

Vinyl Chloride–Vinyl Acetate Kinetic Modeling. I. Determination of Radical Efficiency Factor

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Synopsis

Using dead end polymerization procedures, the copolymerization of vinylchloride–vinyl acetate was studied in laboratory scale reactors. Predictive kinetic models based on modified Hamielec equations were developed which were valid up to the limit of the experiments, 35% conversion. The efficiency factor (f) for the *t*-butylperneodecanoate initiator was determined for a range of initiator concentrations in a comonomer mixture.

INTRODUCTION

The polymerization of vinyl chloride can be modelled accurately by kinetic equations developed by Hamielec and co-workers.^{1,2} These kinetic equations have been important in developing efficient commercial manufacturing processes for polymerization of vinyl chloride.³ The copolymers of vinyl chloride, in particular the vinyl acetate copolymers (with vinyl acetate content of 5–20%), are important items of commerce.⁴ The development of predictive kinetic equations for the polymerization of vinyl chloride–vinyl acetate copolymers represents a significantly greater challenge in comparison to the vinyl chloride homopolymer in that the comonomer mixture will partition between the gas, liquid (water and comonomer), and solid phases in different ratios. Recent work⁵ has indicated that, for vinyl chloride–vinyl acetate copolymerization, the anticipated comonomer ratio was not observed at the site of polymerization due to this partitioning effect.

Our efforts to perfect an accurate vinyl chloride–vinyl acetate kinetic model have required that we develop procedures to terminate and sample a copolymerization in a manner which would not shift the comonomer ratio in the liquid, vapor, and solid phases. We have already reported on the development of a sampling device which can remove the three phases from a reaction vessel without shifting the comonomer composition.⁶ Our experimental studies on vinyl chloride–vinyl acetate copolymerization have permitted us to examine the efficiency factor (f) for perester initiators in the presence of vinyl chloride–vinyl acetate comonomers and to measure the change in the value of f at different initiator levels.

EXPERIMENTAL

Raw Materials

Water. Tap water was passed through a deionization column and then double distilled under a purge of nitrogen.

Suspension Agent. Polyvinyl pyrrolidone obtained from the GAF Corp. used as received.

Vinyl Chloride. CP-grade obtained from B. F. Goodrich used as received.

Vinyl Acetate obtained from Fisher Scientific used as received.

***t*-Butyl Perneodecanoate** (75% active in mineral spirits) obtained from Lucidol used as received.

Sodium Bicarbonate reagent grade obtained from J. T. Baker Chemical Company.

Polymerization Procedure

Reactor. Ingenieubureau SFS 1.5-L glass-jacketed reactor with bottom sampling valve temperature control to $\pm 0.5^\circ\text{C}$.

Recipe

(1) Water 500 g; (2) poly(vinyl pyrrolidone) 0.30 g; (3) sodium bicarbonate 0.20 g; (4) vinyl acetate 48 g; (5) *t*-butyl per neodecanoate, as indicated; (6) vinyl chloride 252 g.

Charge Procedure

Components 1, 2, and 3 were premixed and charged to the reactor under a stream of nitrogen with the agitator at 250 rpm. The reactor content were cooled to 10°C and the reactor was sealed and evacuated to 25 mm absolute pressure and components 4 and 5 were sucked into the reactor. Component 6 was added at 500 rpm and the entire content of the reactor was heated to 65°C . The heat-up cycle took approximately 8 min. The reactions were carried to the indicated time.

Test Procedures

Bound Vinyl Acetate Content by IR adsorption at 5.74 microns in 1,2-dichloroethylene solution.

Inherent Viscosity. ASTM Procedure D-1243-60A.

DISCUSSION

Talamini⁷ has shown that the comonomer equilibrium between the monomer, polymer, water, and gas phases must be considered throughout the homopolymerization of vinyl chloride. In the homopolymerization of vinyl chloride a separate polymer phase exists in the monomer phase at levels of as low as 0.1% polymer formation, and this separate polymer phase needs to be considered in any kinetic modelling. In order to establish an experimental environment for measuring the copolymer kinetic equations of vinyl chloride-vinyl acetate copolymers, it was first necessary to determine

the phase equilibrium of vinyl chloride and vinyl acetate monomers in a copolymer. Several techniques were considered to terminate a copolymerization:

- (1) thermal quenching;
- (2) radical scavenging;
- (3) dead-end polymerization (DEP).

