

# Structure and properties of polyvinyl chloride physical gels

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In this work, the structure and physical properties of polyvinyl chloride (PVC) gels prepared from the solutions of bromobenzene (BrBz) and dioxane (DOA) under different gelation conditions are studied. The average size of the junction point for PVC gels in the initial gelation state are the combination of *ca.* two to three chains in width and *ca.* six to eight syndiotactic sequences in length to form a fibril-like network structure, irrespective of the species of solvents used, the molecular weight and the concentration of the polymer. Because the size of the junction point/microcrystal is too small, the results of wide angle X-ray diffraction (WAXD) shows only a broad intensity peak, implying that the crystallinity is very low for PVC gels. However, the X-ray intensity peak of amorphous scattering in PVC/DOA gel is sharper than that in PVA/BrBz gel, indicating that PVC/DOA gel has a thicker network structure due to a larger degree of polymer aggregation. The morphology of the gel is investigated from the observation of dried gel prepared from the freeze-drying method using electron microscopy. The results show that the gel morphology consists of a fibril-like structure and the mesh size of the network decreases with increasing polymer concentration. The difference in physical properties, such as the modulus of gels, may be considered to be mainly due to the aggregation degree of amorphous chains related to the solvent type, the concentration and molecular weight of polymer. © 1997 Elsevier Science Ltd.

(Keywords: polyvinyl chloride; physical gel; network structure)

## INTRODUCTION

It is well known that some crystalline polymer solutions can form into thermoreversible physical gels when they were cooled<sup>1–3</sup>. The attraction of polymer gel to researchers lies in the variation of the network structure and physical properties of the physical gels. The formation of polyvinyl chloride (PVC) physical gels are generally classified into the crystallization-induced gelation<sup>4–7</sup>, and then the microcrystals could be only formed by the association of syndiotactic sequences as junction points in the network structure of gels. It is well known that atactic PVC is a low crystalline polymer, and the gelation of PVC solution occurs under a great amount of the solvent, so that the crystallization becomes more difficult, resulting in a very low crystalline gel.

Guerrero and Keller<sup>8–10</sup> have already reported that the network structure of PVC gels was due to the formation of junction points caused by the arrangement of polymer chains. They also indicated that the crystallinity of PVC gels was strongly related to the polymer–solvent interaction. These results may imply that the gelation ability and the physical properties of gels are related to the polymer–solvent interaction, i.e. hydrogen bonding ability of the solvent. Recently, Soenen and Berghmans<sup>11</sup> also pointed out that the polymer–solvent interaction affected the thermal behaviour of PVC gels, and the liquid–liquid phase separation was observed in the poor solvent gels, while no noticeable phase separation occurred in the good solvent ones. Then, the melting point of the gel,  $T_m^G$ , prepared from good solvent was higher than that from poor solvent. These results let us consider that the difference in  $T_m^G$  of PVC gel may be mainly due to the different

polymer–solvent interaction that may result in different degrees of polymer aggregation. However, in our previous study<sup>12</sup> for polyvinyl alcohol (PVA) gels prepared from ethylene glycol (EG) and *N*-methylpyrrolidone (NMP) solutions, we showed that the  $T_m^G$  of PVA/EG gel, which tended to shift to a higher temperature with increasing syneresis, was higher than that of PVA/NMP gel. On the other hand, the WAXD results clearly showed a remarkable difference in crystallinity between PVA/NMP and PVA/EG gels, i.e. PVA/EG gel has a higher crystallinity than PVA/NMP gel does. The (101) diffraction of PVA crystal was clearly observed in PVA/EG gel, indicating that a larger size of the crystallite was formed. It should be noticeable that the affinities to PVA, i.e. the solubility of PVA in NMP is larger than that in EG<sup>13,14</sup>. As mentioned above, how the structure and properties of gel affected by the effect of the solvent occur in PVC gels must be a very important subject that attracts our interest.

On the observation of gel morphology, Tohyama and Miller<sup>15</sup> showed that the morphology of poly(*r*-benzyl-L-glutamate) gel has a mesh-like structure with a mesh size of 1  $\mu\text{m}$  which consists of ramified fibres of diameter ranging from 10 nm to over 100 nm. Yang and Geil<sup>5</sup> used the freeze-etching technique to prepare a PVC gel for observing gel morphology by means of electron microscopy. On the other hand, Mutin and Guenet<sup>6</sup> also determined the PVC gel morphology using optical microscopy. They all showed that the gel morphology consists of a fibrous network, and the mesh size of PVC gel in good solvent is smaller than that in poor solvent. In this work, we also studied the gel morphology which may change with gelation conditions by means of electron microscopy and by preparing dried gels using a freeze-drying technique differed from the freeze-etching technique.

