

Bulk Polymerization of Vinyl Chloride-Commercial Initiator Systems

A. H. ABDEL-ALIM* and A. E. HAMIELEC, *Chemical Engineering Department, McMaster University, Hamilton, Ontario, Canada*

Synopsis

The applicability of a model after Talamini for the bulk polymerization of vinyl chloride with several commercial initiators has been examined. The model agrees well with experimental rate data for the initiators: diisopropyl peroxydicarbonate, diisobutyl peroxydicarbonate, *t*-butyl peroxyvalate, lauroyl peroxide and benzoyl peroxide.

Bulk polymerization of vinyl chloride is a typical example of what is known as "heterogeneous polymerization." The polymer being insoluble in its own monomer precipitates during the course of reaction giving rise to a two-phase polymerizing system.

Many workers have studied the bulk polymerization of vinyl chloride experimentally, and a common observation was autocatalysis from the onset of the reaction. Many models have been proposed to describe the kinetics of the reaction. A review of these is given by Talamini and Peggion.¹ Most of the models proposed to date fit experimental rates up to relatively small conversions and involve parameters which have not been measured over a useful temperature range.

In a previous publication,² we proposed a model which accurately predicts the molecular weight distribution as well as the conversion to high levels. The model assumes a two-phase polymerization, in a monomer-rich and polymer-rich phase. The composition of each phase remains constant, but as reaction proceeds, the mass of polymer-rich phase grows while the monomer-rich phase diminishes. Since the reaction rate per unit volume is higher in the polymer-rich phase, due to gel effect, there is an acceleration in the overall reaction rate.

Under these heterogeneous conditions, the polymer molecules aggregate, forming monomer-swollen particles insoluble in the monomer. These aggregates are roughly spherical in shape; their size depends on the conversion in the early stages since they grow a little after precipitation from about 0.2 to about 1 micron in diameter.³ The size distribution, solubility, and stability depend on the polymerization temperature. An average

* Present address: Research Department, Imperial Oil Canada Ltd., Sarnia, Ontario, Canada.

aggregate diameter of 0.25 micron was reported using light scattering^{4,5,6} and GPC and electron microscopy.⁷ Particles of diameter 800 Å and less were recently reported⁸ in γ -ray-initiated bulk polymerization of vinyl chloride at 0°C.

Phase interaction may or may not be important depending on the state of subdivision. If the particles are very small in diameter, then radical diffusion between phases might be important due to the large surface area for mass transfer. Models were presented that emphasize the significance of interaction between the phases.^{9,10} Practically, this does not seem to be the situation, and the insignificance of radical interphase diffusion can be illustrated by the following order-of-magnitude calculations.

At steady state and for a 1-liter volume of reaction mixture, the following radical balance holds:

rate of radical production by initiation + rate of radical transport by bulk flow of monomer converting into polymer - net rate of radical transport by diffusion out of the polymer - rate of radical destruction by termination = 0

$$\therefore 2f k_d I + \left(\frac{dV}{dt} \right) [R^\cdot]_1 - k_D a ([R^\cdot]_2 - [R^\cdot]_1) - k_t [R^\cdot]_2^2 = 0 \quad (1)$$

where I = the initiator concentration, in moles/l., (dV/dt) = average rate of bulk flow of monomer converting into polymer this is approximately equal to $1/t_1$, t_1 being the time required for one liter of monomer to convert to polymer; Units are l./sec, $[R^\cdot]_1$ = radical concentration in monomer, in g-moles/l., $[R^\cdot]_2$ = radical concentration in polymer, g-moles/l., k_D = a constant representing radical transfer coefficient, a = mass transfer area per unit volume, units of $k_D a$ being hr^{-1} , f = initiator efficiency, taken as one, k_d = initiator dissociation rate constant, in hr^{-1} , and k_t = termination rate constant in l./mole-hr.

