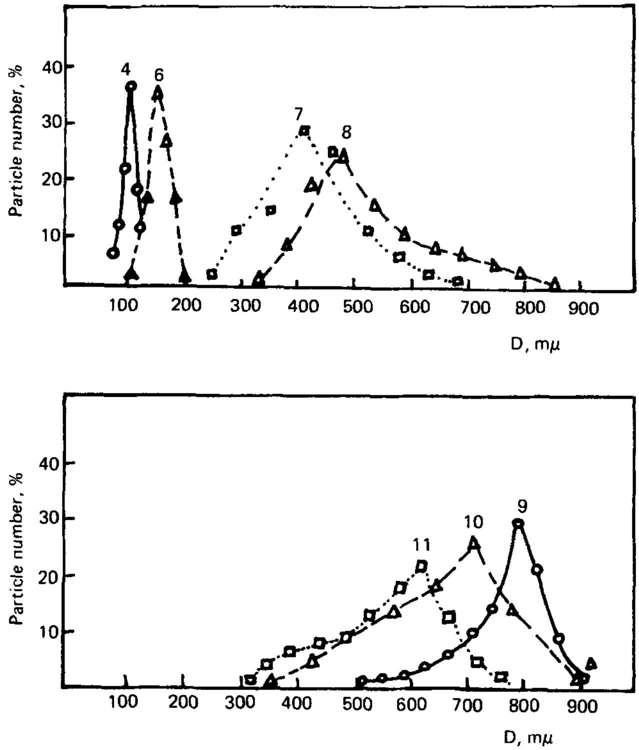

FIG. 5. Variation of the distribution curve of the polymer particle diameters with the progress of the process.

speed and included both effects. The decrease of the polymerization rate with an increase of the stirrer speed may be due to the contact between the reaction mixture and atmospheric oxygen. After 400 r/min conversion, increases result because the diffusion phenomena may indirectly affect the rate of polymerization.

The structure of the polymerization products is modified by the agitation rate (Fig. 7).

When films of VAc-DBM copolymers were successively extracted in boiling water and boiling benzene, only two fractions were separated: a small fraction soluble in water and another one soluble in benzene. The lack of insoluble fractions may be explained by the existence of a strong chain transfer agent introduced with DBM. In the presence of this small molecular transfer agent, crosslinking onto the PVA chain does not take place. This strong chain transfer agent is the comonomer DBM [17].

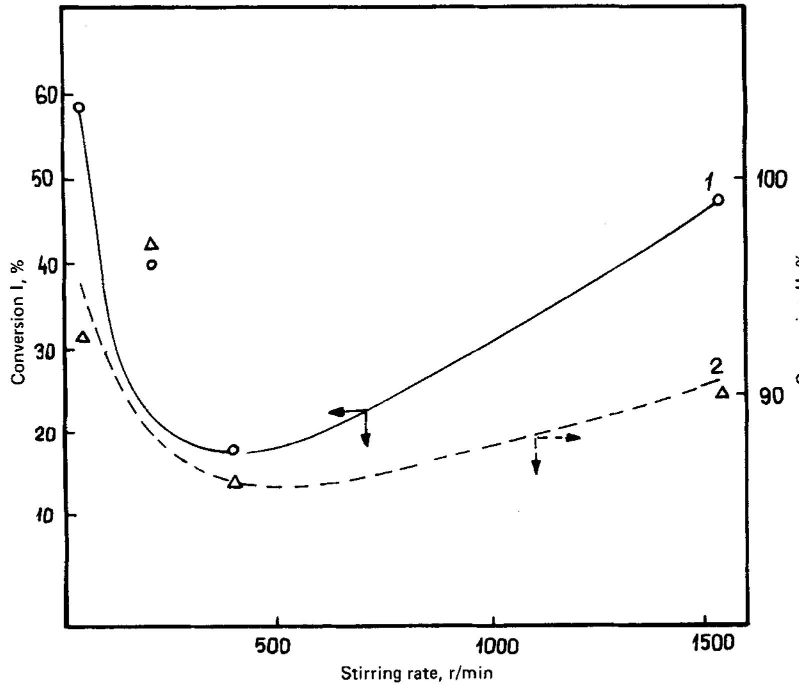

FIG. 6. Influence of stirring speed on conversion.

Over 200 r/min, the water-soluble fractions are less than the amount of PVA and the coemulsifier. These results can be explained on the basis of the formation of graft copolymers of VAc-DBM onto PVA and the coemulsifier. This fact suggests that these graft copolymers are benzene soluble and have a high P(VAc-DBM) content. The different content of water-soluble fractions may be ascribable to an inefficient stirring rate. At small speeds the transfer to coemulsifier and PVA may be higher because the contact of the radicals with oxygen is smaller. The level of water-soluble fraction is smaller as in the homopolymerization of VAc for high stirring speeds. Copolymers with higher water-soluble fractions had lower glass transition temperatures (Fig. 8). This suggests that water-soluble fractions are plasticizers for the final copolymer films.

