Effect of Electrolyte on the Emulsifier-Free Emulsion Polymerization of Vinyl Acetate

A. B. MOUSTAFA,[1] A. A. ABDEL-HAKIM,[1] S. M. SAYYAH,[2] G. A. MOHAMED[1]

[1] Department of Polymers and Pigments, National Research Center, Dokki, Cairo, Egypt

[2] Chemistry Department, Faculty of Science, Beni Suef Branch, Cairo University

ABSTRACT: The emulsifier-free emulsion polymerization of vinyl acetate was carried out in the absence or in the presence of some electrolytes such as sodium chloride, calcium chloride, aluminum chloride, sodium sulphate, and ammonium phosphate at 50°C using potassium persulphate–sodium bisulphite as a redox initiation system. The viscosity average molecular weights of the polymers obtained were also determined. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 711–715, 1997

INTRODUCTION

The polymerization of vinyl acetate has been carried out in the presence of an emulsifier by many investigators.[1–6] We have started to polymerize vinyl acetate without using any emulsifier[7] to study some parameters and to avoid the problem of getting rid of the emulsifier when the polymer is subjected to molecular weights or structure determination and also to avoid any probable interaction that could take place between the monomer and the surfactant or between the surfactant and the initiator; this interaction may affect both the rate of polymerization and the average molecular weights of the polymers obtained. In this article, we explore the effect of type and concentration of some electrolytes on the emulsifier-free emulsion polymerization of vinyl acetate.

EXPERIMENTAL

Materials

Vinyl acetate monomer stabilized by 14 ppm hydroquinone provided by BDH was redistilled before use and stored at 20°C. Potassium persulphate and sodium bisulphite were recrystallized from water by methanol; the final crystals were vacuum dried. The electrolytes NaCl, $CaCl_2$, $AlCl_3$, Na_2SO_4, and $(NH_4)_3PO_4$ were obtained from El-Nile Mining Company. The water used was purified by distillation.

Polymerization of Vinyl Acetate

The 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 50°C in the absence or in the presence of different concentrations of sodium chloride, calcium chloride, aluminum chloride, ammonium phosphate, and sodium sulphate in an autmatically controlled water bath. All experiments were run with mechanical stirring at 500 rpm. This speed is in the range at which 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 on a watch glass, the reaction was stopped using 7 ppm hydroqui-

Table I   Effect of Electrolytes on the Polymerization of Vinyl Acetate

Number of Experiments	Electrolyte	Concentration (%)	Conversion (%)	Initial Rate ($\times 10^4$ g mol/L.S.)	$\bar{M}v \times 10^{-8}$
1	—	—	81.6	2.7600	2.1410
2		0.1	65.0	1.3150	3.7282
3	NaCl	0.3	50.0	1.0465	4.0738
4		0.5	40.6	0.7105	4.3260
5		0.1	65.0	2.2010	2.7621
6	$CaCl_2$	0.3	50.0	0.8740	3.5125
7		0.5	37.3	0.6750	3.9468
8		0.1	54.1	1.7610	4.0090
9	$ALCl_3$	0.3	42.2	1.4907	5.3420
10		0.5	28.5	1.2914	6.6390
11		0.1	65.0	0.8220	2.9982
12	Na_2SO_4	0.3	47.5	0.7420	3.7282
13		0.5	35.1	0.6220	4.4246
14		0.1	97.5	2.5370	1.3110
15	$(NH_4)_3PO_4$	0.3	93.0	2.4220	2.1068
16		0.5	87.6	2.2940	2.1902

Materials: 100 ml vinyl acetate (1.162 g mol/L) redistilled in water; $K_2S_2O_8$ (0.014 g mol/L) and $NaHSO_3$ (0.076 g mol/L) redox system at 50°C.

none and the content of the watch glass was evaporated at room temperature and then dried to constant weight at 40°C in a vacuum oven. Since sampling time is known, the percent conversion of the total monomer can be easily determined. The purification and precipitation of the polymer were made by the method described by Grassie.[8]

Determination of the Intrinsic Viscosity

The intrinsic viscosity [η] for each polymer was determined by the usual method of extrapolation. The viscosity average molecular weights ($\bar{M}v$) for the respective polymers were calculated from the corresponding intrinsic viscosity values (η] by using Nakajima's equation:[9]

$$[\eta] = 48 \times 10^{-6} \, (\bar{M}_v)^{0.8}$$

The viscosity measurements were carried out in acetone at 25°C.

