

Kinetics of Heterogeneous Polymerization of Vinylidene Chloride. I. Mechanism and Modeling

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Received 16 January 2003; accepted 23 July 2003

ABSTRACT: The similarities and differences between the heterogeneous polymerization of vinylidene chloride (VDC) and vinyl chloride (VC) were compared and analyzed. The effect of the poly(vinylidene chloride)(PVDC) crystal morphology on the kinetics of VDC polymerization was discussed. Based on the assumption that polymerization occurs in the monomer phase and on the edges of the PVDC lamellar crystals, a mechanism of VDC polymerization is pro-

posed and then a kinetic model for VDC bulk/suspension polymerization is developed according to the elementary reactions. The model can be used to predict polymerization rate and conversion. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2576–2581, 2004

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

INTRODUCTION

Vinylidene chloride (VDC) polymer has long been an important commercial material,¹ which was among the first synthetic polymers to be commercialized before 1940. However, so far the kinetics of VDC polymerization has scarcely been studied and the kinetic data are noticeably absent, especially over the entire conversion range. A set of kinetic data over the entire conversion range reported by Robert² in 1943 has been perpetually cited in the literature.^{1,3} The kinetic model proposed by Wessling⁴ in 1971 is still the only significant paradigm that considers the morphology of the poly(vinylidene chloride) (PVDC) crystal, although this case is defective for the ongoing development of VDC polymers. Investigations of the kinetics of VDC polymerization have become increasingly more important along with the extensive development and application of new products of VDC polymer in recent years.^{1–8}

Comparatively, the kinetics of vinyl chloride (VC) polymerization has been extensively studied.^{9–11} Some excellent mechanisms and kinetic models for VC polymerization have been proposed. The experience for studying kinetics of VC polymerization is very important and can be used to study the kinetics of VDC polymerization.

In the present article, the similarities and differences between heterogeneous free-radical polymerization of VDC and VC are discussed. Based on the discussion, a mechanism is proposed according to the feature of VDC polymerization. A kinetic model for VDC bulk/suspension polymerization is developed from the elementary reactions. The present model can be used to predict polymerization rate and conversion. The authors expect to offer a theoretical foundation for the study of VDC copolymerization kinetics through this work.

THEORETICAL ANALYSIS

VDC polymerization is a typical heterogeneous free-radical polymerization like VC polymerization. Therefore, the kinetic behaviors for both show some similarities. For example, both PVDC and poly(vinyl chloride) (PVC) are insoluble in their own monomers, and so the polymers precipitate from their own monomer phases at very low conversion in the polymerization process. Autoacceleration appears at the very start as a result of the effect of polymer phase.^{1,4,9–11} However, the polymerization kinetic behaviors of these two monomers also demonstrate a series of significant differences, which are summarized and discussed in the following subsections.

Difference of polymer swellability

PVC is practically insoluble (<0.01%) in VC, but PVC may be swollen with about 30% VC monomer. Thus, VC polymerization occurs in the monomer and the polymer-rich phases simultaneously.^{9–11} The addition

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Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 20166001.

Contract grant sponsor: Nature Science Foundation of Jiangxi Province, China.

of "dead" PVC to the system will cause a significant increase in the rate of polymerization because the polymerization rate within the polymer phase is faster than that in the monomer phase.^{13,14} For VDC polymerization, however, the polymer (PVDC) cannot be swollen by VDC monomer. Hence, no reaction will occur within the solid phase. Polymerization can occur only in the monomer phase and on the surface of polymer.⁴ In contrast to VC polymerization, no increase in rate was observed on adding "dead" PVDC to the system. This lack of enhancement of the reaction by "dead" polymer is believed to be attributable to poisoning of the surface of PVDC by some component of the air.^{13,14}

Difference of chain transfer

In VC polymerization, there is a significant amount of chain transfer to monomer caused by head-to-head addition of the monomer double bond to the radical center.^{10,11} It plays a very important role in controlling molecular weight and such that the molecular weight of PVC is practically independent of initiator concentration in the polymerization temperature range of 40–65°C.^{9–11} In VDC polymerization, however, no significant head-to-head addition can be present because the 1,1-disubstitution of chlorine atoms causes steric interactions^{1,4} and so there is no significant quantity of chain transfer to monomer. Therefore, the molecular weight of PVDC is an inverse function of the initiator concentration,¹⁵ like that of most polymers.

