Study on Suspension Copolymerization Rate of Vinyl Chloride/*N*-phenylmaleimide

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ABSTRACT: The copolymerization rate of vinyl chloride(VC)/*N*-phenylmaleimide (PMI) was investigated. The cross termination constant φ was measured to be 8.3 by using nonlinear least square fitting. The value showed that the cross termination was significant. A model of the copolymerization rate of VC/PMI was obtained. Using the calculated modeling parameters, the effects of temperature and initiator concentration on the copolymerization rate were predicted. The predicted values were in good agreement with the experimental data. Acrylonitrile, a third monomer, was selected to reduce the range of copolymer composition of this system, but it further lowered the copolymerization rate. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2649–2656, 1999

Key words: vinyl chloride; *N*-phenylmaleimide; suspension copolymerization; copolymerization rate

INTRODUCTION

Polyvinylchloride (PVC) is a widely used thermoplastic polymer due to its unique chemical and physical properties. Many "modified" PVC resins have been developed to increase the impact strength. In recent years, PVC with good heat resistance has been developed also for new applications.[1,2]

The goal of this study was assessment of vinyl chloride monomer copolymerization with a monomer such as N-substituted maleimide monomer, whose incorporation into the backbone chain could present a considerable and promising interest. Since the latter has a structure of the 1,2-ethylenic type and a five-member planar ring that completely hinders the rotation of the imide residues around the backbone chain of the macromolecules, it must lead to copolymers with a great structural stiffness as well as high heat resistance.

Most of the literature concerning the copolymerization of N-substituted maleimide with vinyl chloride was reported in patents.[3–7] In these patents, the copolymerization technology, such as feeding modes, suspending agents, and product development, were mainly claimed. But the parameters of vinyl chloride/N-substituted maleimide copolymerization were not presented.[1,2] In addition, the copolymerization rate of these system has not yet been examined.

In this paper, the copolymerization of vinyl chloride and N-phenylmaleimide in suspension with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator was investigated. The main objective of this study was to investigate the effects of various factors on the copolymerization rate of vinyl chloride and *N*-phenylmaleimide.

EXPERIMENTAL

Materials

N-phenylmaleimide (PMI) was prepared by the Searle[8] method, recrystallized several times from

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the ethanol/water (volume ratio 1 : 2), and characterized by nuclear magnetic resonance, infrared (IR) spectra, and differential scanning calorimeter (DSC) in order to make sure that it was free from unreacted maleic anhydride and uncyclized maleamic acid. The purity of PMI was measured by elemental analysis.

Anal. Calcd. for $C_{10}H_7O_2N$(173.17): C, 69.39%; H, 4.074%; N, 8.088%. Found: C, 69.335%; H, 4.070%; N, 8.102%. IR spectrum(KBr): 3100, 1708, 1600, 1509, 1393, 1146, 830,755 and 697cm^{-1}. ^{1}H-NMR spectrum (δ), CDCl$_3$, 6.85ppm-(2H,—CH=CH—), 7.41ppm(5H, aromatics).

Vinyl chloride (VC) was of polymerization grade. Acrylonitrile (AN) was distilled before using.

Initiators

AIBN was purified by fractional crystallized by a two-stage procedure from ethanol four times, and then dried and stored in a dark cool place. Its melting point was determined with a Perkin-Elmer DSC-7 differential scanning calorimeter and found to be 104.2°C. Dicyclohexyl peroxydicarbonate (DCPD) and bis(2-phenoxy ethyl) peroxydicarbonate (BPPD) were washed twice with methyl alcohol before use.

Solvents and Precipitants

Tetrahydrofuran and ethanol were distilled before use.

Others

Hydroxypropylmethylcellulose (65SH50) and hydrolyzed poly(vinyl alcohol) (KH20) from Synthesis Chemical Co. of Japan were used as suspending agents.

Copolymerization

The copolymerization was carried out in a stainless steel tube. All the vessels were washed before use with distilled water, and dried under vacuum at 100°C for 24 h.