RESULTS AND DISCUSSION

Aqueous polymerization of vinyl acetate was carried out in the absence or in the presence of different types and concentrations of electrolytes (NaCl, $CaCl_2$, and $AlCl_3$). The conditions and the data obtained are given in Table I.

From Table I, it is observed that, using different percentage of NaCl (0.1, 0.3, and 0.5%) as electrolyte affected both the rate of polymerization and molecular weight of the polymer. It was found that the initial rate of polymerization decreased from 2.7 to 0.7×10^{-4} g mol/L.S. and that the conversion decreased from 81.6 to 40.6%, but the molecular weight increased from 2.1 to 4.3 $\times 10^8$ g/mol. The results are represented in Figure 1. From the figure it is clear that the rate of polymerization increased slowly with time and
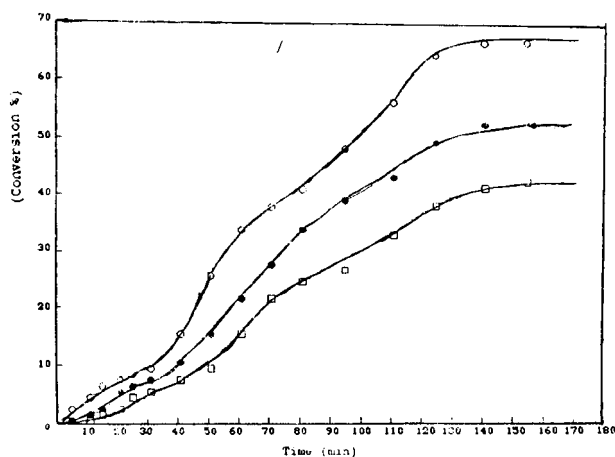

Figure 1 Effect of NaCl percentage on the rate of polymerization of vinyl acetate; (○) 0.1% NaCl; (●) 0.3% NaCl; (□) 0.5% NaCl.
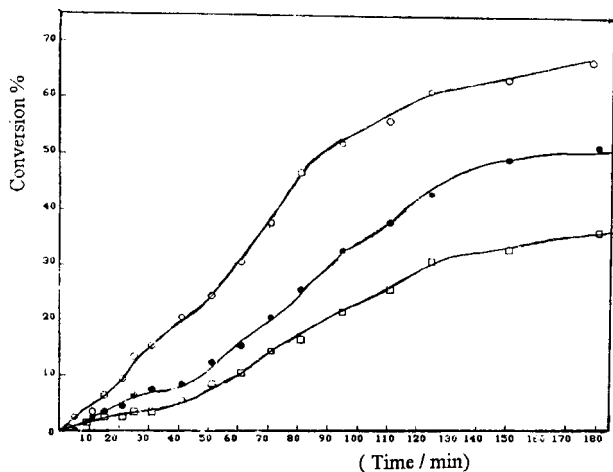
Figure 2 Effect of $CaCl_2$ percentage on the rate of polymerization of vinyl acetate; ($\bigcirc$) 0.1% $CaCl_2$; ($\bullet$) 0.3% $CaCl_2$; ($\square$) 0.5% $CaCl_2$.

Figure 3 Effect of $AlCl_3$ percentage on the rate of polymerization of vinyl acetate; ($\bigcirc$) 0.1% $AlCl_3$; ($\bullet$) 0.3% $AlCl_3$; ($\square$) 0.5% $AlCl_3$.

that the effect of increasing the concentration is small at first but is more obvious at higher conversion percentage. Also, the effect of $CaCl_2$ and $AlCl_3$ as di- and trivalent electrolyte (Ca^{2+}, Al^{3+}) on the polymerization processes of vinyl acetate monomer was determined under the same conditions given in Table I, using different percentages of $CaCl_2$ (0.1, 0.3, 0.5%). The results are presented in Figure 2. From the figure it can be seen that the rate of polymerization decreased from 2.7 $\times$ 10^{-4} to 0.6 $\times$ 10^{-4} g mol/L.S. and that the conversion decreased from 81.6 to 37.3%. Using different percentages of $AlCl_3$ (0.1, 0.3, 0.5%), the polymerization of vinyl acetate was carried out, and the rate of polymerization was determined and found to decrease from 2.7 $\times$ 10^{-4} to 1.2 $\times$ 10^{-4} g mol/L.S. and the conversion to decrease from 81 to 28%, but the molecular weight increased from 2.1 $\times$ 10^8 to 6.6 $\times$ 10^8 g/mol. The results are presented in Figure 3.

