

Review

KINETICS OF VINYL CHLORIDE (CO)POLYMERIZATION AT HIGH CONVERSION

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Abstract This paper provides a summarized review on the kinetics of vinyl chloride homopolymerization in the absence and presence of chain transfer agents, of VC/DAP(diallyl phthalate) copolymerization with chain extension and/or slightly crosslinking functions, and of vinylidene chloride/VC random copolymerization. Models of rate, degree of polymerization or molecular weight, copolymer composition, gel fraction and crosslinking density were proposed and interpreted mechanistically.

Keywords Vinyl chloride, Chain transfer, Polymerization kinetics, Copolymerization, Crosslinking

Polyvinyl chloride(PVC) is a large-tonnage polymer. The degree of polymerization (DP) and particle characteristics (average particle size and its distribution, and morphology) are the dominant characteristic parameters of PVC. It may be divided into two main aspects for studying the effects of various factors on these two parameters and also for controlling them: (1) mechanistic or kinetic aspects, including the kinetics of initiator decomposition, the kinetics of polymerization, heat transfer and temperature control, aiming at controlling the polymerization rate and DP of PVC; (2) particle formation mechanism aspects concerning dispersants, liquid-liquid dispersion, agitation and mixing in the reactor, aiming at controlling the particle size and morphology of PVC. Studies on random, slightly crosslinking and graft copolymerizations may be also carried out along these two aspects though there will be some differences between these copolymerizations and the homopolymerization of PVC. This paper will give a summarized review on our recent research work of kinetics of vinyl chloride (co)polymerization at high conversion.

RATE MODELS OF VINYL CHLORIDE POLYMERIZATION

The DP of general-purpose PVC prepared at the temperature range of 45~70°C is independent of the initiator concentration and monomer conversion, but is only controlled by the polymerization temperature since the chain transfer reaction to vinyl chloride (VC) is a controlling factor of DP . The polymerization rate may thus be regulated by temperature only. This mechanistic feature will simplify research work on the factors affecting the polymerization rate and DP , and will make it more convenient in terms of their regulation and control.

Two-Phase Mechanistic Model^{1, 2)}

Until the mid-sixties only initiators with lower activity, such as 2, 2'-azobisisobutyronitrile (AIBN), were used in the polymerization of vinyl chloride (VC). At the same time, the rate model was limited to experimental correlation in the form of series or power equations. In 1966

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Talamini^[3] proposed the two-phase mechanistic model for the VC polymerization. Thereafter, Aldel-Alim, et al.^[4], made some modifications to the model, but these were limited to the use of lower active initiators, which was far from commercial practice.

PVC/VC is a partially miscible system. PVC is practically insoluble in VC monomer (< 0.01%), but VC may be soluble in PVC up to 30%. At the beginning of VC polymerization, PVC will precipitate out and separate into two phases. In the conversion range of 0~70%, the VC polymerization takes place in the monomer phase (0.01%) and the polymer-rich phase separately. The authors of the paper proposed a set of hypotheses: initiation may take place in the two phases, but propagation and termination occur mainly in the polymer-rich phase; primary or oligomeric radicals will diffuse from the monomer phase into polymer-rich phase and continue to propagate or terminate with long chain radicals in the latter phase, but the chain radical in the polymer-rich phase cannot diffuse back to the monomer phase; *DP* is controlled by the chain transfer reaction to the monomer; both the volume contraction and the decrease of initiator concentration in the polymerization process are considered, etc. A series of elementary reactions were listed and an improved mechanistic model of conversion rate (dC/dt) was derived on the basis of these hypotheses.

$$\frac{dC}{dt} = 2Df \frac{k_p k_d}{k_a} [I]_0 + k_p \left(\frac{f k_d}{k_{t2}} \right)^{\frac{1}{2}} [I]_0^{\frac{1}{2}} \left[\frac{D' \rho_p A^2}{V_0 (\rho_m + A \rho_p)} \right]^{\frac{1}{2}} C^{\frac{1}{2}} \quad (1a)$$

where

$$D = \frac{2V_1}{1 + \sqrt{1 + 8\psi^2 V_1^2}}, \quad D' = \frac{2V_0}{1 + \sqrt{1 + 8\psi^2 V_1^2}}, \quad \psi = \frac{\sqrt{R_{i1} k_{t1}}}{k_a}, \quad A = \left(\frac{M}{P} \right)_2$$

ρ = density, k_a = rate constant for free radical adsorption, V_0 = initial volume, V = volume, M or m = monomer, P or p = polymer, subscripts 1 and 2 = monomer phase and polymer-rich phase, respectively. Other symbols are the same as those used in general textbooks.

