

# Several Features of Vinyl Chloride–Diallyl Phthalate Suspension Copolymerization

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**ABSTRACT:** Vinyl chloride–diallyl phthalate (VC–DAP) suspension copolymerization was carried out in a 5-L autoclave and 200-mL stainless steel vessel at 45°C. The apparent reactivity ratios of VC–DAP suspension copolymerization system were calculated as  $r_{VC} = 0.77$  and  $r_{DAP} = 0.37$ . It shows that VC–DAP copolymer contains no gel when the feed concentration of DAP ( $f_2^0$ ) is lower than a critical concentration ( $f_{cr}$ , inside the range of 0.466–0.493 mmol/mol VC at 80–85% conversion), the polymerization degree (DP) of copolymer increases with the increase of  $f_2^0$  and conversion. VC–DAP copolymer is composed of gel and sol fractions when  $f_2^0$  is larger than  $f_{cr}$ . The DP of sol fraction decreases as  $f_2^0$  increases, but the gel content and the crosslinking density of gel increase. The gel content also increases as conversion increases. The results also show that the index of polydispersity of molecular weight of sol changes with  $f_2^0$ , a maximum value appears when  $f_2^0$  is close to  $f_{cr}$ . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 156–162, 2000

**Key words:** vinyl chloride; diallyl phthalate; suspension copolymerization; gel content

## INTRODUCTION

High-molecular-weight poly(vinyl chloride) (HMW-PVC) and lightly chemically crosslinked PVC (C-PVC), which can be used to prepare matte PVC products and PVC thermoplastic elastomer, developed rapidly.<sup>1–4</sup> According to the principle of vinyl chloride (VC) polymerization, the molecule weight of PVC increases with the decrease of polymerization temperature for the isothermal polymerization without chain transfer agent.<sup>5,6</sup> Thus, HMW-PVC can be synthesized by VC polymerization at a low polymerization temperature (<40°C). The rate of polymerization is directly related to the polymerization temperature such that the manufacture of HMW-PVC by low-temperature VC polymerization is a slow, costly pro-

cess; a high activity initiator or high concentration of initiator should be used to increase the rate of polymerization. Alternatively, HMW-PVC can be prepared by VC–divinyl monomer suspension copolymerization at a relatively high temperature (>40°C).<sup>7</sup> C-PVC can also be prepared by VC–divinyl monomer suspension copolymerization as the usage of divinyl monomer increases.<sup>8,9</sup> VC–divinyl monomer copolymerization belongs to the free-radical crosslinking copolymerization. The mechanism and modeling of free-radical crosslinking copolymerization have been studied by many researchers, but most of them were concerned with the homogeneous system.<sup>10–12</sup> It is not suitable to use their results to deal with the heterogeneous system, such as a VC–divinyl monomer suspension copolymerization system.

The modeling of and experiments on VC–divinyl monomer suspension copolymerization were carried out in our laboratory. Some modeling results have been published recently.<sup>13,14</sup> In

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**Table I** Typical Recipe for Suspension Polymerization

Reagent	5-L Autoclave	200-mL Vessel
Monomer:		
VC	1000 g	40 g
DAP	varied	varied
Deionized water	2000 mL	80 mL
Dispersing agent:		
65SH-50	135 mL (2.0 wt %)	1.4 mL (2.0 wt %)
KH20	35 mL (2.0 wt %)	1.4 mL (2.0 wt %)
Initiator DCPD	1.80 g	0.075 g

this article, experimental results on VC-diallyl phthalate suspension copolymerization at 45°C will be reported.

## EXPERIMENTAL

### Main Reagents

Vinyl chloride (VC) monomer is of polymerization grade. Diallyl phthalate (DAP) is chemically pure and supplied by Qingpu Synthetic Reagent Factory, Shanghai, China. Hydroxypropylmethylcellulose (HPMC, 65SH-50) and partially hydrolyzed poly(vinyl alcohol) (PVA, KH20) are supplied by Nippon Synthetic Chemical Ltd. Co. and are used as dispersing agents. Dicyclohexyl peroxydicarbonate (DCPD) is used as initiator after purification by twice methyl alcohol wash. Tetrahydrofuran (THF) and nitrobenzene used as solvents are analytically pure.

### Polymerization

Polymerization was carried out in a 5-L jacketed autoclave equipped with a paddle-type agitator and a 200-mL stainless steel vessel turned over top-to-bottom in a thermostated water bath.

