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Network structure and chain mobility of freeze-dried polyvinyl chloride/dioxane gels

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In this work, the network structure and chain mobility of dried polyvinyl chloride/dioxane (PVC/DOA) gels prepared by the freeze-drying method are studied by SEM, FTIR, WAXD, EDTA and pulsed NMR analyses. The results of *FT*i.r. and WAXD show no remarkable change in the crystallinity of either dried or wet PVC gels; however, the elasticity of wet gels and the gelation time of semi-dilute solutions exhibit remarkable changes with increasing concentration, C and molecular weight, M_w of the polymer. From SEM results, the dried gel morphology consists of a fibril-like structure and the mesh size of the gel network decreases, resulting in the glass transition temperature (T_g) shifting to higher temperatures with increasing M_w and C. The results of pulsed NMR (CPMG method) for wet gels show that spin–spin relaxation time, T_2^s and T_1^l, respectively, related to the immobile and mobile components decrease, and the fractional amount of the immobile component, f^s increases, while that of the mobile component, f^l decreases with increasing M_w and C. On the other hand, similar results are also found in freeze-dried gels from the pulsed NMR experiment (FID method). These facts in both wet and dried gels are considered to be due to the reduction of chain mobility related to the increase in the aggregation of polymer chains or the number of junction points in the gel network. The change in elasticity of PVC/DOA gels must be mainly related to the chain mobility of the network structure but not to the crystallinity of gels. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyvinyl chloride; freeze-dried gel; chain mobility)

INTRODUCTION

Studies on physical polymer gels attract much interest because the relationship between the network structure and the physical properties is very complicated[1–9]. The formation of polyvinyl chloride (PVC) physical gels is generally classified as crystallization-induced gelation[10]. It is well known that atactic PVC is a low crystalline polymer and gelation of PVC solution occurs under a great amount of solvent, therefore the crystallization becomes more difficult. Generally, it is considered that microcrystals can only be formed by the association of syndiotactic PVC chains. However, the network structure is very difficult to determine, because a large amount of solvent exists within gels. For example, in our previous study[4] the X-ray intensity curve of PVC gel only showed an amorphous scattering peak, which must be mainly due to the scattering of solvents. How to prepare a dried gel is very important for determining the real network structure of gels.

The gel morphology has been reported by Aubert[11,12], Hikmet *et al.*[13] and Prasad *et al.*[14] from the SEM observations of dried polystyrene gels. They showed that the morphology of PS gel exhibits either an open strut-like network or smooth spherical globules. On the other hand, the morphology of PVC gel has also been investigated by Yang and Geil[1] from SEM observation of a freeze–fracture gel. Mutin and Guenet[2] also determined gel morphology using optical microscopy. Their results showed that gel morphology consists of a fibrous network. However, there is no certainty that what the real gel structure can be certified corresponds to the actual properties of PVC gels. Recently, the dynamic phenomenon in many heterogeneous polymer systems (e.g. polymer gels, polymer blends, and polymer solutions) has been studied by pulsed NMR[15–21]. The decaying signals of heterogeneous materials could be decomposed into two or three components with various spin–spin relaxation times, T_2, which indicates that the difference in molecular mobility must be related to the structural heterogeneity. In our previous results[4], it is found that the average size of junction point/microcrystal in the gel network is the combination of 2–3 chains in width and about 6–8 syndiotactic sequences in length for the formation of a PVC gel with a fibril-like network structure, irrespective of the species of solvents used and the molecular weight and concentration of the polymer. However, the physical properties of PVC gels increase remarkably as the molecular weight and concentration of the polymer are increased. These facts may imply that the increase in the number of junction points or the aggregation degree of polymer chains enhances the physical properties of PVC gels.

In this work, the freeze-drying method was used for preparing dried PVC gel by extracting the solvent from the frozen gel at a very low temperature under vacuum. Because no remarkable shrinkage (less than 1%) of the gel volume occurred after freeze-drying, the network structure of freeze-dried gel may be considered to be the same as that of wet gel. Then, the morphology of dried gel is determined by electron microscopy for studying the relationship between network structure and chain mobility of PVC gels.

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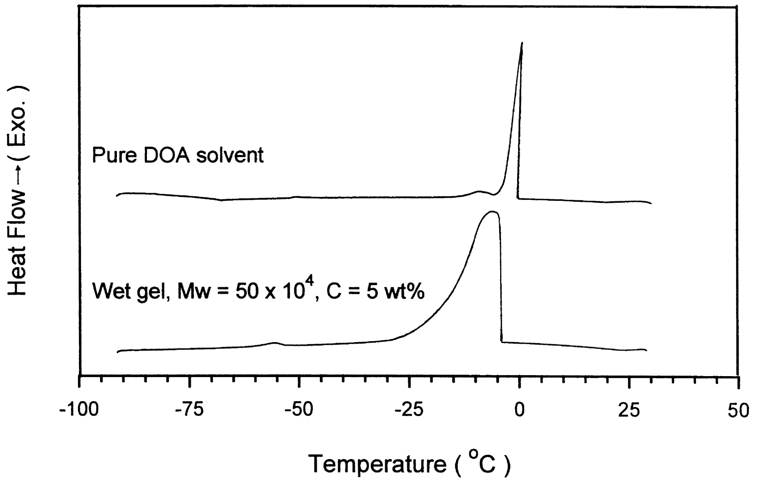

Figure 1 DSC thermogram of PVC/DOA wet gel and pure DOA solvent

EXPERIMENTAL

Materials

The PVCs used in this work were laboratory-grade powders (Aldrich Chemical Co. Ltd, USA). The solvent, dioxane (DOA), was analytical grade and purified by distillation before use. The characteristics of PVCs used in this work are shown in *Table 1*. The syndiotacticity of PVCs with different weight-average molecular weights ($M_w = 50.0 \times 10^4$, 20.5×10^4, 15.8×10^4, 8.3×10^4), determined from ^{13}C NMR, is roughly the same[4]. It means that the tacticity would not affect the structure and properties of gels in this study. The homogeneous PVC solutions with various concentrations of PVC were obtained by heating at 110–120°C for 2 h and were then cooled at a cooling rate of 10°C min^{-1} to 30°C for 24 h to form gels.

