Macromolecules **1998,** *31,* 7472−7478

Rheological Images of Poly(vinyl chloride) Gels. 5. Effect of Molecular Weight Distribution

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Received December 30, 1997; Revised Manuscript Received August 5, 1998

ABSTRACT: Three blends were prepared from a high molecular weight of poly(vinyl chloride) (PVC) (M_w = 173 000, M_w/M_n = 2.0) and a low molecular weight PVC (M_w = 39 400, M_w/M_n = 1.7). Dynamic viscoelastic properties of these PVC blends in bis(2-ethylhexyl) phthalate (DOP) were measured at 40 °C as a function of polymer concentration, and the effect of long chains on gelation has been studied. The scaling exponent n at the gel point was found to be constant (=0.75), independent of molecular weight and molecular weight distribution. The critical concentration c_g for the sol−gel transition still followed the relation $c_g \propto M_w^{-1}$, which was unchangeable with the molecular weight distribution and was also in good agreement with the previous results. As a result, c_g was well expressed by a mixing rule, $1/c_g = w_1/c_{g1} + w_2/c_{g2}$, where w_i is the weight fraction of the component polymer i. The gel strength S_g at the gel point did not obey the relation $S_g \propto M_w^{-1}$, but scaled as $S_g \propto M_z^{-1}$ to show the effect of long chains on gelation. In the postgel state, the gel elasticity determined by the quasi-equilibrium modulus G_e still followed the scaling law, $G_e \propto \epsilon^z$, where ϵ is the relative distance to the gel point and z = 2.6 for the (PVC blend)/DOP samples, but the G_e values at the same ϵ were observed to be dominated by the long chains of PVC.

Introduction

The typical gelation of a physically gelling material is rheologically described by three stages: pregelation (sol), sol−gel transition, and postgelation (gel). The following three scaling laws[1−7] are applied correspondingly to the three stages of gelation:

$$\eta_0 \propto \epsilon^{-\gamma} \qquad \text{for pregelation} \qquad (1)$$

$$G' \sim G'' \propto \omega^n \qquad \text{at the gel point} \qquad (2)$$

$$G_e \propto \epsilon^z \qquad \text{for postgelation} \qquad (3)$$

where η_0 is the zero shear viscosity, G' is the dynamic storage modulus, G'' is the dynamic loss modulus, G_e is the quasi-equilibrium modulus, ω is the angular frequency, ϵ is the relative distance (=$|c - c_g|/c_g$, where c is the polymer concentration) to the gel point c_g, and γ, n, and z are the scaling exponents for the three scaling laws, respectively.

We have conducted a series of rheological studies of poly(vinyl chloride) (PVC) gels to examine the above scaling laws.[8−11] It has been observed that (1) the zero shear viscosity η_0 diverged according to the scaling law of eq 1 where γ was 1.5; (2) the dynamic moduli at the gel point were characterized by the power law of eq 2 where n was 0.75; and (3) the elasticity evolution beyond the gel point, expressed by the quasi-equilibrium modulus G_e, scaled with the relative distance ϵ by the power law of eq 3 with z of 2.6. It should be emphasized here that all three scaling exponents (γ, n, and z) were found to be independent of the PVC molecular weight (the weight-average molecular weight ranged from about 40 000 to 173 000) studied. The PVCs used in the previous studies[8−11] were linear polymers and had polydispersity indices (M_w/M_n) of about 2. Also, we observed that the critical concentration c_g for the sol−gel transition and the gel strength S_g at the gel point deceased as $c_g \propto M_w^{-1}$ and $S_g \propto M_w^{-1}$, respectively. The molecular weight dependence of c_g or S_g suggests that both the critical gel concentration and the gel strength are significantly affected by the molecular weight of polymer. However, it is not studied here how the molecular weight distribution (MWD) would alter the scaling laws. As the percolation model[2] describes the probability of cluster connections passing through the system, one may imagine that the longer polymer chains have a higher probability for the percolation than that the shorter chains because it can be considered that some connections exist already in longer chains. On the other hand, a large portion of free ends of shorter chains should limit their contribution to formation of the gel network. No theoretical predictions have been proposed to deal with the effect of MWD on the scaling laws for physical gelation.

This kind of interest has motivated us to conduct the present study on how MWD can influence the scaling laws for physical gelation. A simple way to broaden MWD of PVC, is to mix a low MW PVC with a high MW PVC. Of previously studied PVCs, we selected the lowest MW one (M_w = 39 400) and the highest one (M_w = 173 000) to make the PVC blends for preparation of three gelling systems with three blend compositions.

