

NOTES

Measurements of Propagation Rate Constant from Emulsion Polymerization

INTRODUCTION

Any polymerization reaction can be used to determine the reaction if the governing kinetics are well understood. The use of emulsion polymerization for determination of the propagation rate constant (k_p) is specially attractive because it can yield the absolute value of k_p not coupled with other kinetic parameters, as in bulk polymerization. Using phase II of emulsion polymerization for the measurement of k_p has been tried by various investigators such as Smith,¹ and Morton, Sataliello, and Landfield.²

However, while k_p is not coupled with other rate constants, it is coupled with other parameters such as monomer concentration in the latex particle and latex particle size. This seriously limits the advantages of employing emulsion polymerization as the additional measurements required are time consuming and can limit accuracy and repeatability. These inconveniences can largely be eliminated by using controlled seed polymerization, whose kinetics are relevant to phase III of emulsion polymerization and is the subject of this note.

THEORY

Kinetics of one-phase seed emulsion polymerization systems are completely characterized by two dimensionless parameters, α and m , defined in eqs. (1) and (2), respectively.³

$$\alpha \equiv V_p / (k_t \tau) \quad (1)$$

$$m \equiv k_0 S / k_t \quad (2)$$

So-called "ideal behavior" is observed when α is sufficiently small and m is zero, and the polymerization rate can be expressed by eq. (3),

$$-\frac{d}{dt} ([M] V_p) = \frac{k_p [M]}{2 N_{AV}} \quad (3)$$

where the factor of 1/2 indicates that there is an average of one-half a radical per particle. Equation (3) gives about 10% error when $\alpha = 0.1$ and $m = 0$, so $\alpha < 0.1$ may be considered the range in which eq. (3) can be used. All variables in eq. (3) can be expressed in terms of conversion, x , as shown in the Nomenclature, and substitution gives a differential eq. (4) in terms of x

$$\frac{V_{p\infty} dx}{1 - \epsilon dt} = \frac{k_p}{2 N_{AV}} \frac{1 - x}{1 - \epsilon x} \quad (4)$$

Equation (4) can be integrated with the initial condition $x = 0$ at $t = 0$, to give eq. (5)

$$V_{p\infty} \left(\frac{\epsilon}{1 - \epsilon} x + \ln \frac{1}{1 - x} \right) = \frac{k_p}{2 N_{AV}} t \quad (5)$$

With eq. (5), a plot of

$$V_{p\infty} \left(\frac{\epsilon}{1 - \epsilon} x + \ln \frac{1}{1 - x} \right)$$

versus time should give a straight line with slope $k_p / (2 N_{AV})$. Moreover, various runs of polymerization with different seed diameter, initiator level, or other factors, should all lie on the same line. The following considerations are necessary to make sure that the data used fulfill the conditions for using eq. (4).

(1) Most systems show initial inhibition-retardation period, and that period should be deleted from consideration. This may be done by visual inspection of the plot, but it is advantageous to exclude from consideration data before conversion reaches 10%.

(2) Particle-size measurements before and after polymerization should show no new particle generation or coagulation. This requires use of enough stabilizer to give at least 30 or 40% surface coverage to the surface area of swelled-latex particles. The initial monomer:polymer ratio should be less than the limit of swelling to prevent the appearance of monomer droplets, which can cause the new particle generation. Much of this information is available from the literature.⁴

(3) Although estimates of α and m values are usually available, running polymerizations with different initiator levels or with different diameter seed latices to compare the slope of the plot can serve as a positive check for the absence of desorption ($m = 0$) and α smaller than 0.1. One cannot obtain the same slope when either of the parameters lie outside the range where eq. (4) is applicable. According to Ugelstad, Mörk, and Aasen,⁵ n remains at the value of half for a range of α values provided that m value is small ($0.1 \sim 0.001$ for $m = 10^{-4}$ in the absence of aqueous phase termination), and the proposed method can still be applied. Due to lack of reliable methods to determine m , this possibility has not been pursued.

(4) High-conversion data should be deleted as the decrease of the termination rate constant by the gel effect can make α value too high. Visual check of deviation from straight line is usually sufficient. Because it was possible to obtain k_p values from methyl methacrylate (MMA), where the gel effect is known to be very serious, most other monomers with lesser gel effect are expected to pose little problems with this method.

EXPERIMENT

Styrene (STY) and MMA were used for polymerization. STY data are taken from the literature,⁶ and MMA data are obtained from current experiments. In Table I, the polymerization recipes are summarized. The polymerization procedures were those of conventional batch emulsion polymerization with stirring and nitrogen bubbling in a reactor immersed in a constant-temperature water bath. Monomers were purified by caustic washing followed by double distillation *in vacuo*. Particle size were measured by turbidity.⁶ The effects of particle-size distributions were not further investigated.

RESULTS AND DISCUSSION

Time conversion data from styrene polymerization at 50°C were plotted in Figure 1 according to eq. (4) with inhibition time correction.

A-1, A-2, and A-3 had the same polymerization recipes and showed good reproducibility.