Accurately weighed PMI and AIBN were placed in a 200-mL stainless steel tube and swept with nitrogen. VC was added into the tube by a metering pump, then the sealed tubes were shaken in order to dissolve PMI in VC. Then the quantitative distilled water and suspending agents were put into the tubes by metering pump. Copolymerization was carried out in a water bath

thermostated at 50, 60, or 70°C. The tubes were turned to homogenize the system. The sealed tubes with the reaction mass were removed after an appropriate time interval and cooled immediately to stop the copolymerization. The contents were poured out and washed several times with distilled water, then dried under vacuum at 60°C, and weighed. The weighed mixture was dissolved in tetrahydrofuran, then poured into a large amount of ethanol, reprecipitated, and dried under vacuum at 60°C. Weighing the copolymer provided the weight conversion of VC/PMI copolymerization.

Copolymer Analysis

The composition of copolymer was calculated on the basis of the nitrogen content in the copolymer measured by an elemental analyzer (CARLO ERBA-1106).

The glass transition temperature (T_g) was measured using a Perkin-Elmer DSC-7. The 6–15 mg samples were scanned at a heating rate of 20°C/min under nitrogen.

RESULTS AND DISCUSSION

Copolymerization Process Analysis of VC/PMI

Free radical copolymerization of VC (M_1) and PMI (M_2) with AIBN as initiator was performed in a batch suspension process. The reactivity ratios of the two monomers (VC and PMI) are $r_1 = 0.03$, $r_2 = 3.82$,[1] respectively, showing that PMI is more active than VC. It may be expected that the cross termination will take place and that the copolymer composition is not constant during the batch process due to the great difference of these two reactivity ratios. The comparison of the conversion-time curve of VC homopolymerization to VC/PMI copolymerization is shown in Figure 1. It can be seen that the copolymerization rate was lower than homopolymerization rate.

Being different from the styrene/PMI [9] system, a charge-transfer complex (CTC) could not form between VC and PMI, since both the induction effect and donor effect of the Cl atom of VC are weak. This can be concluded from the polarity (e) and the resonance effect (Q), $e_1 = 0.2$, $e_2 = 1.7$, and $Q_1 = 0.044$, $Q_2 = 2.0$. Although the polymerization reactivity of PMI was high, the steric effect of the substituent of PMI played an important role beyond the high reactivity, namely, the large

Figure 1 Comparison between conversion-time curves of VC homopolymerization and VC/PMI copolymerization at 60°C, AIBN = 0.1% (wt).

phenyl hindered the propagation of the radical. On the other hand, the formation of a resonance-stabilized PMI radical involving intramolecular tautomerzation not only decreased the reactivity of PMI radical,[10] but also served as a monomolecular chain-terminating step, which will lower the copolymerization rate.

The content of PMI monomer in the recipe was not too large due to the limited solubility of PMI in the VC monomer. Generally, the solubility of PMI in VC was less than 30 g/100 g VC.

We could predict how the copolymer composition varies with molar conversion from the well-known Mayo–Lewis equation.[11] We defined n as the step of conversion, and i is the step of calculation, $i = 1, 2, 3, \ldots, n$. Let

$$pt = \frac{1}{n} \times \sum_{j=1,2} [M_j]_0 \qquad (1)$$

$[M_j]_0$ is the initial concentration of the two monomers, $j = 1, 2$.