Freeze-drying of 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 gel. The solvent will be sublimated from the frozen gel during freeze-drying under vacuum. The freeze-dried gel was prepared as follows: the homogeneous PVC/DOA solution was cooled to room temperature to form a wet gel and then the gel was placed into the freeze-drying equipment at −50°C, where it was quickly frozen to form an ice-like solid. Under a vacuuming condition for more than 2 weeks, a dried-pore material could be obtained. The surface morphology of freeze-dried PVC gel was measured by a scanning electron microscopy (SEM; Cambridge S-360).

The freezing temperature of PVC gel was determined by Du-Pont 2000 DSC equipment. About 10 mg of PVC gel was measured from 30°C to −90°C at a cooling rate of 5°C min^{-1}. *Figure 1* shows the DSC result of PVC gel and pure DOA solvent. The freezing temperature range of PVC gel is significantly lower than that of DOA solvent. In order to avoid the effect of freezing point depression due to the colligative property of the solvent, the freeze-drying process took place at −50°C.

Table 1 Characteristics of samples used. Tacticity was measured by ^{13}C-NMR (P_{rr} syndiotactic; P_{rm}: atactic; P_{mm}: isotactic)

Sample No.	$M_w \times 10^{-4}$	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

The residual solvent in the freeze-dried PVC gel was checked by using a Digilab Division BIO-RAD spc-3200 FTIR system. *Figure 2* shows the FTIR results for freeze-dried PVC gel and original PVC powder. The absorbance intensity curves between the freeze-dried PVC gel and the original PVC powder show no remarkable difference and there is no other absorbance peak due to the solvent, indicating that the DOA solvent is almost completely removed from wet PVC gel during freeze-drying under vacuum.

Measurements

The modulus of wet gel was obtained using ball indentation experiments proposed by Hertz[22,23]

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

where E represents Young's modulus (dynes cm^{-2}), F represents the force of sphere against the gel surface (dynes), r represents the radius of sphere (cm), and h

