

NOTES

The Effect of Agitation on the Conversion of Vinyl Acetate Emulsion Polymerization

INTRODUCTION

The effect of agitation on the conversion in a batch emulsion polymerization has never been the main research parameter in a research program. This is probably due to rather conflicting results obtained by various workers. In the case of acrylonitrile, Dainton and Seaman¹ noted that, for a homogeneous aqueous system, the stirring decreased the steady state and that the total polymerization was generally decreased. Moore and Parts² also found that stirring in a nonstabilized system decreased the reaction rate and they suggested the presence of two reactions: a homogeneous one taking place between molecules of largely dissolved species and an heterogeneous one involving the already formed polymer. Shunmukam et al.³ observed that the shaking and the stirring of the styrene emulsion lowered the polymerization rate and increased the induction period. This was disputed by Schoot et al.⁴ Omi et al.⁵ however, came to the conclusion that the emulsion polymerization of styrene was not affected by stirring, as long as emulsification conditions were the same. Nomura et al.⁶ established the presence of an optimum range of stirring speed for the emulsion polymerization of styrene. This optimum was also observed by Rollin et al.⁷ for styrene, but, instead of working in a batch reactor, they used a tubular reactor; they also expressed this optimum in terms of Reynolds number of the unreacted monomer and found that the optimum occurred in the transition zone.

Evans et al.⁸ studied the emulsion polymerization of vinylidene chloride and noted that polymerization proceeded according to a three-stage mechanism: During the first stage the rate of polymerization decreases with increasing stirring speed, at the second stage the rate of polymerization increases with increasing stirring speed, and the third stage is independent of stirring speed.

For vinyl acetate Zollars⁹ found that the agitation level had no significant effect on the reaction rate contradicting some earlier studies by Stannett et al.¹⁰ In some recent work, conducted with a tubular reactor Dalpe¹¹ found that an optimum in conversion existed also for vinyl acetate, a somewhat similar phenomena described by other workers for styrene.⁷

In this note we would like to discuss the results obtained for batch emulsion polymerization of vinyl acetate. The variable studied were agitation and level of surfactant. The emulsion obtained were characterized for the conversion and molecular weight.

EXPERIMENTAL

Materials

The vinyl acetate was distilled under vacuum at 45°C in order to remove the inhibitor. Sodium lauryl sulfate (SLS) the surfactant, and potassium persulfate, the initiator, were used as provided by the suppliers. Distilled and demineralized water used throughout except for one instance discussed later on. The polymerizations reactions were carried out in a 1000 mL glass reactor at 60°C according to the formulation scheme given in Table I.

The stirring assembly was made up of a glass rod with a Teflon paddle of 6 cm in length. The water was first added to the reactor and then the surfactant. The agitation is maintained at 170 rpm and the nitrogen is bubbled through the mixture for 30 min, after which the purified vinyl acetate is added to the reactor. The nitrogen bubbling operation is maintained for 20 min; the temperature of the preemulsion is then raised to the desired polymerization conditions. When the required temperature is reached the initiator solution is added to the reactor: This is time zero for the polymerization. A nitrogen blanket is maintained throughout the polymerization and the reaction is sampled every 5 min for the first 30 min and then every 10 min. At time zero, the

TABLE I
Emulsion Formulation

Constant parameters	
Demineralized water (total charge)	450 mL
Vinyl Acetate (monomer)	180 mL
Potassium persulfate—Initiator ^a K ₂ S ₂ O ₈	0.11 g
Variable parameter	
Sodium lauryl sulfate-surfactant ^b	1.7 g
	3.3 g
	5.0 g
	10.0 g
Volume ratio monomer/water	0.38

^aThe 0.11 g of K₂S₂O₈ was actually dissolved in 25 mL of water.

^bThis corresponded respectively to 1.4, 2.7, 4.1, and 8.1 times the CMC, being taken as 2.6 g of SLS/L.¹²

agitator is set at the desired agitation level. Three levels of agitation were studied 75, 150, and 220 rpm. Details of some of these steps may be found elsewhere.¹³

Selected samples were analyzed for their molecular weight and distribution of molecular weight by a Waters 150-C GPC using THF as solvent.

RESULTS AND DISCUSSION

Effect of Agitation

Some preliminary experiments were run at 60°C using undistilled monomer and with an agitation of 150 rpm; this gave a maximum conversion of 58% in spite of the fact that the level of initiator was 1.05 g/L. Other experiments were run at 70°C and the agitation was increased to 250 rpm; this led to no induction period and a nearly vertical conversion curve. The maximum conversion attained in this case was 60%.