In ordinary chains of PVC, there is a significant amount of branching.^{9,10} However, both NMR and infrared spectra show that no significant amounts of branching exist in the chains of PVDC.^{4,11} Determination of the branching coefficient for PVDC (n) by the method of Houwink gives $n = 1$. This unusually low value and the marked tendency to crystallize constitute strong evidence that the chains of PVDC are not branched,^{1,4,11} which indicates no significant quantity of chain transfer to polymer and to monomer in the VDC polymerization process, which is significantly different from that in VC polymerization.

Difference of polymer morphology

The morphology of as-polymerized PVDC is quite different from that of PVC. Nearly spherical aggregates form in the PVC system,¹⁰ whereas anisotropic growth occurs in the PVDC system.¹ The highly crystalline particles of PVDC precipitated during polymerization are aggregates of thin lamellar crystals.¹⁶ The substructures are 5–10 nm thick and 100 or more times in other dimensions.¹⁶ PVDC is known to crystallize in the form of folded-chain crystals^{1,4,16,17} that can be described by the Keller model.

The morphology of as-polymerized PVDC is a consequence of its highly crystalline nature. Like most crystalline polymers, it precipitates from solution in the form of lamellar-folded chain crystals when the solvent medium is thermodynamically favorable (i.e., where the Flory–Huggins interaction parameter χ is less than $\frac{1}{2}$). Solubility study on PVDC suggests that the monomer should be a thermodynamically favorable solvent for amorphous PVDC.⁴ Therefore, the polymer chains should not precipitate until they contact a crystalline surface or combine with other molecules to form a crystal nucleus.^{4,17,18} This may be the main reason that anisotropic growth occurs for PVDC.

MECHANISM OF VDC POLYMERIZATION

Based on the preceding properties of VDC polymerization and the results of studies reported in the literature,^{1,4,16} one can summarize the main dynamic features of VDC polymerization as follows.

Conversion $X < X_0$

A homogeneous polymerization occurs at very low conversion ($X < X_0$), but the stage will be neglected in the present model because X_0 is very small ($X_0 < 0.1\%$).

Conversion $X < X_0 < X_f$

At some point (X_0) early in the polymerization the VDC monomer will become supersaturated with PVDC and PVDC crystals will begin to precipitate. The rate of nucleation of PVDC particles should be very high at the start but should fall quickly to zero as the supply of polymer is exhausted. Then, provided the rate of crystal growth is sufficient to consume polymer as quickly as it forms, no new particles will develop.

In the period ($X_0 < X < X_f$) the reaction occurs in the monomer phase and on the crystalline surface of PVDC. No reaction occurs within the PVDC crystals because PVDC cannot be swollen by its own monomer. Polymer chains can be attached to the crystalline surface with the active end dangling out in a layer of monomer on the crystalline surface of PVDC. Monomer units continue to add to the end until it is long enough to traverse the lamellar thickness and then growth will continue on the opposite side of the lamella. The process will be repeated until the chain is terminated by an incoming radical. In terms of the view of Wessling,⁴ the reactions are confined to the crystalline surface of the edges of the lamellar crystals. The two sides of lamellar crystal constitute an amorphous surface, which cannot attach polymer radicals, and so no surface reactions occur on them. In fact, the surface reactions take place in a thin layer of monomer

on the crystalline surface of the edges of the lamellar crystals, which is called the surface layer for short. On the other hand, the polymer that forms in the monomer phase can also precipitate quickly to the crystalline surface of PVDC.

Conversion $X > X_f$

The above case will continue until the critical conversion X_f at which the monomer in liquid phase is just exhausted, although there is still a considerable amount of monomer attached to the surface and in the tiny capillary of polymer. After the conversion X_f , the pressure and the polymerization rate will gradually decrease with conversion. It is because the capillary in polymer deflates with conversion, which causes the capillarity to become stronger, and the thickness of the monomer layer attached to the crystalline surface decreases or falls partially to zero because of the consumption of monomer to produce polymer without the supply of monomer from the liquid phase.