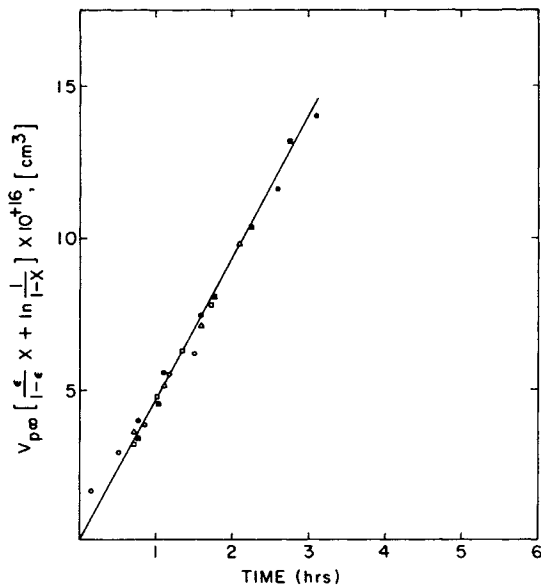


Fig. 1. Styrene polymerizations at 50°C. ●, A-1; Δ, A-2; ■, A-3; ○, B; □, C.

TABLE I
Polymerization Recipes

Monomer	Run No.	Seed diam.	M:p ratio	Initiator conc. ^a	Emulsifier conc. ^b	Polym. temp., °C	% Final solid cont.
Styrene	A-1	1210 Å	2.4	0.20	0.57	50	36.4
	A-2	1210	2.4	0.20	0.57	50	36.4
	A-3	1210	2.4	0.20	0.57	50	36.4
	B	916	1.5	0.21	0.94	50	34.9
	C	1110	2.1	0.26	0.68	50	34.9
MMA	A-1	640	2.7	0.0027	0.09	60	20.0
	A-2	405	2.7	0.245	0.12	60	20.0
	B	520	1.25	0.020	0.33 ^c	50	20.0
	C-1	520	1.25	0.066	0.55 ^c	40	20.0
	C-2	730	1.25	0.007	0.01 ^c	40	20.0

^a Potassium persulfate, wt % of aq. phase.

^b Sodium lauryl sulfate, wt % of aq. phase.

^c +0.3% of Dowfax 2A1, 46% solution.

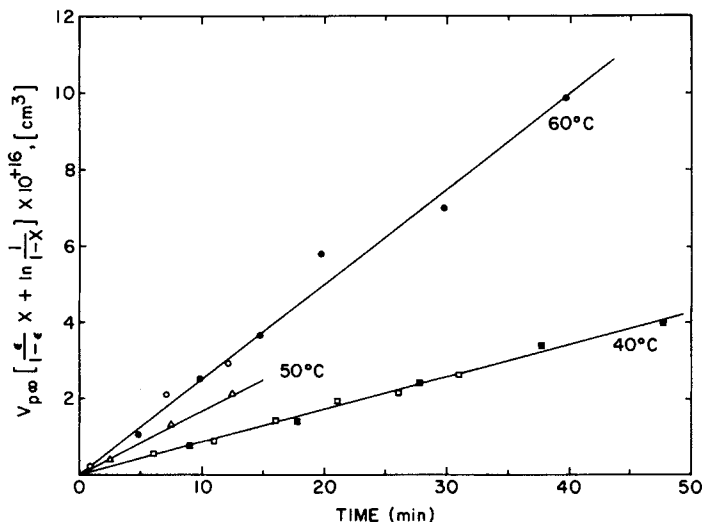


Fig. 2. MMA polymerizations. ●, A-1; ○, A-2; △, B; □, C-1; ■, C-2.

Although there is uncertainty in the values of the initiator decomposition rate constant and termination rate constant, the relative ratio of initial α values are readily calculated as 1:0.22:0.76 for A:B:C.

Because of possible gel effect, the α value may change continuously during the course of the reaction; but, this does not complicate the analysis as high conversion data where the plot deviates from a straight line will be discarded anyway.

The constancy of the slope with these variations in initial α value confirms ideal behavior as expected.

Similar plots for methyl methacrylate at 40, 50, and 60°C are shown in Figure 2.

The initial α ratios were 1:22.6 for A-1:A-2 at 60°C, and 1:0.29 for C-1:C-2 at 40°C. Again same slopes confirm ideal behavior.

The k_p values obtained from the slope of Figures 1 and 2 are shown with some representative literature values in Table II. For styrene, the reported values at 50°C are as follows: [units: (liter/mol, sec)] 123 by Matheson, et al.,⁷ 223 and 206 by Gerrens,⁹ and 156 from this work looks to be very reasonable.

For MMA, the values reported by Matheson et al.,⁷ Shultz, et al.,⁸ and Gerrens⁹ are plotted with this work in Figure 3. Figure 3 also shows the values from this method are compatible with conventional methods.

Linear regression of the literature values shown in Figure 3 gave the best Arrhenius fit of eq. (6).

$$\ln k_p = 16.6 - \frac{3500}{T} \quad (6)$$

The three data points obtained in this work gave a maximum deviation of 5% from eq. (6).

