

Kinetics of Heterogeneous Polymerization of Vinylidene Chloride. II. Discussion of Model

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ABSTRACT: In the present article, the kinetic model for vinylidene chloride polymerization obtained in the previous article was analyzed and simplified. A series of kinetic experiments was carried out in stainless-steel batch reactors to evaluate the model. The kinetic parameters were estimated by using these experimental data. The theoretical model prediction was compared with the experimental data. The

result shows that the present model is in good agreement with experimental data over nearly the entire conversion range. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2582–2587, 2004

Key words: vinylidene chloride (VDC); polymerization; mechanism; kinetics; model

INTRODUCTION

The kinetic model of vinylidene chloride (VDC) polymerization was derived in the previous article of this series. However, so far the kinetic parameters K^* and K'_{de} in the model have not been determined accurately because the kinetic data of VDC polymerization is still noticeably absent, especially over the entire conversion range. Therefore, the model in the previous article has been properly simplified in the present article to decrease the number of kinetic parameters. To evaluate the present simplified model and estimate its kinetic parameters, a series of kinetic experiments were carried out for VDC suspension polymerization. The present model prediction is in good agreement with experimental data over nearly the entire conversion range.

SIMPLIFICATION OF MODEL

For the kinetic model obtained in the previous article, it is clear that if K^* and K'_{de} are expressed with appropriate constants, one can obtain simplified models. For example,

(1) If $K^* = 1$ and $K'_{de} = 0$, eq. (27a) in the previous article becomes

$$\frac{dX}{dt} = k_1 H [I]^{1/2} \left(\frac{V}{V_0} \right)^{1/2} \left(\frac{V_2}{V_0} \right)^{1/2} \quad (1)$$

$K^* = 1$ is consistent with $r_c = 1$ (i.e., the critical chain length for precipitation is one monomeric unit). All the radicals will precipitate and transfer to the crystalline surface layer of the polymer before further propagation. $K'_{de} = 0$ indicates that the radicals on the surface do not desorb. Under this condition, all of the polymerization occurs on the surface layer.

In fact, eq. (1) is none other than Wessling's model. Let $k = k_1 H P^{1/2}$ and substituting $[I] = I/V$ and $V_2/V_0 = M_2/M_0 = P X^{1/2}$ into eq. (1), it becomes the form of Wessling's model reported in the literature¹ as follows:

$$\frac{dX}{dt} = k \left(\frac{I}{V_0} \right)^{1/2} X^{1/4} \quad (2)$$

If $I = I_0 \exp(k_d t)$ is substituted into eq. (2) by considering initiator consumption and the power of X is changed to α ($\neq \frac{1}{2}$) by considering the effect of a common monomer on the morphology of the polymer, then eq. (2) becomes the model used in our previous article² as follows:

$$\frac{dX}{dt} = k [I]_0^{1/2} X^\alpha \exp\left(-\frac{1}{2} k_d t\right) \quad (3)$$

This shows that both Wessling's model¹ and the model used in our previous article² are special cases of the model obtained in the previous article, but the explanation for their kinetic meaning is more definite here than that in Jin and Hua¹ and Lu et al.²

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(2) If $K^* = 0$ and $K'_{de} = 0$, eq. (27b) in the previous article becomes

$$\frac{dX}{dt} = k_{p1} \left(\frac{fk_d}{k_{t1}} \right)^{1/2} [I]^{1/2} \left[\left(\frac{M_1}{M_0} \right) + H \left(\frac{M_2}{M_0} \right) \right] \quad (4)$$

$K^* = 0$ is consistent with $r_c = \infty$, which indicates that precipitation of radicals does not occur during polymerization, and where $K'_{de} = 0$ indicates that the radical transfer reaches equilibrium between the monomer phase and the surface layer. Under this condition, eq. (4) suggests that the polymerizations occur in both the surface layer and the monomer phase independently, which is similar to Talamini's model^{3,4} for VC polymerization. An important difference between eq. (4) and Talamini's model is that the meaning of M_2 in the VDC system is different from that in the VC system.

