Some Parameters Affecting the Emulsifier-Free Emulsion Polymerization of Vinyl Acetate

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SYNOPSIS

The kinetics of emulsifier-free emulsion polymerization of vinyl acetate using the redox initiation system of potassium persulfate–potassium metabisulfite was studied. The effect of the reaction conditions on the rate of polymerization was also investigated. The polymerization proceeded smoothly until high conversion and yielded stable emulsions. The apparent activation energy for the polymerization system was calculated and the effect of some inorganic substances on the rate of polymerization was also revealed. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

The emulsion polymerization of vinyl acetate using potassium persulfate as an initiator was investigated by many authors.[1-5] Also, several studies were done in the field of emulsion polymerization of vinyl acetate using different redox pair initiation systems.[6-13] Different redox initiation systems consisting of a persulfate salt together with a reducing agent in the presence of different multivalent metal ions were investigated.[14-17] Vinyl acetate can, of course, be readily polymerized using hydrogen peroxide–zinc formaldehyde sulfoxylate[18] at 80°C. Most of these processes were carried out at high temperatures, but none of these function suitably for commercial purposes. The present study describes the development of a redox pair initiation system which consists of potassium persulfate–potassium metabisulfite to obtain a stable emulsion of high conversion at low temperature in the absence of an emulsifier and the effect of some inorganic substances on the rate of polymerization.

EXPERIMENTAL

Materials

The vinyl acetate monomer stabilized with 14 ppm hydroquinone, provided by BDH, was redistilled be-

fore use and stored at $-20°C$; potassium persulfate and potassium metabisulfite were recrystallized from water by methanol. The final crystals were vacuum-dried. Titanium dioxide (Rutile) was a product of Kromos CL300. Calcium carbonate was obtained from the EL-Nile Mining Co. All the water used was purified by double distillation.

Polymerization of Vinyl Acetate

The following ingredients were mixed in a 250 mL three-necked round-bottom flask. The order of addition was water, initiator, and, finally, the vinyl acetate monomer. The polymerization reactions were carried out at the required temperature in an automatically controlled water bath. All experiments were run with mechanical stirring at 500 rpm. This speed is in the range where the agitation has no noticeable effect on the rate of polymerization. Samples of the reaction mixture were taken at various intervals. These samples were relatively small so that the overall composition in the reaction vessel was not seriously affected. Once the sample was removed and put in a watch glass, the reaction was stopped using 7 ppm hydroquinone and the content of the watch glass was evaporated at room temperature, then dried until constant weight at 40°C in a vacuum oven. Since sampling time is known, the percent conversion of the total monomer is easily calculated. The purification and precipitation of the polymer were made by the method described by Grassie.[19]
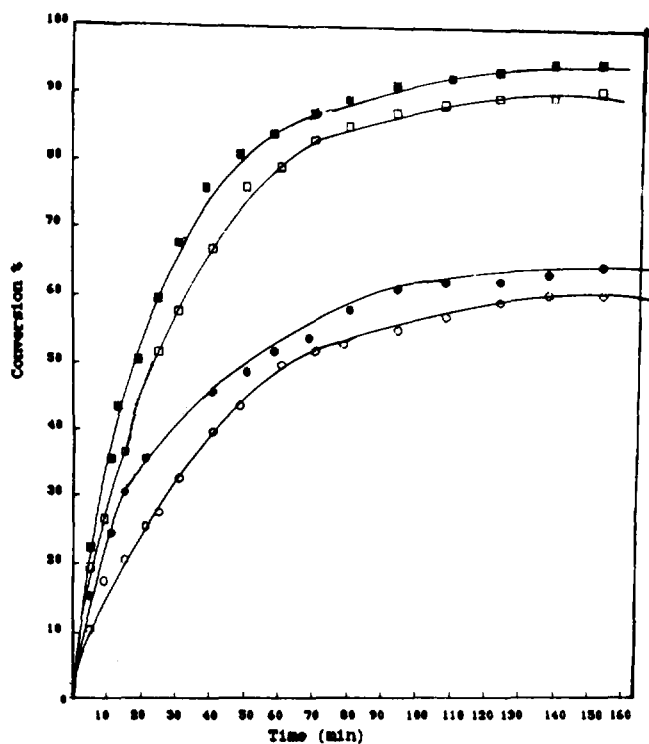
Figure 1   Conversion time curve effect of initiator using redox system $(K_2S_2O_8)/(K_2S_2O_5)$ = (○) 0.01, (●) 0.02, (□) 0.03, and (■) 0.04 g mol/L. Vinyl acetate = 1.162 g mol/L.