The plots of the log initial rate of the polymerization for the three cationic electrolytes used ($NaCl$, $CaCl_2$, $AlCl_3$) against electrolyte concentration are shown in Figure 4. From the figure it is obvious that the same tendency in the rate of the polymerization was obtained using different types of electrolytes, but at different values. The conversion percentages and rates of polymerization decreased with increasing electrolyte concentrations.

For studying the effect of anionic radicals of the electrolytes, the polymerization of vinyl acetate monomer was carried out under the same condition given in Table I in the presence of Na_2SO_4 as
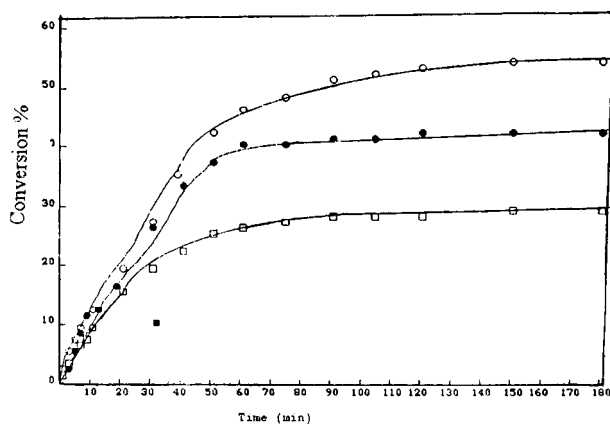
divalent anionic radical and $(NH_4)_3PO_4$ as trivalent anionic radical, taking into consideration that $NaCl$ represents a monovalent cationic and anionic radical electrolyte. Using different percentages of Na_2SO_4 as electrolyte, it can be observed that the rate of polymerization decreased from 2.7 $\times$ 10^{-4} to 0.6 $\times$ 10^{-4} g mol/L.S. but that the molecular weight increased from 2.1 $\times$ 10^8 to 4 $\times$ 10^8 g m/mol. The conversion time curves are presented in Figure 5. Using different percentages of $(NH_4)_3PO_4$ as trivalent anionic electrolyte also revealed a decrease in the initial rate of polymerization. This rate decreased from 2.7 $\times$ 10^{-4} to 2.5 $\times$ 10^{-4} g mol/L.S., and the conversion increased from 81 to 97%, as shown in the conversion-time curves presented in Figure 6.

Plots of the log initial rate of the polymerization for the two anionic electrolytes used [Na_2SO_4, $(NH_4)_3PO_4$] against electrolyte concentrations
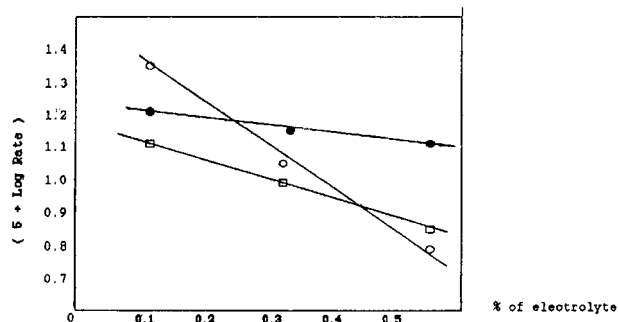

Figure 4 Logarithmic plot of initial rate of polymerization versus the percentage of electrolyte; ($\bigcirc$) 0.1%, 0.3%, 0.5% $CaCl_2$; ($\bullet$) 0.1%, 0.3%, 0.5% $AlCl_3$; ($\square$) 0.1%, 0.3%, 0.5% $NaCl$.
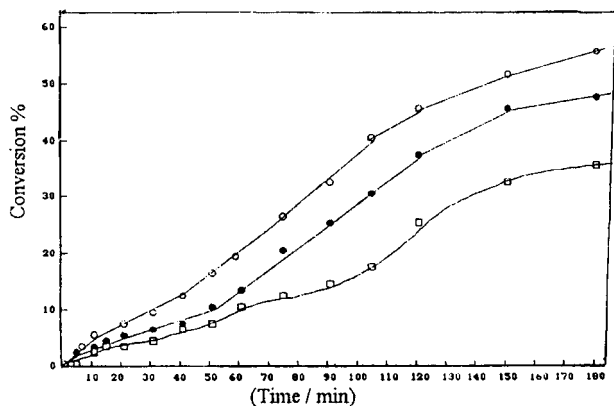
Figure 5 Effect of Na_2SO_4 percentage on the rate of polymerization of vinyl acetate; ($\bigcirc$) 0.1% Na_2SO_4 ($\bullet$) 0.3% Na_2SO_4; ($\square$) 0.5% Na_2SO_4.