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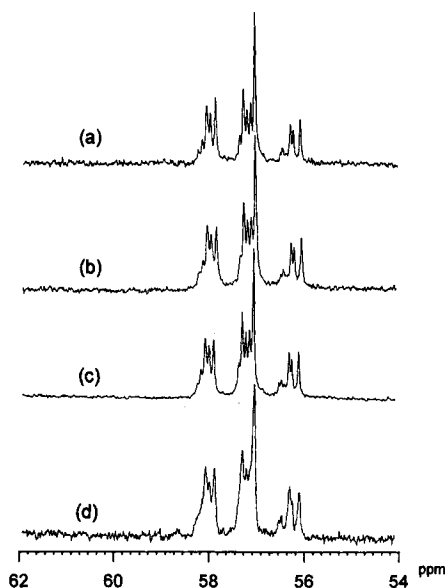
## EXPERIMENTAL

## Materials

The PVCs used in this work were laboratory grade powders (Aldrich Chemical Co. Ltd., USA). The solvents were analytical grade and purified by distillation before using. The tacticities of PVCs with different molecular weights were obtained by using the  $^{13}\text{C}$ -n.m.r. decoupled spectra for scanning 2000 times at  $90^\circ\text{C}$  to obtain a safe signal-to-noise ratio signal<sup>16</sup>. The  $^{13}\text{C}$ -n.m.r. instrument used was the Barian unity plus 400 MHz, and the solvent used was dioxane- $d_8$ . The results were as shown in Figure 1, the areas of the different signal peaks represent the tacticity of the PVC. The characteristics of PVCs used in this work are shown in Table 1, from which the syndiotacticity of PVCs with different molecular weights can be seen to be roughly the same. This means that the effect of the tacticity would not affect the structure and properties of gels in this study.

## Freeze-drying of the PVC gels

The freeze-drying principle of polymer gels is to let the molecular mobility of polymer and solvents be extremely frozen at a low temperature below the freezing point of the solvent. The solvent will be sublimated from the frozen gel under vacuum. Because no remarkable shrinkage (less than 1%) of gel volume occurs during the freeze-drying process, the network structure of freeze-dried gel may be considered to be the same as that of wet gel. The freeze-dried gels were



**Figure 1** The  $^{13}\text{C}$ -n.m.r. spectrum of PVCs used in this study: (a)  $M_w = 50 \times 10^4$ ; (b)  $M_w = 20.5 \times 10^4$ ; (c)  $M_w = 15.8 \times 10^4$ ; (d)  $M_w = 8.3 \times 10^4$ .

**Table 1** Characteristics of samples used. Tacticity was measured by  $^{13}\text{C}$ -n.m.r. ( $P_r$ , syndiotactic;  $P_m$ , atactic;  $P_{mm}$ , isotactic)

Sample no.	Molecular weight $\times 10^{-4}$	$P_{rr}$	$P_{rm}$	$P_{mm}$
1	50.0	0.32	0.48	0.20
2	20.5	0.35	0.46	0.19
3	15.8	0.29	0.49	0.22
4	8.2	0.31	0.49	0.20
Average		0.32	0.48	0.20

prepared as follows: the polymer solution was cooled to room temperature to form the gel and then was placed into freeze-drying equipment at  $-50^\circ\text{C}$ , where the polymer gel was quickly frozen to form an ice-like solid. Under vacuuming conditions for more than two weeks, a freeze-dried gel could be obtained for the electron microscopy (Cambridge S-360) measurements.

## Measurements

A 'test tube upside-down' method was used for determining the gel melting points,  $T_m^G$  values, of PVC gels prepared from different conditions of the gelation. The PVC and solvent were placed in sealed glass tubes of an inner diameter of 12 mm, and then were heated until dissolved into a homogeneous solution. The solutions were cooled to room temperature for two days to be formed gels. The test tubes with gels after being kept upside down in a thermostat oven at heating rate of  $0.5^\circ\text{C min}^{-1}$  to let the gel in the test tube heat evenly. The temperature at which the gel begin to flow was defined as the  $T_m^G$  of the gel.

The determination of viscosity for semi-dilute solutions were carried out with a spindle viscometer at different temperatures (Brookfield viscometer model LVIDV-II).

The modulus of the gel was obtained using ball indentation experiments proposed by Hertz<sup>17,18</sup>:

$$E = \frac{3(1 - \nu^2)F}{4r^{1/2}h^{3/2}} \quad (1)$$

where  $E$  represents Young's modulus ( $\text{dynes cm}^{-2}$ ),  $F$  represents the force of sphere against the gels surface (dynes),  $r$  represents the radius of sphere (cm),  $h$  represents the depth of indentation of sphere (cm), and the  $\nu$  represents the Poisson's ratio, with the typical value for the elastomer of  $\nu = 0.5$ .

The wide angle X-ray diffraction (WAXD) intensity curves of gels were measured with a graphite-monochromatized Cu  $K\alpha$  radiation generated at 40 kV and 100 mA in a Rigaku D/max diffractometer at scanning speed of  $2\theta = 1 \text{ deg min}^{-1}$ .

## RESULTS AND DISCUSSION

Figures 2 and 3 show the gel melting temperature,  $T_m^G$  and the Young's modulus,  $E$ , as a function of the polymer concentration for PVC gels with different molecular weights, respectively. The results show that the physical properties of gels increased significantly with increasing polymer concentration and molecular weight. At a given polymer concentration and molecular weight, the  $T_m^G$  and  $E$  of PVC/BrBz gels are higher than those of PVC/DOA gels. These results indicate that the differences in physical properties may be due to the structural changes of the gels. Generally, the physical properties of physical gels are considered to be dominated by the size and the number of the junction point/microcrystal, chain mobility in the network structure, and the degree of molecular interaction between polymer and solvent. As mentioned in the Introduction, our previous study<sup>12</sup> showed that the  $T_m^G$  of PVA/EG gel was higher than that of PVA/NMP gel, because a larger size of the crystallite was formed in PVA/EG gel. Therefore, the size of the junction point may change with the gelation conditions in PVC systems. However, the difference in crystallinity of PVC gels is not observed in the results of WAXD (shown latter) which show only an amorphous scattering peak, irrespective of gelation conditions in this study. Under this situation, the investigation of