Thermal quenching by rapid decrease in the polymerization temperature was unacceptable as was also the injection of a radical scavenging agent as techniques of polymerization terminating processes which would not affect the comonomer phase equilibrium. The dead-end polymerization process, where a very low level of initiator is used in the copolymerization, was found to be highly reproducible in conversion vs. time relationship for the vinyl chloride-vinyl acetate copolymerization. In the DEP process the copolymerization ends because of a depletion in the free radical source.

The copolymerization of vinyl chloride-vinyl acetate with low levels of *t*-butylperneodecanoate (tBPND) initiator was studied as a model for the DEP process. Using three different levels of tBPND, we were able to identify polymerization systems which were self-terminating in a highly reproducible manner. These experimental data are noted in Table I. The inherent viscosity of the copolymer resin was unaffected by the initiator level or conversion up to 35%. By comparison, Cotman and co-workers⁸ have shown that in the homopolymerization of vinyl chloride there is an increase in inherent viscosity with conversion. This rather flat response of inherent viscosity to conversion for the vinyl chloride-vinyl acetate copolymers is probably due to the increased in the chain transfer coefficient for the unreacted comonomer mixture which is increasing in vinyl acetate content as the copolymerization proceeds. The limiting conversion achieved in each of the three series of experiments was found to be directly related to the initial level of tBPND over the experimental conditions studied. No attempt

TABLE I
Depleted Initiator Copolymerization Experiments

Run no.	Initiator level (μ L)	Time (h)	Yield (%)	IV ^a (dL/g)	% BVAc ^b
1	20	2.0	6.8	0.531	8.61
2	20	4.0	11.9	0.538	8.80
3	20	6.0	12.3	0.529	8.81
4	20	8.0	13.9	0.540	8.87
5	20	12.0	15.1	0.528	8.98
6	40	2.0	10.9	0.531	8.79
7	40	4.0	18.0	0.527	9.13
8	40	6.0	21.1	0.542	9.04
9	40	8.0	23.8	0.523	9.11
10	40	12.0	25.2	0.525	9.19
11	60	2.0	14.2	0.535	8.97
12	60	6.0	29.8	0.538	9.18
13	60	8.0	31.4	0.531	9.38
14	60	12.0	34.2	0.535	9.62

^a IV = inherent viscosity.

^b % BVAc = % bound vinyl acetate (%).

was made to run at lower initiator levels to determine the curvature as the conversion/initiator concentration approached zero.

The cumulative copolymer composition varies with conversion in a manner which follows the reactivity ratio of $R_{\text{VCM}} = 2.47$ and $R_{\text{VAC}} = 1.99$. This is illustrated in Figure 1.

We examined both the Tobolsky procedure⁹ and the Hamielec procedure¹ to model the copolymer kinetics of vinyl chloride-vinyl acetate. The Tobolsky procedure is most useful for homogeneous monomer/polymer systems. It was unsuccessful in predicting the copolymer kinetics for our experiments. The Hamielec procedure¹ (summarized in the Appendix) was successful in predicting the copolymer kinetics for vinyl chloride-vinyl acetate, over the conversion range of 0–35%. Based on our understanding of the Hamielec model (Appendix) and using the following constants:

$$K_d - (t \text{ butyl perneodecanoate initiator at } 65^\circ\text{C})$$

$$= \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{0.75} = 0.924 \text{ h}^{-1}$$

$$\begin{aligned} [I_0] (20 \mu\text{L}) &= 2 \times 10^{-2} \text{ cc } [0.75] 0.85 \frac{\text{g}}{\text{cc}} \frac{1}{245.37 \text{ g/mol}} \cdot \frac{1}{0.363 \text{ L}} \\ &= 1.4315 \times 10^{-4} [\text{M}]P \\ &= 48.01 \end{aligned}$$