From the previous article, it is known that the equations to calculate M_1 and M_2 are as follows:

$$M_1 = M_0(1 - X) - M_2 \quad (5)$$

$$M_2 = PM_0X^{1/2} \quad (6)$$

By substituting eqs. (5) and (6) into eq. (4), one can rewrite the polymerization rate as

$$\frac{dX}{dt} = k_1 [I]^{1/2} (1 - X + QX^{1/2}) \quad (7)$$

where $Q = (H - 1)P$ and $k_1 = k_{p1}(fk_d/k_{t1})^{1/2}$. If the consumption of initiator is considered in eq. (7), then one obtains

$$\frac{dX}{dt} = k_1 [I]_0^{1/2} (1 - X + QX^{1/2}) \exp\left(\frac{1}{2}k_d t\right) \quad (8)$$

Equation (8) describes the kinetic behavior of VDC polymerization in the range of $X_0 < X < X_f$ or does approximatively in $0 \leq X \leq X_f$. The effects of the decrease of Q attributed to aggregation involving multiparticle contacts on polymerization rate is contrary to the effect of the increase of initiator concentration attributed to the constriction of volume during polymerization. Therefore, they are together neglected in eq. (8) by roughly considering that they counteract each other.

Equation (8) is easily solved analytically with the initial condition $X = X_0 = 0$ at $t = 0$. It can be integrated as follows:

$$\int_0^X \frac{dX}{(1 - X + QX^{1/2})} = \int_0^t k_1 [I]_0^{1/2} \exp\left(\frac{1}{2}k_d t\right) dt, \quad X < X_f \quad (9)$$

The integral result can be expressed with a simple form as

$$Z = k_1 Y \quad (10)$$

where

$$Y = \left(\frac{2[I]_0^{1/2}}{k_d} \right) [1 - \exp(-\frac{1}{2}k_d t)] \quad (11)$$

$$Z = \frac{1}{\sqrt{Q^2 + 1}} \left[C_1 \ln \left| \frac{C_1}{\sqrt{X} - C_1} \right| - C_2 \ln \left| \frac{C_2}{\sqrt{X} - C_2} \right| \right] \quad (12)$$

In eq. (12)

$$C_1 = \frac{Q + \sqrt{Q^2 + 4}}{2}, \quad C_2 = \frac{Q - \sqrt{Q^2 + 4}}{2}$$

After the conversion X_f , the case becomes very complex. To describe the kinetic behavior in the range of conversion, eq. (8) is rewritten with Ahmed's approximate method⁵ as follows:

$$\frac{dX}{dt} = k_1 [I]_0^{1/2} (1 - X + QX^{1/2}) \left(\frac{1 - X}{1 - X_f} \right) \exp\left(\frac{1}{2}k_d t\right) \quad (13)$$

The fact is that both K^* and K'_{de} are between 0 and 1. However, it is troubling that so far K^* and K'_{de} in VDC polymerization have not accurately been determined like that in VC polymerization and so the model containing both K^* and K'_{de} obtained in the previous article cannot accurately be used now. Therefore, eq. (8) and (13) will be used as the present model to describe the kinetic behavior of VDC polymerization in the present article. It will be proved below that eqs. (8) and (13) are in good agreement with our experimental data.

EXPERIMENTAL

To evaluate the present model and estimate the kinetic parameters, a series of kinetic experiments was made for VDC polymerization.

Materials

VDC monomer (industrial grade), from Zhejiang Juhua Group Co. (China) was distilled twice in an atmosphere of nitrogen. The second distillation was done immediately before use. Lauryl peroxide (LPO; Dow Chemical Co., Midland, MI) was used as initiator. Acetone semicarbazone (ATSC; Shanghai Chemical Reagent Co., China) was used as inhibitor. Both LPO and ATSC were used as received. Hydroxy-propyl methyl cellulose (HPMC; Dow Chemical Co.) was

used as suspending agent. Deionized water was used in all experiments.

Determination of conversion

The 200-mL stainless-steel reactor was filled with a weighed amount of deionized water containing suspending agent and a weighed amount of VDC containing LPO. The oxygen in the reactors was swept by nitrogen three times. The reactors were then fixed on a rotational axle, which was immersed in a water bath. The polymerization temperature was well controlled at definite values. The reactors were removed from the water bath at different time intervals and cooled immediately. The inhibitor was added to the reactor, and the reactant was poured out, filtrated, washed with water, and dried at 50°C until achieving constant weight, after which its final dry weight was recorded. The conversion was calculated based on the weight of final polymer.

Measurement of reactor pressure

The polymerization recipes were added into a 5-L stainless-steel reactor according to the same method as described above. The stirrer was run for 10 min at room temperature and then the reactor temperature was rapidly raised to the polymerization temperature. The reactor pressure as a function of polymerization time was recorded.