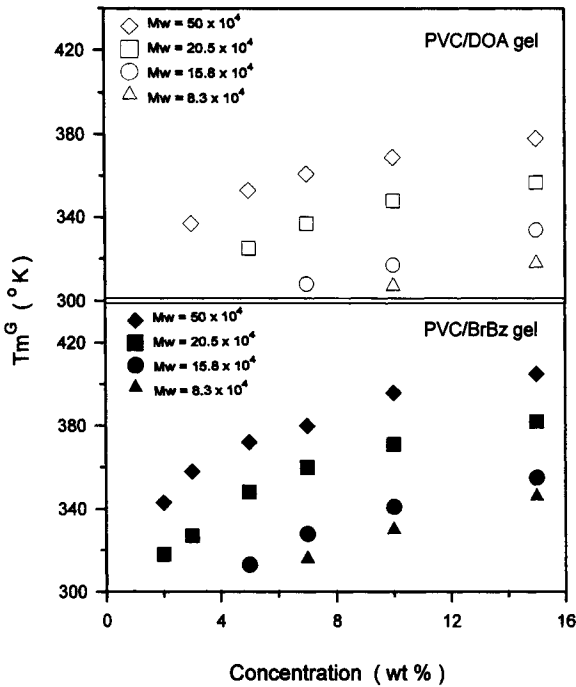


Figure 2 Plot of  $T_m^G$  as a function of concentration for PVC gels with various Mws

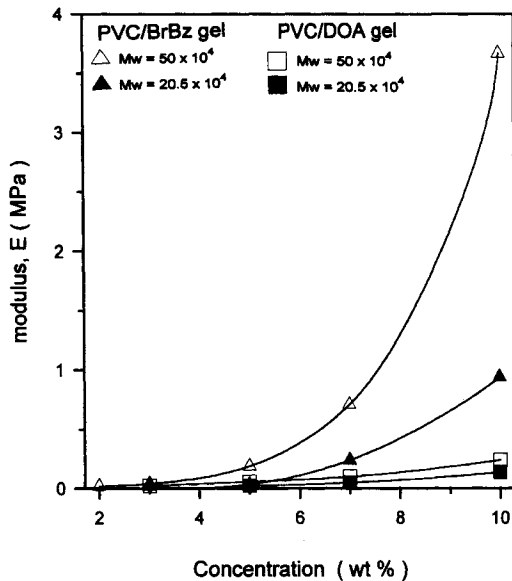


Figure 3 Plot of  $E$  as a function of concentration for PVC gels with various Mws

the size of the junction point for PVC gels becomes very difficult.

Fortunately, Ferry and Eldridge<sup>19</sup> and Harrison *et al.*<sup>20</sup> have provided a convenient relation as shown in equations (2) and (3), for calculating the average number of polymer chains held together in a junction point. Figure 4a and b show respectively the plots of  $1/T_m^G$  versus  $\ln Mw$  and  $1/T_m^G$  versus  $\ln C$ , and indicate a linear relationship between them. This implies that the Ferry–Eldridge relation may apply to the PVC gel system in our study.

$$\left[ \frac{\partial \ln Mw}{\partial (1/T_m^G)} \right]_{N,C} = \frac{\Delta H_m}{R} \quad (2)$$

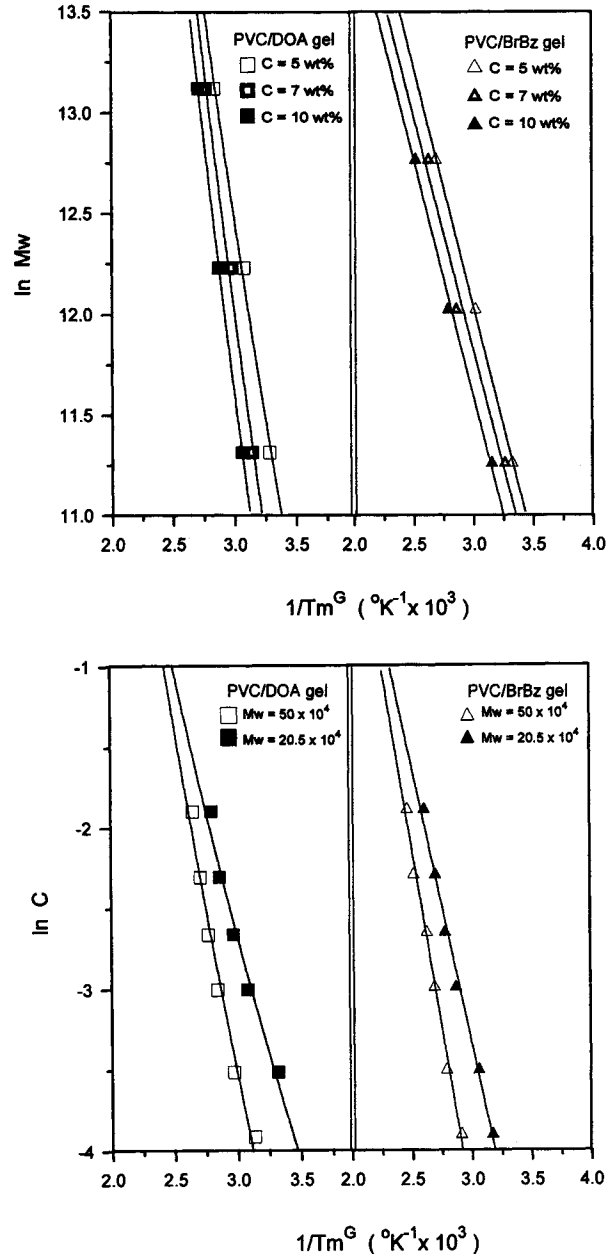


Figure 4 (a) Plot of  $\ln Mw$  versus  $1/T_m^G$  for PVC gels with various concentrations. (b) Plot of  $\ln C$  versus  $1/T_m^G$  for PVC gels with various Mws