At the stage of steady reaction ($X_0 < X < X_f$), a mechanism for the heterogeneous polymerization of VDC should include reactions in the monomer phase and the surface layer. The kinetic behavior of reaction in the monomer phase is similar to homogeneous polymerization but the formed polymer will precipitate quickly to the crystalline surface of PVDC. In the surface layer, the polymer radicals attached to the crystalline surface of PVDC should be terminated more slowly than in the monomer phase because they cannot move freely, so that the radical concentration in the surface layer is higher and the rate of polymerization is more rapid.

In terms of the above conclusion, the mechanism of VDC polymerization is proposed and shown in Table I. It can be seen from Table I that there are initiation, propagation, chain transfer, and termination steps in both the monomer phase and the surface layer. Radicals with different chain length can transfer between the monomer phase and the surface layer, and the chains of polymer formed in the monomer phase precipitate quickly to the crystalline surface.

MODEL DEVELOPMENT

For kinetic modeling, it is reasonable to assume that reactions occur in the monomer phase and the surface layer simultaneously from the very start of the polymerization up to the conversion X_f and after the conversion X_f , reactions occur only in the surface layer. Therefore, a model valid over the entire conversion range must describe two-section polymerization before and single-section polymerization after conversion X_f . Thus, when conversion is before X_f , the following equations apply for a batch reactor:

TABLE I
Mechanism of VDC Polymerization

Elementary reaction	In monomer phase (1)	In the surface layer (2)
Initiation	$I \xrightarrow{K_{s1}} 2R_0$	$I \xrightarrow{K_{s2}} 2R_0$
	$R_0 + M \xrightarrow{k_{i1}} R_1$	$R_0 + M \xrightarrow{k_{i2}} R_1$
Propagation	$R_r + M \xrightarrow{k_{p1}} R_{r+1}$	$R_r + M \xrightarrow{k_{p2}} R_{r+1}$
Chain transfer	$R_r + M \xrightarrow{k_{m1}} P_r + R_1$	$R_r + M \xrightarrow{k_{m2}} P_r + R_1$
	$R_r + P_s \xrightarrow{k_{p1}} P_r + R_s$	$R_r + P_s \xrightarrow{k_{p2}} P_r + R_s$
Termination	$R_r + R_s \xrightarrow{k_{t1}} P_{r+s}$	$R_r + R_s \xrightarrow{k_{t2}} P_{r+s}$
	$R_r + R_s \xrightarrow{k_{t1}} P_r + P_s$	$R_r + R_s \xrightarrow{k_{t2}} P_r + P_s$
Radical transfer		$(R_r)_1 \xleftarrow{k_{a,r} \leq r_c} (R_r)_2$
		$(R_r)_1 \xrightarrow{k_{a,r} > r_c} (R_r)_2$
Polymers precipitate		$(P_r)_1 \xrightarrow{k} (P_r)_2$

$$-\frac{dM}{dt} = k_{p1}[R]_1[M]_1V_1 + k_{p2}[R]_2[M]_2V_2 \quad (1)$$

The polymerization rate in terms of conversion per unit time can be expressed as

$$\frac{dX}{dt} = k_{p1}[R]_1 \frac{M_1}{M_0} + k_{p2}[R]_2 \frac{M_2}{M_0} \quad (2)$$

where $[R]_1$ and $[R]_2$ are the concentrations of radical; $[M]_1$ and $[M]_2$ are the molar concentrations of monomer and M_1 and M_2 are the number of moles of monomer in the monomer phase and the surface layer, respectively; and M_0 is the initial number of moles of monomer VDC in the system.