From classical Mayo–Lewis equation, we gained the instantaneous composition of the two monomer units, $F_{1,i}$ and $F_{2,i}$ (or $F_{j,i}, j = 1, 2$),

$$F_{2,i} = \frac{r_2[M_2]_i^2 + [M_1]_i[M_2]_i}{r_1[M_1]_i^2 + 2[M_1]_i[M_2]_i + r_2[M_2]_i^2} \qquad (2)$$

$$F_{1,i} = \frac{r_1[M_1]_i^2 + [M_1]_i[M_2]_i}{r_1[M_1]_i^2 + 2[M_1]_i[M_2]_i + r_2[M_2]_i^2} \qquad (3)$$

where $[M_1]_i$ and $[M_2]_i$ was the concentration of monomer 1 and 2 in copolymerization system, which could be written by $[M_j]_i$.

$$[M_j]_i = [M_j]_i - 1 - F_{j,i-1} \times pt \qquad (4)$$

Defining a parameter $pc_{j,i}$ $(j = 1, 2)$,

$$pc_{j,i} = pc_{j,i-1} + F_{j,i} \times pt \qquad (5)$$

Then the integral composition of the two monomers were obtained:

$$\bar{F}_{j,i} = pc_{j,i} / \sum_{j=1,2} pc_{j,i} \qquad (6)$$

With the above model formulae, we could estimated the variety of copolymer composition during copolymerization process.

The relationship between instantaneous composition (F) and molar conversion for VC/PMI copolymerization system (Fig. 2) according to eqs. (1)–(6) indicated that the more active PMI monomer was consumed nearly completely when the weight conversion was only 23%. In fact, in the later period of copolymerization, there will be mainly homopolymerization of VC monomer. The overall product of VC/PMI copolymerization was a mixture of VC/PMI copolymer and VC homopolymer. In the batch suspension copolymerization system, the integral composition of copolymer varied greatly with the conversion (Fig. 3). The model value from eqs. (1)–(6) approximately fitted with the experimental data for VC/PMI suspension copolymerization.

The batch copolymer with two glass transition temperatures (T_g) also indicated their heterogeneous nature, as shown in Table I. The lower T_g (88.0°C) represented PVC chains, whereas the higher one (130.4°C), represented poly(VC/PMI) of a roughly constant composition. The rigidity of the copolymer chain increased with the increas-

Figure 2 Calculated curve of instantaneous composition vs molar conversion for VC/PMI, Temp = 60°C.

ing of PMI content; consequently, T_{g2} rose. In order to gain homogeneous VC/PMI copolymer structure, the more active monomer, PMI, should be added portionwise or successively to make the reaction proceeds under monomer-starved conditions. Because PMI is in a solid state at room temperature (its melting point is 89.8°C), there was much difficult in portionwise feeding.

Effects of Initiator on Copolymerization Rate

In free radical polymerization, the concentration of initiator plays an important role on the poly-

Table I T_g of VC/PMI Batch Copolymers (°C)

PMI Content (wt %)	T_{g1}	T_{g2}
5	88.0	130.4
10	87.9	137.7
20	88.2	143.6
30	88.3	173.8

merization rate. It is obvious that raising the initiator concentration can lead to the increasing of copolymerization rate of VC/PMI.

The copolymerization rate R_p can be expressed as the Walling[12] formula:

$$R_p = -\frac{d[M_1] + d[M_2]}{dt}$$

$$= \frac{R_i^{1/2}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)}{(\delta_1^2 r_1^2[M_1]^2 + 2\varphi\delta_1\delta_2 r_1 r_2[M_1][M_2] + \delta_2^2 r_2^2[M_2]^2)^{1/2}} \quad (7)$$

which can be simplified as

$$R_p = K[I]^n[M]^m \quad (8)$$

Taking the logarithm of two sides of eq. (8), we obtained

$$\ln R_p = n \ln[I] + C' \quad (9)$$

Figure 3 The curve of integral composition of VC/PMI (90/10) copolymer vs conversion at 60°C with AIBN as initiator.

Figure 4 Relationship of ln R_p^0 and ln[I] (VC : PMI = 90 : 10, Temp = 60°C).

Figure 5   Plot of R_p^0 against $[M_2]$, Temp = 60°C, AIBN = 0.2%.

Figure 6   Comparison of $\ln R_p^0 \sim 1/T$ between model value and experimental data. VC:PMI = 90 : 10, with AIBN as initiator.