Figure 7 Logarithmic plot of initial rate of polymerization versus the percentage of electrolyte; ($\bigcirc$) 0.1%, 0.3%, 0.5% (Na_2SO_4); ($\bullet$) 0.1%, 0.3%, 0.5% ($(NH_4)_3PO_4$; ($\square$) 0.1%, 0.3%, 0.5% (NaCl).

are shown in Figure 7. From the figure it can be found that the initial rate of polymerization decreased with increasing electrolyte concentration and that the relationship is linear.

From the previous results, it is clear that the presence of electrolyte in the polymerization reaction conditions for either cationic electrolyte or anionic radical electrolyte in the polymerization of vinyl acetate monomer caused a decrease in the conversion percentage and initial rate of polymerization but increased the average molecular
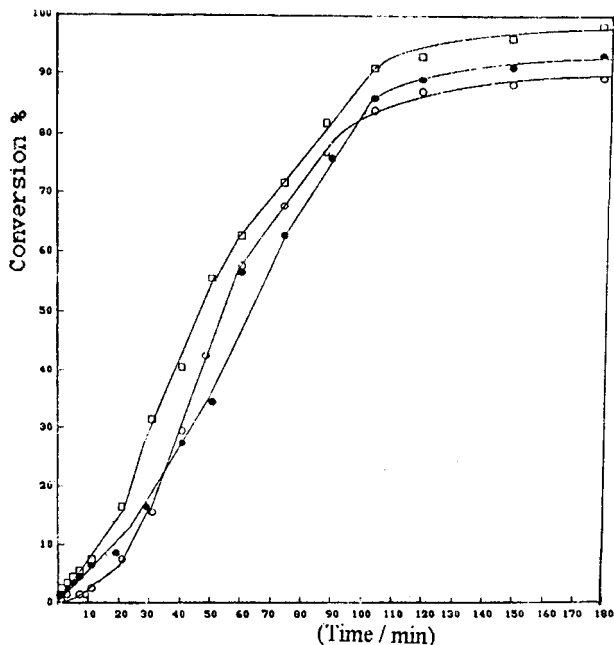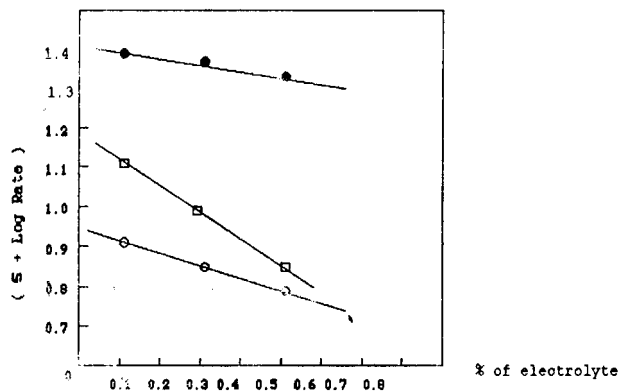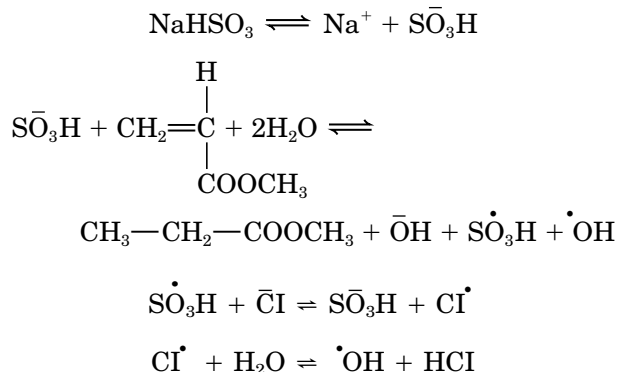