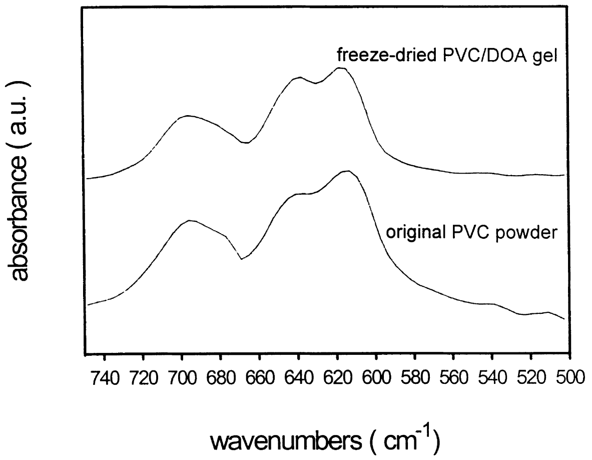

Figure 2 FTIR spectra of freeze-dried PVC/DOA gel and original PVC powder

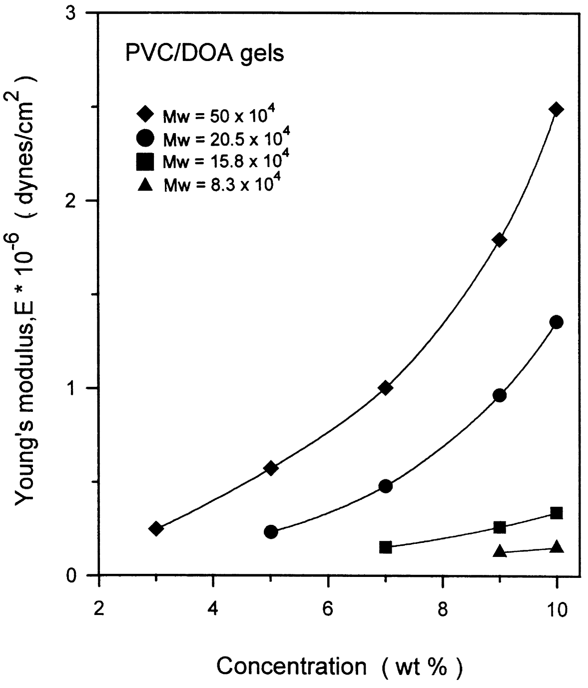

Figure 3 Plot of E as a function of M_w for PVC/DOA gels with various C

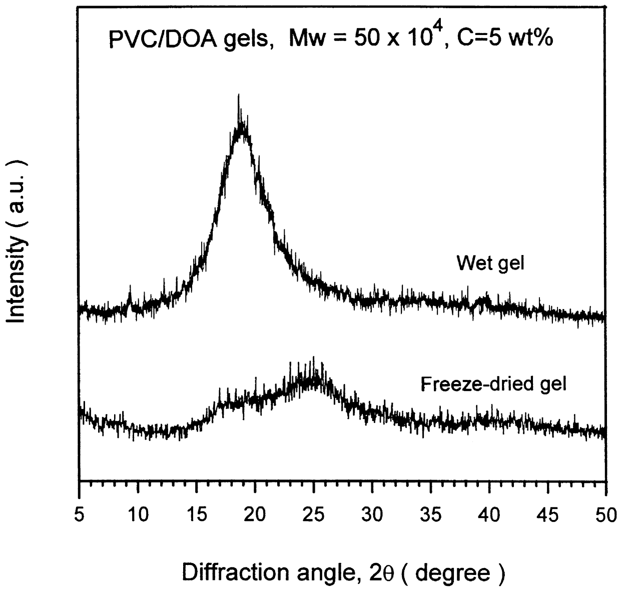

Figure 4 WAXD intensity curves of wet and freeze-dried PVC/DOA gels

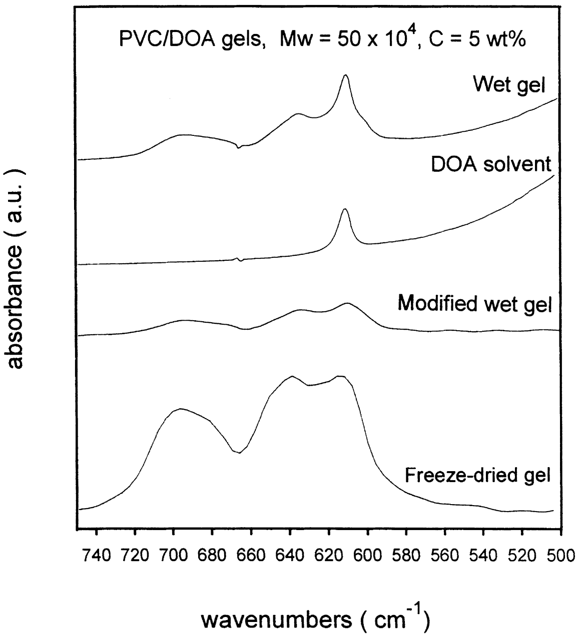

Figure 5 FTIR spectra of wet and freeze-dried PVC/DOA gels

represents the depth of indentation of sphere (cm), and the ν represents Poisson's ratio, with the typical value for elastomer of $\nu = 0.5$.

The gelation times were measured using a gelation timer (Techne Co., UK) operating at a fixed temperature of 20°C. The gelation timer consists of a flat, weighted disc which is connected by a link to a synchronous motor. The disk falls under gravity in the polymer solution. At the gel point the rigidity of the polymer is sufficient to support the weight of the disc, and causes the link to be compressed to stop the synchronous motor. The time at which the synchronous motor stopped is defined as the gelation time.

The infrared spectra were measured by using a Digilab Division BIO-RAD spc-3200 FTIR system. The absorbency ratio of 604/690 cm^{-1} and 640/690 cm^{-1} are the regulativity index of the PVC chain. The peaks at 604 cm^{-1} or 640 cm^{-1} and 690 cm^{-1} were assigned to the crystalline and the amorphous sequences, respectively[24].

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

The dielectric thermal analysis (DETA) was carried out with the GABO eplexor 150-N dielectric thermal analysis instruction. About 2 mm thickness and 20 mm diameter of circular freeze-dried gel was placed in a sample plan, the tan δ was recorded at 100 Hz frequency from − 100 to 100°C at a heating rate of 2°C min^{-1}.

^1H pulsed NMR measurements were performed with a MARAN-20 pulsed NMR spectrometer operating at a fixed frequency of 20 MHz at 30°C. The recovery time of the spectrometer following a sequence of pulses was 15 μs. The spin–spin relaxation time, T_2 measurements were carried out using the solid echo[25] (free induction decay, FID) pulsed sequence $(90°_x\tau 90°_y)$ ($P90° = 2.8$ μs) available for short T_2 sample, e.g. dried gel system, to avoid the effect of the dead time after the pulse, and Carr–Purcell–Meiboom–Gill (CPMG)[26] pulsed sequence $[90°_x\tau(180°_y 2\tau)_n]$ ($P90° = 2.8$ μs, $P180° = 5.6$ μs, and $n = 4000$) available for long T_2 sample, e.g. wet gel system, to eliminate the effect of heterogeneity in the static magnetic field.

RESULTS AND DISCUSSION

Figure 3 shows Young's modulus, E of wet gels as functions of the molecular weight, M_w and the concentration, C, of polymer. The result indicates that Young's modulus of PVC/DOA gel increases significantly with increasing M_w and C, implying that the difference in Young's modulus must be due to the structural change of gels. However, the network structure is very difficult to determine because of the large amount of solvent within gels. Dorrestijn *et al.*[3] have reported that the presence of crystalline PVC could not be proved by WAXD and DSC investigations. The greatest

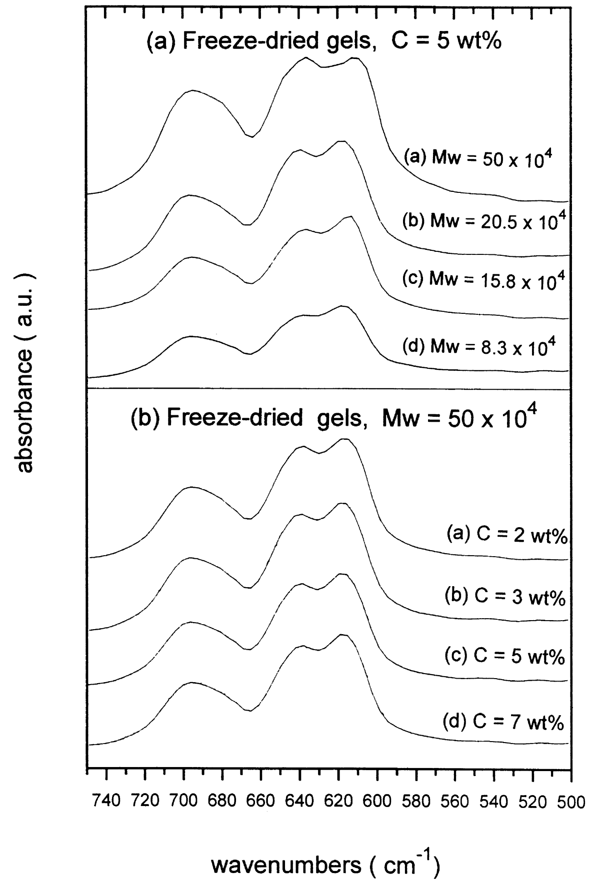

Figure 6 FTIR spectra of freeze-dried PVC/DOA gels with various M_w and C

doubt for studying the gel morphology is that there is no certainty that what is eventually seen corresponds to the actual gel structure in the wet state. In this study, the dried gel is obtained using the freeze-drying method where the solvent is sublimated from the frozen gel under vacuum at a low temperature. Because no remarkable shrinkage (less than 1%) of gel volume occurs after freeze-drying, the structure of freeze-dried gel may be considered to be the same as that of wet gel.