An order-of-magnitude calculation will be carried out to assess the significance of each of the terms in eq. (1) above. Let us consider bulk polymerization at 50°C. Initiator concentration is 0.8×10^{-3} mole AIBN/mole VC. Under these conditions the reaction time is about 10 hr.¹¹

k_t is in the order of 10^9 l./mole-sec

k_d is in the order of 10^{-2} hr^{-1}

The radical transfer area per unit volume (a) is difficult to determine since it varies with time and depends primarily on the aggregation process. This area is a maximum if the surface area of all the spherical aggregates is available for transfer. Undoubtedly (a) will be much less than this extreme. For the purpose of the present rough calculations, this will be considered the case,

$\therefore a$ = surface area of one spherical aggregate \times number of aggregates per liter

$$= 4\pi(1250 \times 10^{-8})^2 + \frac{1000 \times 0.5}{\frac{4}{3}\pi(1250 \times 10^{-8})^3}$$

The porosity is taken as 0.5; therefore, a is in the order of 10^8 cm²/l., and

$$k_D \simeq \frac{D}{r_0}$$

where D is the radical diffusion coefficient $\simeq 10^{-10}$ cm²/sec (ref. 10), r_0 is radius of the spherical aggregate $\simeq 1250 \times 10^{-8}$ cm, and k_D is in the order of 10^{-5} cm/sec.

$[R^\cdot]_1$ and $[R^\cdot]_2$ are of the same order of magnitude, even though $[R^\cdot]_2$ is larger than $[R^\cdot]_1$. Accordingly, $[R^\cdot]$ will be used for any of them or their difference;

$$\therefore 2fk_a I \text{ is of the order of } 2 \times 1 \times \frac{10^{-2}}{3600} \times \frac{0.8 \times 10^{-3}}{0.0625}, \text{ i.e., } 10^{-9} \text{ mole/sec}$$

$$\left(\frac{dV}{dt}\right) [R^\cdot] \text{ is of the order of } \frac{1}{10 \times 3600} [R^\cdot], \text{ i.e., } 3 \times 10^{-5} [R^\cdot] \text{ mole/sec}$$

$$k_D a [R^\cdot] \text{ is of the order of } 10^{-5} \times 10^8 \times 10^{-3} [R^\cdot], \text{ i.e., } [R^\cdot] \text{ moles/sec}$$

$$k_t [R^\cdot]^2 \text{ is of the order of } 10^9 [R^\cdot]^2 \text{ moles/sec.}$$

When the above quantities are substituted in eq. (1) and the equation is solved for $[R^\cdot]$, it is found that

$$[R^\cdot] \text{ is in the order of } 10^{-9} \text{ mole/l.}$$

This means that the transport by bulk flow is completely insignificant, and initiation, termination, and diffusion are of equal significance.

In the above calculations, a was taken as that of isolated spherical aggregates of diameter approximately 2500 Å. Obviously, this leads to a very large surface area. It is highly unlikely that the particles are made up of single aggregates, especially in the absence of stabilizers. Actually, these aggregates agglomerate to form larger polymer particles of diameter ranging from 80 to 200 microns.¹²⁻¹⁴ The above calculations may now be repeated for a more realistic case, namely, the particles having an average diameter of about 100 microns. The quantity $k_D a$ is inversely proportional to the diameter squared. This makes the diffusion term in eq. (1) smaller by a factor of 400², or 1.6×10^5 . For this case, the term $k_D a [R^\cdot]$ will be in the order of $10^{-5} [R^\cdot]$. When eq. (1) is solved for $[R^\cdot]$, it is found that $[R^\cdot]$ is again in the order of 10^{-9} g-mole/l., but now the diffusion term is completely insignificant. This seems to be more realistic, since the polymer precipitated particles were noticed to be in the range of 100 microns in diameter.

The mathematical treatment of our model is given elsewhere.² The model contains four parameters. Only one of these four parameters depends on the initiator used, namely, k_a , the initiator decomposition constant. The remaining three parameters are properties of the monomer-polymer system and are independent of the initiator.