Influence of Coemulsifier Distribution

In semicontinuous emulsion polymerization the distribution of the emulsifier between the initial reactor charge (R) and the continuously

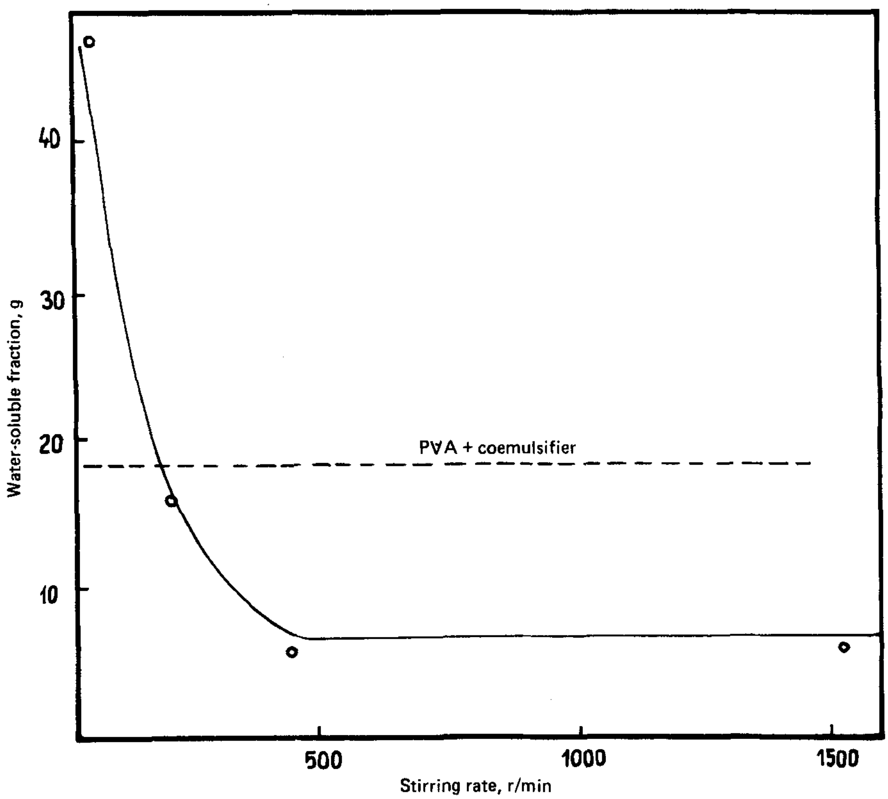

FIG. 7. Stirring effect on the concentration of water-soluble fractions.

introduced monomer (M) plays an important role [1, 12, 13, 18]. In a study concerning acrylic monomers, Snuparek established that if the amount of emulsifier fed continuously with monomer is high, the final surface tension of the emulsions are low and the final particle diameters are large.

We previously reported [1] on the effect of R/M of coemulsifier in semicontinuous emulsion polymerization of VAc. At high $(R/M)_E$ values, smaller particle diameters, conversion, and polymer-insoluble fractions were obtained.

The influence of coemulsifier distribution on conversion in the copolymerization of VAc-DBM is shown in Fig. 9.

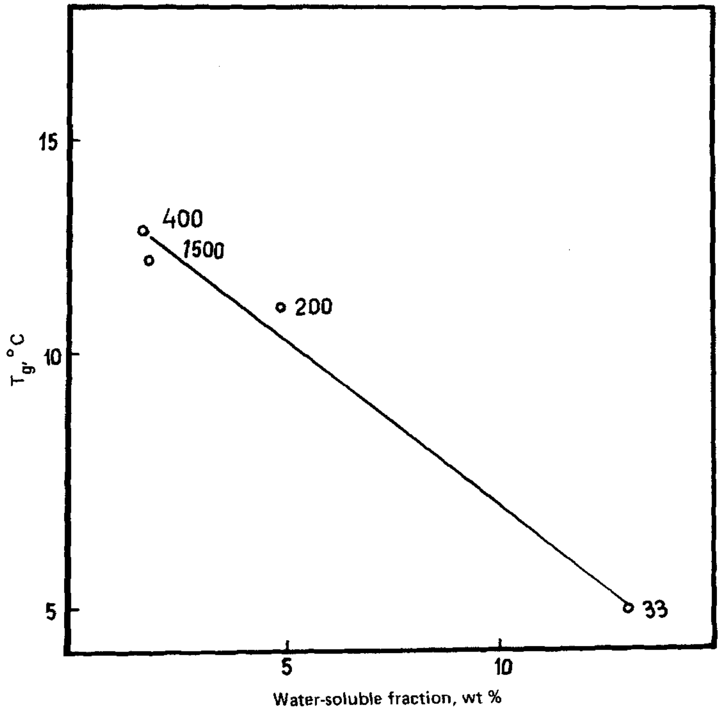

FIG. 8. Correlation of the water-soluble fraction content and T_g (values indicate stirring speed in r/min).