C' was a constant; n was the order of copolymerization rate to the initiator concentration. The relationship between initial copolymerization rate (R_p^0) and initiator concentration ($[I]$) is showed in Figure 4. From the figure, the value of n was 0.78, which stated that monomolecular chain termination existed along with dimolecular chain termination in the VC/PMI copolymerization system.

Effects of Monomer Ratio on Copolymerization Rate

The copolymerization rate of VC/PMI was lower than that of VC homopolymerization as indicated above; moreover, it decreased with the increasing of PMI content (as shown in Fig. 5).

As detailed above, the copolymerization rate R_p can be noted as Walling formula [eq. (7)]. In the equation, there were a few parameters, in which

Table II   Data for Nonlinear Least Square Fitting[a]

Parameters	Value	Ref.
f	0.77	13
$k_d =$	1.47×10^{15}	14
	$\times \exp(-128.4 \times 10^3/RT)$	
δ_1	3.8	This paper
r_1	0.03	1
r_2	3.82	1

[a] $R_i = 2fk_d[I]$; Temp. of copolymerization = 60°C.

$$\varphi = \frac{2k_{t12}}{2(k_{t11}k_{t22})^{1/2}}, \quad \delta_1 = \left(\frac{2k_{t11}}{k_{11}^2}\right)^{1/2},$$

$$\delta_2 = \left(\frac{2k_{t22}}{k_{22}^2}\right)^{1/2} \quad (10)$$

where k_{t11} and k_{t22} refer to the homotermination rate constants and k_{t12} is for the cross termination reaction. The φ is a cross-termination constant, which is a measure of cross termination reaction. The cross-termination reaction is dominant, if $\varphi > 1$. However, self-termination of the radical is dominant, if $\varphi < 1$. It is obvious that the rate of VC/PMI copolymerization would be lowered if φ was large. When the conversion of VC($[M_1]$)/PMI($[M_2]$) was low, the rate of VC/PMI copolymerization could be characterized by the Walling formula [eq. (7)]. If R_i, δ_1, r_1, r_2, and so on were known from literature, nonlinear least square fitting could be utilized to fit the experimental data with eq. (1); then the values of φ and δ_2 was obtained. There was a hypothesis of dimolecular chain termination of copolymerization in eq. (7). However, in VC/PMI copolymerization, monomolecular chain termination existed along with dimolecular chain termination. The order of copolymerization rate vs initiator concentration was 0.78, from experimental data above, which was used in the fitting experimental data. The data for nonlinear least square fitting was summarized in Table II.

Figure 7 The calculated curve of PMI composition in copolymer or terpolymer vs conversion. For terpolymerization: VC : 80; PMI : 10; Other monomers: 10, Temp = 60°C.

Figure 8 The comparison of copolymerization rate for VC/PMI, VC/PMI/AN, VC/PMI/MMA, VC/PMI = 90/10, VC/PMI/AN(MMA) = 80/10/10 at 60°c, with AIBN, DCPD, AND BPPD as initiator.

Using the data of Figure 5, by a series of calculations, φ = 8.3 and δ_2 = 10.41 were gained. The results indicate that cross termination for VC/PMI copolymerization occurs, which leads to a lowering of the copolymerization rate. This was more evidence of the lowering rate of VC/PMI copolymerization.

Molar fraction was introduced to substitute for mole concentration of monomers of eq. (7) as follows:

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} = \frac{[M_1]}{[M]} \qquad (11)$$

$$f_2 = \frac{[M_2]}{[M_1] + [M_2]} = \frac{[M_2]}{[M]} \qquad (12)$$

where f_1 and f_2 are the mole fraction of VC and PMI, respectively. $[M]$ is the total monomer concentration.