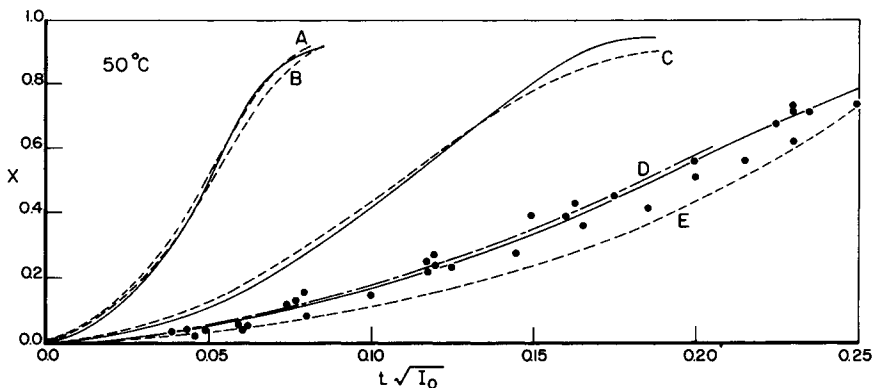


Fig. 1. Experimental data for four commercial initiators compared with present model predictions-bulk polymerization of vinyl chloride: curve A, diisopropyl peroxydicarbonate²⁰; curve B, di(*sec*-butyl) peroxydicarbonate²⁰; curve C, *t*-butyl peroxyvalate²⁰; curve D, lauroyl peroxide¹⁹; curve E, lauroyl peroxide²⁰; (●) lauroyl peroxide¹¹; (—) model prediction.

In the previous study,² AIBN was used as the chemical initiator. Values of the model parameters were estimated by fitting the model response to the experimental data using a special regression analysis routine.¹⁵

As the proposed model indicates, different initiators give rise to different conversion curves due to different k_d values. It is possible, therefore, to predict conversion data using other initiators once k_d for the particular initiator is known.

Conversion data for different commercial initiators at 50°C are available in the commercial literature, and this permits one to test the model over a wide range of initiator systems of commercial interest. Data for five different initiators were examined. Table I lists these initiators, their decomposition characteristics, and the source of the data. Figures 1 and 2 compare model predictions with experimental rate data for the bulk polymerization of vinyl chloride. The dashed lines and the dots are experimental data. The solid lines are the model predictions. These were not fitted to the experimental points but were generated using k_d values given in Table I as reported in the corresponding references. Values of the other parameters at 50°C were taken from our previous work using AIBN.² k_d for the initiators in curves A and B in Figure 1 is the same at 50°C, accordingly only one curve could be predicted. Although there is some scatter of the data obtained from different sources, the agreement is good. Data in Figure 2 are all for benzoyl peroxide at 50°C. There is considerable scatter and disagreement among the various sets of experimental rate data. In both Figures 1 and 2, data for lauroyl peroxide and benzoyl peroxide, respectively, of reference 11 agree best with our model predictions. In both figures, t is the reaction time in hours and I_0 is the initial initiator concentration in g-moles/g-mole VC. Conversion data at different initiator con-

TABLE I
Commercial Initiators and Decomposition Data Used for the Bulk Polymerization of VC at 50°C

Name	Formula and weight	Frequency factor A , hr ⁻¹	Activation energy E , kcal/mole	k_d at 50°C, hr ⁻¹	Ref.	Concentration used, mole/mole VC
Diisopropyl peroxydicarbonate	C ₉ H ₁₄ O ₆ 206.18	1.786 × 10 ¹⁸	28.7	0.678 × 10 ⁻¹	20	1.02 × 10 ⁻⁴
Di(<i>sec</i> -butyl) peroxydicarbonate	C ₁₀ H ₁₈ O ₆ 234.0	1.478 × 10 ¹⁷	27.1	0.679 × 10 ⁻¹	20	6.7 × 10 ⁻⁶
<i>t</i> -Butyl peroxyvalate	C ₉ H ₁₈ O ₃ 174.2	1.274 × 10 ⁻¹⁸	29.1	0.259 × 10 ⁻¹	20	2.7 × 10 ⁻⁴
Lauroyl peroxide	C ₂₄ H ₄₈ O ₄ 398.63	1.353 × 10 ¹⁹	31.3	0.894 × 10 ⁻²	11 19	4.7 × 10 ⁻⁴ to
Benzoyl peroxide	C ₁₄ H ₁₀ O ₄ 242	2.33 × 10 ¹⁷	29.7	1.862 × 10 ⁻³	20 11 16 17 18	5.5 × 10 ⁻³ 7.5 × 10 ⁻⁴ to 10.3 × 10 ⁻³