Measurement of molecular weight

Hexamethylphosphoramide (HMPA) was used as a solvent and distilled under reduced pressure before use. Solution viscosities were determined in Ubbelohde dilution viscosimeters (Cannon-Ubbelohde, State College, PA) at 25°C in a bath controlled to

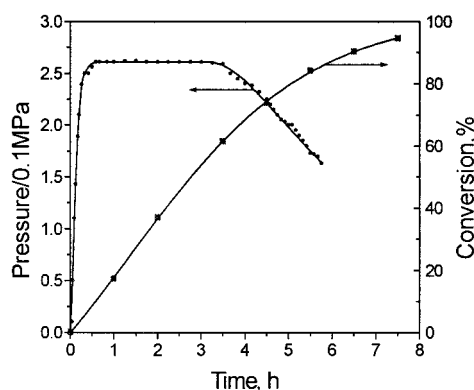


Figure 1 Pressure–time and conversion–time curves of VDC suspension polymerization with LPO as initiator at 70°C.

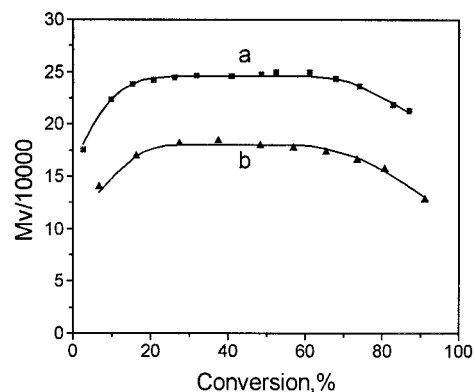


Figure 2 Conversion versus viscosity-average molecular weight of PVDC prepared with LPO as initiator at different temperatures. Temperature: (a) 50°C, (b) 60°C. LPO: 0.8 wt % (based on monomer).

$\pm 0.02^\circ\text{C}$. The molecular weight of PVDC can be calculated using eq. (14) as follows⁶:

$$[\eta] = 2.53 \times 10^{-4} Mv^{0.65} \text{ (dL/g)} \quad (14)$$

where $[\eta]$ is the intrinsic viscosity and Mv is the viscosity-average molecular weight.

DISCUSSION OF THE MODEL

Kinetic parameter

To predict and simulate using the present model for VDC polymerization, the kinetic parameters X_0 , X_f , Q , k_1 , and k_d must first be estimated.

It is reasonable to assume $X_0 \approx 0$ in terms of the above paragraph and so eq. (8) can be used for $X < X_f$. For $X > X_f$, eq. (13) is used.

At the critical conversion X_f , the polymerization rate, the reactor pressure, and molecular weight of polymer all begin to decrease in VC polymerization⁷⁻⁹ as well as in VDC polymerization. To estimate X_f in VDC polymerization, the reactor pressure and molecular weight of PVDC were determined and the results are shown in Figures 1 and 2. One can see from Figures 1 and 2 that $X_f \approx 0.65$. Shapes of these curves in VDC polymerization are similar to those in VC polymerization,⁷⁻⁹ but $X_f \approx 0.70$ for VC polymerization. It may be seen from the following paragraphs that the polymerization rate will also gradually decrease after 65% conversion in VDC polymerization.

Based on eq. (10), Q and k_1 can be estimated using our conversion–time data before the conversion X_f . The results show that the average value of Q is about 1.55 under various experimental conditions in the present work and k_1 obtained with the above method at different temperatures can be estimated again, using a least-squares fit, as

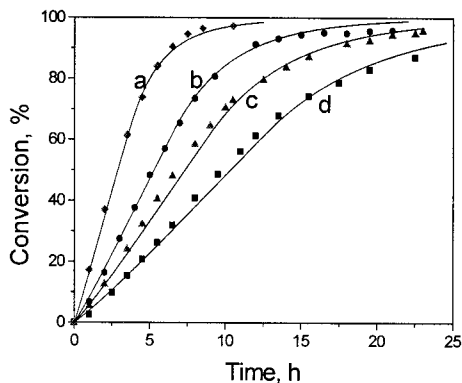


Figure 3 Conversion–time curves of VDC suspension polymerization with LPO as initiator at different temperature. LPO: 0.8 wt % (based on monomer). Temperature: (a) 70°C, (b) 60°C, (c) 55°C, (d) 50°C. Water/monomer ratio: 2 : 1. Points: experimental results. Lines: theoretical model prediction.