The parameter φ, δ_2, δ_1, r_1, and r_2 in Eq.7 was substituted with actual data and fitting results. Equation (7) was written as

$$R_p = 4.76 \times 10^7 \exp(-7.722 \times 10^3/T)$$

$$\times [I]^{0.78} \frac{[M](0.03 + 1.94f_2 + 1.85f_2^2)}{(0.013 + 75.22f_2 + 1503.1f_2^2)^{1/2}} \qquad (13)$$

This model equation was only suited to VC/PMI copolymerization system in a limit range. The effects of reaction temperature on the copolymerization rate could be predicted quantitatively by this model equation.

Effects of Reaction Temperature on the Copolymerization Rate

It was obvious that the rate of free radical copolymerization increased with ascending reaction

Table III The Reactivity Ratio of Monomers

Reactivity Ratio	VC	PMI	AN	MMA	St	α-MeSt
VC	—	0.03	0.02	0.1	0.02	0.033
PMI	3.82	—	∞	0.30	0.01	0.04
AN	3.28	∞	—	—	—	—
MMA	10	0.91	—	—	—	—
St	17	0.07	—	—	—	—
α-MeSt	3.44	0.003	—	—	—	—

Figure 9 The effects of the amount of AN on R_p at 60°C with AIBN, DCPD, and BPPD as initiator.

temperature. Without exception, it may be applied to VC/PMI copolymerization system also. VC/PMI suspension copolymerization was carried out at 50, 60, and 70°C, respectively; the rates of VC/PMI copolymerization were obtained. The curve of ln R_p^0 and $1/T$ are showed in Figure 6; ○ was experimental data and the solid line was gained from calculating model eq. (13). The figure indicates that the calculated curve agreed with the experimental data.

Effects of the Third Monomer on the Copolymerization Rate

The composition of VC/PMI copolymer varied greatly with the conversion in batch suspension copolymerization as detailed above. A third monomer was added in order to minimize the composition variation. AN, MMA, styrene(St), and α-methylstyrene (α-MeSt) were selected to attain the goal. The varying instantaneous composition

of terpolymer with conversion was calculated according to Mayo-Lewis equation as shown in Figure 7. All the monomer reactivity ratios could be obtained from literature[15–17] or on the basis of the value of Q and e,[18] and are summarized in Table III.

Figure 7 indicated that the third monomer reduced the range of compositions with conversion. The system with AN was best among them. The addition of a third monomer would further lower the reaction rate of polymerization, for example, AN and MMA, seen in Figure 8. The copolymerization rate of VC/PMI/AN system also decreased with increasing of AN contents (Fig. 9).

The rate of VC/PMI/AN copolymerization was too low to commercialize. It was necessary to study the possibility of raising the copolymerization rate. The experimental results are summarized in Table IV.

Highly active initiator and increasing the concentration of initiator could raise the copolymerization rate.

CONCLUSION

The copolymerization rate of VC/PMI was low due to cross termination. The order of copolymerization rate to initiator concentration was 0.78, which was utilized to fitting the experimental data. As a result, the cross termination constant φ was equal to 8.3, which showed that cross termination was significant. Using the calculated modeling parameters, the effects of reaction temperature on the copolymerization rate were predicted. The predicted values were in good agreement with the experimental data. The Mayo–Lewis equation could be used to predict approximately the relationship between copolymer composition and conversion for VC/PMI or VC/PMI/third monomer copolymerization. The third monomer, acrylonitrile, would further lower

Table IV Effects of Initiator on Terpolymerization

VC (wt %)	PMI (wt %)	AN (wt %)	Initiator (wt %)			Polymerization Time (h)	Conversion (wt %)
			DCPD	BPPD	AIBN		
80	10	10		0.5	0.3	20	56
80	10	10	0.2	0.5	0.3	11.5	80.44
80	10	10	0.33	0.25	0.17	8.25	82.80
84.5	10.5	5	0.2	0.5	0.3	5	87.39
71.1	8.9	20	0.2	0.5	0.3	18	81.25

the copolymerization rate. The rate can be raised by increasing the initiator concentration and using highly active initiator.

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