Typical recipes of polymerization are shown in Table I. In order to disperse DAP in VC phase homogeneously, the reagents were charged in the following order: 500 mL deionized water, DAP, and DCPD were added first; the reactor was sealed and deoxygenated; a certain amount of VC monomer was charged then. After agitation for 30 min at room temperature, 1500 mL deionized water and an aqueous solution of dispersing agents

were pumped into the reactor. Temperature was raised, and polymerization was started. Polymerization temperature was controlled at  $45 \pm 0.2^\circ\text{C}$  both for the 5 L and 200 mL reactor by the water bath. Polymerization carried in 5-L reactor was ended when the reaction pressure drop was 0.15 MPa; the conversion of polymerization was controlled to be 80–85% then.

### Structure Characterization

#### Composition

VC-DAP copolymer with low conversion (<10%) prepared by vessel polymerization was washed with methyl alcohol and extracted by alcohol to remove unreacted monomers, then dried under vacuum. The weight percentages of carbon and hydrogen elements of polymer were determined on an element analysis instrument (type 240C, made by PE Co., USA). The composition of polymer was calculated from the element analysis results.

#### Gel Content

A certain amount of the dry copolymer ( $W_1$ ) was extracted in a Soxhlet extractor with THF at 70–80°C for 72 h, and the final residue was dried and weighted ( $W_2$ ). The gel content ( $w_g$ ) is expressed as:  $w_g = (W_2/W_1) \times 100\%$ .

#### Crosslinking Density of Gel

The average molecular weight between crosslinks and the crosslinking density of gel were determined by swelling measurements. The weighted PVC sample was allowed to swell in THF for 1 h at 60°C and 24 h at room temperature. The swollen gel was precipitated by centrifugal at a rate of 3000 r/min for 10 min, and the volume of swollen gel was recorded. The average molecular weight between crosslinks ( $\bar{M}_c$ ) is calculated using the following Flory-Rehner equation<sup>15</sup>:

$$\ln(1 - v_2) + v_2 + \chi v_2^2 = -\frac{\rho V_1}{M_c} v_2^{1/3}$$

in which  $v_2$  is the volume fraction of gel in the swollen system,  $\chi$  is the interaction parameter of PVC and THF ( $\chi = 0.14$ , see Brandup and Immergut<sup>16</sup>),  $V_1$  is the mole volume of THF, and  $\rho$  is the density of PVC ( $\rho = 1.4 \text{ g/cm}^3$ ). The crosslinking density of gel ( $v$ ) is expressed as  $v = \rho/\bar{M}_c$ .

### The Average Polymerization Degree of Sol Fraction

The average polymerization degree (DP) of PVC sol was calculated from the viscosity of its dilute solution in nitrobenzene according to the National Standard of China GB/T 5761-93, as follows:

$$DP = 500[10^{[\eta]^{0.168}} - 1]$$

$$[\eta] = \frac{\sqrt{2}}{c} \cdot \sqrt{\eta_{sp} - \ln \eta_r}$$

### Molecular Weight Distribution of Sol Fraction

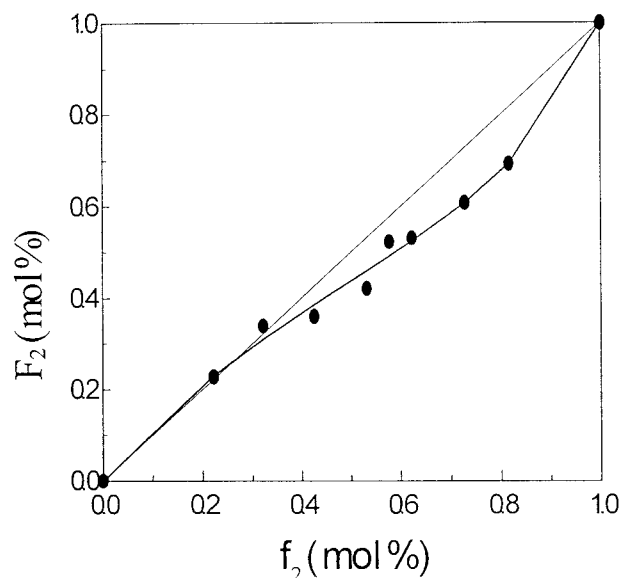
The molecular weight distribution (MWD) of sol was determined by a Waters 150C gel permeation chromatography (GPC) instrument at 25°C with THF as the mobile phase. Three columns, 10<sup>3</sup> and 10<sup>6</sup> nm and a linear column, were used. About 1.0 μL of PVC-THF solution containing about 0.1 wt % PVC was injected. Several polystyrene samples with a narrow molecular weight distribution and a known molecular weight were used to obtain the GPC calibration curve.