RESULTS AND DISCUSSION

Dependence of the Rate of Polymerization on the Initiator Concentration

Figure 1 shows the conversion–time plots for the polymerization of the vinyl acetate monomer at

40°C. From the figure, it is obvious that both the initial rate of polymerization as well as the maximum conversion were increased with increasing of the initiator concentration. This could be explained by stating that increasing the redox initiator concentration increased the rate of production of primary free radicals and, consequently, increased both the initial rate of polymerization and maximum conversion. The data are given in Table I. From Table I, it is found that both the conversion percentage and initial rate of polymerization increase with increase of the initiator concentration.

Figure 2 shows the double logarithmic plot of the polymerization rate vs. initiator concentration. The rate of polymerization is calculated from the slope of the relation of the monomer conversion vs. time plot shown in Figure 1. The order of the reaction with respect to the initiator concentration was calculated from Figure 2 and was found to be 0.86.

Effect of Temperature on the Rate of Emulsifier-free Emulsion Polymerization of Vinyl Acetate

The effect of polymerization temperature on the conversion percentage and the rate of the polymerization was studied. The results are shown in Figure 3 and given in Table I. From the figure, it is observed that both the conversion percentage and the initial rate of polymerization increased with increasing the temperature from 30 to 50°C.

The apparent activation energy (E_a) at different temperatures, 30, 40, and 50°C, was calculated and found to be 15 kJ/mol from Figure 3 and Table I by using Arrhenius plotting of the initial rate (R) against $1/T$. The results of plotting are shown in Figure 4. From the slope of this relation, the appar-

Table I   Effect of Emulsion Polymerization Conditions on the Initial Rate and Conversion Percentage Using 100 mL H_2O and 1.162 g mol/L Monomer for a Period of 150 Min

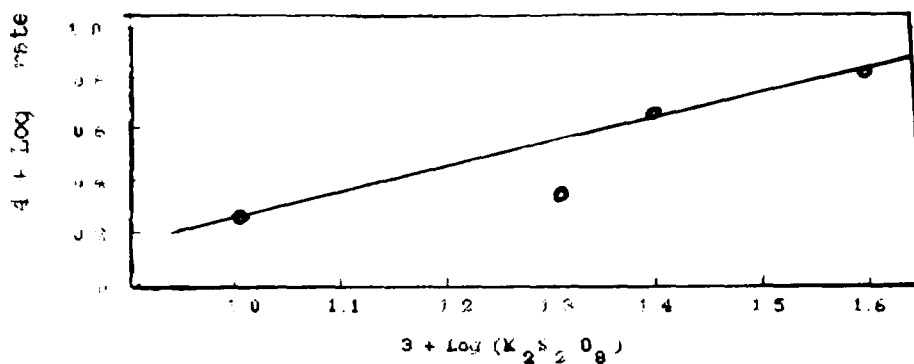| Exp No.	Redox Initiation System (g mol/L)		Reaction Temp (°C)	Conversion (%)	Initial Rate × 10^4 (g mol/L s)	E_a (kJ mol/mol)
	$K_2S_2O_8$	$K_2S_2O_5$				
1	0.01	0.01	40	59.2	1.761	—
2	0.02	0.02	40	62.2	2.422	—
3	0.03	0.03	40	89.5	5.305	—
4	0.04	0.04	40	92.5	5.692	—
5	0.02	0.02	30	43.8	2.153	—
6	0.02	0.02	40	62.2	2.422	15.282
7	0.02	0.02	50	96.1	3.229	—