These results showed that the reaction conditions were poor, and both the temperature and the agitation were too high so that the reaction was out of control. Due to the closeness of the monomer boiling point and the reaction temperature a fair amount of monomer was lost through the nitrogen system.

The initiation of the polymerization is increased due to the high level of initiator and of agitation and also due to the higher temperature the polymerization was conducted. Taking these

TABLE II
Operating Conditions vs. Reaction Rate

Experiment no.	Operating conditions		Maximum conversion (%)	Reaction rate (% min ⁻¹)	Plateau (min)
	[SLS]	Agitation (rpm)			
B-1		75	67	1.5	80 +
B-2	2.7 ×	150	98.5	3.0	50
B-3	[CMC]	220	95	3.7	50
B-4		75	55.5	0.9	80 +
B-5	1.4 ×	150	89	2.7	70
B-6	[CMC]	220	93	2.5	55
B-7	8.1 ×	75	98.5	7.4	40
B-8	[CMC]				
	4.0 ×	150	70	3.1	60
	[CMC]				

^a[CMC] = 2.6 g/L water.

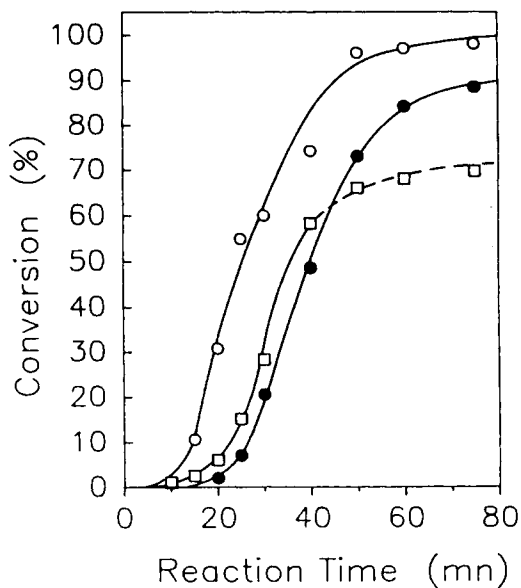


Fig. 1. Conversion vs. time—agitation 150 rpm: (●) [SLS] = $1.4 \times$ [CMC]; (○) [SLS] = $2.7 \times$ [CMC]; (□) [SLS] = $4 \times$ [CMC].

factors into account, the other experiments were run in such a way that the effect on the polymerization by these parameters could be studied. They are given in the material part.

In Table II are given the results of the batch polymerization. It summarizes the main points of the conversion vs. reaction time (see Figs. 1 and 2). At a low level of agitation—75 rpm—where the phase separation is quite evident, the maximum conversion is low except when the concentration of surfactant is relatively high: $8.1 \times$ [CMC]. At that concentration the conversion reaches

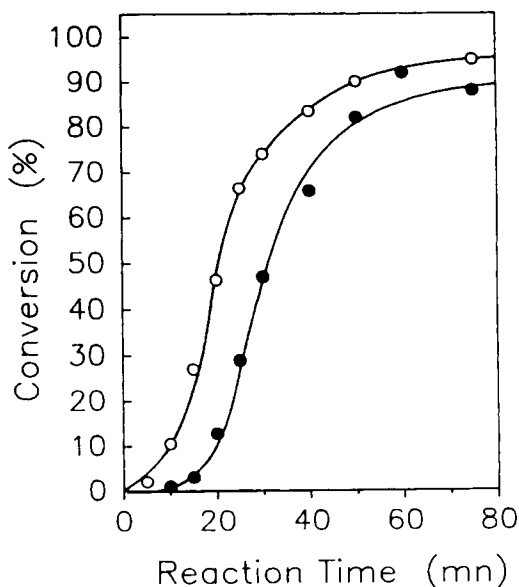


Fig. 2. Conversion vs. time—agitation 220 rpm: (●) [SLS] = $1.4 \times$ [CMC]; (○) [SLS] = $2.7 \times$ [CMC].

95%; also to be noted is the high conversion rate. The relative dispersity about the conversion curve indicates the poor control of the polymerization.

The phase separation renders more difficult the access of the micelle by the monomer as well as for the homogeneous particle nucleation formation. The lower level of surfactant leads to a lower rate of polymerization as well as a lower conversion. This phase separation makes much less vinyl acetate available in the aqueous phase. The polymerization would be controlled by the rate of diffusion of the monomer in the water as well as by the level of surfactant.

At a higher agitation rates of 150 and 220 rpm, which are closer to normal operating conditions, relatively high conversions are reached. One notes the similarity between the experiments of Figures 1 and 2. For the two levels of agitation, the formulation using 2.7 times the CMC gave higher conversions. This confirms results of other workers,¹⁴ who noted an increase in reaction rate and conversion with an increase in surfactant level. For a more normal agitation level there is an increase in the reaction rate with an increase in the surfactant. This might be caused by the greater amount of micelles present. The contribution of these micelles are, however, less important as compared to the styrene case.