Figure 4 shows WAXD intensity curves of wet and dried gels. The result shows that only an amorphous scattering peak due to the scattering intensity of solvents could be observed in the wet gel. On the other hand, the freeze-dried gel shows a typical PVC WAXD intensity curve, although the crystallinity of dried gel is too low to produce sharply crystalline diffraction peaks. *Figure 5* shows the *FT*i.r. spectra of the wet and dried gels. The peaks at 604 and 640 cm^{-1} are assigned to crystalline sequences, and that at 690 cm^{-1} is assigned to the amorphous ones[24]. The spectrum of modified sample is PVC/DOA wet gel subtracted from that of DOA. There is no remarkable difference in the ratio of 604/690 and 640/690 cm^{-1} between wet and dried gels, indicating that the degree of regular chain arrangement of freeze-dried gel is roughly the same as that of wet gel. The effect of structural change on the physical properties of PVC gels with M_w and C has been investigated by Dorrestijn *et al.*[3] They pointed out that the number and the size of junction points in the gel network increased with increasing M_w and C. However, in our previous study[4] for PVC gels, no remarkable change in the average size of junction point/microcrystal was found as M_w and C were increased. WAXD and *FT*i.r. results as shown above indicate that it may only increase the degree of PVC chain aggregation or the number of junction points but not the crystallinity of PVC gel with increasing M_w and C.

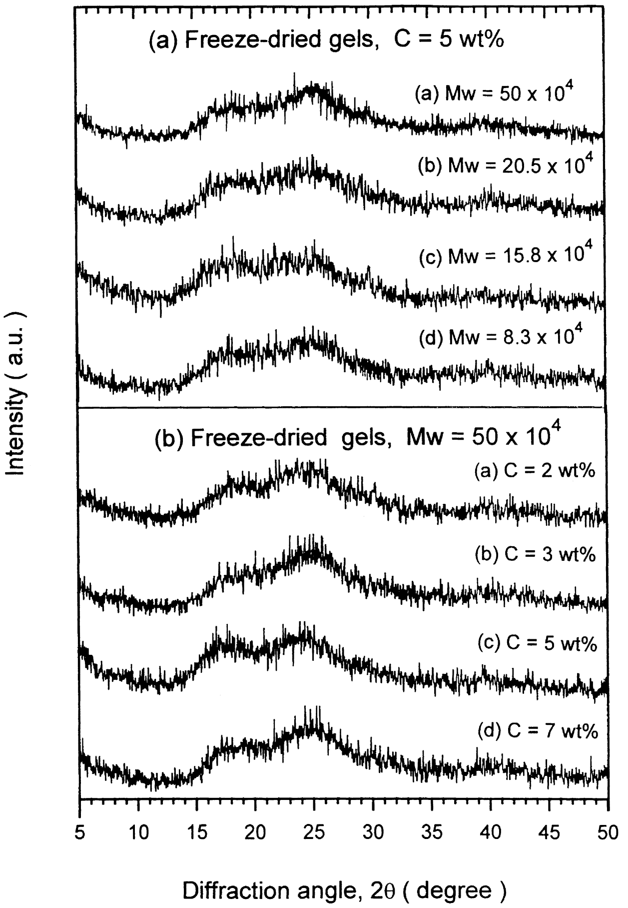

Figure 7 WAXD intensity curves of freeze-dried PVC gels with various M_w and C

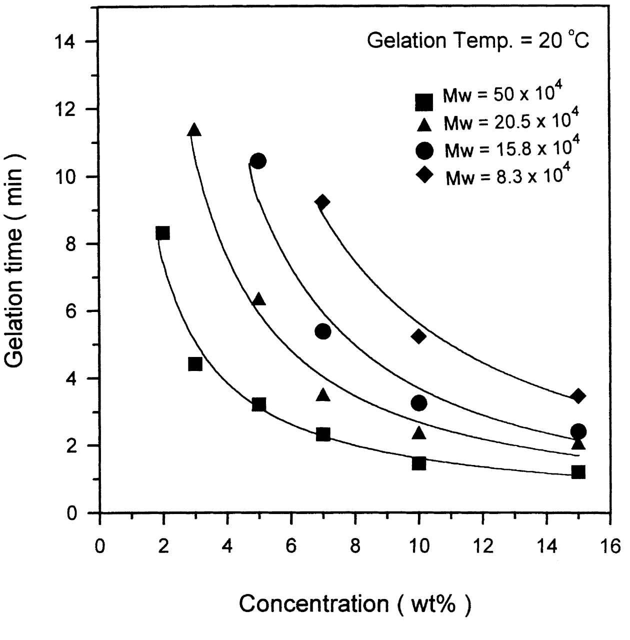

Figure 8 Plot of gelation time as functions of M_w and C at 20°C

Figure 6a and *b* shows the *FT*i.r. spectra of freeze-dried

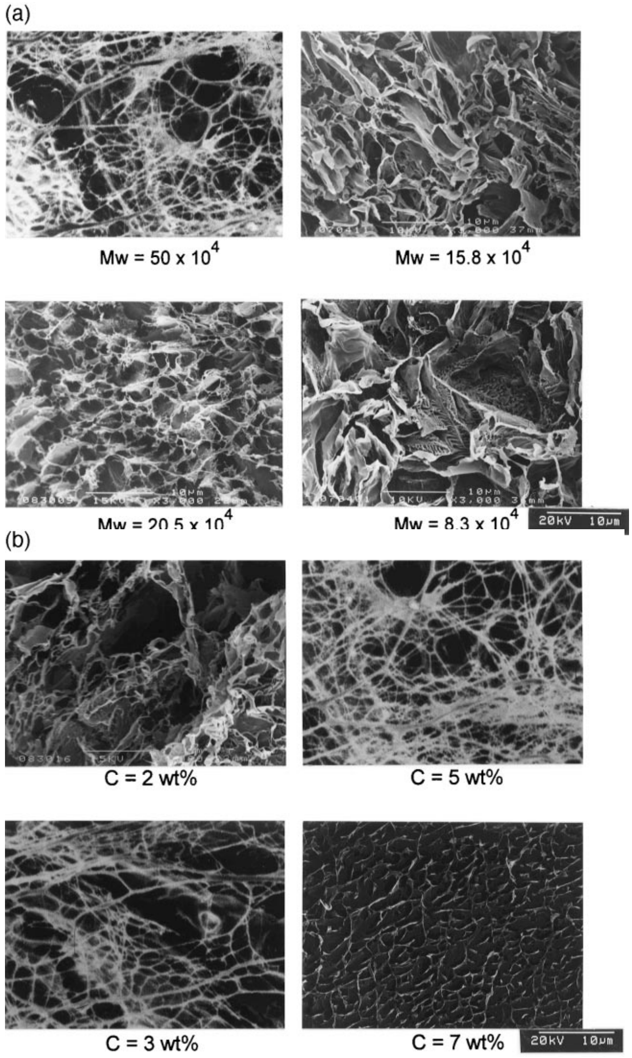

Figure 9 (a) SEM photographs of $C = 5$ wt% freeze-dried gels with various M_w. (b) SEM photographs of $M_w = 50 \times 10^4$ freeze-dried gels with various C