The equations to calculate M_1 and M_2 are developed as follows:

$$M_1 = M_0(1 - X) - M_2 \quad (3)$$

Based on the Wessling lamellar crystal model,^{4,16} M_2 can be expressed as⁴

$$M_2 = \frac{\rho V_2}{M_m} = \frac{\rho d}{M_m} A$$

$$= \frac{\rho d}{M_m} \left[\frac{4hV_p(q+1)^2}{q} \right]^{1/2} \left(\frac{N}{M_0} \right)^{1/2} M_0 X^{1/2} \quad (4)$$

where ρ is the density of VDC, M_m is the molecular weight of VDC, d is the thickness of the surface layer in which the surface reaction occurs, A is the area of the crystalline surface of PVDC, V_2 is the volume of monomer in the surface layer, h is the thickness of lamellar crystal, q is the ratio of large dimensions of lamellar crystal, V_p is the molar volume of PVDC, and N is the particle number of the polymer. Let

$$P = \frac{\rho d}{M_m} \left[\frac{4hV_p(q+1)^2}{q} \right]^{1/2} \left(\frac{N}{M_0} \right)^{1/2} \quad (5)$$

Then eq. (4) may then be expressed as

$$M_2 = PM_0 X^{1/2} \quad (6)$$

where P is a complicated value. It is a function of crystal morphology, densities of monomer and polymer, particle number, and so forth. However, the study of Wessling⁴ indicated that it can approximately be assumed as constant under some conditions.

The equations to calculate $[R]_1$ and $[R]_2$ are developed as follows.

From the previous section, one may note that there is no mass transfer of radicals from the monomer phase to the surface layer when the chain length $r \leq r_c$. Radicals with $r > r_c$ can transfer from the monomer phase to the surface layer by precipitation and capture. On the other hand, desorption of radicals from the crystalline surface is limited to the radicals with chain length $r \leq r_c$. Thus the total radical balance for the two sections in the system can be expressed as follows:

$$\frac{d(R)_1}{V_1 dt} = R_{I1} - k_{p1}[M]_1[R_{rc}]_1 - k_{t1}[R]_1^2$$

$$+ K_{de} \sum_{r=1}^{rc} [R_r]_2 V_2 / V_1 = 0 \quad (7)$$

$$\frac{d(R)_2}{V_2 dt} = R_{I2} + k_{p1}[M]_1[R_{rc}]_1 V_1 / V_2$$

$$- k_{t2}[R]_2^2 - K_{de} \sum_{r=1}^{rc} [R_r]_2 = 0 \quad (8)$$

where $(R)_1$ and $(R)_2$ are radical number of moles, and R_{I1} and R_{I2} are the initiation rates in the monomer phase and the surface layer, respectively.

To calculate $[R_{rc}]$ and $K_{de} \sum_{r=1}^{rc} [R_r]_2$, the involved radical balances are expressed as follows:

$$\frac{d(R_1)_1}{V_1 dt} = R_{I1} - k_{p1}[M]_1[R_1]_1 - k_{t1}[R]_1[R_1]_1$$

$$+ k_{fm1}[M]_1[R_1]_1 + K_{de}[R_1]_2 V_2 / V_1 = 0 \quad (9)$$

$$\frac{d(R_1)_2}{V_2 dt} = R_{I2} - k_{p2}[M]_2[R_1]_2 - k_{t2}[R]_2[R_1]_2$$

$$+ k_{fm2}[M]_2[R_1]_2 - K_{de}[R_1]_2 = 0 \quad (10)$$

$$\frac{d(R_{rc})_1}{V_1 dt} = k_{p1}[M]_1[R_{rc-1}]_1 - k_{p1}[M]_1[R_{rc}]_1$$

$$- k_{t1}[R]_1[R_{rc}]_1 = 0 \quad (11)$$

$$\frac{d(R_r)_2}{V_2 dt} = k_{p2}[M]_2[R_{r-1}]_2 - k_{p2}[M]_2[R_r]_2$$

$$- k_{t2}[R]_2[R_r]_2 = 0 \quad (12)$$

where $(R_1)_1$ and $(R_1)_2$ are the number of moles of radical with chain length $r = 1$ in the monomer phase and the surface layer, respectively.