The conversion increases and then decreases with $(R/M)_E$. This suggests that the coemulsifier has a double effect. At a small concentration of coemulsifier at the beginning of the process (small $(R/M)_E$), the coemulsifier acts as a stabilizer for the polymer particles. The conversion of monomers increases with increases in the particle number and stability. Over a certain coemulsifier concentration its chain transfer effect is more pronounced. The radicals which appear from chain transfer reactions are less active, and the conversion is smaller.

The water-soluble fraction variation with $(R/M)_E$ values follows the conversion curve as in the homopolymerization of VAc [1], but the absolute values are smaller (Fig. 10).

The explanation for the smaller amount of water-soluble fraction at higher $(R/M)_E$ values is the same as in the case of the homopolym-

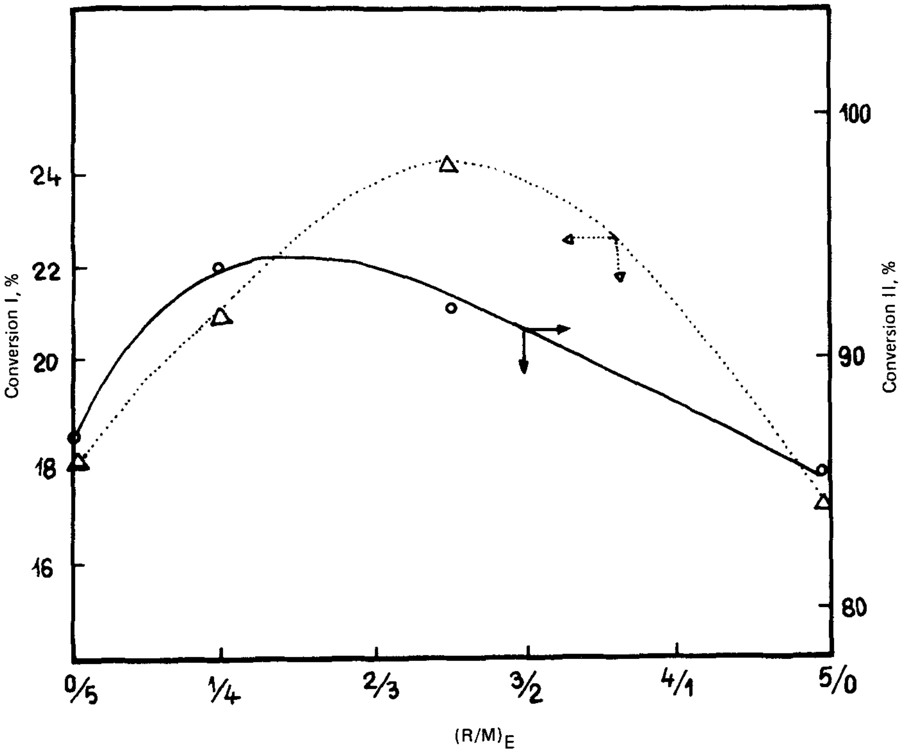

FIG. 9. Influence of $(R/M)_E$ on conversion.

erization of VAc. At higher $(R/M)_E$ values the ratio of coemulsifier over growing radicals is higher. The probability of chain transfer reaction is higher, too. This suggests that the chain transfer reaction to coemulsifier also takes place in the copolymerization of VAc-DBM. A concurrent chain transfer agent is DBM.

In conclusion, the copolymerization of VAc-DBM is a complex process. Monomer conversion and particle number oscillate with reaction time. The stirring rate and the distribution of the coemulsifier between the initial reactor charge and the continuously introduced monomer influence monomer conversion and copolymer structure. The coemulsifier and the comonomer, DBM, act as chain transfer agents.

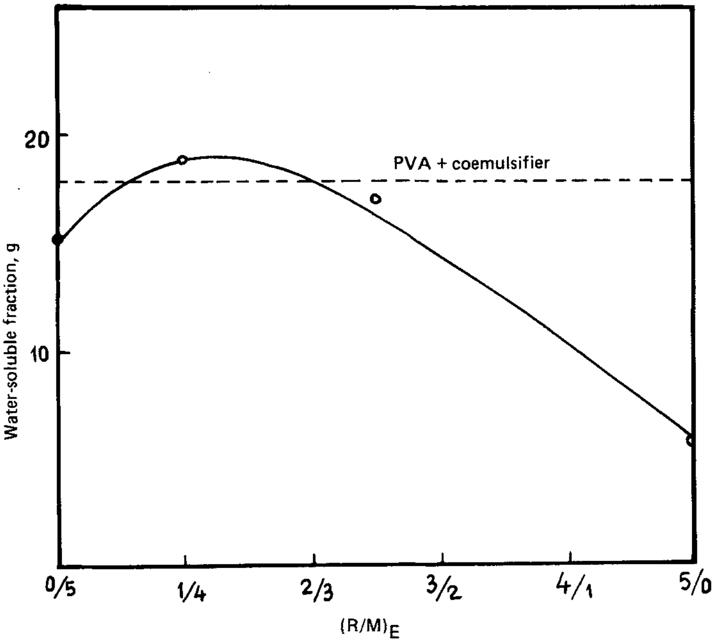

FIG. 10. Variation of water-soluble fraction with $(R/M)_E$.

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