## RESULTS AND DISCUSSION

### The Apparent Reactivity Ratios of VC-DAP Suspension Copolymerization System

VC-DAP copolymerization leads to form linear polymer chains with pendent double bonds (primary chains) first, which are likely to react subsequently with radicals to form branched or crosslinked polymer. The intermolecular crosslinking reaction is the main approach to form branched or crosslinked polymer. Intramolecular crosslinking and cyclization reactions, which are not favored to form a branched or crosslinked polymer, would exist beside the intermolecular crosslinking reaction, so the system can be very complicated.

The reactivity ratios are important parameters for a copolymerization system. Matsumoto et al.<sup>17</sup> calculated the reactivity ratios of VC-DAP solution copolymerization system (benzene, 60°C) using the Mayo-Lewis composition equation considering the cyclization reaction and not considering it; no obvious difference in the reactivity ratios between two cases was found. VC-DAP suspension copolymerization is different from solution copolymerization, and it is useful to study the



**Figure 1** The relationship of  $f_2$  and  $F_2$  of VC-DAP suspension copolymerization at 45°C.

reactivity ratios of the VC-DAP suspension copolymerization system.

VC-DAP suspension copolymerization was carried at 45°C. The relationship between the feed molar composition of DAP ( $f_2$ ) and the composition of DAP in the corresponding low conversion (<10%) VC-DAP copolymer ( $F_2$ ) are shown in Figure 1.

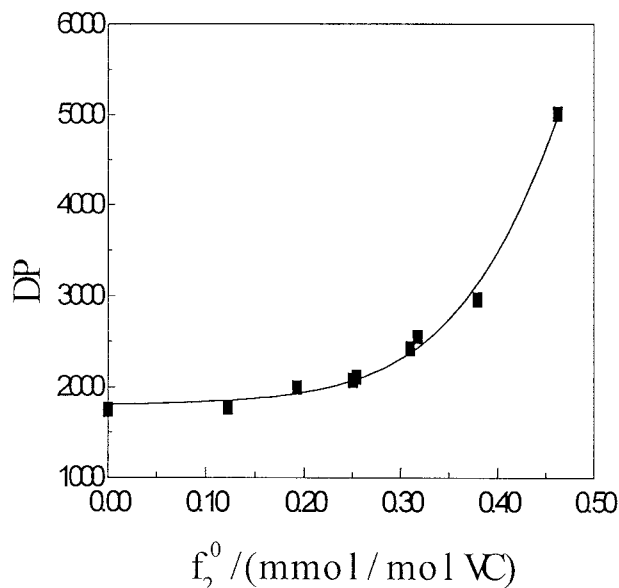
Using the following Mayo-Lewis equation, the data was treated by the nonlinear regression method:

$$F_2 = \frac{r_{DAP}f_2^2 + f_2 \cdot f_1}{r_{VC}f_1^2 + 2f_1 \cdot f_2 r_{DAP}f_2^2}$$

The regression curve is also shown in Figure 1. The apparent reactivity ratios are obtained as  $r_{VC} = 0.77$  and  $r_{DAP} = 0.37$ .

### Effects of $f_2^0$ on the DP of VC-DAP Copolymer Before the Gel Point

According to the mechanism of vinyl/divinyl monomer copolymerization, the gel point appears when the feed concentration of divinyl monomer exceeds a critical value at the certain polymerization condition. This would also happen for the VC-DAP suspension copolymerization system. The VC-DAP copolymer synthesized before the gel point was soluble in certain solvents (such as THF). The VC-DAP copolymer synthesized after



**Figure 2** Effects of  $f_2^0$  ( $<f_{cr}$ ) on the DP of the VC-DAP copolymer.

the gel point was composed of the gel and sol fraction. The gel fraction was not soluble in all solvents. It is difficult to determine the critical concentration of DAP ( $f_{cr}$ ) corresponding to the gel point exactly. It was found that HMW-PVC (DP > 5000) with no gel was formed by VC-DAP copolymerization when the feed concentration of DAP was 0.466 mmol/mol VC, and C-PVC with very low gel content (1.44%) was formed when the feed concentration of DAP was 0.493 mmol/mol VC. So,  $f_{cr}$  was inside the range of 0.466–0.493 mmol/mol VC for VC-DAP suspension copolymerization at 80–85% conversion and 45°C. When the feed concentration of DAP ( $f_2^0$ ) is smaller than  $f_{cr}$ , DAP only acts as chain extension agent for PVC chains. The effect of  $f_2^0$  on the DP of VC-DAP copolymer is shown in Figure 2.

