Preparation and Application of Low Molecular Weight Poly(vinyl chloride). IV. Preparation and Characteristics of Poly(vinyl chloride) with Broad Molecular Weight Distribution

KIKUO YAMAMOTO,* TAKASHI MAEHARA, KATSUO MITANI, and YUKIO MIZUTANI

Tokuyama Soda Co., Ltd., Mikage-cho, Tokuyama-city, Yamaguchi, 745 Japan

SYNOPSIS

Poly(vinyl chloride) (PVC) with a broad molecular weight distribution (BMD-PVC) was prepared by suspension polymerization in the presence of PVC with relatively lower molecular weight (LMW-PVC), which was prepared by suspension polymerization in the presence of 2-mercaptoethanol as a chain-transfer agent. It is elucidated using porosity measurement, scanning electron microscopy (SEM), and energy dispersion X-ray microscopy (EDXM) that the resultant BMD-PVC grains have an interesting internal structure at the level of primary particles. Discoloration time and fusion time of the BMD-PVC was studied. Discoloration time and fusion time of BMD-PVC is particularly dependent on the polymerization degree (Pw) of LMW-PVC and LMW-PVC content in the BMD-PVC samples. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used polymers in the world. Also, PVC is generally prepared by suspension polymerization. The suspension polymerization of vinyl chloride (VC) has so far been studied by many investigators.[1] In particular, the morphology formation of PVC particle by suspension or bulk polymerization has been studied by Davidson and Witenhafer[2] and Barclay.[3]

It is well known that PVC grain consists of three types of particles,[4] as follows:

1. Primary particle 1 μm
2. Agglomerate particle 3–10 μm
3. Grain 50–200 μm.

Krezewki and Sieglaff[5] studied the morphology and

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* To whom correspondence should be addressed at Sun Arrow Chemical Co., Ltd., 1-2 Halumi-cho, Tokuyama-City, 745 Japan.

properties of PVC obtained by suspension polymerization under various conditions.

The mechanical properties of PVC grains with various porosities can affect the breakability of the particle during extrusion molding. Mechanical properties of PVC are generally independent on the fusion level.[6] We have reported that PVC with relatively low molecular weight (LMW-PVC) prepared by suspension polymerization in the presence of the mercapto compounds have good thermal stability, and blended PVC of LMW-PVC and PVC with relatively high molecular weight has improved thermal stability and fusion time.[7]

In this article, PVC with a broad molecular weight distribution (BMD-PVC) was prepared by suspension polymerization. First, LMW-PVC was prepared by suspension polymerization in the presence of a chain-transfer agent, and then the LMW-PVC was filtered and dried. Subsequently, HMW-PVC was prepared by suspension polymerization in the presence of LMW-PVC. Morphology and discoloration time and fusion time of the resultant BMD-PVC were investigated.

conditions the material does cure completely. It is important to take into account also that the heat obtained as a sum of the heat ΔH_{iso} and the residual heat ΔH_{res} obtained in a dynamic postcuring after each isothermal experiment in no case exceeds 300 J/g, a value rather far from the total heat obtained dynamically. This is because in isothermal tests part of the reaction heat cannot be recorded by the calorimeter. As pointed out by several authors,[12,13] at low temperatures at the start and end of the reaction the heat cannot be detected by DSC if it falls below the sensitivity of the apparatus, and at high temperatures part of the reaction heat may be lost during the heating of the sample and the stabilization of the DSC.

For a more precise calculation of the degree of conversion and the reaction rate, it will be necessary to correct eq. (5), bearing in mind the above considerations.