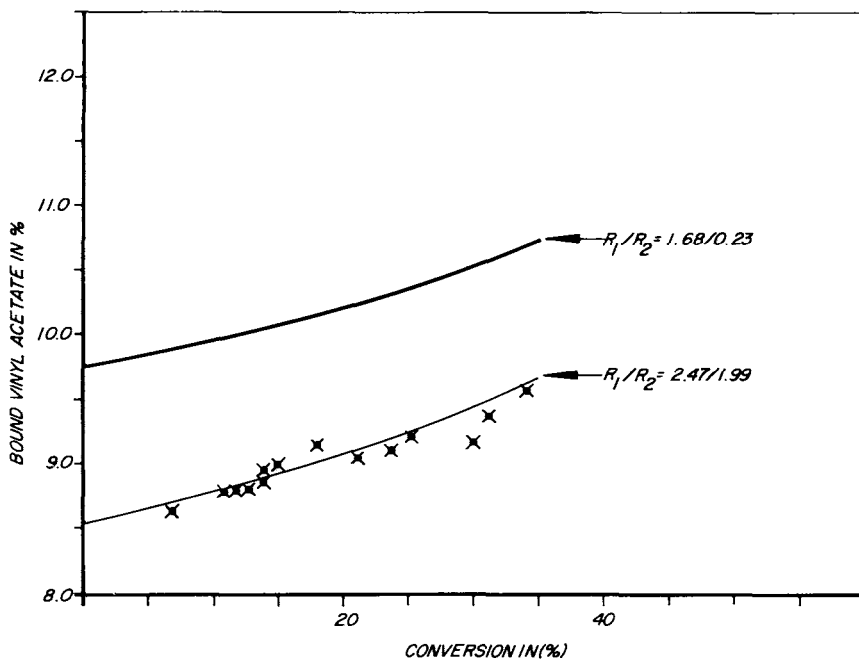


Fig. 1. Bound vinyl acetate content vs. polymer conversion: (x) experimental point.

The graphical representation of conversion vs. time for these copolymerizations is illustrated in Figure 2. The initial slope of the conversion vs. time curve was used to calculate K_1 as

$$K_1 = \frac{dx/dt}{[I_0]}$$

For the three levels of initiator we fit a K_1 value of

$[I_0]$ (μL)	K_1
20	2.888
40	2.600
60	2.450

From these K_1 data points, assuming a radical efficiency (f) for the lowest initiator level of 1.0, we were able to estimate the change in f as the initiator is increased as

$$\frac{K_{1(40 \mu\text{L})}^2}{K_{1(20 \mu\text{L})}^2} = \frac{f_{40}}{f_{20}}$$