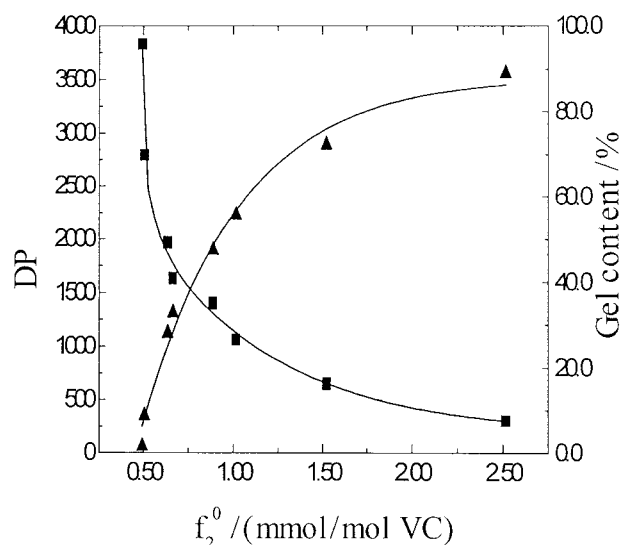
Figure 2 shows that DP increases slowly with the increase of  $f_2^0$  when  $f_2^0$  is small, but it increases quickly when  $f_2^0$  is close to  $f_{cr}$ . For the VC-DAP copolymerization system, one allylic group of DAP will copolymerize with VC first, leading to the formation of a linear PVC primary chain with a pendent double bond (PDB). When the PDB is reinitiated by a radical and bonded with another macromolecule radical, by chance, the branched PVC with a higher molecular weight is formed as a result. PVC primary chains contain more PDBs and exhibit a larger probability of chain extension as  $f_2^0$  increases, DP of VC-DAP copolymer increases then. HWM-PVC with no gel fraction can

be synthesized as  $f_2^0$  is controlled to be lower than  $f_{cr}$ .

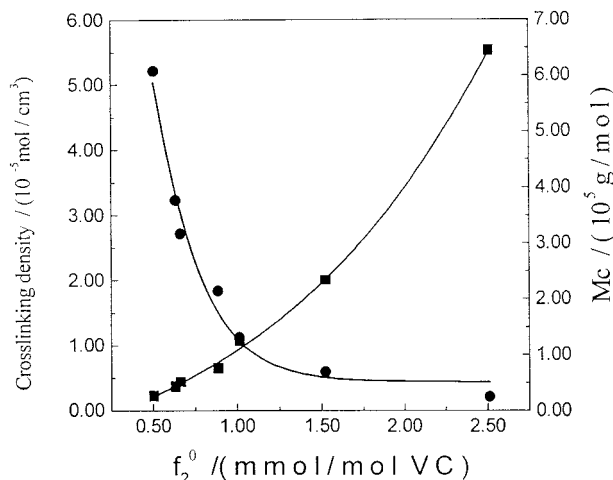
#### Effects of $f_2^0$ on the Gel Content and DP of Sol After the Gel Point

As  $f_2^0$  increases to be larger than  $f_{cr}$ , some primary chains would have sufficient number of DAP units and PDBs to be reinitiated and crosslinked with other macromolecule radicals to form the gel. DAP molecules have chain extension and crosslinking functions in this case. As shown in Figure 3, the gel content of VC-DAP copolymer increases, and DP of sol decreases as  $f_2^0$  increases.

For VC-DAP copolymerization, the formation of the gel is a stepwise process. The initial gel appears as sufficient primary chains connected together to form a polymer with an indefinite molecular weight. The initial gel grows up as more primary chains crosslinked with it, subsequently. The primary chains contains more DAP units and PDBs and thus have a larger probability of participating in crosslinking reaction as  $f_2^0$  increases. So the gel content increases as  $f_2^0$  increases. On the other hand, there are chain length (molecular weight) and composition distributions for primary chains. The longer primary chains contain more DAP units and PDBs and have larger probability of participating in chain crosslinking reaction and becoming the gel. More long primary chains tend to form the gel as  $f_2^0$  increases; the DP of sol decreases as a result.



**Figure 3** Effects of  $f_2^0$  ( $>f_{cr}$ ) on the gel content ( $\blacktriangle$ ) and DP of sol ( $\blacksquare$ ) of the VC-DAP copolymer.