The corrected degree of conversion and the corrected reaction rate are defined as:

$$\alpha_t^c = \frac{\Delta H_t^c}{\Delta H_{tot}} \qquad \left(\frac{d\alpha}{dt}\right)_t^c = \frac{(dH/dt)_t^c}{\Delta H_{tot}} \qquad (6)$$

where ΔH_t^c and $(dH/dt)_t^c$ would be, respectively, the corrected isothermal heat released in a time t and the corrected calorific power generated in a time t if a heat equal to $\Delta H_{tot} - \Delta H_{res}$ could be detected isothermally. As ΔH_t^c and $(dH/dt)_t^c$ cannot be determined experimentally, it is possible to calculate them if we accept the following relations as correct:

$$\frac{\Delta H_t}{\Delta H_{iso}} = \frac{\Delta H_t^c}{\Delta H_{tot} - \Delta H_{res}} \qquad (7)$$

$$\frac{(dH/dt)_t}{\Delta H_{iso}} = \frac{(dH/dt)_t^c}{\Delta H_{tot} - \Delta H_{res}}. \qquad (8)$$

From here it is possible to find the values of ΔH_t^c and $(dH/dt)_t^c$. Replacing them in expressions (6), we obtain the corrected degree of conversion in time t and the corrected reaction rate in a time t, with the value:

$$\alpha_t^c = \frac{\Delta H_t(\Delta H_{tot} - \Delta H_{res})}{\Delta H_{iso}\Delta H_{tot}}$$

$$= \alpha_t\left(\frac{\Delta H_{tot} - \Delta H_{res}}{\Delta H_{tot}}\right) \qquad (9)$$

$$\left(\frac{d\alpha}{dt}\right)_t^c = \frac{(dH/dt)_t(\Delta H_{tot} - \Delta H_{res})}{\Delta H_{iso}\Delta H_{tot}}$$

$$= \left(\frac{d\alpha}{dt}\right)_t\left(\frac{\Delta H_{tot} - \Delta H_{res}}{\Delta H_{tot}}\right). \qquad (10)$$

Figure 1 shows the degree of conversion according to time using eqs. (5), (9), and that which would be obtained by using eq. (5) modified according to $\alpha_t' = (\Delta H_t/\Delta H_{iso}) \cdot (\Delta H_{iso}/\Delta H_{tot})$. It is considered that the most correct option corresponds to eqs. (9) and (10), which are those used in this work to evaluate the degree of conversion and the reaction rate at a time t.

For the kinetic analysis of the curing process for the three catalytic systems investigated we used eq. (4), applying to it different degrees of conversion. The curing times were obtained from the curves degree of conversion versus curing time at different temperatures. These curves were calculated from isothermal experiments in DSC using eq. (9).

Figure 2 shows the curves α versus t at different curing temperatures, and the method for obtaining the curing times for a given degree of conversion at different temperatures for a system using DEA as a promoter. For each degree of conversion it is possible to correlate the logarithm of curing time against the inverse of the temperature by using eq. (4). Figure 3 shows the curves ln t versus $1/T$ for the same system, and Table I shows the linear regressions of these curves with the value of the ordinate at the origin, the slope of the straight lines, which is directly related to the activation energy, and the regression coefficient.

This same study was made with the same proportions of resin, initiator, and promoter with the other two promoters (DMA and DMPT) in order
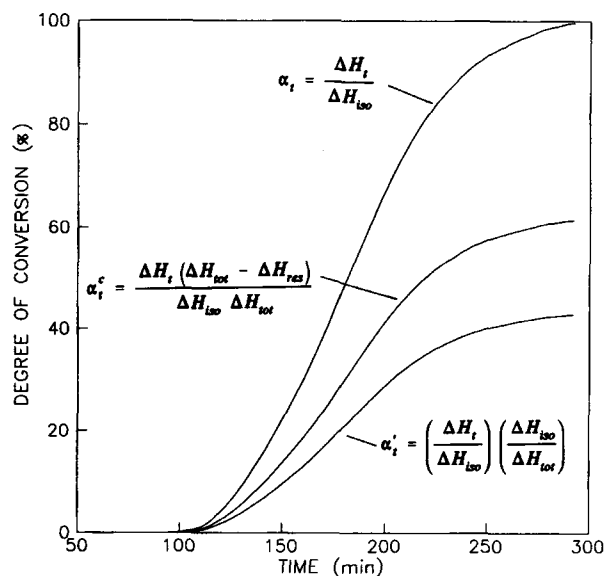

Figure 1 Degree of conversion as a function of time calculated according to different expressions. System with 0.1% DMA. $T = 15°C$.