PVC/DOA gels with different M_w and C, respectively. The result indicates that no remarkable changes in the 604/690 and 640/690 cm^{-1} absorption intensity ratios are observed among dried gels. *Figure 7a* and *b* shows the WAXD intensity curves of dried gels. The result also indicates that nearly the same X-ray intensity curves are observed in these dried gels and the crystallinity of gels is still very low. In our previous study[4], the thermodynamic equilibrium principles based on the theories proposed by Ferry and Eldrige[31], and Takahashi *et al*.[32–34] were used for calculating the average size of the junction point/microcrystal in the network structure of PVC gels. The result showed that polymer chains are insufficient to form a larger size of crystal when the average size of the junction point in gel consists merely of approximately 2–3 chains in width and approximately 6–8 syndiotactic sequences in length, irrespective of M_w and C. It is reasonable to consider that the number of junction point/microcrystal increases with increasing M_w and C, although the size of the junction point/microcrystal is too small to be reflected on the change of crystallinity.

Figure 8 shows the gelation time of PVC/DOA solution as functions of M_w and C at 20°C. The gelation time of the solution decreases with increasing M_w and C, indicating that junction points formed by the chain association easily occur in the solutions with higher M_w and C. The distance between polymer chains is more closed in polymer solution with higher M_w and C to increase the opportunity of the intermolecular association for forming junction points. These facts as mentioned above for PVC gels let us consider that the change in the elasticity of wet gel may be mainly dominated by the increase in the number of the junction point/microcrystal or the degree of 'amorphous' chain aggregation in gels with increasing M_w and C.

Figure 9a and *b* shows the SEM photographs of freeze-dried PVC gels with different M_w and C, respectively. From *Figure 9a*, the gels with lower molecular weights ($M_w = 8.3 \times 10^4$ and 15.8×10^4) could not exhibit a complete network structure at $C = 5$ wt%, while those with higher M_w values showed a complete fibril-like network structure with a mesh size of about 1–10 μm. Mutin *et al*.[9] have determined the gel morphology of PVC/cyclohexanone/hexanol gel using optical microscopy and reported that the mesh size of network structure of PVC gel was about 5–10 μm. On the other hand, *Figure 9b* shows that the complete network structure could not be observed for 2 wt% gel with $M_w = 50 \times 10^4$, and the gel network becomes more complete as C is increased. Combination of SEM results in *Figure 9a* and *b* shows that the mesh size of PVC gel network decreases with increasing M_w and C. It is reasonable that the increase in M_w and C must make the polymer chains associate more easily with each other to increase the number of junction points for forming a smaller mesh size of network structure with a higher elasticity. The morphologies of PS and PE gels have been reported by Prasad *et al*.[14] Their results indicated that the gelation mechanism was induced by liquid–liquid phase separation, and the gels exhibit either an open strut-like network structure or smooth spherical globules depending on the concentration of polymer. They also considered that the former was attributed to gelation inside the spinodal region whereas the latter resulted from the gelation in the metastable region. However, the fibril-like structure in PVC/DOA gel is very different from the strut-like or the spherical structures in PE and PS ones, this may be due to the difference in the degree of liquid–liquid phase separation among these gels preparing from various solvents and gelation conditions. It is well known that atactic PVC is a low crystalline polymer compared with PE and isotactic PS. The liquid–liquid phase separation accompanied by crystallization is comparatively less obvious, resulting in a low crystalline and transparent PVC/DOA gel with a fibril-like network. This may be the main reason why the crystallinity has no remarkable change with increasing M_w and C in PVC gels.

Figure 10a and *b* shows the tan δ obtained from DETA analysis as a function of temperature for PVC gels with different M_w and C, respectively. There are three peaks in the range of the measuring temperature. The peak in the vicinity of 60°C in the curve is the molecular motion of PVC main chain, T_α (T_g) and that at 10–35°C is related to mobility of local molecule chain, T_β, and that at −30 to −40°C is related to chain end mobility, T_γ[35]. The result shows that the T_g of dried gel, which shifts from 55°C to 64°C with increasing M_w and C. This indicates that the reduction of molecular mobility is considered to be due to the decrease in free volume of polymer chain and the increase in the degree of chain aggregation or the number of junction points in gels. On the other hand, T_γ of dried gel shifts from −40 to −20°C with increasing M_w but not remarkably changes with increasing C, implying that the