Figure 2   Log initial rate of polymerization vs. log initiator concentrations.
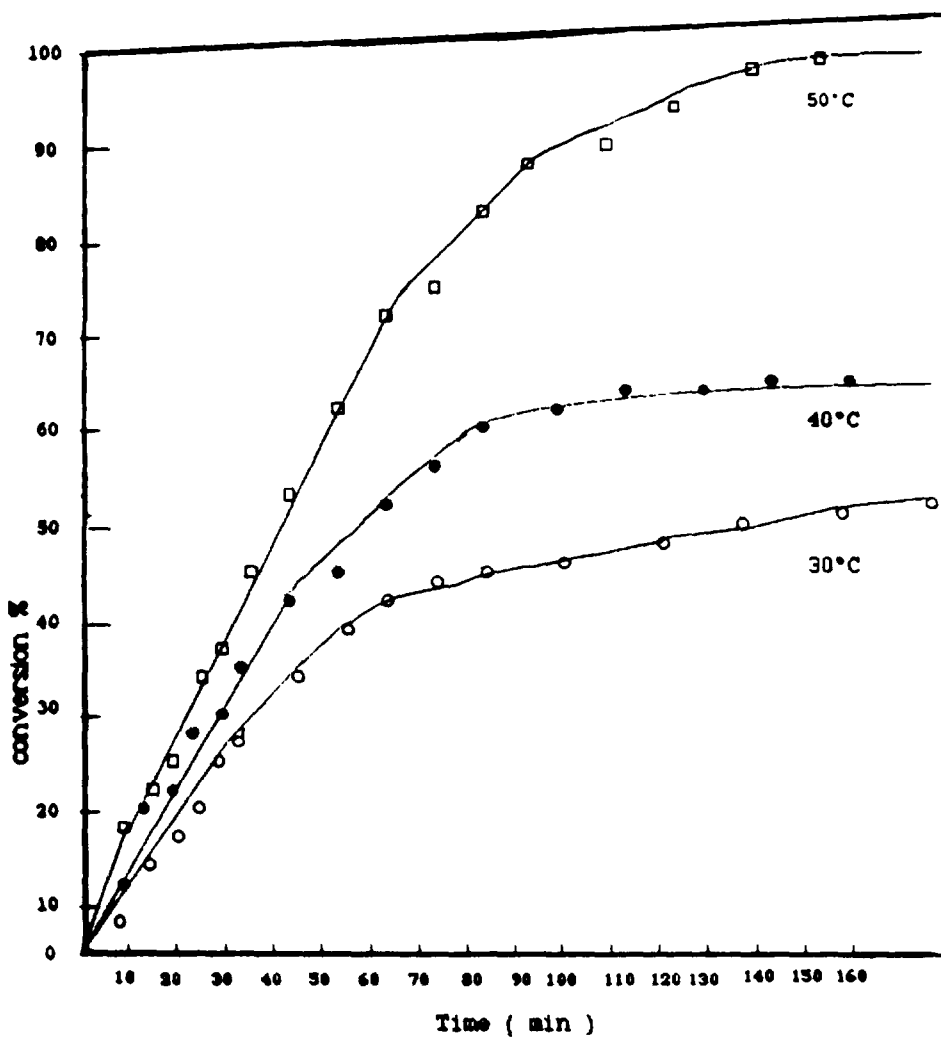

Figure 3   Rate dependence of temperature (30, 40, 50°C). Vinyl acetate = 1.162 g mol/ L; initiator = 0.02 g mol/L.
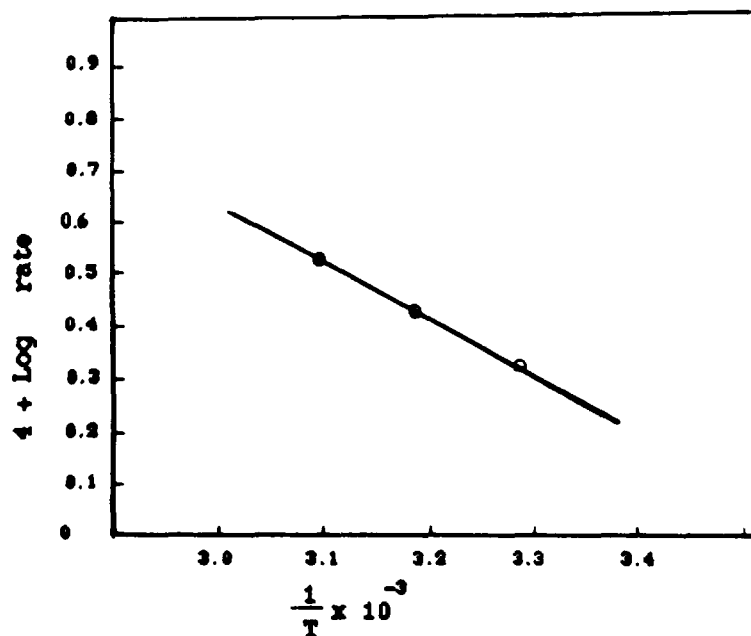
Figure 4   Arrhenius plot of the initial rate of polymerization vs. $1/T$.

ent activation energy was calculated by multiplying the value of the slope by 4.57 to obtain its value in calories; then by multiplying by 4.18, we obtain its value in joules. Its value agrees well with that reported in other similar polymerization systems.