From eq. (9), one obtains

$$[R_1]_1 = \frac{R_{I1} + k_{fm1}[M]_1[R_1]_1}{k_{p1}[M]_1 + k_{t1}[R]_1 - K_{de} V_2 / V_1} \quad (13)$$

From the information on microstructure of PVDC, one knows that the chain transfer to monomer in VDC polymerization is much less than that in VC polymerization. Therefore, $R_{I1} \gg k_{fm1}[M]_1[R_1]_1$. It can be assumed like VC polymerization that $k_{p1}[M]_1 \gg k_{t1}[R]_1 - K_{de} V_2 / V_1$. By substituting these into eq. (13), one obtains

$$[R_1]_1 = \frac{R_{I1}}{k_{p1}[M]_1} \quad (14)$$

From eq. (10), one obtains

$$[R_1]_2 = \frac{R_{I2} + k_{fm2}[M]_2[R_1]_2}{k_{p2}[M]_2 + k_{t2}[R]_2 + K_{de}} \quad (15)$$

Similarly, $k_{p2}[M]_2 \gg k_{t2}[R]_2 + K_{de}$ and $R_{I2} \gg k_{fm2}[M]_2[R_1]_2$ can be assumed and then one obtains

$$[R_1]_2 = \frac{R_{I2}}{k_{p2}[M]_2} \quad (16)$$

From eqs. (11) and (12) one obtains

$$[R_{rc}]_1 = \frac{k_{p1}[M]_1[R_{rc-1}]_1}{k_{p1}[M]_1 + k_{t1}[R]_1} = \left(\frac{1}{1 + \tau_1}\right)[R_{rc-1}]_1$$

$$= \left(\frac{1}{1 + \tau_1}\right)^{rc-1} [R]_1 \quad (17)$$

$$[R_r]_2 = \frac{k_{p2}[M]_2[R_{r-1}]_2}{k_{p2}[M]_2 + k_{t2}[R]_2} = \left(\frac{1}{1 + \tau_2}\right)[R_{r-1}]_2$$

$$= \left(\frac{1}{1 + \tau_2}\right)^{r-1} [R]_2 \quad (18)$$

In eqs. (17) and (18)

$$\tau_1 = \frac{k_{t1}[R]_1}{k_{p1}[M]_1}, \quad \tau_2 = \frac{k_{t2}[R]_2}{k_{p2}[M]_2}$$

By substituting eqs. (14) and (16) into eqs. (17) and (18) one obtains

$$[R_{rc}]_1 = \left(\frac{1}{1 + \tau_1}\right)^{rc-1} \frac{R_{I1}}{k_{p1}[M]_1} = K^* \frac{R_{I1}}{k_{p1}[M]_1} \quad (19)$$

$$[R_r]_2 = \left(\frac{1}{1 + \tau_2}\right)^{r-1} \frac{R_{I2}}{k_{p2}[M]_2} \quad (20)$$

Thus

$$K_{de} \sum_{r=1}^{rc} [R_r]_2 = K_{de} \sum_{r=1}^{rc} \left(\frac{1}{1 + \tau_2}\right)^{r-1} \frac{R_{I2}}{k_{p2}[M]_2} = K'_{de} R_{I2} \quad (21)$$

where the desorption rate parameter of radicals is

$$K'_{de} = \frac{K_{de}}{k_{p2}[M]_2} \sum_{r=1}^{rc} \left(\frac{1}{1 + \tau_2}\right)^{r-1}$$

and the precipitation parameter of radicals is

$$K^* = \left(\frac{1}{1 + \tau_1}\right)^{rc-1}$$

By substituting eqs. (19) and (21) into eqs. (7) and (8), one obtains

$$R_{I1} - K^* R_{I1} - k_{t1}[R]_1^2 + K'_{de} R_{I2} V_2 / V_1 = 0 \quad (22)$$

$$R_{I2} + K^* R_{I1} V_1 / V_2 - k_{t2}[R]_2^2 - K'_{de} R_{I2} = 0 \quad (23)$$