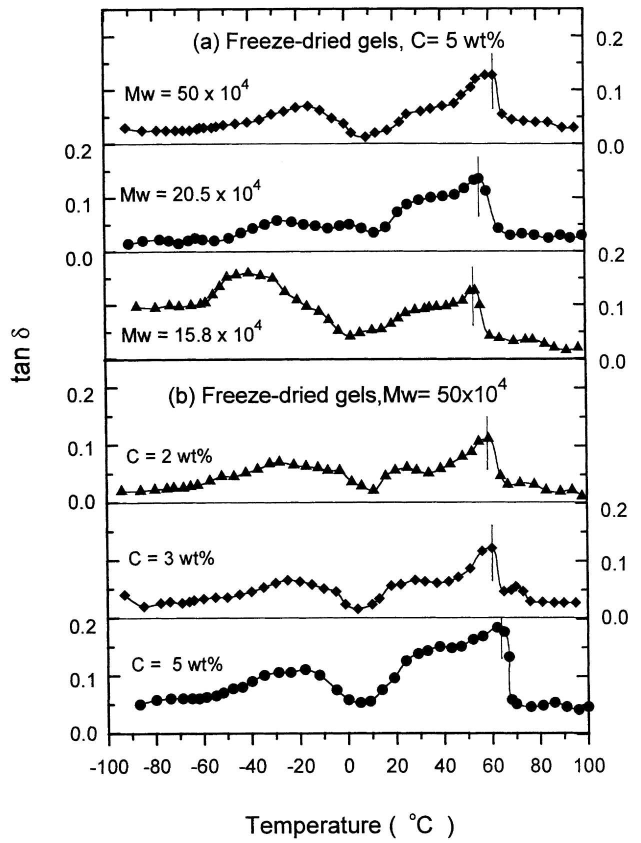

Figure 10 Loss tangent delta, tan δ, as a function of temperature for freeze-dried gels with various M_w and C

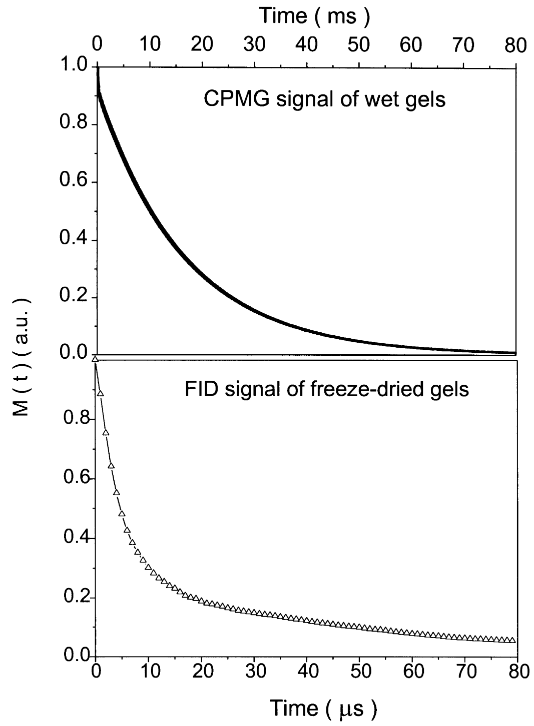

Figure 11 Decaying signals of CPMG and FID for wet and dried gels ($M_w = 50 \times 10^4$, $C = 5$ wt%)

chain end effect on T_γ is more obvious in M_w than that in C. The wider distributions of T_β and T_γ indicate that the heterogeneous network structure and the different chain length between junction points are formed in PVC/DOA gels, resulting in various kinds of molecular relaxation motion and mobility energy[36,37].

Physical gel systems often exhibit a heterogeneous structure[15–22], which leads to the heterogeneity in molecular mobility with a multi-exponential decay of transverse magnetization in pulsed NMR. The decaying signal of transverse magnetization, $M(t)$, for a polymer gel system is expressed as a function of the correlation time of molecular motion, τ_c, by the following equation[27,28]:

$$M(t) = M_0 \exp\{-\sigma_0^2\tau_c^2[\exp(-t/\tau_c) + t/\tau_c - 1]\} \quad (2)$$

where M_0 is a constant proportional to the total number of nuclei with magnetic moment and σ_0^2 is the second moment in the rigid lattice[29]. σ_0^2, which reflects the interaction among nuclear spins, is given by

$$\sigma_0^2 = (6/5)I(I+1)g^2\mu_N^2 N^{-1} \sum_i \sum_j \langle r_{ij}^{-6} \rangle \quad (3)$$

where I is the spin of the nucleus with magnetic moment ($I = 1/2$ for ^{1}H), g is the g factor, μ_N is the nuclear magnetization, N is the total number of nuclei with magnetic moment, and r_{ij} is the distance between nuclei i and j. The decaying signal of the transverse magnetization, $M(t)$ is expressed empirically following the Weibull function[30]:

$$M(t) = M_0 \exp[-(1/a)(t/T_2)^a] \quad (4)$$

where a is the shape parameter, $1 \le a \le 2$, which could express the characteristic of polymer material.

For $\tau_C\sigma_0 \ll 1$, the T_2 signals could be disposed to the soft domain of polymer material ($a = 1$).

$$M(t) = M_0 \exp(-t/T_2) \quad (5)$$

$$T_2 \sim (\sigma_0^2\tau_C)^{-1} \quad (6)$$

For $\tau_C\sigma_0 \gg 1$, the T_2 signal could be disposed to the rigid domain of polymer material ($a = 2$).

$$M(t) = M_0 \exp[-1/2(t/T_2)^2] \quad (7)$$

$$T_2 \sim \sigma_0^{-1} \quad (8)$$

The change of T_2 should be related to both the changes of τ_C and σ_0^2 based on the microscopic foundation. The molecular mobility strongly depends on the network structure of gels, and the appearance of the junction point/cross-link of network structure is attributed to the increase of σ_0^2, i.e. the decrease in T_2. The analysis of the decaying process is made by using the nonlinear least-squares method, which fits the experimental data into the following equation:

$$M(t) = M_{0A} \exp\left\{-\frac{1}{2}(t/T_{2A})^2\right\} + M_{0B} \exp(-t/T_{2B}) \quad (9)$$

where M_{oi} is the magnetic moment of ith component, and T_{2i} is the spin–spin relaxation time of ith component. From this fitting procedure, we found that the decaying signals of PVC/DOA gel could be roughly decomposed into two components. The fast decaying component is from the chain mobility in the junction domain (polymer rich) and the slow decaying one is from between junction domains (polymer poor). By connecting the results obtained from CPMG and solid echo (FID) methods, each component with various T_2 can be obtained separately without the effect of dead time after $90°_x$ pulse and the heterogeneity of magnetic field. The fractional amount f of each