$$k_1 = 2.926 \times 10^9 \exp\left(-\frac{62600}{RT}\right), \frac{(\text{L/mol})^{1/2}}{h} \quad (15)$$

The decomposition rate constant (k_d) of LPO has been estimated by some investigators. The temperature dependency of k_d can be estimated as

$$k_d = 2.78 \times 10^{18} \exp\left(-\frac{127,200}{RT}\right) (1/h) \quad (16)$$

Conversion

Conversion change with time for VDC suspension polymerization was measured to evaluate the present model. The results are shown in Figures 3–5(points). The curves in Figures 3–5 are the predicted results using the present model. It can be seen that the theo-

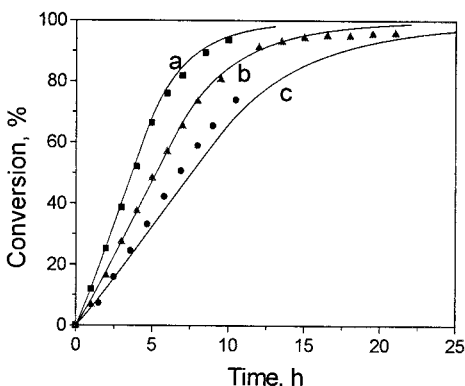


Figure 4 Conversion–time curves of VDC suspension polymerization with LPO as initiator at 60°C. LPO: (a) 1.6 wt %, (b) 0.8 wt %, (c) 0.4 wt % (based on monomer). Water/monomer ratio: 2 : 1. Points: experimental results. Lines: theoretical model prediction.

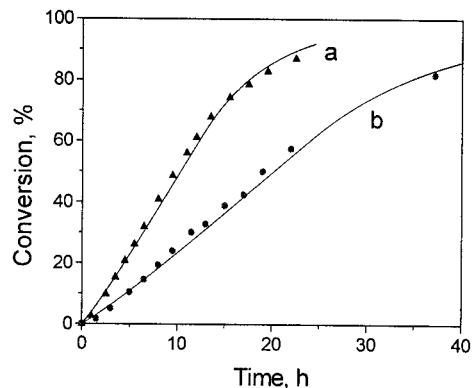


Figure 5 Conversion–time curves of VDC suspension polymerization with LPO as initiator at 50°C. LPO: (a) 0.8 wt %, (b) 0.2 wt % (based on monomer). Water/monomer ratio: 2 : 1. Points: experimental results. Lines: theoretical model prediction.

retical model prediction is in good agreement with experimental data over nearly the entire conversion range.

Polymerization rate

The curves in Figure 6 are typical conversion–time curves for VC polymerization (from Xie et al.,^{7,8} Kiparissides et al.,⁹ and Crosato-Arnaldi et al.¹⁰). By comparing Figure 6 with Figures 3–5, one can see that the autoacceleration effect in VDC polymerization is different from that in VC polymerization. For VDC polymerization, the autoacceleration period is very short and then the polymerization rate is a fairly constant value until about 65% conversion,^{11,12} which is often called the steady-stage region.¹¹ For VC polymerization, however, the autoacceleration period is long and the reaction is characterized by an obviously increasing rate until about 70% conversion.^{7–10}

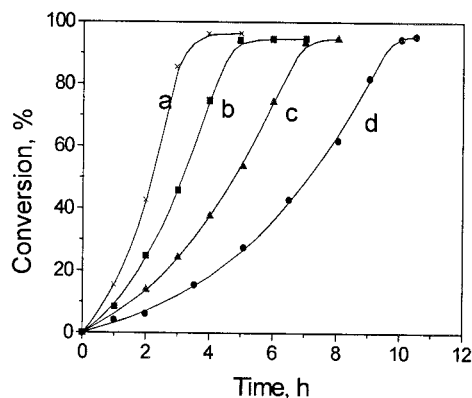


Figure 6 Conversion–time curves of VC suspension polymerization with LPO as initiator at 50°C [LPO] × 10³ (mol/mol VC): (a) 6.60, (b) 3.38, (c) 1.57, (d) 0.83. [From Xie et al.,^{7,8} Kiparissides et al.,⁹ and Crosato-Arnaldi et al.¹⁰]

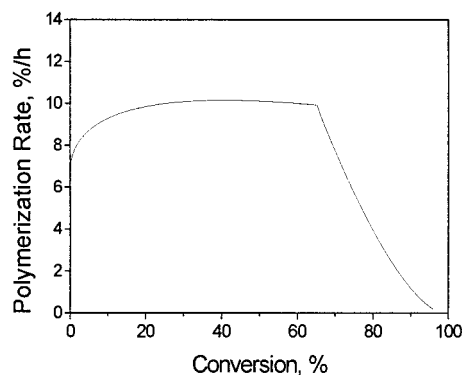


Figure 7 Polymerization rate–conversion curve simulated with the present model for VDC suspension polymerization with LPO as initiator at 60°C. LPO: 0.8 wt% (based on monomer).