One remembers that, for a system like styrene when a droplet is sheared broken by agitation, the surface to be stabilized is increased and thus decreases by the same amount the surfactant

TABLE III
Experimental Conditions and Polydispersity

Experimental conditions	Sample no.	Time (min)	Conversion (%)	M_n ($\times 10^5$)	M_w ($\times 10^6$)	PD
B-1 [SLS] = $2.7 \times$ (CMC) ^a V = 75 RPM	3	15	4.4	2.66	1.03	3.88
	4	20	12.4	5.15	1.54	2.98
	5	25	20.4	4.43	1.64	3.71
	7	40	41.5	2.45	1.88	7.70
	9	60	61.1	2.78	1.82	6.54
B-2 V = 150 RPM [SLS] = $2.7 \times$ (CMC)	4	20	30.7	8.22	1.83	2.22
	5	25	54.9	5.00	1.96	3.92
	7	40	74.2	11.90	2.66	2.23
B-3 [SLS] = $2.7 \times$ (CMC) V = 220 RPM	2	10	10.5	2.70	1.18	4.37
	4	20	46.3	3.17	1.75	5.52
	5	25	66.4	6.14	2.25	3.66
	7	40	83.4	5.77	2.69	4.66
B-4 [SLS] = $1.4 \times$ (CMC) V = 75 RPM	10	75	94.9	4.12	2.73	6.63
	2	10	3.8	2.55	1.34	5.27
	3	15	11.2	2.67	0.99	3.72
	6	30	24.6	2.72	1.33	4.89
B-5 [SLS] = $1.4 \times$ (CMC) V = 150 RPM	7	40	32.4	1.65	1.13	6.89
	10	75	55.7	2.02	1.50	7.44
	6	30	20.5	5.82	1.60	2.74
	7	40	48.6	7.00	2.85	1.68
B-6 [SLS] = $1.4 \times$ (CMC) V = 220 RPM	9	60	84.2	10.30	3.86	1.90
	4	20	12.7	3.11	1.30	4.20
	5	25	28.9	2.67	1.64	6.16
B-7 [SLS] = $8.1 \times$ (CMC) V-75 RPM	7	40	65.8	3.23	2.43	7.52
	3	15	14.8	4.91	1.37	2.79
	4	20	37.9	4.60	1.77	3.85
	6	30	77.0	6.12	2.28	3.72
B-8 [SLS] = $4.0 \times$ (CMC) V = 150 RPM	7	40	98.5	3.85	2.31	5.99
	5	25	15.1	3.57	1.45	4.07
	6	30	28.3	4.37	1.67	3.81
	7	40	58.3	4.59	2.11	4.60
	10	75	69.7	4.25	2.67	6.29

^a (CMC) = 2.6 g/L water (52).

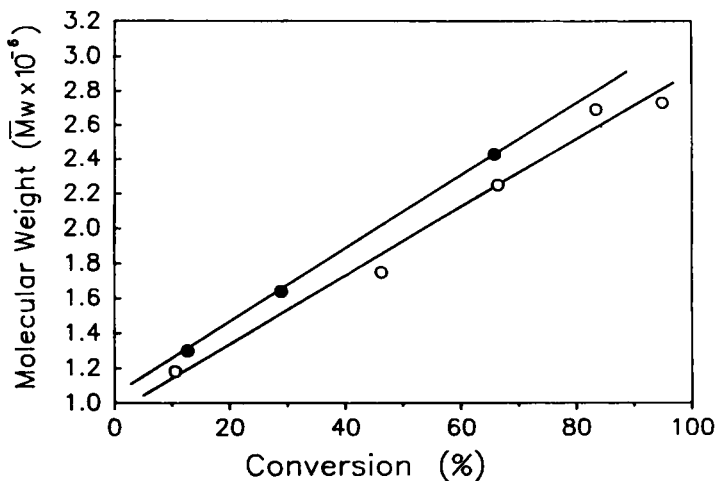


Fig. 3. Molecular weight ($M_w \times 10^6$) vs. conversion—agitation 220 rpm: (●) $[SLS] = 1.4 \times [CMC]$; (○) $[SLS] = 2.7 \times [CMC]$.

available for micelle formation. This leads to lowering of the number of polymer particle and eventually to a lower polymerization rate.¹⁵ In the case of vinyl acetate as one obtains a rather constant rate of polymerization (Figs. 1 and 2), it means that the agitations has little influence in this case and as a consequence the role of the surfactant is also decreased. This is to say that the initiation mechanism by homogeneous nucleation must play an important role.