$$\left[ \frac{\partial \ln C}{\partial (1/T_m^G)} \right]_{N,Mw} = \frac{\Delta H_m}{R(N-1)} = \frac{\Delta H_c}{R} \quad (3)$$

Here  $\Delta H_m$  is the enthalpy of formation per junction point and  $\Delta H_c$  is the enthalpy of formation per molecule entering into the junction point, the values of  $\Delta H_m$  and  $\Delta H_c$  can be obtained from the slope of the linear relationship in Figure 4a and b according to the Ferry–Eldridge relation. Then using the calculated values of  $\Delta H_m$  and  $\Delta H_c$ , the number of polymer chains held together in each junction point,  $N = 1 + (\Delta H_m/\Delta H_c)$  will be determined.

Figure 5 shows respectively the average number of PVC chains held together in each junction point,  $N$ , as a function of molecular weight,  $Mw$ , and concentration,  $C$ , for PVC/BrBz gels and PVC/DOA gels. The results indicate that  $N$  maintains roughly the same value of about 2 to 3, irrespective of the molecular weight and concentration of

polymer and the species of solvents. This also means that each junction point/microcrystal has almost the same width.

On the other hand, Takahashi *et al.*<sup>21-23</sup> have also proposed a formula, as shown in equation (4), for calculating the average number of syndiotactic sequences corresponding to the average size of each junction point in length for the gels.

$$\frac{1}{T_m^G} = \frac{\zeta}{(\zeta\Delta h_f + \zeta B'V_p - 2\sigma_{ec})} \left( \frac{\Delta h_f}{T_m^o} + \frac{RV_p}{V_s} - R \ln X_A \right) - \frac{R}{(\zeta\Delta h_f + \zeta B'V_p - 2\sigma_{ec})} \ln v_p X \quad (4)$$

$$B' = \frac{\chi_1 RT}{V_p} \quad (5)$$

Here  $T_m^G$  is the melting temperature of gel,  $v_p$  is the volume fraction of the polymer in the gel,  $x$  is the number of the repeating unit in the polymer,  $\zeta$  is the number of syndiotactic sequences which have entered into a junction point/microcrystal,  $\Delta h_f$  is the heat of fusion per repeating unit,  $T_m^o$  is the equilibrium melting temperature,  $X_A$  is the mole fraction of syndiotactic content in the polymer,  $B'$  is the interaction energy density characteristic of the 'polymer-solvent' pair,  $\sigma_{ec}$  is the end interfacial free energy per crystalline sequence, and  $V_p$  and  $V_s$  are the molar volumes of the polymer and solvent,  $\chi_1$  is the Flory interaction parameter,

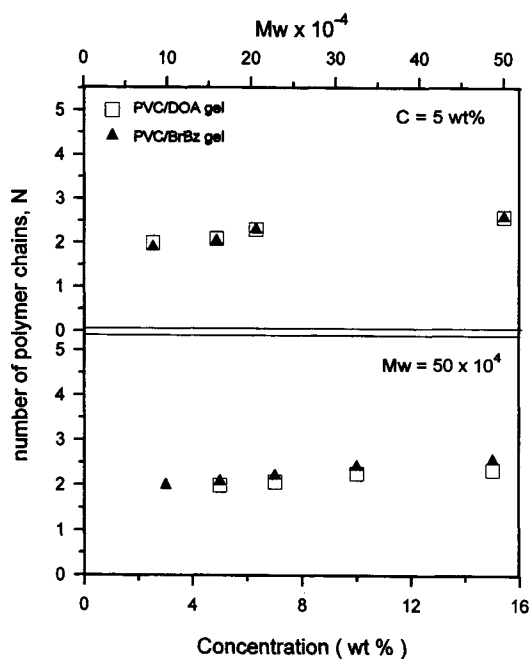


Figure 5 Plot of number of polymer chains,  $N$ , as functions of  $M_w$  and concentration

and  $R$  is the gas constant, respectively. All parameters used for calculation in equations (4) and (5) are listed in Table 2. Figure 6a and b show the plots of  $1/T_m^G$  versus  $\ln v_p x$  for PVC gels with different molecular weights and concentrations, respectively. From the slope and intercept in the linear