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10.1021/ma971889f CCC: $15.00

Table 1. Molecular Characteristics of Poly(vinyl chloride)s (PVC) and Their Blends

PVC	PVC4: PVC17	$M_w/10^3$ [a]	$M_z/10^3$ [b]	$M_w/10^3$ [b]	$M_n/10^3$ [b]	M_w/M_n[b]
PVC4		39.4	58.2	40.0	23.7	1.69
PVC17		173	271	155	77.9	1.99
PVC3-1	3:1	72.8	185	70.0	28.5	2.46
PVC1-1	1:1	106	236	98.1	35.5	2.76
PVC1-3	1:3	140	261	127	49.9	2.55

[a] Measured by light scattering in THF at 25 °C for PVC4 and PVC17. For the others (blends), M_w was calculated from those of the component PVCs. [b] Determined using GPC with a universal calibration by polystyrene standards.

Each gelling series of PVC blend in bis(2-ethylhexyl) phthalate (DOP) was prepared to undergo the rheological range from the pregelation to the postgelation by changing polymer concentration. The dynamic viscoelastic measurements have been carried out on the (PVC blend)/DOP samples to allow examination of the effect of long chains on the gelation.

Experimental Section

Materials. Two poly(vinyl chloride)s (PVC), designated as PVC4 and PVC17, were used in this study. As described in the previous studies,[8–11] the polymers were made at about 50 °C by suspension polymerization. Prior to molecular characterization and sample preparation, two PVCs were purified by using tetrahydrofuran (THF)/methanol as the solvent/precipitant. Characterization by light scattering in THF at 25 °C provided the weight-average molecular weight M_w: 3.94×10^4 for PVC4 and 1.73×10^5 for PVC17. In this work, we performed the GPC measurements with a universal calibration by polystyrene standards. This procedure gives the M_w values close to those measured using light scattering, as shown in Table 1. The polydispersity index (M_w/M_n) becomes somewhat smaller than before, but it is considered that they are within the experimental errors. In this study, we prefer to use the weight-average molecular weights determined by light scattering to discuss the effect of molecular weight on gelation because they are more reliable, but we have to use the GPC results to analyze the effect of molecular weight distribution on gelation since light scattering does not provide the information about molecular weight distribution. The ^{13}C NMR experiments showed that two PVCs had similar tacticities.[8]

To study the effect of molecular weight distribution on gelation, we prepared the gelling systems made from a blend of a high molecular weight (MW) PVC (PVC17) and a low MW PVC (PVC4). Three gelling series with three compositions (i.e., PVC4:PVC17 = 1:3, 1:1, and 3:1 in weight) were prepared at room temperature from THF solutions (about 70 wt % of THF) of the PVCs and DOP. The PVC concentration in each series was varied to cover the range from the pregel state to the postgel state. No stabilizers or additives were added.

Molecular characteristics of the PVC blends have also been measured using GPC with a universal calibration. The results are presented in Table 1 to show that the obtained M_w values are almost the same as those calculated from M_w (measured by light scattering) of the component PVCs. Mixing of the two PVCs with three ratios results in the broader molecular weight distributions ($M_w/M_n \geq 2.5$).

The evaporation of THF from each solution proceeded at room temperature (about 30 °C), and it took longer than 2 weeks. After THF evaporated completely, transparent and viscoelastic samples were obtained. Since a sufficiently long time was taken for the evaporation and the equilibrium of gelation prior to rheological measurements, each sample was stable with time. The rheological reproducibility was confirmed from some selected samples.

Rheological Measurements. The PVC/DOP sample was transferred from the flat laboratory dish into the dynamic rheometer (Rheometric Scientific, ARES 100FRTN1). Then, depending on the viscoelastic properties of each sample, 25 or 50 mm diameter parallel plates were used for the dynamic measurements. Shear storage modulus G' and loss modulus G'' were measured as a function of angular frequency ω at 40 °C. The measuring temperature was chosen to minimize the effect of forming temperatures (the room temperature might change with season). Prior to each measurement, a reasonable time was taken at 40 °C for the sample to be stable. Depending on the viscoelastic properties of each sample, the linearity of dynamic viscoelasticity was ensured by applying the suitable amplitude of shear.