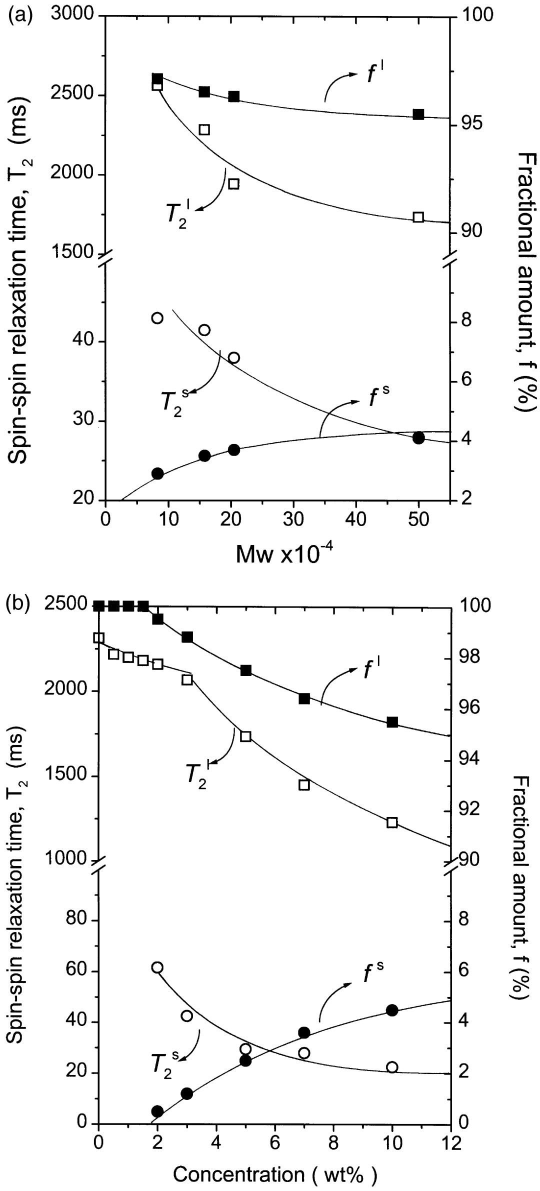

Figure 12 (a) Spin–spin relaxation time, T_2, and fraction amount, *f*, from CPMG signals of each component in wet gels as a function of M_w (C = 5 wt%): (□): T_2^l; (○): T_2^s; (■): f^l; (●): f^s. (b) Spin–spin relaxation time, T_2, and fraction amount, *f*, from CPMG signals of each component in wet gels as a function of C ($M_w = 50 \times 10^4$): (□): T_2^l; (○): T_2^s; (■): f^l; (●): f^s

component is obtained from $f^s = [M_{0A}/M(t)] \times 100\%$ and that $f^l = [M_{0B}/M(t)] \times 100\%$, respectively. *Figure 11* shows the decaying signals of wet (CPMG) and dried gels (FID). The CPMG and FID decaying signals are decomposed into two components using equation (9) for calculating T_2 and *f* of each component. *Figure 12a* and *b* show T_2 and *f* of two components with different chain mobilities, which are separated from the results of CPMG decaying signals in wet gels as functions of M_w and *C*, respectively. The component with the long $T_2(T_2^l)$ and the short $T_2(T_2^s)$, and the fractional amount of long $T_2(f^l)$ and fractional amount of short $T_2(f^s)$ originate from polymer-poor and polymer-rich domains in gels, respectively. In *Figure 12b*, only a T_2^l component is detected for the samples with *C* below 2 wt% ($M_w = 50 \times 10^4$), while two components, T_2^l and T_2^s are observed at higher *C* regions, indicating that the gelation induced by liquid–liquid separation of PVC/DOA solution only takes place at *C* above 2 wt% in this work. Ikehara *et al.*[15] studied the relation between volume phase transition process and spin diffusion in the heterogeneous structure of acrylamide gels by pulsed NMR. They showed that the discontinuous change of chain mobility was observed at the transition point of the volume change for ionized gels with acetone content of the mixed solvent above 50%, while homogeneous behaviours were observed at acetone content below 50%. This means that polymer chains start to aggregate with each other at the transition point. Combination of SEM and pulsed NMR results indicates that PVC/DOA gels cannot be formed with a complete network structure at lower M_w and *C*, because these gels are attributed to the gelation from comparatively homogenous solution. *Figure 12a* and *b* also shows that T_2^s decreases with increasing M_w and *C*. This is due to the fact that the polymer chains associate with each other for forming the polymer-rich region to increase the immobile chains in gels. On the other hand, the value of T_2^l also decreases remarkably with increasing M_w and *C*, and this may be due to the increment of the solvents bound with polymer chain. The states of bound solvent molecule and free solvent molecule are difficult to distinguish from CPMG signals, although the mobilities must differ from each other in wet gels. The fractional amount of the immobile component/polymer-rich phase, f^s, only increases from about 1% to 5% as M_w and *C* are increased, implying that the phase separation is less remarkable in PVC/DOA gel. This result is in good agreement with that of SEM observation.

The spin–spin relaxation time, T_{2F} and the fractional amount, f_F, from FID signals of each component as functions of M_w and *C* for dried gels are shown in *Figure 13a* and *b*, respectively. We consider that the long $T_2(T_{2F}^l)$ and the short $T_2(T_{2F}^s)$ components come from, respectively, the molecular mobility for between and inner junction points in freeze-dried gels, because the response of chain mobility inner junction points (immobile component) must be faster than that between junction points (mobile component). *Figure 13a* and *b* shows that there is no remarkable change in T_{2F}^s with a value of about 6 μs and the value of T_{2F}^l decreases from about 200 μs to 100 μs as M_w and *C* are increased. The results also show that there is a relative increase in f_F^s and a decrease in f_F^l with increasing M_w and *C*. The scale of T_{2F}^s is similar to that derived by Shiga *et al.*[16] for polyvinyl alcohol–polysodium acrylate gels (PVA–PAA gels). They studied the heterogeneous structure of PVA–PAA hydrogel prepared by repeatedly freezing and thawing the mixed solution, and reported that the cross-linked domain in the gel is mainly formed by PVA chains, with a T_2 with the scale of about 10 μs. It is reasonable that T_{2F}^s has no remarkable change, because the dead time following a 90° pulse is the same in the measurement of FID, and T_{2F}^s is related to the immobile component or the chain mobility inner junction points. On the other hand, it is noteworthy that it has a remarkable decrease in T_{2F}^l with increasing M_w and *C*, indicating the significant reduction of chain mobility in the mobile component or between junction points. However, an unreasonable value of f_F^s, which increases from about 20% to 40% in freeze-dried gels, is much higher than that in wet gels. Because the temperature of pulsed NMR measurement is fixed at 30°C below T_g of PVC (55–64°C in this study), the f_F^s of immobile component is not only related to junction point/microcrystal but also to other immobile components in freeze-dried gels. Therefore, a measured temperature higher than T_g must be chosen for

