Emulsion polymerization of vinyl propionate using a newly developed redox pair initiation system

M. M. H. Ayoub*, S. M. Shendy and A. S. Badran
Department of Polymers and Pigments, National Research Center, Dokki, Cairo, Egypt
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The kinetics of emulsion polymerization of vinyl propionate (VP) using the redox system potassium persulfate (KPS)/acetone–sodium bisulfite (ASBS) as redox pair initiation system is studied at 25°C. The effect of different initiator concentrations on the rate of polymerization and on the number and size of particles of the formed emulsion latices is established. The polymerization proceeded smoothly till high conversion and yielded stable emulsion latices. The rate of polymerization was found to be dependent on the initiator concentration to the 2/5 power.

(Keywords: emulsion polymerization; vinyl propionate; kinetics)

INTRODUCTION

The emulsion polymerization of vinyl acetate using persulfate salt as initiator has been investigated by many authors[1–3]. Research has been done in the field of emulsion polymerization of vinyl acetate using different redox pair initiation systems[4–8]. Most of the polymerization processes were run at higher temperature, but none of these are suitable for commercial purposes at lower temperatures. Badran *et al.*[9–12] polymerized vinyl acetate by using different developed redox pair initiation systems that consist of a persulfate salt with bisulfite adducts as reducing agents. They found that the polymerization proceeded smoothly till high conversion and yielded stable emulsion latices. The effect of such redox systems on the emulsion polymerization of vinyl propionate has not yet been studied.

The aim of the present work is to study the kinetics and mechanism of emulsion polymerization of vinyl propionate using potassium persulfate with acetone–sodium bisulfite as a newly developed redox pair initiation system at low temperature. Also, the kinetics are followed by the light scattering technique.

EXPERIMENTAL

Materials

Vinyl propionate (VP) was obtained from Polyscience Inc. and was used as received ($MW = 100.12$, $d = 0.92$ at 20°C). Potassium persulfate (KPS) was obtained from Fisher Scientific Co. and was recrystallized from water with methanol. The final crystals were vacuum dried. Poly(vinyl alcohol) was obtained from Polyscience Inc. ($MW = 3000$, 87% hydrolysed) and was purified by dissolving in water and reprecipitating in acetone. Hydroquinone was obtained from Eastman Kodak Co. Water was purified by double distillation. The acetone–sodium bisulfite adduct (ASBS) was prepared by the addition reaction of sodium bisulfite on the carbonyl group of acetone. All other reagents were analytical grade.

Emulsion polymerization

The bottle polymerization technique was used for emulsion polymerization, according to the general recipe given in *Table 1*. Different concentrations of ASBS and KPS as redox initiator were dissolved in 90.0 ml of water containing surfactant in a 4 ounce glass bottle. Monomer was then added to the bottle. The bottle was immediately sealed with a butyl-rubber-gasket-lined perforated metal cap. Nitrogen purging was then performed for 15 min to minimize the amount of oxygen in the bottle. The bottle was clamped on the shaft of a thermostated water bath at 25°C and rotated end-over-end at 45 rev min^{-1}. A timer was started at the commencement of the polymerization to indicate when the samples were to be taken.

Determination of conversion. At various time intervals, a sample of the latex was removed from the bottle, and the percentage conversion of vinyl propionate to poly(vinyl propionate) (PVP) was determined. By plotting percentage conversion *versus* time, the rate of the polymerization reaction was determined from the slope of the straight-line portion of the curve at conversion nearly 20–80%.

Determination of particle size by dynamic light scattering. The particle size of the resulting emulsion latices was followed by dynamic light scattering (d.l.s.) (Autosizer IIc, Malvern Instruments Co.), which is based on the time and frequency fluctuations in the scattered light intensity of a sample. The variations of both particle size (D_z) and number of polymer particles per unit volume of water (N_t) for the obtained latices were investigated.