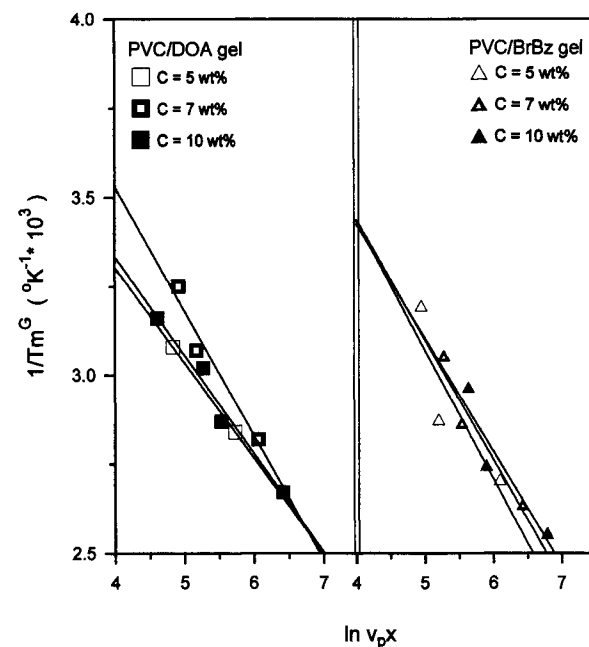
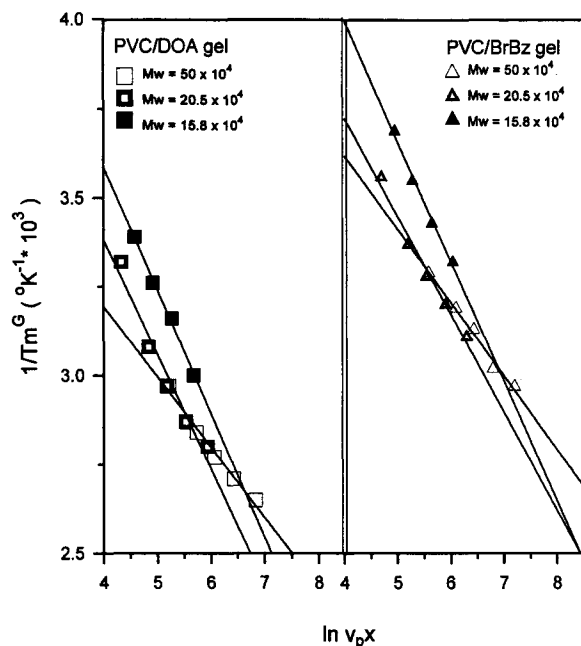


Figure 6 (a) Plot of  $\ln v_p x$  versus  $1/T_m^G$  for PVC gels with various  $M_w$ s. (b) Plot of  $\ln v_p x$  versus  $1/T_m^G$  for PVC gels with various concentrations

Table 2 Values of parameters used for the calculations in this study

	$T_m^o$ <sup>a</sup> (K)	$\Delta h_f^o$ <sup>a</sup> (J mole <sup>-1</sup> )	$X_A$ (%)	$V_p$ (cm <sup>3</sup> mole <sup>-1</sup> )	$\chi_1$ <sup>b</sup>	$B'$ (J cm <sup>-3</sup> )	$V_s$ (cm <sup>3</sup> mole <sup>-1</sup> )	$v_p^c$ (% v/v)
PVC	583	3300	32 <sup>d</sup>	46.25				
DOA					0.09	2.68	85.21	5.43
BrBz					-0.06	-1.42	104.75	5.62

<sup>a</sup>  $T_m^o$  and  $\Delta h_f^o$  are taken from Ref. <sup>29</sup>

<sup>b</sup>  $\chi_1$  is taken from Ref. <sup>30</sup>

<sup>c</sup> Values used for the calculation in equation (7)

<sup>d</sup> Syndiotactic content is taken from Table 1

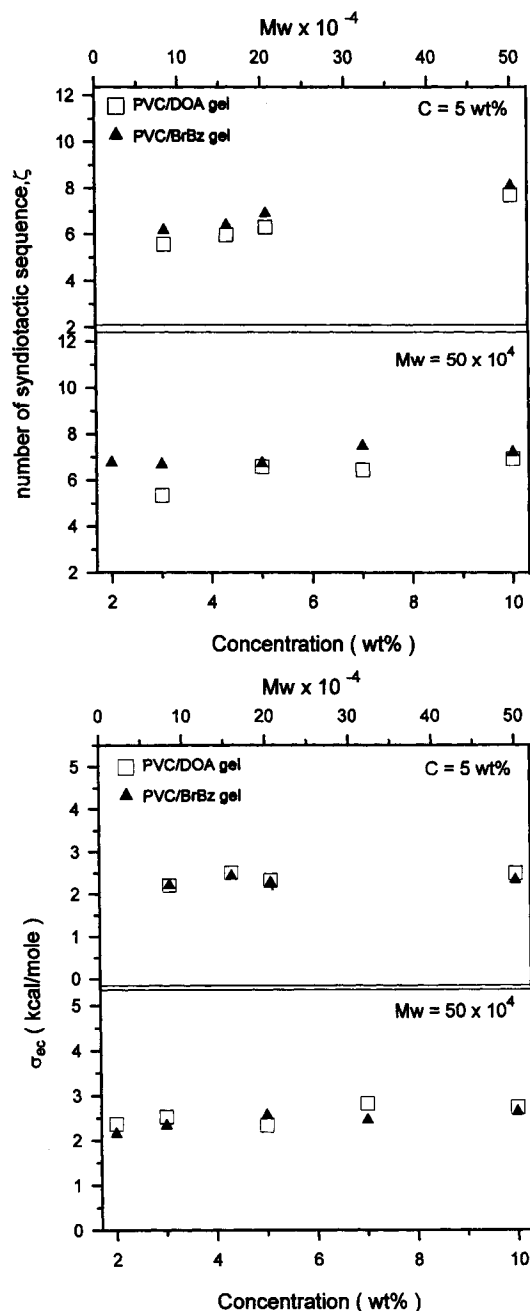


Figure 7 (a) Plot of  $\zeta$  as functions of  $M_w$  and concentration. (b) Plot of  $\sigma_{ec}$  as functions of  $M_w$  and concentration