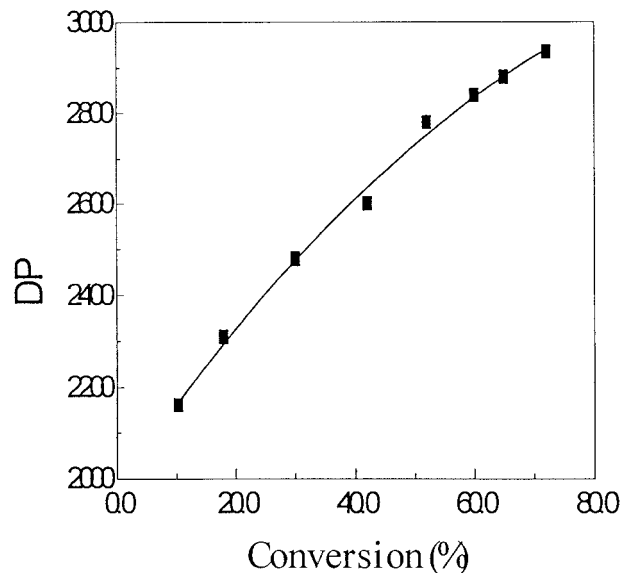
**Figure 4** Effects of  $f_2^0$  ( $>f_{cr}$ ) on the crosslinking density (■) and  $\overline{M}_c$  (●) of the PVC gel.

Chemically crosslinked PVC with different amount of gel content can be synthesized when  $f_2^0$  is larger than  $f_{cr}$ .

#### Effects of $f_2^0$ on the Crosslinking Density and $\overline{M}_c$ of PVC Gel

The crosslinking density and  $\overline{M}_c$  are important structural parameters for crosslinked polymer. Effects of  $f_2^0$  on the crosslinking density and  $\overline{M}_c$  of PVC gel are shown in Figure 4.

Figure 4 shows that the crosslinking density increases and  $\overline{M}_c$  decrease as  $f_2^0$  increases.  $\overline{M}_c$  of PVC gel is larger than that of irradiated crosslinked PVC, and the crosslinking density is lower.<sup>18</sup> Furthermore,  $\overline{M}_c$  of PVC gel prepared at low  $f_2^0$  is larger than the molecular weight of VC homopolymer prepared at 45°C ( $\overline{M}_w = 1.19 \times 10^5$  g/mol,  $\overline{M}_n = 6.81 \times 10^5$  g/mol, determined by GPC), so PVC prepared by VC–DAP copolymerization is lightly chemically crosslinked in most cases. The molecular weight of the PVC primary chains that tended to form the gel is much higher than that of the commercial VC homopolymer, so  $\overline{M}_c$  of the gel is high when  $f_2^0$  is relatively low. It is also found that the crosslinking density is lower than the corresponding concentration of DAP in VC–DAP copolymer when  $f_2^0$  is low since some DAP molecules are contained in the sol fraction or are consumed by intramolecular crosslinking and cyclization reactions. The crosslinking density of gel increases rapidly with the increase of  $f_2^0$  (or gel content) when  $f_2^0$  (or gel

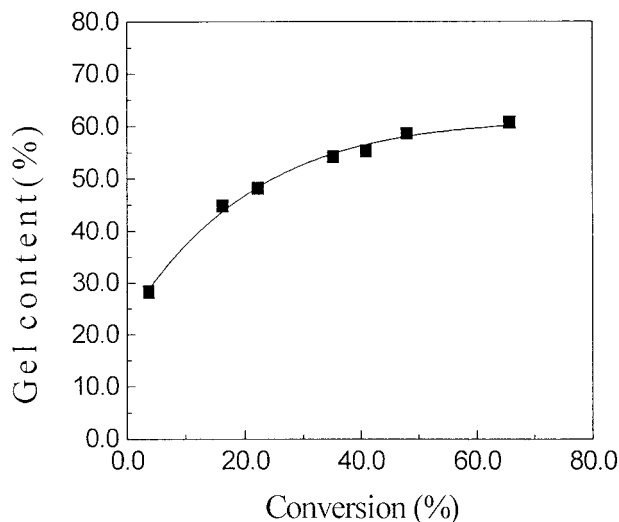


**Figure 5** Effect of conversion on the DP of the VC–DAP copolymer ( $f_2^0 = 0.427$  mmol/mol VC).

content) is relatively high. In that case, the crosslinking density calculated from swelling measurement contains much contribution of trapped chain entanglements.