Table II   Preparation of PVC by Suspensiom Polymerization in the Presence of LMW-PVC Powder

Resin No.	LMW-PVC		Polymerization of HMW-PVC					
	P_w	g	VC g	Temp. °C	Time hr	PVA g	MC g	Yield %
A	—	—	360	57	5	1.6	0.72	66.0
B1	400	8	360	57	5	1.6	0.72	70.6
B2	400	15	360	57	5	1.6	0.72	67.5
B3	400	30	360	57	5	1.6	0.72	68.5
B4	400	35	360	57	5	1.6	0.72	66.8

water: 1000 g
PVA: poly(vinyl alcohol)
MC: methyl cellulose

No. A is prepared by suspension polymerization without LMW-PVC, and it is PVC with a relatively high molecular weight (HMW-PVC).

Nos. B-1, B-2, B-3, and B-4 were prepared in the presence of various amounts of LMW-PVC. The resultant PVC with a broad molecular weight distribution (BMD-PVC) consisted of LMW-PVC and HMW-PVC. The attained yield of PVC was to 66% in the case of No. A. In a previous article, it was found that LMW-PVC, which is obtained in the presence of a particular mercapto compound as a chain-transfer agent, has good discoloration time and fusion time.[7] LMW-PVC obtained as shown in Table I has similar properties. Table III shows some properties of the resultant BMD-PVC. The Pw of BMD-PVC (B series) is lower than that of No. A and decreases with increasing LMW-PVC content. Moreover, M_w/M_n increases with increasing LMW-PVC content, as shown Table III. Both pore volume and pore radius of BMD-PVC increase with decreasing LMW-PVC content.

Morphology

Both pore volume and pore radius generally suggest a packing state of PVC grains consisting of primary particles and agglomerate particles. Table III shows that the pore volumes and the pore radii of BMD-PVC (Nos. B-3, -4) become larger than those of Nos. A, B-1, and B-2. Figure 1 shows a scanning electron micrograph (SEM) of the surface structure for No. A, which is HMW-PVC itself ($Pw = 1013$, $M_w/M_n = 2.1$). These grains have an agglomerated surface structure. Moreover, a large empty space is observed at the surface of the grains.

Figure 2(a) shows an SEM of the surface structure of No. B-3 (LMW-PVC content 11.2%), which consists of LMW-PVC and HMW-PVC. Figure 2(b) shows the distribution of the sulfur atom in the same grains, taken using S—Kα with the aid of energy diffraction X-ray micrography (XMA). The sulfur atom (white point) comes from 2-mercaptoethanol, which was used as a chain-transfer agent during the

Table III   Properties of BMD-PVC Obtained by Suspension Polymerization in the Presence of LMW-PVC

Resin No.	BMD-PVC				Bulk density cm³/g	Pore volume cm³/g	Pore radius × 10⁻³ Å
	LMW-PVC wt %	HMW-PVC wt %	P_w	M_w/M_n			
A	0	100	1013	2.1	0.38	0.13	0.95
B-1	3.1	96.9	910	2.2	0.42	0.12	0.80
B-2	5.9	94.1	890	2.3	0.40	0.13	0.90
B-3	11.2	88.8	850	2.9	0.39	0.14	1.00
B-4	13.3	86.7	730	3.3	0.42	0.15	1.00
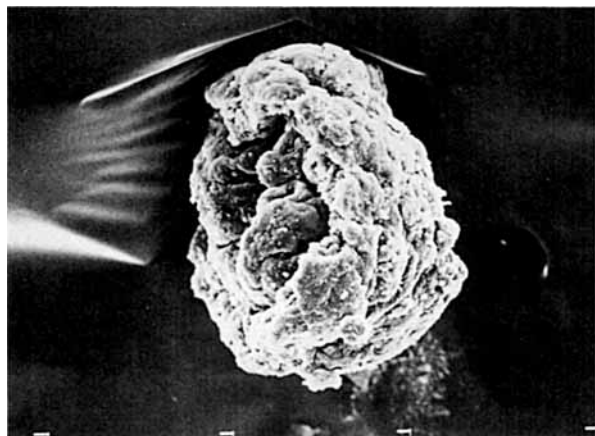
Figure 1 Scanning electron micrograph of surface structure of PVC grain (resin A).