relationship in Figure 6a and b, the  $\zeta$  and  $\sigma_{ec}$  could be obtained from equation (4). Figure 7a and b show the calculated values of  $\zeta$  and  $\sigma_{ec}$  as functions of  $M_w$  and  $C$  for PVC gels, respectively. The results indicate that the average number of syndiotactic sequences and the end interfacial energy for each junction point have no remarkable change among the different gels prepared from various conditions of the gelation and maintain roughly the same range of  $\zeta = 6 \sim 8$  and  $\sigma_{ec} \approx 2.3 \text{ kcal mol}^{-1}$ . Comparison of the results reported by Takahashi *et al.*<sup>21,22</sup> shows that the  $\zeta$  in this study is comparatively small because of the lower syndiotactic content of PVC used in this study, but the value of  $\sigma_{ec}$  is roughly the same. Combination of these results with those mentioned above indicates that the average size of the junction point/microcrystal shows no remarkable change with the sample preparation condition in the initial state of gelation.

Figure 8 shows the WAXD intensity curves of PVC gels.

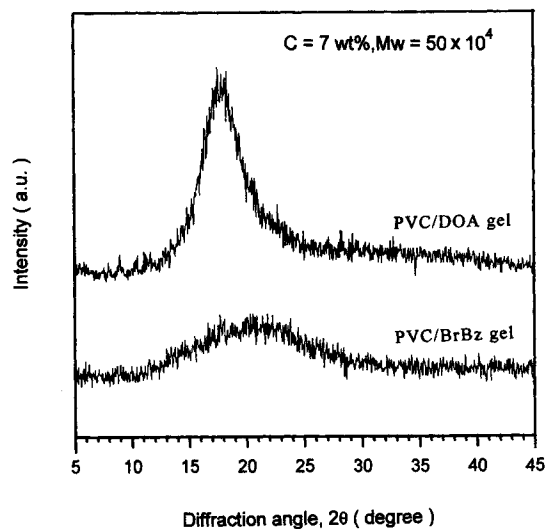


Figure 8 WAXD intensity curves of PVC gels

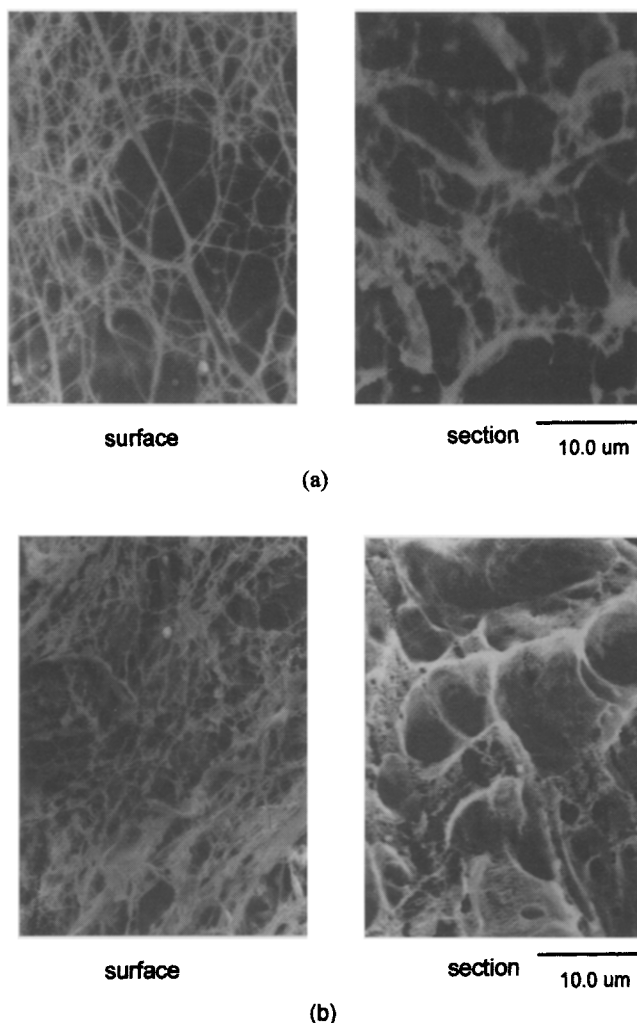


Figure 9 SEM photographs of freeze-dried PVC/DOA gels at a given  $M_w = 50 \times 10^4$ : (a) 3 wt.%, (b) 5 wt.%

The result shows that only an amorphous scattering peak is observed in both PVC/BrBz gel and PVC/DOA gel, indicating that the size of the junction point/microcrystal is too small to produce a crystalline diffraction pattern in X-ray intensity curves. However, the peak of amorphous scattering in PVC/DOA gel is much sharper than that in PVC/BrBz gel, implying that PVC/DOA gel has a thicker

network structure due to a larger degree of polymer aggregation, i.e. heterogeneous network structure in PVC/DOA gels.