Equation (1a) may be simplified to:

$$\frac{dC}{dt} = \alpha + \beta C^{1/2} \quad (1b)$$

This shows that the polymerization rate is proportional to the square root of the conversion. This has been checked with VC polymerization experiments with AIBN, ABVN (azobisdimethylvaleronitrile) and DCPD (dicyclohexyl peroxydicarbonate) as initiators of lower, medium and higher activity in the temperature range of 50 ~ 62 °C^[1]. This indicates that the hypotheses for modeling are rational.

Experimental Model^[2, 5, 6]

A number of kinetic parameters which are difficult to measure are needed in the application of the above mechanistic model. An experimental model for correlating conversion with time was proposed to meet the need of industrial control as follows.

$$C = kt^n \quad (2)$$

where k is the initial rate (% / h), n is the acceleration factor (= 1 ~ 2.2) (see Refs.[5, 6]). Equation (2) gave a good agreement with the experimental conversion-time data in the temperature range of 50~62 °C in the presense of various types of initiators with half-lives of 2 ~ 74 h. Meanwhile, it was discovered that the n values approach heat distribution indexes R (the ratio of maximum conversion rate to average conversion rate). The value of n or R mainly depends on the half life of the initiators, and the polymerization time will have considerable effect on n . n values have been collected in Refs.[5, 6] and may be used to design the recipe of initiators. The acceleration factor, n , is 1 when the half-life equals 2 h, i.e., it is equivalent to the homogeneous polymerization rate. It is a constant aim to increase the heat transfer or productive capacity of the reactor. An initiator

system complexed from initiators with lower and higher activities may be used if no single initiator with proper half-life can be selected.

In the suspension-swelling graft copolymerization process of chloropolyethylene (CPE)-g-VC, the conversion-time relationship may be also estimated from an experimental model^[7] though CPE will retard the graft copolymerization somewhat at the earlier stage of the process. Ref.[8] gave the ternary equilibrium of CPE-VC-PVC system, which is important fundamental information in the process.

Theoretical Consumption of Initiator^[5, 6]

From the average of more than 10 initiator recipes, it may be concluded that the theoretical consumption of initiator (N_t , mol/ton VC) in VC polymerization under normal polymerization conditions approaches a constant value (1 ± 0.1 mol/ton VC). The amount of initiator (N_0 , mol/ton VC) in the recipe of VC polymerization may thus be estimated from this rule so as to save on experiment time and reagents.

$$N_t = N_0 (1 - [I] / [I]_0) = 1 \pm 0.1 \text{ mol/ton VC} \quad (3)$$

where $[I]_0$ and $[I]$ are the concentration of the initiator at the beginning of polymerization ($t = 0$) and time t .

There are two abnormal cases of deviations from the theoretical consumption of initiator: (1) the theoretical consumption may be lowered to 0.8 mol/ton VC in the case of longer polymerization time caused by much lower amounts of initiator; and (2) it will increase to 1.2~2.0 mol/ton VC in the case of shorter polymerization times when more initiator is used. Estimation of the initiator amount under these two abnormal cases will result in greater deviation.

DEGREE OF POLYMERIZATION OF POLYVINYL CHLORIDE

Suspension-PVC may be divided into three main types from their difference in the DP : (1) general purpose, $DP = 700\sim 1500$; (2) higher DP ($= 1600\sim 4000$) for thermoplastic elastomer; (3) lower DP ($= 700\sim 400$) for injection molding and for transparent rigid sheet.