Rate Dependence of Medium

The initial rate data for the polymerization reaction using different percentages of acetone with water as

media are shown in Table II and represented in Figure 5. From Figure 5, it is obvious that the initial rate of polymerization as well as the maximum conversion decrease with increase of acetone percentage in the medium (from 15 to 50%).

Figure 6 shows the logarithmic plot of the polymerization rate (g mol/L s) vs. the percentage of acetone in the medium. The relation was found to be a straight line.

Table II   Factors Affecting the Emulsion Polymerization of Vinyl Acetate for a Period of 150 Min at 40°C Using the Redox System $(K_2S_2O_8)/(K_2S_2O_5)$ = 0.02 g mol/L

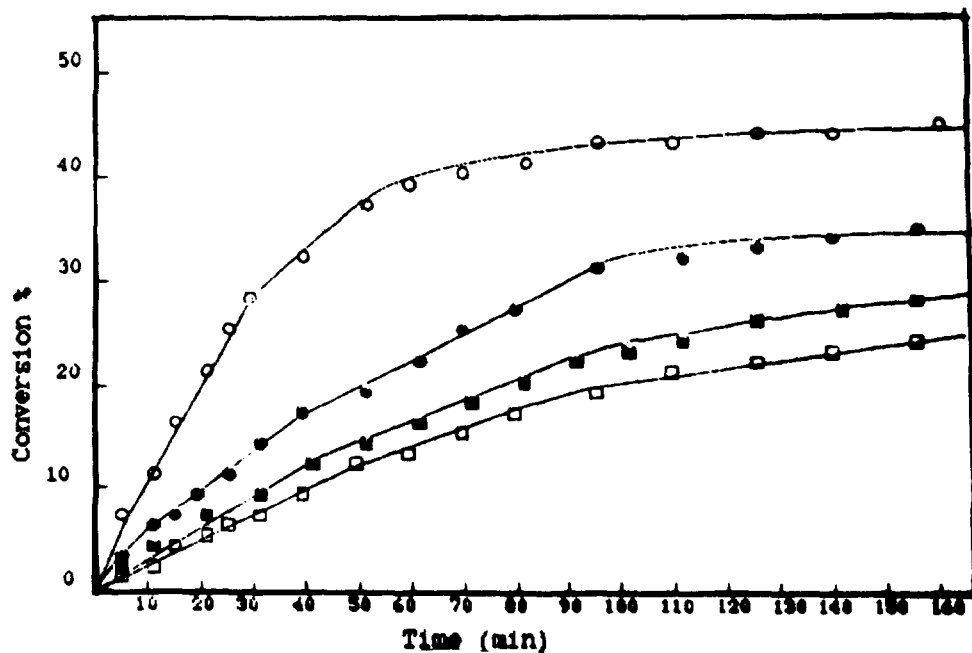| Exp No.	Vinyl Acetate (g mol/L)	Water (mL)	Acetone (mL)	TiO_2 (%)	$CaCO_3$ (%)	Conversion (%)	Initial Rate $\times$ 10^4 (g mol/L s)
1	1.162	100	0.0	0.0	0.0	62.2	2.422
2	1.162	85	15	—	—	45.1	1.937
3	1.162	75	25	—	—	35.5	0.7913
4	1.162	60	40	—	—	26.0	0.74
5	1.162	50	50	—	—	24.6	0.527
6	1.162	100	—	0.1	—	40.2	0.8074
7	1.162	100	—	0.3	—	33.6	0.6459
8	1.162	100	—	0.5	—	22.7	0.4213
9	1.162	100	—	—	0.1	40.5	4.30
10	1.162	100	—	—	0.3	31.5	1.514
11	1.162	100	—	—	0.5	20.5	0.9689

Figure 5 Effect of acetone percentage on the polymerization of vinyl acetate = 1.162 g mol/L. Initiator = 0.02 g mol/L. Acetone percentage: (O) 15%; (●) 25%; (■) 40%; (□) 50%.