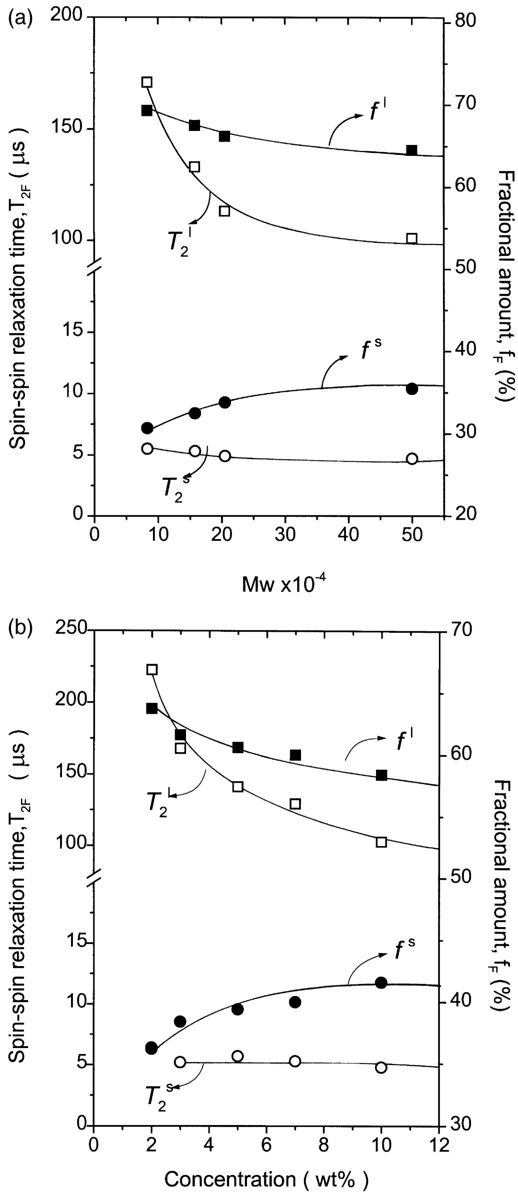

Figure 13 (a) Spin–spin relaxation time, T_{2F}, and the fraction amount, f_F, from FID signals of each component in freeze-dried gels as a function of M_w ($C = 5$ wt%): (□): T^l_{2F}; (○): T^s_{2F}; (■): f^l_F; (●): f^s_F. (b) Spin–spin relaxation time, T_{2F}, and the fraction amount, f_F, from FID signals of each component in freeze-dried gels as a function of C ($M_w = 50 \times 10^4$): (□): T^l_{2F}; (○): T^s_{2F}; (■): f^l_F; (●): f^s_F

determining the real amount of junction points. Unfortunately, a significant shrinkage of the gel volume occurred at the temperature above 45°C because of the porous structure of freeze-dried gels. Regardless of the circumstance described above, combination of the results in SEM and pulsed NMR for wet and dried gels indicates that the change of chain mobility and fractional amount in both mobile and immobile components is accompanied by the structural change of gel network due to the increases of M_w and C. For only the qualitative explanation, the enhancement of elasticity for PVC/DOA gels may be mainly due to the increases in the degree of PVC chain aggregation and the number of junction points but not to that in the crystalline structure such as the size of junction point/microcrystal or the crystallinity.

SUMMARY

In this work, the network structure and chain mobility of dried polyvinyl chloride/dioxane (PVC/DOA) gels prepared by the freeze-drying method were studied. First, the results of WAXD and *FT*i.r. indicate that the crystallinity of dried gels is very low and has no remarkable change as M_w and C are increased, implying that the degree of the regular arrangement of molecular chains has no significant difference in gels. Then, the result of SEM observation shows that the gel morphology consists of a fibril-like structure and the mesh size decreases with increasing M_w and C. The elasticity of wet gel significantly increases and the glass transition temperature, T_g, of freeze-dried gel shifts to higher temperature with increasing M_w and C. This means that the increases in the degree of aggregation and the number of junction points result in the reduction of the molecular mobility of gels. The result from CPMG signals of pulsed NMR shows only a T^l_2 component is detected for the samples with C below 2 wt%, while two components, T^l_2 and T^s_2 are observed at higher C regions, indicating that the gelation induced by liquid–liquid separation of PVC/DOA solution only takes place at C above 2 wt% in this study. The values of T^s_2 and T^l_2 decrease with increasing M_w and C, and this is related to the fact that the polymer chains associate with each other in forming the polymer-rich region and the increment of the solvents bound with polymer chains to increase the immobile molecular chain in the gels, respectively. The fractional amount of the immobile component/polymer rich phase, f^s, only increases from about 1% to 5% as M_w and C are increased, implying that the phase separation is less remarkable in PVC/DOA gelation. On the other hand, the results in FID signals in pulsed NMR for dried gels show that there is no remarkably change in T^s_{2F} with a value of about 6 μs. This indicates that T^s_{2F} is related to the immobile component or the chain mobility inner junction points. T^l_{2F} decreases remarkably as M_w and C are increased. This is due to the significant reduction of chain mobility in the soft component or between junction points. The fractional amount of the immobile component f^s_F of freeze-dried gels is much higher than those in wet gels, because the f^s_F is not only related to the number of junction points but also to other immobile components in freeze-dried gels. The enhancement of elasticity for PVC/DOA gels may be mainly due to the increases in the degree of PVC chain aggregation and the number of junction points but not to that in the crystalline structure such as the size of junction point/microcrystal or the crystallinity.

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