polymerization. It is shown that BMD-PVC (No. B-3) is of heterogeneous agglomerate particles (1–10 μm) and also that LMW-PVC grains are dispersed at the surface of BMD-PVC.

Many of the sulfur atoms are observed around the surface area of No. B-3, which shows that LMW-PVC are heterogeneously dispersed in BMD-PVC. Nos. B-1, -2, and -4 with different LMW-PVC contents show a surface structure similar to that of No. B-3.

On the other hand, Figure 3(a) shows the fractured structure of No. B-3. The internal structure of No. B-3 is made of homogeneously agglomerated particles (1–5 μm).

Figure 3(b) shows the internal fractured section of No. B-3, showing the distribution of the sulfur atoms, assigned to LMW-PVC. Around the surface area of BMD-PVC grain, the dispersion of sulfur atoms (LMW-PVC) is uniformly observed. From the observation of the fractured structure of BMD-PVC, it is elucidated that some amount of LMW-PVC exists around the HMW-PVC. It suggests that BMD-PVC consists of three types of grains as follows: HMW-PVC grain, LMW-PVC grain, and grain consisting of LMW-PVC and HMW-PVC.

Discoloration Time

Figure 4 shows discoloration time–Pw curves for BMD-PVC. Beyond a Pw of 850, the discoloration time of BMD-PVC decreases with increasing Pw. Therefore, it is indicated that the discoloration time
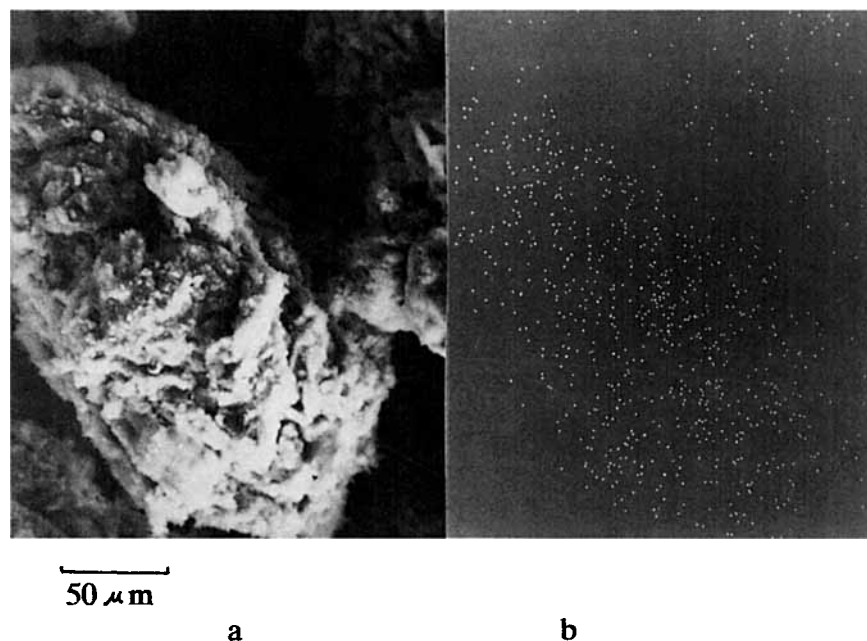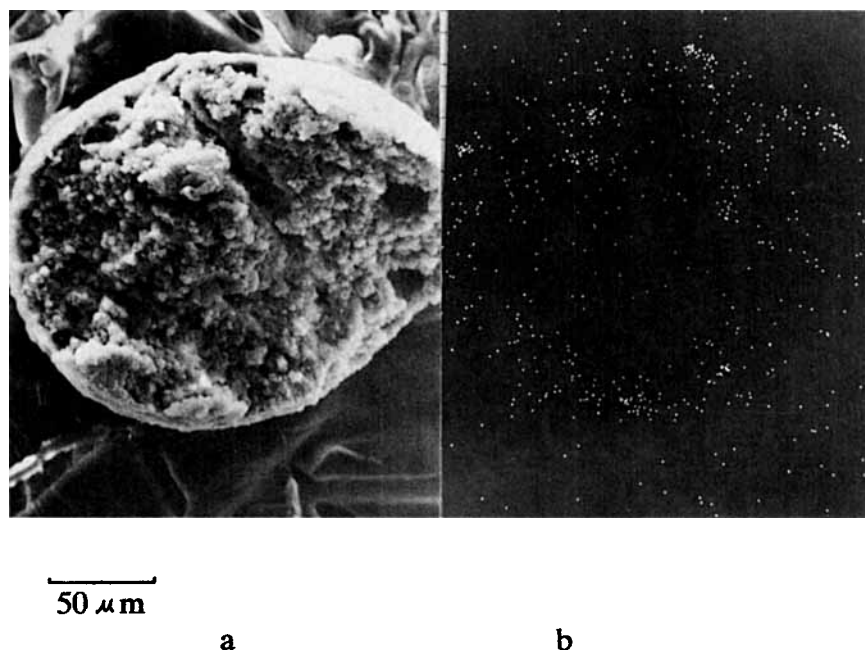