A generalized equation of kinetic chain length at lower conversion or instantaneous DP at disproportionation termination may be derived from the mechanism of free radical polymerization.

$$\frac{1}{\bar{p}} = \frac{1}{\bar{p}_0} + C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} \quad (4)$$

The average DP at higher conversion should be integrated and averaged from the instantaneous DP over the entire conversion. But the form of eq. (4) may also be used to represent the DP at higher conversion if the effect of conversion on DP can be neglected. But C_M , C_I , C_S are preferably defined as the apparent- or pseudo-chain transfer constants, and their values will be somewhat different from microscopic chain transfer constants.

Single-Factor Control by Polymerization Temperature^[9]

The chain transfer to monomer is the main termination mode in the VC polymerization. $DP(\bar{P})$ of general purpose PVC (700~1500) is independent of the initiator concentration and conversion. Thus, the integrated average DP equation may be represented by that of the instantaneous DP . In this case, DP of PVC is controlled by the polymerization temperature or chain transfer constant to monomer only in the following equation.

$$\frac{1}{\bar{p}} = C_M = 13400 \exp(-45000 / RT) \quad (5)$$

C_M is calculated to be 1.23×10^{-3} at 60°C .

Two-Factor Control by Polymerization Temperature and Initiator Concentration^[9]

The DP of PVC may be lowered by decreasing the polymerization temperature. But the chain transfer to initiator cannot be neglected in the preparation of PVC with higher DP (1700~2500) at lower temperature below 45°C in the presence of DCPD ($= 0.393 \sim 1.179$ mmol/mol VC) as initiator, as shown in Table 1. P_1 is calculated from eq. (5), while P_2 is experimental data and may be reduced to eq. (6). The difference between them will increase with the decrease in temperature, i.e., the effect of initiator concentration on DP becomes predominant gradually and should not be neglected.

Table 1. Relationship between DP of PVC and polymerization temperature

$T(^{\circ}\text{C})$	60	55	50	45	40	35	30	25
P_1	849	1087	1402	1825	2395	3170	4236	5714
P_2	846	1082	1394	1806	1340	3014	3753	4271
ΔP	3	5	8	19	53	156	483	1443

Initiator [DCPD] = 0.393~1.179 mmol/mol VC

$$\frac{1}{P} = C_M + C_I \frac{[I]}{[M]} = 13400 \exp\left[-\frac{45000}{RT}\right] + 100 \exp\left[-\frac{20500}{RT}\right] \left(\frac{[I]}{[M]}\right) \quad (6)$$

The temperature difference for heat transfer and the productive capacity of the reactor will decrease with lower polymerization temperatures. Therefore, PVC with $DP > 2500$ is rarely prepared by lowering the polymerization temperature only, but may be synthesized from the copolymerization of VC with small amount of divinyls as chain extension or slightly crosslinking agent.

Two-factor Control by Polymerization Temperature and Chain Transfer Agent Concentration^[10,11]

PVC with lower DP (700 ~ 400) may be prepared at higher polymerization temperatures. But the chain transfer agent, such as mercaptoethanol is usually added to regulate DP of PVC in order to avoid too high a vapor pressure of VC in the reactor at higher temperature and to decrease the degree of branching. The interaction between the chain transfer agent and initiator^[10] and its effect on DP ^[11] are factors that must be considered.

Chain transfer agents such as mercaptoethanol are reducing agents and will react with peroxide initiators, with the exception of lauryl peroxide. Usually, excess mercaptoethanol and peroxide initiator should be used in the recipe of VC polymerization. But mercaptoethanol and azo-initiator may be used together and still give good results^[11].

The effect of chain transfer reaction of chain transfer agents on DP should be considered, but the effect of the same to initiators on DP may be neglected in the preparation of PVC with lower DP (700~400) at higher temperatures (55~70°C) in the presence of mercaptoethanol as the chain transfer agent and ABVN as the initiator. The equation of instantaneous DP may be used to represent the integrated average DP with apparent chain transfer constant if the effect of conversion on DP is small or the final conversion approaches a constant. DP equation of PVC may be correlated from experimental data as follows:

$$\frac{1}{P} = C_M + C_S \frac{[S]}{[M]} = 6718 \exp\left[-\frac{42,820}{RT}\right] + 383,100 \exp\left[-\frac{33,800}{RT}\right] \left(\frac{[S]}{[M]}\right) \quad (7)$$

The apparent chain transfer constant of mercaptoethanol (C_s) at 60°C is 1.893.