TABLE II
 k_p Values (liter/gmol, sec)

	Temp., °C	This result	Literature
STY	50	156	123 by Matheson ⁷
MMA	60	500	515 by Schultz et al. ⁸
	50	340	270 by Matheson ⁷ ^a
	40	171	195 by Matheson ⁷

^a Also 224 by Gerrens⁹ and 229 by Schultz⁸ at 45°C.

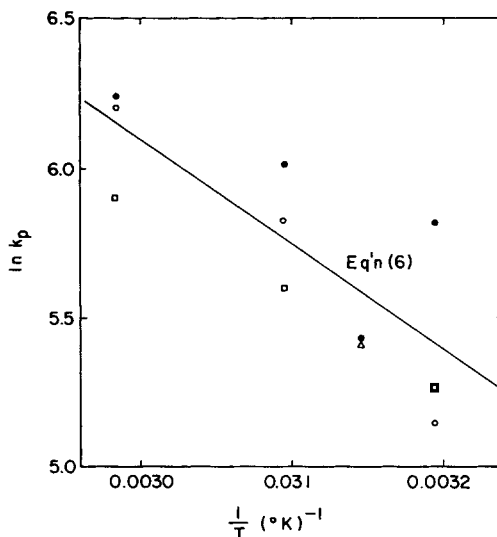


Fig. 3. Comparison with reported values. \circ , this work; \bullet Schulz, et al.⁸; \square , Matheson, et al.⁷; Δ , Gerrens⁹; —, eq. (6).

These results confirm the fact that the presented method yields reliable values for k_p . Compared to Smith's method, it can be easily recognized that this method has the following advantages:

(1) Measurements of monomer concentrations in the latex particle is not necessary, which required considerable amount of time and effort and also is an additional source of error in Smith's method.

(2) Particle-size measurements are mostly waived as one seed latex of known particle size can be used to generate a series of different α values where the resulting latex particle size (v_∞) can be predicted accurately from the knowledge of seed latex particle size. It should be noted that uniform particle-size latices are commercially available and can possibly eliminate any errors coming from particle-size distribution which is inevitable in Smith's method. Uniform latices have not been tested in this work.

(3) Effects of adsorbed soap layers are avoided. It should be noted that in Smith's method, the surface coverage defined as the ratio of adsorbed surface area of soap to the surface area of latex particles changes continuously from 1 to a final value of about 0.3 ~ 0.4.

In this work, the surface coverage is kept constant at 0.4 and unpredictable complication by adsorbed soap layers is avoided as enough nonadsorbed surface is available during the whole course of reaction.

CONCLUDING REMARKS

As the proposed method gives very reasonable values from only time conversion data, without using special instruments or techniques, the author believes it can be easily performed in any laboratory and should find many practices.

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Nomenclature

- k_0 radical desorption constant (cm/mol sec)
- k_p propagation rate constant (1/mol sec)
- k_t termination rate constant (1/mol sec) or (cm³/mol sec)
- [M] concentration of monomer (mol/liter)

$$[M]_0 \frac{1-x}{1-\epsilon x} = [M]$$

where $[M]_0$ is concentration of monomer at $x = 0$

m dimensionless parameter defined by eq. (2)

N_{AV} Avogadro's number

S surface area of a latex particle (cm^2)

t time after start of reaction (min) or (sec)

V_p volume of a latex particle [cm^3] $\equiv \frac{V_{p\infty}}{1-\epsilon}(1-\epsilon x)$

$V_{p\infty}$ volume of latex particle at complete conversion [cm^3]

x fractional conversion

α dimensionless parameter defined by eq. (1)

ϵ volume shrinkage factor

$$\epsilon \equiv \frac{V_{p0} - V_{p\infty}}{V_{p0}}$$

where V_{p0} is volume of a latex particle at zero conversion (cm^3)

τ time interval between initiator radical into a latex particle (sec)

References

1. W. V. Smith, (a) *J. Am. Chem. Soc.*, **70**, 3695 (1948); (b) **71**, 4077 (1949).
2. M. Morton, P. P. Salatiello, and H. Landfield, (a) *J. Polym. Sci.*, **8**, 111 (1952); (b) **8**, 215 (1952), (c) **8**, 279 (1952).
3. W. H. Stockmayer, *J. Polym. Sci.*, **24**, 314 (1957).
4. J. L. Gardon, *J. Polym. Sci. Part A1*, **6**, 643, (1970).
5. J. Ugelstad, P. C. Mörk, and J. O. Aasen, *J. Polym. Sci., Part A1*, **5**, 2281 (1967).
6. D. R. James, M.S. thesis, University of Idaho, Moscow, Idaho 1976.
7. M. S. Matheson, et al., *J. Am. Chem. Soc.*, **71**, 497, (1949).
8. V. Schultz et al., (a) *Z. Phys. Chem. (Frankfurt am Main)*, **27**, 1 (1960); (b) **67**, 741, (1963).
9. H. Gerrens, *Ber. Bunsenges. Phys. Chem.*, **67**, 741, (1963).

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