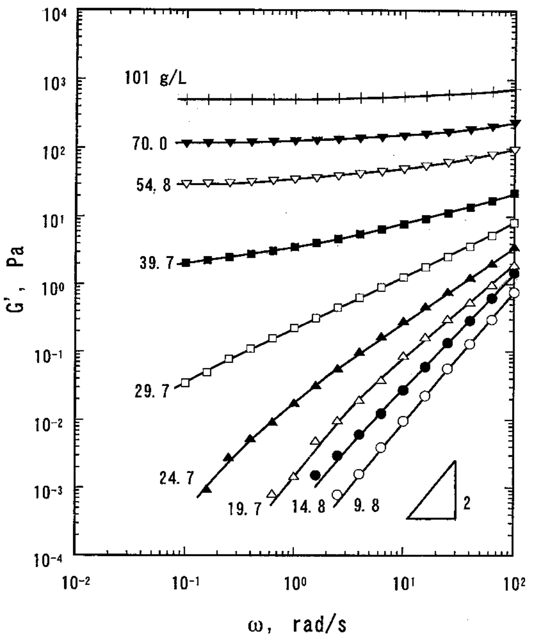

Figure 1. Storage modulus G' of PVC3-1/DOP as a function of angular frequency ω for various concentrations of PVC3-1, as indicated.

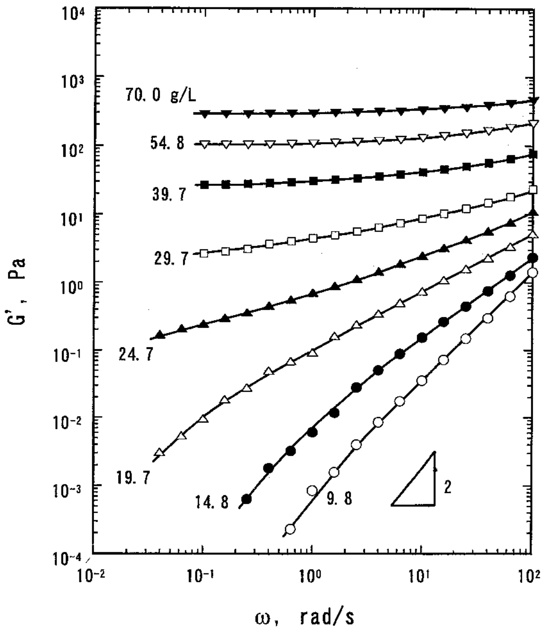

Figure 2. Storage modulus G' of PVC1-1/DOP as a function of angular frequency ω for various concentrations of PVC1-1, as indicated.

Results

Dynamic Viscoelastic Properties of (PVC Blend)/DOP. Figures 1–3 present the dynamic storage modulus G' as a function of angular frequency ω for the

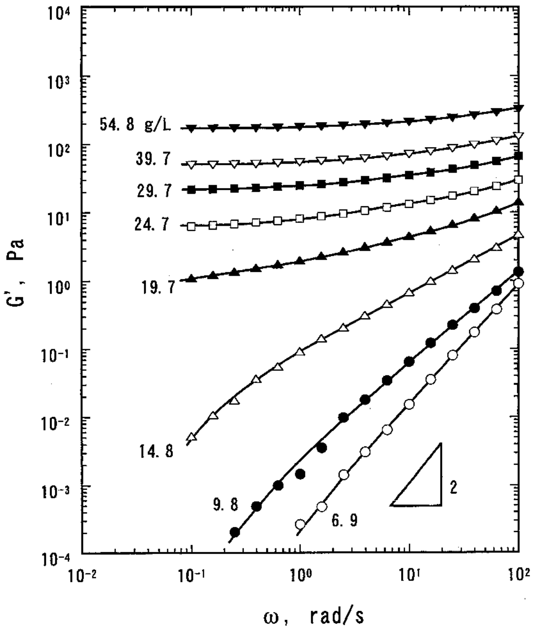

Figure 3. Storage modulus G' of PVC1-3/DOP as a function of angular frequency ω for various concentrations of PVC1-3, as indicated.

PVC3-1/DOP, PVC1-1/DOP, and PVC1-3/DOP samples, respectively. The polymer composition of each PVC blend is given in Table 1. All the polymer concentrations are indicated in each figure. The PVC/DOP samples show the following liquidlike terminal behavior at very low concentrations:

$$G'(\omega) \propto \omega^2 \qquad (\text{at } \omega \to 0) \tag{4}$$

while $G'(\omega)$ deviates from the above relation as the PVC concentration increases. After the PVC concentration exceeds a certain amount, the behavior of $G'(\omega)$ = constant, independent of ω, is observed, indicating formation of a gel network. The variation from the pregel state to the postgel state is phenomenally consistent with that observed in the PVC/DOP systems where the PVCs had a polydispersity index (M_w/M_n) of about 2.[8]