VC/DIALLYL PHTHALATE (DAP) COPOLYMERIZATION WITH CHAIN EXTENSION AND SLIGHTLY CROSSLINKING FUNCTIONS^[12-16]

The preparation of PVC with higher DP at lower polymerization temperature is limited because of the considerable decrease in temperature difference for heat transfer. DP of PVC with more than 2500 is rarely prepared by this method. But DP may be raised to a higher value, such as up to 3000 ~ 4000, in the VC/DAP copolymerization via chain extension or slight crosslinkage.

DAP is an appropriate comonomer among various types of divinyl monomers. The reactivity ratios of VC and DAP were measured at 45°C: $r_1 = 0.77$, $r_2 = 0.37$. A critical initial concentration of DAP exists in the VC/DAP copolymerization: $f_{cr} = 0.47 \sim 0.49$ mmol/mol VC. DAP acts as a chain extension agent to increase the DP of PVC when $f_2^0 < f_{cr}$. For example, the DP of PVC may be increased from 1800 to 3200 at 45°C when $f_2^0 = 0.40$. On the other hand, both chain extension and slightly crosslinking reactions will take place when $f_2^0 > f_{cr}$. The copolymer thus formed will consist of sol and gel fractions. The DP of the sol fraction decreases with an increase in DAP amount. At the same time, the gel content increases, the swelling ratio decreases, the crosslinking density increases, and the molecular weight between two crosslinking points decreases. The experimental results of VC/DAP with $f_2^0 = 0.67$ mmol/mol VC at 45°C are as follows: the DP of sol fraction is over 2000, the gel content is about 32.7%, the swelling ratio is up to 64.5, the lower crosslinking density (1.56×10^{-6} mol/g) and higher molecular weight between two crosslinking points are up to 320,000 (much higher than that of homo PVC = 69,000 at 45°C). But such slight crosslinkage does not affect the processibility.

Based on the experiments of VC/DAP crosslinking copolymerization, the model of molecular weight before the gel point^[13], the combined statistical and kinetic model of sol/gel partition^[14], the model of gel fraction^[15] and the model of crosslinking density^[16] after gel point were proposed.

COPOLYMERIZATION OF VINYLIDENE CHLORIDE/VINYL CHLORIDE (VDC/VC)

VDC/VC copolymer is a packaging material with excellent barrier property. Copolymer composition and molecular weight are the main factors which affect the barrier property, film formation behavior and strength.

Copolymer Composition^[17,18]

Polyvinylidene chloride (PVDC) is an insoluble crystalline polymer in most organic solvents and cannot melt for processing. Copolymerization of VDC with a certain amount of VC (such as 15 ~ 20%) will lower the crystallinity, increase the fluidity of melt and enhance the processibility, but only gives a little influence on the barrier property. The problem is to balance these comprehensive properties.

The reactivity ratios of VDC/VC were measured at three temperatures, among which $r_1 = 2.98$, $r_2 = 0.175$ at 45°C. From these data it may be expected that the copolymer composition distribution of VDC/VC copolymer from monomer feed of 85/15 weight ratio once charged at the beginning of the copolymerization will not be too broad.

From the differential equation of copolymerization, the relationship between the instantaneous composition of the copolymer F_1 and monomer feed composition f_1 may be expressed as follows:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (8)$$

f_1 will change with conversion, the integrated equation is as follows:

$$C = 1 - \left[\frac{f_1}{f_1^0} \right]^\alpha \left[\frac{f_2}{f_2^0} \right]^\beta \left[\frac{f_1^0 - \delta}{f_1 - \delta} \right]^\gamma \quad (9)$$