By solving eqs. (22) and (23) one can obtain the polymer radical concentrations in the monomer phase and the surface layer respectively, as follows:

$$[R]_1 = \frac{1}{k_{t1}^{1/2}} [(1 - K^*) R_{I1} + K'_{de} R_{I2} V_2 / V_1]^{1/2} \quad (24)$$

$$[R]_2 = \frac{1}{k_{t2}^{1/2}} [(1 - K'_{de}) R_{I2} + K^* R_{I1} V_1 / V_2]^{1/2} \quad (25)$$

By substituting eqs. (24) and (25) into eq. (2), one can rewrite the polymerization rate as

$$\frac{dX}{dt} = \frac{k_{p1}}{k_{t1}^{1/2}} \left[(1 - K^*) R_{I1} + K'_{de} R_{I2} \frac{V_2}{V_1} \right]^{1/2} \frac{M_1}{M_0}$$

$$+ \frac{k_{p2}}{k_{t2}^{1/2}} \left[(1 - K'_{de}) R_{I2} + K^* R_{I1} \frac{V_1}{V_2} \right]^{1/2} \frac{M_2}{M_0} \quad (26)$$

Equation (26) is a basic form of the present kinetic model for VDC heterogeneous polymerization. Comparing eq. (26) with the kinetic model of VC polymerization in the literature,^{9,10} it can be seen that there are two obvious differences between them, although their forms are sort of similar. One difference is that in the kinetic model of VC polymerization^{9,10} the chain transfer to monomer plays a very important role, whereas it is neglected in eq. (26) because of the lack of a significant amount of chain transfer to monomer in the VDC polymerization process. Another difference is that the meaning of M_2 in eq. (26) differs from M_2 in the kinetic model of VC polymerization. For VC polymerization^{9,10} M_2 indicates the amount of monomer swollen within the polymer (PVC), whereas for VDC polymerization M_2 is the amount of monomer in the surface layer.

If the density of VDC, initiator concentration, and initiation rate in the monomer phase are equal to those in the surface layer, then one obtains

$$R_{I2} = R_{I1} = f k_d [I], \quad \frac{M_1}{M_0} = \frac{V_1}{V_0}, \quad \frac{M_2}{M_0} = \frac{V_2}{V_0}$$

where V_0 is the initial total volume of monomer. Furthermore, let

$$k_1 = k_{p1} \left(\frac{f k_d}{k_{t1}} \right)^{1/2}, \quad H = \frac{k_{p2}}{k_{t2}^{1/2}} / \frac{k_{p1}}{k_{t1}^{1/2}}$$

where $H \gg 1$ is attributed to $k_{t2} \ll k_{t1}$. Then eq. (26) can be rewritten as follows:

$$\frac{dX}{dt} = k_1[I]^{1/2} \left\{ \left[(1 - K^*) \frac{V_1}{V_0} + K'_{de} \frac{V_2}{V_0} \right]^{1/2} \left(\frac{V_1}{V_0} \right)^{1/2} + H \left[(1 - K'_{de}) \frac{V_2}{V_0} + K^* \frac{V_1}{V_0} \right]^{1/2} \left(\frac{V_2}{V_0} \right)^{1/2} \right\} \quad (27a)$$

$$\frac{dX}{dt} = k_1[I]^{1/2} \left\{ \left[(1 - K^*) \frac{M_1}{M_0} + K'_{de} \frac{M_2}{M_0} \right]^{1/2} \left(\frac{M_1}{M_0} \right)^{1/2} + H \left[(1 - K'_{de}) \frac{M_2}{M_0} + K^* \frac{M_1}{M_0} \right]^{1/2} \left(\frac{M_2}{M_0} \right)^{1/2} \right\} \quad (27b)$$

CONCLUSIONS

The similarities and differences between the heterogeneous polymerization of VDC and VC were compared and analyzed. The result shows that the kinetic behavior of VDC heterogeneous polymerization is significantly different from that of VC polymerization. Based on assuming that polymerization occurs in the monomer phase and the surface layer on the edges of the PVDC lamellar crystals, a mechanism of VDC polymerization is proposed and then a kinetic model for VDC polymerization is developed according to the elementary reactions. The present model can be used to predict polymerization rate and conversion.

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