Effect of TiO₂ Percent on the Rate of Polymerization

TiO₂ was used as a white pigment for the poly(vinyl acetate) emulsion latex in surface coating technology; therefore, it is very important to study the effect of presence of TiO₂ in the polymerization process medium. The polymerization of vinyl acetate of 1.162 g mol/L was carried out using 0.02 g mol/L of

potassium persulfate and 0.02 g mol/L potassium metabisulfite at 40°C using different percentages of TiO₂ (0.1–0.5%) for a period of 150 min. and the data are given in Table II and represented in Figure 7.

It is obvious that the initial rate of polymerization as well as the maximum conversion decrease with increase of percentage of TiO₂ in the medium. The initial rate data for the polymerization reaction using
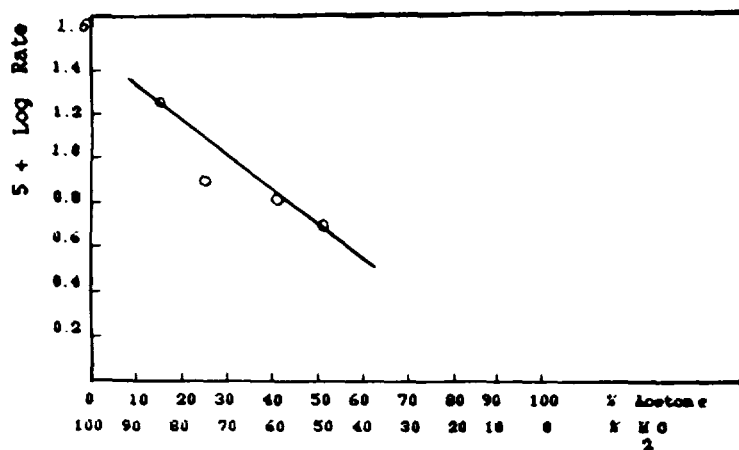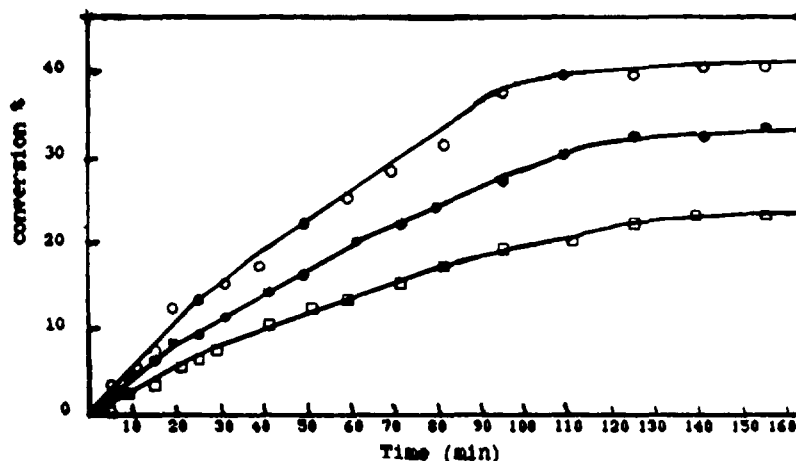

Figure 6 Logarithmic plot of the initial rate of polymerization vs. percentage of acetone on the medium: 15%; 25%; 40%; 50%.

Figure 7 Effect of TiO_2 amounts on the rate of polymerization. Vinyl acetate = 1.162 g mol/L; initiator = 0.2 g mol/L; TiO_2 = (○) 0.1%, (●) 0.3%, and (□) 0.5%.

different percentages of TiO_2 are shown in Table II. From Table II, it is found that addition of TiO_2 decreased the rate of polymerization due to the fewer number of radicals formed in its presence.

Figure 8 shows the logarithmic plot of polymerization rate (g mol/L s) vs. the percentage of TiO_2 in the reaction medium. The power of the polymerization with respect to percentage of TiO_2 was 0.8.

Effect of $CaCO_3$ Percent on the Rate of Polymerization

Figure 9 shows the conversion–time plots for the polymerization of vinyl acetate at 40°C using $CaCO_3$ for a period of 2.5 h. It is obvious that both the

initial rate of polymerization as well as the maximum conversion decrease with increase of the percentage of $CaCO_3$ in the reaction medium. The initial rate data for the polymerization reaction using different percentages of $CaCO_3$ are shown in Table II.

Figure 10 shows the logarithmic plot of the polymerization rate (g mol/L s) vs. the percentage of $CaCO_3$ in the reaction medium. The relation was found to be a straight line with a slope of 1.5.