#### Effect of the Conversion of Polymerization on the Structure of VC–DAP Copolymer

The molecular weight of VC homopolymer is mainly dependent on the polymerization temper-



**Figure 6** Effect of conversion on the gel content of the VC–DAP copolymer ( $f_2^0 = 1.137$  mmol/mol VC).



**Table II** Effect of  $f_2^0$  on MWD of Sol Fraction of the VC-DAP Copolymer

$f_2^0$ (mmol mol VC)	0	0.122	0.250	0.386	0.505	0.666	1.522	2.513
Index of Polydispersity	1.75	1.95	2.45	2.86	3.00	2.09	1.71	1.57

ature, and conversion has little effect on the molecular weight under the isothermal polymerization condition.<sup>5</sup> According to the mechanism of VC-DAP copolymerization, conversion would influence the molecular weight and the gel content of the VC-DAP copolymer. Figure 5 shows the effect of conversion on the DP of the VC-DAP copolymer as  $f_2^0 < f_{cr}$ . Figure 6 shows the effect of conversion on the gel content of the VC-DAP copolymer as  $f_2^0 > f_{cr}$ .

Figure 5 shows that the DP of the VC-DAP copolymer increases with the increase of conversion when  $f_2^0 < f_{cr}$ . Figure 6 shows that the gel content of the VC-DAP copolymer increases with increase of conversion when  $f_2^0 > f_{cr}$ . Since the molar concentration of DAP ( $f_2$ ) is very low and the molar concentration of VC is close to 1 in the experiments, while  $r_{VC}$  and  $r_{DAP}$  are smaller than 1 and  $r_{DAP} < r_{VC}$ , the Mayo-Lewis equation can be deduced as  $F_2 = f_2/f_{VC}$ . Thus,  $F_2 > f_2$  and DAP is consumed faster than VC in VC-DAP copolymerization when  $f_2$  is low. On the other hand, the reactivity ratio of double bond of VC ( $r'_{VC}$ ) is larger than 1 ( $r'_{VC} = 2r_{VC}$ ), while the reactivity ratio of DAP ( $r'_{DAP}$ ) is smaller than 1. ( $r'_{DAP} = r_{DAP}/2$ ). The double bonds of DAP are consumed slower than VC, and the concentration of double bonds increases as copolymerization conversion increases. As a result, DP of the VC-DAP copolymer increases with increase of conversion when  $f_2^0 < f_{cr}$ , and the gel content increase when  $f_2^0 > f_{cr}$ .

#### Effect of $f_2^0$ on MWD of VC-DAP Copolymer

The effect of  $f_2^0$  on MWD of sol fraction of the VC-DAP copolymer is shown in Table II.

It can be seen that the index of polydispersity increases with the increase of  $f_2^0$  as  $f_2^0 < f_{cr}$  and decreases as  $f_2^0 > f_{cr}$ . According to the mechanism of VC-DAP suspension copolymerization, DAP molecules act as chain extension agent before the gel point and the VC-DAP copolymer with long branches is formed. The degree of branching increases as  $f_2^0$  increases, leading to the increase of the index of polydispersity. DAP molecules have the function of chain extension and chain

crosslinking after the gel point. The longer PVC primary chains tend to transfer to gel, and shorter PVC primary chains remain as sol, so the index of polydispersity decreases with increase of  $f_2^0$ .

#### CONCLUSION

The apparent reactivity ratios of VC-DAP suspension copolymerization are calculated as  $r_{VC} = 0.77$  and  $r_{DAP} = 0.37$  at 45°C. The existence of the gel point of VC-DAP suspension copolymerization is verified, and it demonstrated that  $f_{cr}$  is inside the range of 0.466–0.493 mmol/mol VC at 80–85% conversion and 45°C. DAP only acts as chain extension agent, and DP of VC-DAP copolymer increases with the increase of  $f_2^0$  and conversion before the gel point ( $f_2^0 < f_{cr}$ ). DAP exhibits chain extension and chain crosslinking functions, and the VC-DAP copolymer is composed of the gel and sol fraction after the gel point ( $f_2^0 > f_{cr}$ ). The gel content of VC-DAP copolymer increases as  $f_2^0$  and conversion increase, while DP of sol fraction decreases. In addition, the crosslinking density of gel increases and  $\bar{M}_c$  decreases as  $f_2^0$  increases. The index of polydispersity of the VC-DAP copolymer also changes with  $f_2^0$ ; the maximum value appears when  $f_2^0$  is close to  $f_{cr}$ .

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