One can also add here that the graphs obtained here corresponded well to the ones obtained by other workers.^{9,16,17} After the first 15% of conversion, one observes a generally constant reaction rate up to about 80–85%.

Effect of Agitation on the Molecular Weight

The results are given in Table III and Figure 3. At first glance they might seem to be half hazard. If one examines them more closely, one notice that for a rotating speed of 150–220 rpm, the \bar{M}_w runs between 1 and 3.6 million, values which are much higher than the ones obtained at an agitation of 75 rpm. This is due to the lower diffusion associated with the lower agitation.

At 150 rpm as well as for 220 rpm, one obtains a higher molecular weight while using a lower level of surfactant. This may be explained by the smaller number of particles formed due to the lower concentration of surfactant leading to a higher degree of polymerization.

At 75 rpm, it is the inverse phenomena occurring, i.e., polymers of high molecular weight are obtained at high concentration of surfactant. At this agitation level where one assumes a good contribution from the homogeneous nucleation, it is normal to think at high concentration of surfactant one would obtain high molecular weights as the oligomers generated in the aqueous phase would be more easily stabilized and the chances of termination would be decreased.

The polydispersity of the polymers obtained varied between 1.6 and 7.5 (see Table III); it increases with increasing conversion. This is in agreement with other workers¹³ using basically the same formulation. These results are also in good agreement with the results of another group of workers,¹⁸ although not using the same operating conditions.

Like these workers,^{13,14,18} the molecular weight distribution was quite large and followed the normal law of logarithmic distribution. These authors tend to minimize the effect of the surfactant on the molecular weight. This study, however, shows that it has a definite effect.

CONCLUSION

The concentration of the surfactant SLS has only little influence on the polymerization rate and on the maximum conversion if one operates at abnormal agitation conditions and if the

concentration of the surfactant is not exaggerated (i.e., above eight times the CMC); it will permit a stable emulsion.

The molecular weight is affected by the level of surfactant used as well as the reaction time.

References

1. F. S. Dainton and P. H. Seaman, *J. Polym. Sci.*, **39**, 279 (1959).
2. D. E. Moore and A. G. Parts, *Makromol. Chem.*, **37**, 108 (1960).
3. S. R. Shunmukham, V. L. Hallenbeck, and R. L. Guile, *J. Polym. Sci.*, **6**, 691 (1951).
4. C. J. Schoot, J. Baker, and K. H. Klassens, *J. Polym. Sci.*, **7**, 657 (1951).
5. S. Omi, Y. Shiriaishi, H. Sato, and H. Kubota, *J. Chem. Eng. Jpn.*, **2**, 64 (1969).
6. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **16**, 835 (1972).
7. A. L. Rollin, I. Patterson, J. Archambault, and P. Bataille, *Polymerization Reactors and Processes Symposium*, J. N. Henderson and T. C. Bouton, Eds., ACS Symposium Series 104, Am. Chem. Soc. Washington, DC, 1979, p. 113.
8. C. P. Evans, P. M. Hay, L. Marker, R. W. Murray, and O. J. Sweeting, *J. Appl. Polym. Sci.*, **13**, 39 (1961).
9. R. L. Zollars, *J. Appl. Polym. Sci.*, **24**, 1353 (1979).
10. V. Stannett, A. Klein, and M. Litt, *Br. Polym. J.*, **1**, 139 (1975).
11. J. F. Dalpé, M. Sc. thesis, Ecole Polytechnique de Montréal, 1988.
12. *Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut, Eds. Wiley-Interscience, New York, 1974, Vol. II, p. 485.
13. P. Bataille, H. Bourassa, and A. Payette, *J. Coat. Technol.*, **59**, (753), 71 (1987).
14. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, *Emulsion Polymerization*, I. Piirma Series No. 24, 1976, p. 102.
15. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
16. R. Patsiga, M. Litt, and V. Stannett, *J. Phys. Chem.*, **64**, 801 (1960).
17. M. Litt, R. Patsiga, and V. Stannett, *J. Polym. Sci. A - 1*, **8**, 3607 (1970).
18. N. Friis and A. E. Hamielec, *J. Appl. Polym. Sci.*, **19**, 97 (1975).

P. BATAILLE
J.-F. DALPÉ
F. DUBUC
L. LAMOUREUX

Chemical Engineering Department
Ecole Polytechnique De Montréal
P.O. Box 6079, Station "A"
Montreal, Quebec H3C 3A7, Canada

Received June 19, 1989

Accepted July 10, 1989