Suggested Mechanism for the Polymerization Reaction of Vinyl Acetate Using Acetone in the Reaction Medium

This mechanism is shown in Scheme 1.
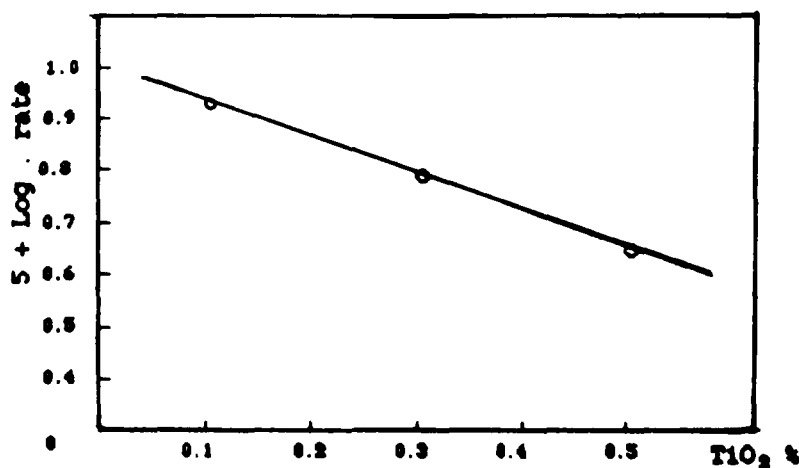
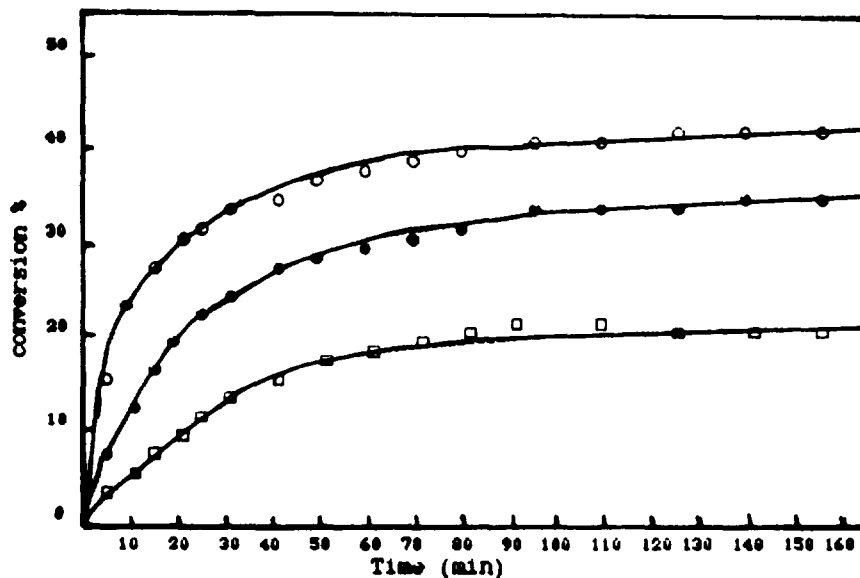**Figure 8** Logarithmic plot of the initial rate of polymerization vs. the TiO_2 percentage: 0.1%; 0.3%; 0.5%.

Figure 9 Effect of $CaCO_3$ percentage on the rate of polymerization. Vinyl acetate = 1.162 g mol/L; initiator = 0.02 g mol/L; $CaCO_3$ = (O) 0.1%, (●) 0.3%, (□) 0.5%.