Figure 2 Scanning electron micrograph of surface structure of BMD-PVC (resin B-3) and mapping of S—Kα emission from the same field area as in SEM.

50 μm

a   b

Figure 3   Scanning electron micrograph of fracture structure of BMD-PVC (resin B-3) and mapping of S—Kα emissions from the same field area as in SEM.

of BMD-PVC is strongly affected by the thermal stability of LMW-PVC. Figure 5 shows the relationship between the discoloration time and the LMW-PVC content in BMD-PVC. The discoloration time of BMD-PVC increases with increasing the LMW-PVC content. In the previous paper, it was found that LMW-PVC obtained by the polymerization in the presence of mercapto compounds has good thermal stability.[7] BMD-PVC also has a
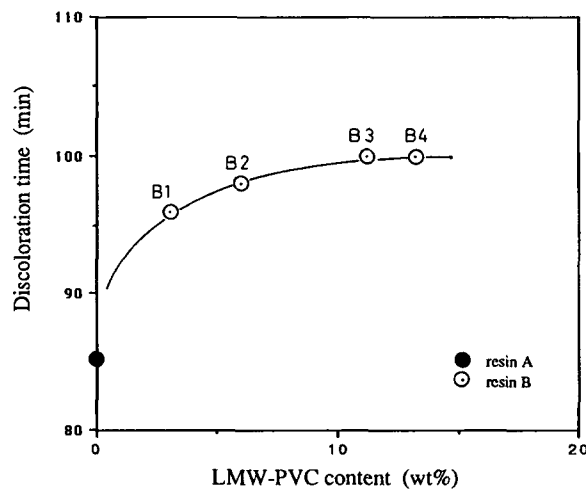
good discoloration time, because LMW-PVC has a good discoloration time.

Fusion Time

BMD-PVC is the grain consisting of LMW-PVC and HMW-PVC, so it is expected that the fusion time decreases with increasing the LMW-PVC content. Figures 6 and 7 show the fusion time–Pw and
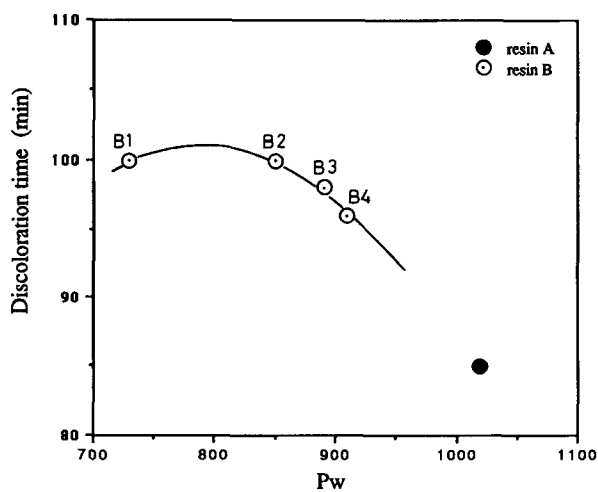
Figure 4   Dependence of discoloration time on Pw of BMD-PVC.