For the copolymerization system of $r_1 > 1$ and M_1 as main monomer, $F_1 \sim f_1$ is usually a linear function in the range of $f_1^0 = 0.65 \sim 1.0$, such as $F_1 = 0.4f_1 + 0.6$ for VDC/VC system. Therefore, a simplified integrated equation may be obtained:

$$C = 1 - \left(\frac{1 - f_1^0}{1 - f_1} \right)^{0.6} \quad (10)$$

The average copolymer composition $\overline{F}_1$ may be calculated from eq. (11) based on the C and f_1 value from eq. (9) or (10).

$$\overline{F}_1 = \frac{f_1^0 - (1 - C)f_1}{C} \quad (11)$$

The full integrated eq. (9) and simplified integrated eq. (10) will give the same degree of accuracy from the comparison of the calculated results with the experimental data, as shown in Table 2.

Table 2. Average copolymer composition

C (%)	5.7	10.6	29.3	42.1	51.8	61.2	67.3	79.8
$\overline{F}_{1,ex}$	0.919	0.914	0.909	0.902	0.899	0.880	0.880	0.857
$\overline{F}_1(\text{Eq9})$	0.917	0.915	0.908	0.902	0.897	0.890	0.885	0.869
$\overline{F}_1(\text{Eq10})$	0.913	0.911	0.905	0.900	0.895	0.889	0.885	0.893

The average copolymer composition $\overline{F}_1$ equals to 91.2 wt% and the VDC content ranges in 94.5~81.5% in the case of VDC/VC feed weight ratio = 85/15 once charged at the beginning of polymerization, and final conversion of 80%.

Molecular Weight^[17, 19]

There are a number of factors, such as polymerization temperature, initiator concentration, conversion, etc., affecting the molecular weight of VDC/VC copolymer. But the molecular weight would level off after the conversion becomes >35%. Therefore, the viscosity-average MW may be correlated with the initiator concentration at 45 °C,

$$\text{DCPD} \quad 1/\overline{M}_\eta = 4.93 \times 10^{-5} I_0^{1/2} + 2.86 \times 10^{-4} I_0 + 6.02 \times 10^{-6} \quad (12)$$

$$\text{IPP} \quad 1/\overline{M}_\eta = 6.83 \times 10^{-5} I_0^{1/2} + 7.24 \times 10^{-5} I_0 + 6.02 \times 10^{-6} \quad (13)$$

where IPP is di-isopropyl peroxydicarbonate. The coefficients of the three terms on the right side of eqs. (12) and (13) represent the contributions of the bimolecular termination, chain transfer to initiator, and chain transfer to monomer to MW of the copolymer. Comparing DCPD with IPP, there is only a little difference between the coefficients of the first term in these two equations, i.e., these two initiators affect the bimolecular termination closely. The coefficient of the second term in eq. (12) is about 4 times that in eq. (13), showing easy chain transfer to DCPD. This is why IPP is preferred in the plant. The equal coefficients of third term indicate the same chain transfer to monomer.

The effect of polymerization temperature on the viscosity-average MW may be expressed as follows:

$$\text{DCPD} \quad \overline{M}_\eta = 0.0468 \exp[37380/RT] \quad (T = 308 \sim 338K) \quad (14)$$

$$\text{IPP} \quad \overline{M}_\eta = 0.0272 \exp[32830/RT] \quad (T = 308 \sim 328K) \quad (15)$$

Polymerization Rate^[17, 20]

VDC/VC copolymerizes more slowly due to the cross-termination. The polymerization time is usually up to 20 h, even if a highly active initiator, such as peroxydicarbonate, is used. Based on

the feature of precipitation polymerization, the rate model of VDC/VC copolymerization was proposed as follows:

$$\frac{dC}{dt} = \alpha C^\beta I_0^\gamma \exp(-\gamma k_d t) \quad (16)$$

where α , β , γ are the model parameters, respectively:

$$\alpha = 9.63 \times 10^8 \exp[-68320 / RT], \quad \beta = -2.75 \times 10^{-9} \exp[44080 / RT], \quad \gamma = 0.310.$$

Usually, there will be no trouble in the heat transfer of the reactor due to the lower rate of heat generation since both the rate of VDC/VC copolymerization and heat of polymerization of VDC are low.

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