CONCLUSION

The emulsifier-free emulsion polymerization of vinyl acetate using the redox initiation system of potassium persulfate–potassium metabisulfite was studied using different initiator concentrations (0.1–0.4 g mol/L) at 40°C. This resulted in an increase in the conversion from 59.2 to 92.5%. The rate of polymerization increased by increasing the temperature from 30 to 50°C and the apparent activation energy was found to be 15.2 kJ/mol. Using acetone in the reaction medium resulted in a decrease in the rate of polymerization. Both of TiO_2 and $CaCO_3$ decreased the rate of polymerization of vinyl acetate.
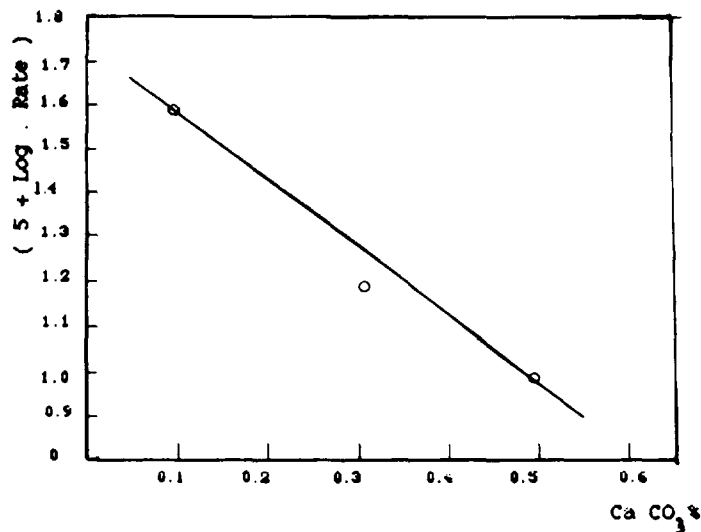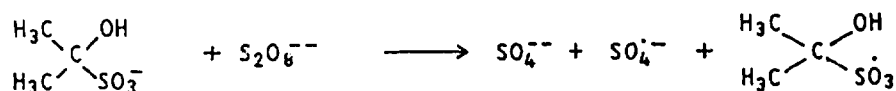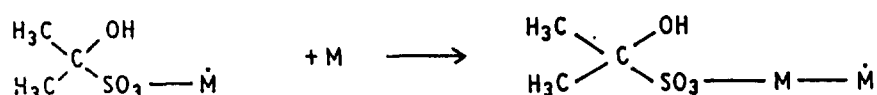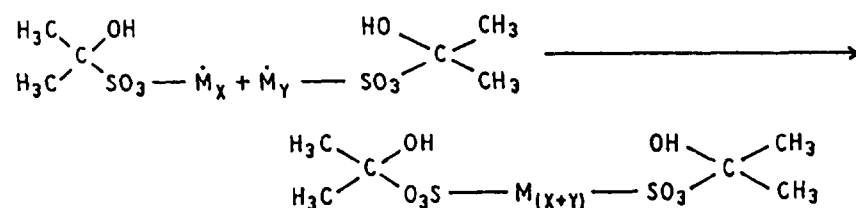

Figure 10 Logarithmic plot of the initial rate of polymerization vs. percentage of $CaCO_3$: 0.1%; 0.3%; 0.5%.

$$\underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3^-}{<}} + S_2O_8^{--} \longrightarrow SO_4^{--} + SO_4^{\cdot-} + \underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}}$$

Initiation

$$\underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}} + M \longrightarrow \underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}}\!\!-\!\!\dot{M}$$

Propagation

$$\underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}}\!\!-\!\!\dot{M} + M \longrightarrow \underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}}\!\!-\!\!M\!\!-\!\!\dot{M}$$

$$\underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}}\!\!-\!\!\dot{M}_{(X-1)} + M \longrightarrow \underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}}\!\!-\!\!\dot{M}_X$$

Termination

$$\underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{SO_3}{<}}\!\!-\!\!\dot{M}_X + \dot{M}_Y\!\!-\!\!SO_3\!\!\overset{HO}{\underset{CH_3}{>}}\!\!C\!\!\overset{CH_3}{\underset{CH_3}{<}} \longrightarrow$$

$$\underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{O_3S}{<}}\!\!-\!\!M_{(X+Y)}\!\!-\!\!SO_3\!\!\overset{OH}{\underset{CH_3}{>}}\!\!C\!\!\overset{CH_3}{\underset{CH_3}{<}}$$

Dimerization

$$\underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{\dot{SO_3}}{<}} + \underset{\dot{SO_3}}{\overset{HO}{>}}\!\!C\!\!\overset{CH_3}{\underset{CH_3}{<}} \longrightarrow \underset{H_3C}{\overset{H_3C}{>}}\!\!C\!\!\overset{OH}{\underset{O_3S}{<}}\!\!-\!\!SO_3\!\!\overset{HO}{\underset{CH_3}{>}}\!\!C\!\!\overset{CH_3}{\underset{CH_3}{<}}$$
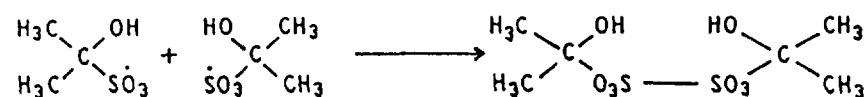
Scheme 1.

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