Figure 5   Dependence of discoloration time on content of LMW-PVC in BMD-PVC.
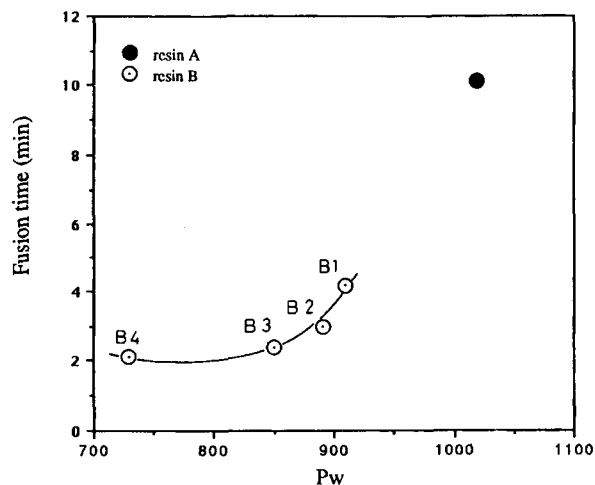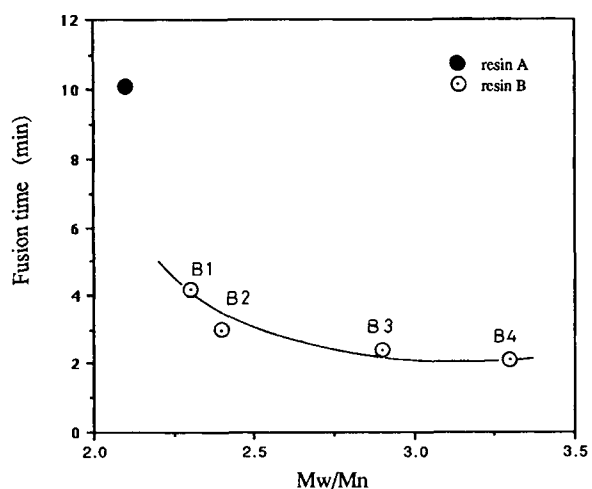
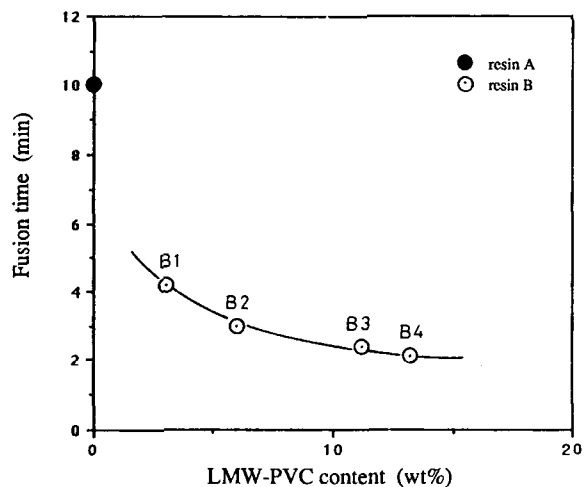**Figure 6** Dependence of fusion time on Pw of BMD-PVC.

Figure 8 Dependence of fusion time on content of LMW-PVC in BMD-PVC.

$-M_w/M_n$ curves of BMD-PVC, respectively.