Figure 9a and b show the SEM photographs of 3 wt.% and 5 wt.% freeze-dried PVC/DOA gels, respectively. From the pictures, it can be clearly observed that the gel morphology is formed by a fibril-like network structure. The mesh size of 5 wt.% gel is smaller than that of the 3 wt.% one. However, the freeze-dried PVC/BrBz gel cannot be obtained, because the freezing point of BrBz is about  $-34^{\circ}\text{C}$  which must depress significantly in the semi-dilute polymer solution state and the molecular interaction between BrBz and PVC may be too strong so that the sublimation of the solvent becomes difficult under a very low temperature. The differences in gel morphology with the solvent type could not be observed in this study. Yang and Geil<sup>5</sup> have used a freeze-etching technique to prepare a dried gel for observing gel morphology by electron microscopy. On the other hand, Mutin and Guenet<sup>6,7</sup> also determined gel morphology using optical microscopy and considered that the mesh structure of the network is related to the polymer concentration from the studies of PVC dilute solutions by light scattering analysis. Combination of the results from Yang and Geil and Mutin and Guenet indicates that the gel morphology consists of a fibrous network, and that the mesh size of PVC gel in good solvent is smaller than that in poor solvent. Figure 9 indicates that the number of the junction point increases and the mesh size decreases with increasing polymer concentration. The mechanical properties such as the modulus of gels may be related to the mobility of polymer chains between junction points.

For calculating the activity energy of polymer solutions, the Arrhenius equation<sup>24</sup> as shown in equation (6) is used.

$$\frac{1}{\eta} = \frac{1}{\eta_0} e^{-\Delta E/RT} \quad (6)$$

Here  $\eta$  is the viscosity of the solution,  $\eta_0$  is the viscosity of infinitely dilute solution, and  $\Delta E$  is the activity energy. Figure 10 shows the plot of  $\ln 1/\eta$  versus  $1/T$ , and the  $\Delta E$  can be obtained from the slope of the linear relationship in the plot. The result indicates that the activity energy of PVC/BrBz solution is about  $17.1 \text{ kJ mole}^{-1}$  while that of PVC/DOA is  $5.8 \text{ kJ mole}^{-1}$ , implying that the mobility of PVC chains in DOA is higher than that in BrBz. This may mean that the aggregation of PVC chains is much easier in PVC/DOA solution, resulting in a heterogeneous network structure under the same degree of the undercooling. This aggregation may be similar to that proposed by Stoks *et al.*<sup>25</sup> for the PVA/EG gels. Soenen and Berghmans<sup>11</sup> have also reported that the liquid-liquid phase separation takes place in poor solvent but not in good solvent for PVC gels. Figure 11 shows the gelation time as a function of polymer concentration under the same undercooling. The gelation time of PVC/BrBz solution is shorter than that of PVC/DOA solution at below  $C = 6 \text{ wt.}\%$ , indicating that the junction points induced by the chains association easily occur in the less liquid-liquid phase separation of semi-dilute PVC/BrBz solution. It is reasonable to consider that the polymer chains are more extended in the good solvents for the semi-dilute solution to increase the opportunity of the intermolecular association for forming junction points. The higher elasticity in PVC/BrBz gels is considered to be related to the homogeneous network structure with a smaller mesh size. The result is corresponding to our previous study<sup>12</sup> for PVA gels. High crystalline PVA gel formed

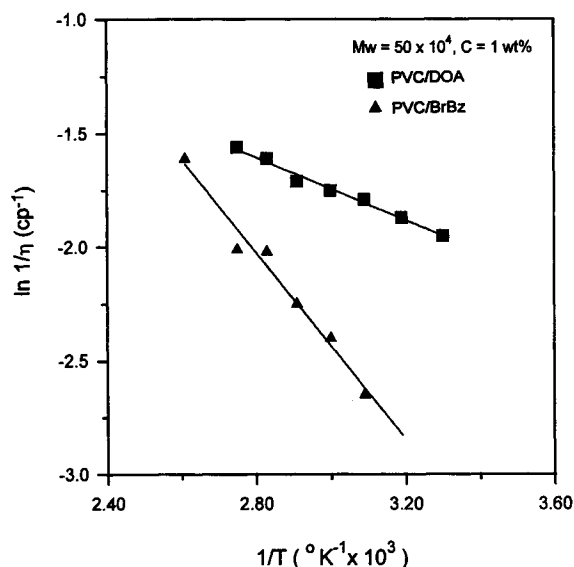


Figure 10 Plot of  $\ln 1/\eta$  versus  $1/T$  for PVC solutions at a given  $M_w = 50 \times 10^4$  and  $C = 1 \text{ wt.}\%$