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*To whom correspondence should be addressed

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Table 1 Recipe used for emulsion polymerization of vinyl propionate at 25°C

Vinyl propionate	10 g
KPS	0.04–0.17 mol l^{-1}
ASBS	(0.05–0.2) × 10^4 mol l^{-1}
Poly(vinyl alcohol)	1.0 ml
Water	90.0 ml

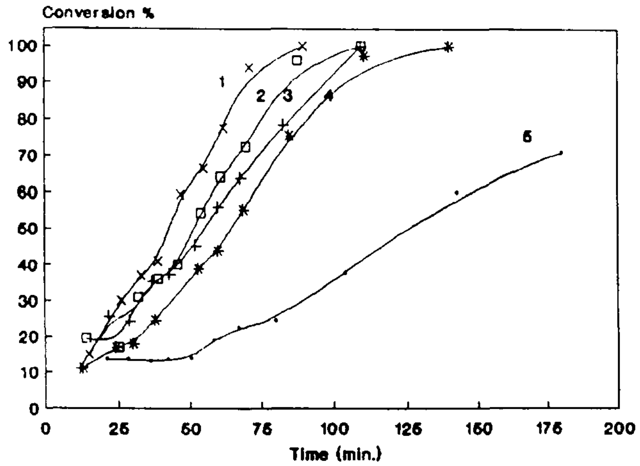

Figure 1 Dependence of the rate of polymerization on redox initiator concentration: $[K_2S_2O_8/ASBS] = 0.04/0.3 \times 10^4$ mol l^{-1}(1); $0.06/0.4 \times 10^4$ mol l^{-1}(2); $0.08/0.6 \times 10^4$ mol l^{-1}(3); $0.13/0.9 \times 10^4$ mol l^{-1}(4); $0.2/1.2 \times 10^4$ mol l^{-1}(5)

RESULTS AND DISCUSSION

Dependence of the rate of polymerization on initiator concentration

Figure 1 shows the conversion *versus* time plots for the emulsion polymerization of vinyl propionate at 25°C. It is obvious that, considering the initial rate of polymerization as well as the maximum conversion, concentration increased the rate of production of primary free radicals and consequently increased the initial rate and maximum conversion. The rate of emulsion polymerization is calculated from the slope of the linear portion of the monomer conversion *versus* time plot shown in *Figure 1*. The order of reaction with respect to the initiator concentration is 2/5, which is calculated from the relationship between logarithm of rate of polymerization and initiator concentration. When the poly(viny propionate) emulsions were formed in the presence of poly(vinyl alcohol) as an emulsifier and with the newly developed potassium persulfate/acetone–sodium bisulfite redox pair initiation system, the polymerization proceeded smoothly till high conversion (*Figure 1*), and the obtained poly(vinyl propionate) emulsions were stable. A potassium persulfate/sodium bisulfite redox system containing the same weight equivalent of bisulfite anion produced unstable emulsions of low conversion. This may be due to the emulsifying effect caused by the acetone adduct in addition to its function as a reducing agent. This behaviour was observed previously in polymerization of poly(vinyl acetate)[12].

Effect of different initiator concentrations on the particle size of the obtained latices

The particle size D_z of the poly(vinyl propionate) emulsion latices obtained in the presence of different initiator concentrations was determined by using the light scattering technique. Also, D_z was determined at different percentage conversions. *Figure 2* shows the relationship between D_z and percentage conversion. From this figure, it is clear that the maximum value of D_z occurs between 25 and 35% conversion, which is due to the presence of a second nucleation stage as a result of using the newly developed redox initiator system. *Figure 3* shows the relation between N_t, the number of polymer particles per unit volume of water, and percentage conversion for the latices prepared at different initiator concentrations. From this figure, it is obvious that N_t increased with conversion. This behaviour is the same for all emulsion latices.

The light scattering studies of the final latices indicated bimodal particle size distributions. This can be explained as follows: one group of latex particles was formed during the first constant-rate period, and another group of particles was nucleated at the start of the second constant-rate period. It can be concluded that a changing emulsion phase during polymerization will create latices with bimodal particle size distribution.

The following mechanism can be suggested for the polymerization reaction:

Initiation

$$(CH_3)_2\text{–}C(OH)SO_3^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{-\cdot} + (CH_3)_2C(OH)\dot{S}O_3$$

$$(CH_3)_2C(OH)\dot{S}O_3 + M \rightarrow (CH_3)_2C(OH)SO_3\ldots\ldots\dot{M}$$

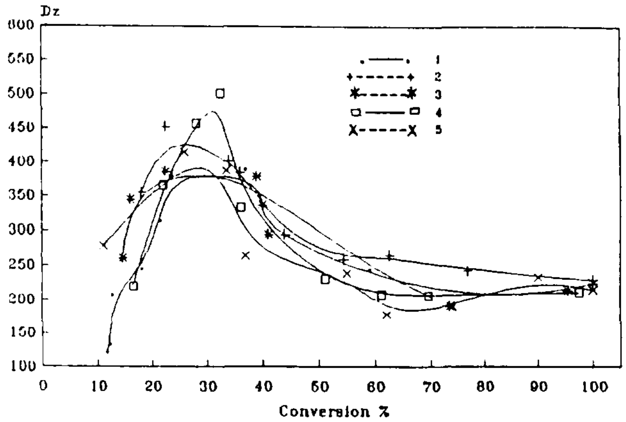

Figure 2 D_z of poly(vinyl propionate) latex particles obtained at different redox initiator concentration vs. percentage conversion: $[K_2S_2O_8/ASBS] = 0.04/0.3 \times 10^4$ mol l^{-1}(1); $0.06/0.4 \times 10^4$ mol l^{-1}(2); $0.08/0.6 \times 10^4$ mol l^{-1}(3); $0.13/0.9 \times 10^4$ mol l^{-1}(4); $0.2/1.2 \times 10^4$ mol l^{-1}(5)

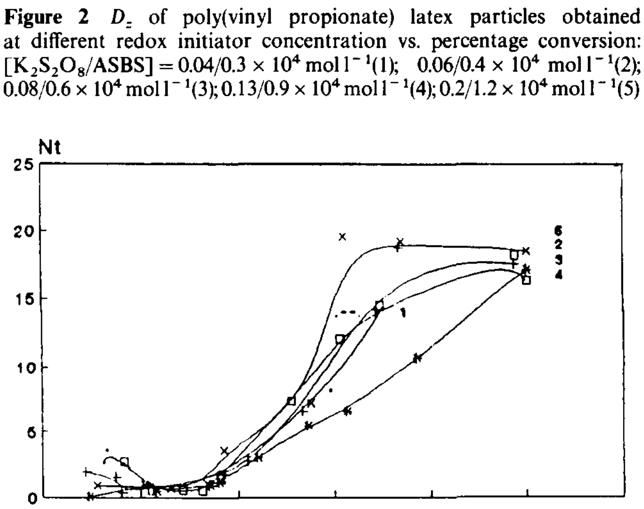

Figure 3 N_t of poly(vinyl propionate) latex particles obtained at different redox initiator concentration vs. percentage conversion: $[K_2S_2O_8/ASBS] = 0.04/0.3 \times 10^4$ mol l^{-1}(1); $0.06/0.4 \times 10^4$ mol l^{-1}(2); $0.08/0.6 \times 10^4$ mol l^{-1}(3); $0.13/0.9 \times 10^4$ mol l^{-1}(4); $0.2/1.2 \times 10^4$ mol l^{-1}(5)

Propagation

$$CH_3)_2C(OH)SO_3.....\dot{M}+M \rightarrow (CH_3)_2C(OH)SO_3.....M.....\dot{M}$$

$$(CH_3)_2C(OH)SO_3.....\dot{M}_{x-1}+M \rightarrow (CH_3)_2C(OH)SO_3.....\dot{M}_x$$

Termination

$$(CH_3)_2C(OH)SO_3.....\dot{M}_x+(CH_3)_2C(OH)SO_3.....\dot{M}_y \rightarrow (CH_3)_2C(OH)SO_3.....M_{x+y}SO_3(OH)C(CH_3)_2$$

Dimerization

$$(CH_3)_2C(OH)\dot{S}O_3+\dot{S}O_3C(OH)(CH_3)_2 \rightarrow (CH_3)_2C(OH)SO_3\text{-}O_3S(OH)C(CH_3)_2$$

CONCLUSION

There are significant differences in the results obtained with the emulsion polymerization of vinyl propionate (VP) using the newly developed redox system potassium persulfate (KPS)/acetone–sodium bisulfite (ASBS) as redox pair initiation system. It is certain that the type of emulsion created at the start of the reaction plays an important role in emulsion polymerization. It has an influence on the rate of polymerization, and the particle size distribution of the obtained latices. The emulsion phase change during polymerization will create latices with bimodal particle size distributions. Small changes in a reaction variable such as initiator concentration will create a tremendous change in the outcome of the reaction and the final product.

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