Below a Pw of 850, the fusion time is constant. Beyond a Pw of 850, the fusion time gradually increases with increasing Pw. On the other hand, the fusion time of BMD-PVC increases with increasing M_w/M_n. In particular, Pw and M_w/M_n of BMD-PVC decrease with increasing LMW-PVC content. The fusion time, hence, is affected by the LMW-PVC content in BMD-PVC.

Figure 8 shows the fusion time–LMW-PVC content curves for BMD-PVC. In fact, the fusion time of BMD-PVC decreases with increasing LMW-PVC content. In particular, BMD-PVC (Nos. B-1, -2, -3) gives a shorter fusion time than that of No. A.

Figure 9 shows the fusion time–pore volume curve for BMD-PVC. The fusion time of BMD-PVC (Nos. B-1, -2, -3) decreases with increasing pore volume. Figure 10 shows the fusion time–pore radius curve for BMD-PVC. The fusion time of BMD-PVC linearly decreases with increasing pore volume. It is elucidated that the fusion time is also affected by the agglomeration of the primary, as reported by Rabinovitch and Summers.[8]

The fusion time of BMD-PVC is strongly affected by the dispersion state and the LMW-PVC in BMD-PVC. Therefore, it is suggested that the discoloration time is much more improved with increasing LMW-PVC content. Moreover, the fusion time is

Figure 7 Dependence of fusion time on M_w/M_n of BMD-PVC.
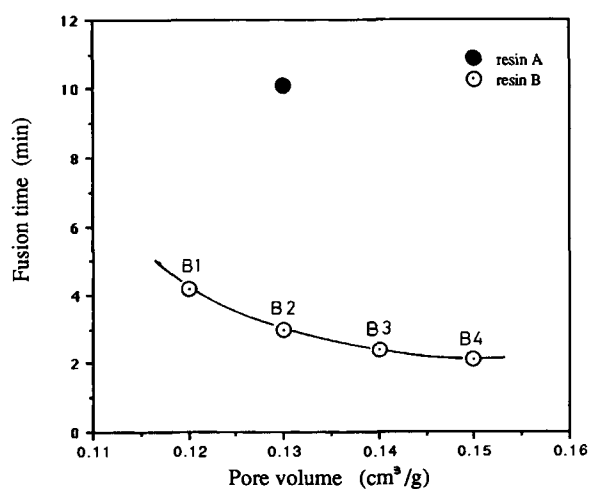
Figure 9 Dependence of fusion time on pore volume of BMD-PVC.
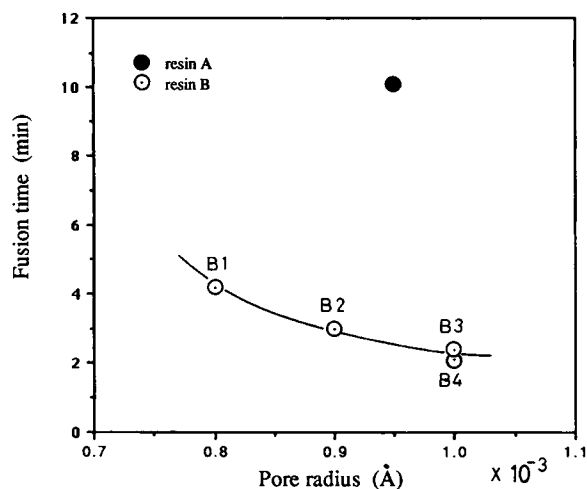
Figure 10   Dependence of fusion time on pore radius of BMD-PVC.

affected by the dispersion state and the content of LMW-PVC particles in BMD-PVC grains.

CONCLUSION

Poly(vinyl chloride) with broad molecular weight was synthesized by suspension polymerization in the presence of LMW-PVC. The resultant BMD-PVC grains are consisting of three types of grains: LMW-PVC grain, HMW-PVC grain, and grain consisting of LMW-PVC and HMW-PVC.

LMW-PVC particles that are partially dispersed at the surface of the BMD-PVC grains consist of LMW-PVC and HMW-PVC. Both the discoloration time and the fusion time of BMD-PVC decrease with increasing LMW-PVC content.

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