$$\left[\frac{2.600}{2.888} \right]^2 = \frac{f_{40}}{1.0}$$

$$f_{40} = 0.810$$

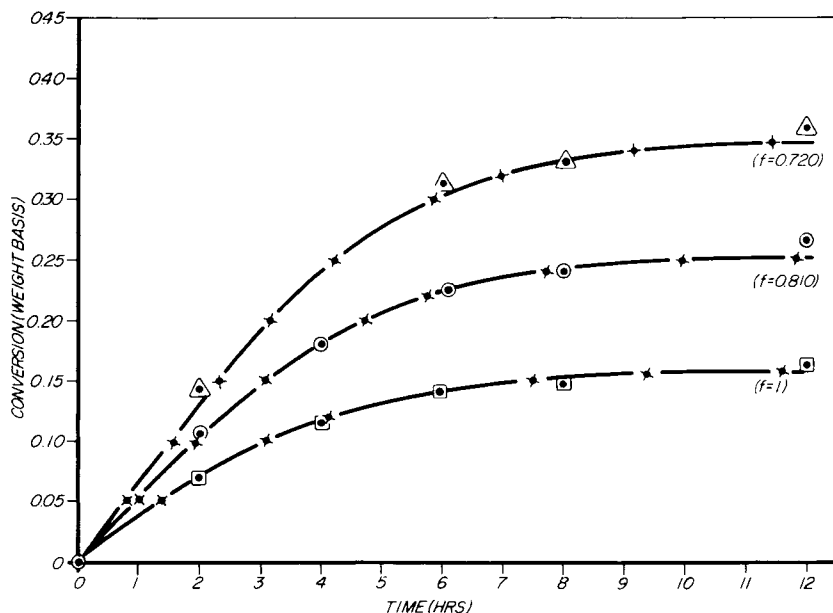


Fig. 2. Dead end polymerization of vinyl chloride-vinyl acetate: (\square) 20 μL injection; (\odot) 40 μL injection; (\triangle) 60 μL injection; (\bullet) modified approach.

Similarly the $f_{60 \mu\text{L}}$ is

$$\left[\frac{2.450}{2.888} \right]^2 = \frac{f_{60 \mu\text{L}}}{f_{20 \mu\text{L}}}$$

$$\left[\frac{2.450}{2.888} \right]^2 = \frac{f_{60 \mu\text{L}}}{1}$$

$$f_{60 \mu\text{L}} = 0.720$$

The decrease that we measure in the relative initiator efficiency factor represents the increased likelihood of primary radical interactions in the polymerization as the initiator concentration is increased. The radical efficiency factor shows a linear decrease with initiator level (in log form). This is shown in Figure 3. This decrease in radical efficiency factor needs to be considered in any modeling of copolymerization kinetics.

SUMMARY AND CONCLUSIONS

The copolymer kinetics for vinyl chloride–vinyl acetate (16% vinyl acetate) can be modeled by a Hamielec equation in the conversion range of 0–35%. The radical efficiency factor can be measured comparatively in a

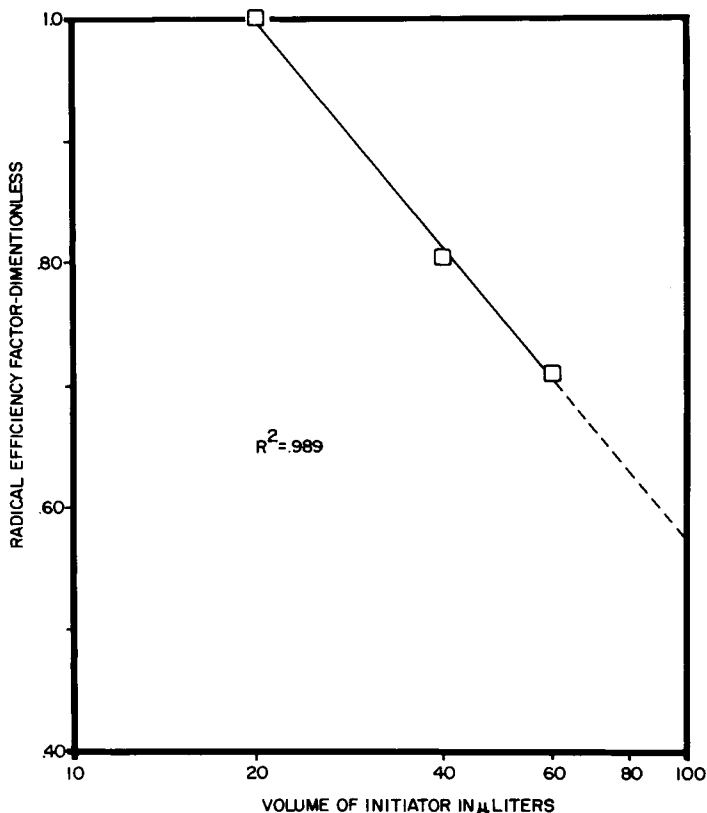


Fig. 3. Radical efficiency factor vs. radical level.

vinyl chloride-vinyl acetate polymerization medium using dead end polymerization procedures. These radical efficiency factors decrease in a predictable manner as the initiator level is increased.

We wish to acknowledge Mr. S. S. Schmidt for the polymerization and characterization efforts and Mr. Phil A. Mango for expert discussions and critical analysis of our efforts.