Figure 6 Effect of $(NH_4)_3PO_4$ percentage on the rate of polymerization of vinyl acetate; ($\square$) 0.1% $(NH_4)_3PO_4$; ($\bullet$) 0.3% $(NH_4)_3PO_4$; ($\bigcirc$) 0.5% $(NH_4)_3PO_4$.

weights obtained. This can be explained in the following way: with respect to the sodium chloride, calcium chloride, and aluminium chloride, the liberated chlorine ion reacts with the bisulfite radicals, giving bisulfite ions and chlorine radicals. The chlorine radicals react with water to result in hydroxyl radicals, which are responsible for the hydroxyl groups that are found in the polymers obtained.[10]

$$NaHSO_3 \rightleftharpoons Na^+ + S\bar{O}_3H$$

$$S\bar{O}_3H + CH_2{=}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}} + 2H_2O \rightleftharpoons$$

$$CH_3{-}CH_2{-}COOCH_3 + \bar{O}H + S\dot{O}_3H + {}^{\bullet}OH$$

$$S\dot{O}_3H + \bar{C}I \rightleftharpoons S\bar{O}_3H + CI^{\bullet}$$

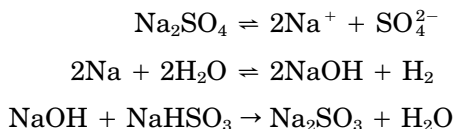$$CI^{\bullet} + H_2O \rightleftharpoons {}^{\bullet}OH + HCI$$

The hydroxyl radical's life time, is less than the bisulphite radical's life time, and thus the total number of radicals is less, resulting in the higher average molecular weights obtained and decreasing the initial rate of polymerization.

In the case of ammonium phosphate, some of the bisulphite radicals are consumed by the ammonium ion formed, and this consumption results in higher mean average molecular weights.

$$(NH_4)_3PO_4 \rightleftharpoons PO_4^{3-} + 3NH_4^+$$

$$NH_4^+ + HS\bar{O}_3 \rightarrow NH_4HSO_3$$
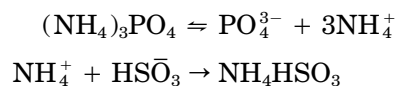
The effect of sodium sulfate can be explained in the following way:

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$

$$2Na + 2H_2O \rightleftharpoons 2NaOH + H_2$$

$$NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O$$

Some of the sodium bisulfite initiator is consumed, resulting in less bisulfite ions and finally less bisulfite radicals and leading to a lower rate of reaction and higher mean average molecular weight.

CONCLUSION

The emulsifer-free emulsion polymerization of vinyl acetate using the redox initiation system of potassium persulfate–sodium bisulfite was studied in the absence or in the presence of some electrolytes. The electrolytes used resulted in a decrease in the initial rate of polymerization and an increase in the viscosity average molecular weights obtained.

REFERENCES

1. A. S. Badran, A. A. Yehya, A. B. Moustafa, and S. M. M. Shendy, *Acta Polym. J.,* **41,** 187 (1990).
2. A. S. Badran, A. A. Yeha, S. M. M. Shendy, and A. B. Moustafa, *Acta Polym. J.,* **42,** 394 (1991).
3. A. S. Badran and S. M. M. Shendy, *Acta Polym. J.,* **42,** 1 (1991).
4. A. S. Badran, A. M. Ramadan, A. B. Moustafa, and K. A. Shaffie, *J. Appl. Polym. Sci.,* **49,** 187 (1993).
5. R. M. Mohsen, A. M. Ramadan, K. A. Shaffi, and A. S. Badran, *Pigment and Resin Technology,* July/August (1993).
6. M. A. Abdel-Ghaffar, A. S. Badran, A. M. Ramadan, and K. A. Shaffi, *J. Elastomer and Plastics,* **27,** 281 (1995).
7. A. B. Moustafa and G. A. Mohamed, *J. Appl. Polym. Sci.,* to appear.
8. Grassie, *Trans. Faraday Soc.,* **48,** 379 (1952).
9. A. Nakajama, *Kobumnshi Kagaku,* **11,** 142 (1954).
10. Premamoy Ghosh, Subhash-Chande, Chadha Asishr Mukher-Jee, and Santir-Palit, *J. Polym. Sci., Part A.,* **2,** 4333 (1969).