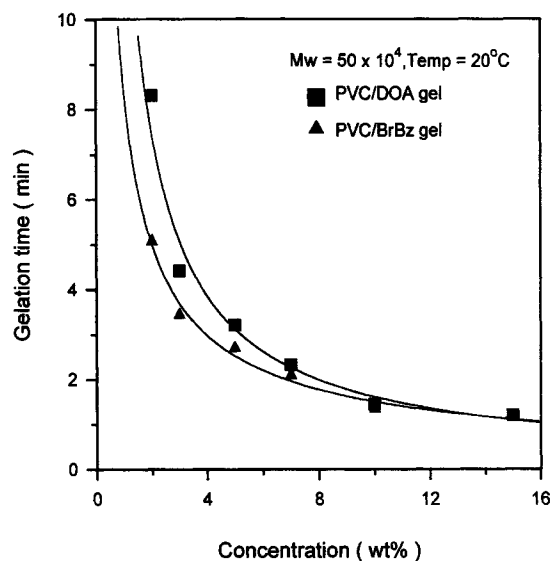


Figure 11 Plot of gelation time as a function of concentration

from poor solvent has a lower value of elasticity compared with that formed from good solvent. In this study, no remarkable differences in crystalline properties are observed between PVC/BrBz gel and PVC/DOA gel from the results of the junction point size and WAXD. These results in both PVA and PVC gels let us consider that the elasticity of physical gels is mainly dominated by the homogeneous degree of network structure with less liquid-solid phase separation, i.e. gel morphology with smaller mesh size due to the larger number of the junction point/microcrystal.

Regarding the melting temperatures,  $T_m^G$  values, of PVC gels, if nearly the same size of junction points/microcrystals formed with the syndiotactic sequences is present, at the same concentration and molecular weight of polymer, then the  $T_m^G$  values of gels should be only affected by the solvent quality. Generally, the gel formed with good solvent has a lower  $T_m^G$  due to the higher solubility. However, the results of this work and Harrison *et al.*<sup>20</sup> show that  $T_m^G$  values of PVC/BrBz gels are higher than those of PVC/DOA gels at the same gelation condition. This phenomenon may be

worthily discussed using the Flory–Huggins<sup>26,27</sup> relation for the melting point depression as shown in equation (7).

$$\frac{1}{T_m^{G'}} - \frac{1}{T_m^0} = \frac{T_m^0 - T_m^{G'}}{T_m^0 T_m^{G'}} = \frac{R}{\Delta h_f} \left( \frac{V_p}{V_s} \right) [(1 - v_p) - \chi_1 (1 - v_p)^2] \quad (7)$$

In equation (7), two parameters which affect  $T_m^{G'}$  are  $V_s$  and  $\chi_1$ . Generally, the molar volume of the solvent used is the same, the  $T_m^{G'}$  values of the gels formed from good solvents must be lower than those from poor solvents, because of the smaller  $\chi_1$ . However, the  $V_s$  is also a very importance factor related to the  $T_m^{G'}$ . Najeh *et al.*<sup>28</sup> have already discussed the effect of  $\chi_1$  and  $V_s$  on the  $T_m^{G'}$  and compression modulus of PVC gels prepared from the solvents with different functional groups such as monoesters and diesters. Their results showed that the gel prepared from the solvent with larger molar volume has a higher  $T_m^{G'}$  at the same  $\chi_1$ . In this work, the degree of melting temperature depression,  $\Delta T = T_m^0 - T_m^{G'}$  are obtained from equation (7) using the parameters as shown in Table 2. The result shows that  $\Delta T$  in PVC/DOA gel (238 K) is larger than in PVC/BrBz gel (229 K), implying PVC/BrBz gel has a higher  $T_m^{G'}$  at a given concentration. Although the calculated value of  $\Delta T$  depends on the  $T_m^0$  and  $\Delta h_f$  of the pure polymer, which may be changed under the various crystallization conditions, the difference in  $\Delta T$  between PVC/BrBz and PVC/DOA gels may be explained from this viewpoint.

## SUMMARY

In this work, the structure and physical properties of PVC gels prepared from the solutions of bromobenzene (BrBz) and dioxane (DOA) under different conditions of gelation have been studied. First, the thermodynamic equilibrium principles based on the theories proposed by Ferry and Eldridge, and Takahashi *et al.* are used for calculating the average size of the junction point/microcrystal in the network structure of PVC gels. The results indicate that the average size of the junction point of PVC gels in the initial gelation state are the combination of *ca.* two to three chains in width and *ca.* six to eight syndiotactic sequences in length to form a fibril-like network structure, irrespective of the species of solvents used, the molecular weight and concentration of the polymer. Because the size of the junction point/microcrystal is too small, the result of WAXD shows only a broad intensity peak, implying that the crystallinity is very low and no remarkable difference among PVC gels. However, the X-ray intensity peak of amorphous scattering in PVC/DOA gel is sharper than that in PVA/BrBz gel, indicating that PVC/DOA gel has a thicker network structure due to a higher degree of the liquid–solid phase separation. The results of the viscosity shows that the PVC/BrBz solution has a higher value of activity energy than PVA/DOA solution does. The gelation time of semi-dilute PVC/BrBz solution is shorter than that of PVC/DOA one, indicating that junction points induced by the chain association easily carry out in the less liquid–liquid phase separation of semi-dilute PVC/BrBz solution. The morphology of the gel is investigated from the observation of dried gel prepared from the freeze-drying method using electron microscopy. The results show that the gel morphology consists of a fibril-like structure and the

mesh size of the network decreases with increasing polymer concentration. The differences in the elasticity of gels may be considered to be mainly due to the mesh size of gel network and the homogeneous degree of polymer chain aggregation related to the molecular interaction between PVC and solvent. Although the molecular interaction between PVC and BrBz is stronger than that between PVC and DOA, the  $T_m^{G'}$  values of PVC/BrBz gels are still higher than those of PVC/DOA. This unreasonable result may be considered not due to the crystalline properties of PVC gels, but to the molar volume of the solvent used.

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