APPENDIX: ABDEL-ALIM-HAMIELEC MODEL DERIVATION

Since the Tobolsky model considers only a homogeneous bulk polymerization, it is limited and cannot adequately model two phase suspension polymerizations. It is known that two phases as in equilibrium in vinyl chloride polymerizations (1) monomer-rich phase oil 21 polymer rich phase. As the reaction proceeds, the mass of the polymer rich phase grows while the monomer rich phase is consumed. Experimental results have confirmed that two phases exist after <1% conversion and continues until about 70% conversion. An assumption of the Hamielec model is that the monomer rich phase is in equilibrium with the growing polymer phase and that the monomer rich phase contains monomer and no polymer.

The reader is urged to consult the reference¹ because the derivation and integration of the resulting equations are fairly involved. The final useful form of the Abdel-Alim-Hamielec model is as follows:

$$t = -\frac{2}{K_d} \ln(1 - H)$$

where

$$H = \frac{K_d}{2K_1 [I_0]^{1/2}} \left(\frac{2}{Q} (\sqrt{1 - BX} - 1) + \frac{\sqrt{Q+B}}{Q\sqrt{Q}} \ln \left\{ \frac{[\sqrt{Q(1-BX)} - \sqrt{Q+B}]/(\sqrt{Q} - \sqrt{Q+B})}{[\sqrt{Q(1-BX)} + \sqrt{Q+B}]/(\sqrt{Q} + \sqrt{Q+B})} \right\} \right)$$

The terms in this equation are defined as follows: t = time (h), K_d = rate constant for decomposition of initiator, $K_1 = (dx/dt)_0/[I_0]^{1/2}$ the initial slope of the curve X vs. $t[I_0]^{1/2}$, $[I_0]$ = initial catalyst concentration, P = constant term for diffusion of monomer into the polymer phase, X_f = mass fraction of polymer in polymer-rich phase, $Q = [P(1 - X_f) - 1]/X_f$, $B = (\rho_p - \rho_m)/\rho_p$, and X = conversion of monomer to polymer. This equation provides an independent method for evaluating both K_d and $K_p/K_t^{1/2}$ along with applications for obtaining f (efficiency) relative to various initiator concentrations. A typical approach to using this equation is as follows:

- (1) Select a low concentration of initiator $[I_0]$ and run experiments to determine conversion (X) vs. time (t).
- (2) Determine the decomposition rate constant K_d (literature).
- (3) Calculate K_1 which is the initial slope of the curve X vs. $t[I_0]^{1/2}$.
- (4) Trial and error on P until a best fit is obtained on lower conversion data points.
- (5) If the upper points do not fit, the decomposition rate constant is in error, go to (2) and repeat the procedure.
- (6) Run another experiment using a higher concentration of initiator and determine conversion vs. time.
- (7) Keeping K_d and P the same as the best fit value obtained above, K_1 is varied until the best fit is obtained for the higher concentration data.
- (8) At this point the efficiency (f) of the initiator has been assumed to be one at the low concentration and $K_p/K_t^{1/2}$ can be directly calculated by

$$K_p/K_t^{1/2} = K_1/fK_d^{1/2} = K_1/(1)K_d^{1/2}$$

(9) The constants $K_p/K_t^{1/2}$ and K_d are now fixed and the relative efficiency (f) can be calculated for the higher concentration assuming $f = 1$ at the lower concentration as follows:

$$\frac{K_1(\text{low})}{K_1(\text{high})} = \frac{(K_p/K_t^{1/2}) (K_d^{1/2}) f^{1/2}(\text{low})}{(K_p/K_t^{1/2}) (K_d^{1/2}) f^{1/2}(\text{high})} = \frac{f^{1/2}(\text{low})}{f^{1/2}(\text{high})} = \frac{1}{f^{1/2}(\text{high})}$$

(10) Continue experiment using higher concentrations of initiator, go to (7) and repeat the procedure.

(11) The same initiators must be used for each run since every initiator has its unique K_d and P values.

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Received November 15, 1984

Accepted December 17, 1984