The curve in Figure 7 is the typical rate curve of VDC polymerization simulated with the present model and the curve in Figure 8 is that of VC polymerization with the kinetic model from Xie et al.⁷ In Figures 7 and 8, the difference of autoacceleration effect between VDC and VC polymerization can be observed more clearly than in Figures 3–6. The model prediction of a significant increase in rate of VDC polymerization at low conversion, such as Figure 7, is in agreement with the experimental results made by Reinhardt¹² and Bengough and Norrish.¹³

The difference of autoacceleration effect between VDC and VC polymerization can be explained as follows.

For VDC polymerization the autoacceleration effect is dependent on the crystalline surface area of PVDC lamellar crystal edge,¹⁴ whereas for VC polymerization the autoacceleration effect is dependent on the total volume of PVC.^{7,8} It is known that the surface area that increases with conversion is slower than the volume of polymer and furthermore the increase in

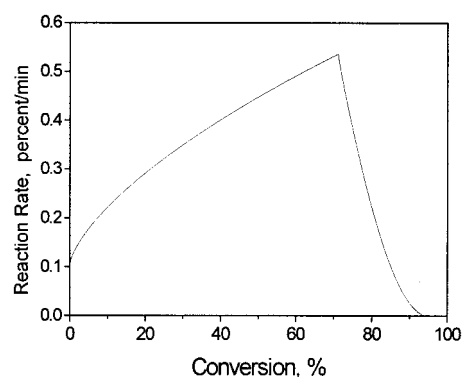


Figure 8 Polymerization rate–conversion curve simulated with the kinetic model (from Xie et al.⁷) for VC suspension polymerization. Perkadox 16-W40 as initiator, $[I]_0 = 0.175$ wt %.

TABLE I
Effect of Initiator Concentration on Molecular Weight of PVDC

LPO (wt %)	M_v
0.2	21.25
0.4	19.40
0.8	17.39
1.6	14.53

surface area is limited by aggregation of PVDC particles; thus the autoacceleration effect in VDC polymerization is not so strong as that in VC polymerization, unless at low conversion. It is known from Wessling's lamella model¹⁴ that the increase of crystalline surface area of PVDC with conversion is fast only at low conversion.

Molecular weight

The change of viscosity-average molecular weight with initiator concentration was determined. The results are shown in Table I, which shows that the molecular weight decreases significantly with the increase of initiator concentration, which is much different from the effect of initiator concentration on the molecular weight of PVC. The molecular weight of PVC is independent of initiator concentration because of significant chain transfer to monomer during VC polymerization, whereas the chain transfer to monomer during VDC polymerization is not so significant as that during VC polymerization.

If the molecular weights of PVDC in Figure 2 and Table I are compared with that of PVC from Xie et al.^{7,8} and Kiparissides et al.,⁹ it can be seen that the molecular weight of PVDC is significantly larger than that of PVC prepared under the same conditions. It also indicates that the chain transfer to monomer during VDC polymerization is not so strong as that during VC polymerization.

Comparison of the present model with the Wessling model

In the Wessling model, polymerization in the monomer phase was neglected and only the surface polymerization was considered, whereas in the present model, polymerizations both in the monomer phase and on the surface were considered. Although the polymerization rate in the surface layer is much larger than the rate in the monomer phase for a unit volume, the amount of monomer in the surface layer is much less than that in the monomer phase. Therefore, it may not be reasonable that polymerization in the monomer phase is neglected in the Wessling model.

CONCLUSIONS

The kinetic model for VDC polymerization obtained in the previous paper is simplified in the present article. The present simplified model does not contain the parameters K^* and K'_{de} , which have not yet been accurately determined. A series of kinetic experiments was carried out to estimate the kinetic parameters and evaluate the present model for VDC heterogeneous polymerization. The present model prediction was compared with the experimental data. The result shows that the model is in good agreement with experimental data and can be used to predict polymerization rate and conversion over nearly the entire conversion range.

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