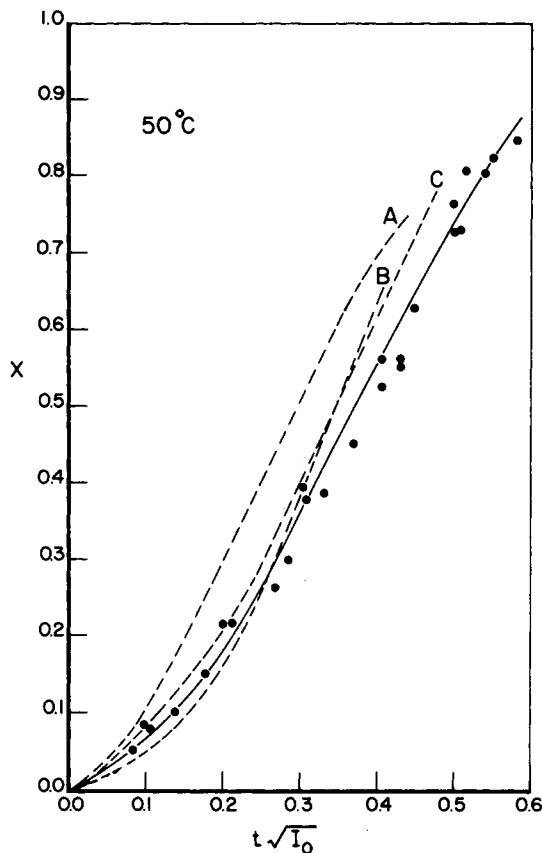


Fig. 2. Experimental rate data for benzoyl peroxide compared with present model prediction-bulk polymerization of vinyl chloride: curve A, ref. 18; curve B, ref. 16; curve C, ref. 17; (●) ref. 11; (—) model prediction.

centrations are known to overlap when plotted versus $t\sqrt{I_0}$, and hence our use of this type of plot.

A basic assumption in our model is that the initiator has the same concentration in both phases at all times. The good agreement found with the five commercial initiators investigated suggests that errors associated with this assumption are small and that therefore our model has a rather wide range of applicability.

References

1. G. Talamini and E. Peggion, in *Vinyl Polymerization*, Vol. 1, G. Ham, Ed., Marcel Dekker, New York, 1967, Chap. 5.
2. A. H. Abdel-Alim and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 783 (1972).
3. J. D. Cotman, M. F. Gonzales, and G. G. Claver, *J. Polym. Sci. A1*, **5**, 1137 (1967).
4. P. Kratochvil, V. Petrus, P. Munk, M. Bohdanecky, and K. Solc, *J. Polym. Sci.*, **C16**, 1257 (1967).

5. Kratochvil, P., *Collection Czech. Chem. Commun.*, **30**, 683 (1965).
6. Kratochvil, P., *Collect. Czech. Chem. Commun.*, **29**, 2290 (1964).
7. A. H. Abdel-Alim and A. E. Hamielec, *J. Appl. Polym. Sci.*, **17**, 3033 (1973).
8. K. Aritz and V. Stannett, *J. Polym. Sci.*, **11**, 1565 (1973).
9. J. Ugelstad, H. Lervik, B. Gardinovacki, and E. Sund, *Pure Appl. Chem.*, **25**, 121 (1971).
10. J. Ugelstad, H. Flogstad, T. Hertzberg, and E. Sund, *Markromol. Chem.*, **164**, 171 (1973).
11. A. Crosato-Arnaldi, P. Gasparini, and G. Talamini, *Makromol. Chem.*, **117**, 140 (1968).
12. Pechiney-St. Gobain, U.S. Pat. 2,715,117 (1955); U.S. Pat. 2,856,272 (1958).
13. Pechiney-St. Gobain, Belg. Pat. 602,397 (1960).
14. Pechiney-St. Gobain, Belg. Pat. 674,371 (1968); 674,372 (1965).
15. A. H. Abdel-Alim, Ph.D. Thesis, McMaster University, 1973.
16. E. Jenckel, Eckmano, and H. Rumbac, *Makromol. Chem.*, **4**, 15 (1949).
17. A. Schindler and J. W. Breitenbach, *Ric. Sci. Suppl.*, **25**, 34 (1955).
18. F. Danusso and G. Perugini, *Chim. Ind. (Milan)*, **35**, 881 (1953).
19. E. Farber and M. Koral, *Soc. Plast. Eng. Tech. Papers*, **13**, 398 (1967).
20. Lucidol Bulletin for Free Radical Initiators for PVC. Technical Bulletin 30.90, Buffalo (August 1970).

Received October 30, 1973

Revised December 8, 1973