Determination of the Gel Point c_g, the Scaling Exponent n, and the Gel Strength S_g. The following scaling law, eq 2, at the gel point gives access to determination of the gel point. Furthermore, eq 2 ensures establishment of the relation

$$G''(\omega)/G'(\omega) = \tan\delta = \tan(n\pi/2) \tag{5}$$

This frequency independence of loss tangent in the vicinity of the gel point has been examined for chemical and physical gels[6-8,11-18] and also been widely used to determine the gel point. The definition of the gel point by this power law is excellent because a gelation variable loses its dependency on frequency and converges at the gel point. The experimental results have shown that this method is reliable and valid for determination of the gel point such as the critical gelation time (or degree of cross-linking)[13,14,18] or the critical gelation concentration.[8]

The gel point was determined from a multifrequency plot of tan δ versus gel concentration in this work. An example of this type of plot is illustrated in Figure 4 for the PVC3-1/DOP samples. All curves pass through the common point at a certain polymer concentration, which is defined as the gel point c_g. It is apparent that the gel point for each gelling system is accurately determined by means of this method. The values of c_g, as shown in Table 2, vary as a function of the composition in PVC blends. We discuss the results in the next section. On the other hand, the scaling exponent n was simply calculated from the gel point using eq 5. Being consistent with the previous results for the PVCs having a M_w/M_n of about 2,[8] the value of n was also found to be constant (=0.75), independent of the PVC molecular weight and MWD.

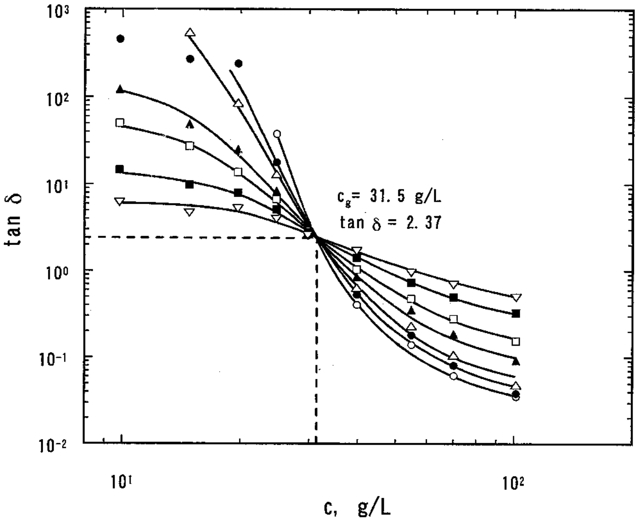

Figure 4. Loss tangent, tan δ, as a function of polymer concentration c for PVC3-1/DOP samples at various angular frequencies (0.1 rad/s, ○; 0.398 rad/s, ●; 1 rad/s, △; 3.98 rad/s, ▲; 10 rad/s, □; 39.8 rad/s, ■; 100 rad/s, ▽).

Table 2. Critical Concentration c_g for the Sol–Gel Transition, the Scaling Exponent n at the Gel Point, and the Gel Strength S_g

series	c_g (g/L)[a]	c_g (g/L)[b]	n	S_g (Pa s^n)
PVC4	66.0		0.753	0.835
PVC3-1	31.5	31.9	0.746	0.219
PVC1-1	21.4	21.0	0.747	0.166
PVC1-3	16.2	15.7	0.751	0.157
PVC17	12.5		0.748	0.154

[a] Experimental values determined using the frequency independence of loss tangent. [b] Calculated values using the blending rule $1/c_g = w_1/c_{g1} + w_2/c_{g2}$, where c_{g1} = 66.0 g/L and c_{g2} = 12.5 g/L.

The shear relaxation modulus $G(t)$ at the gel point exhibits a power law behavior with a slope of $-n$:[6,7,8,11-18]

$$G(t) = S_g t^{-n} \tag{6}$$

Here S_g is the gel strength and has a unit of Pa s^n. The application of the Boltzmann superposition principle[19] to the dynamic moduli G' and G'' using eqs 5 and 6 leads to[7,12,16,17]

$$G'(\omega) = G''(\omega)/\tan(n\pi/2) = S_g\omega^n\Gamma(1-n)\cos(n\pi/2) \tag{7}$$

where $\Gamma(1-n)$ is the gamma function. By knowing n, one can calculate S_g from $G'(\omega)$ or $G''(\omega)$ at the gel point using eq 7.

Taking advantage of eq 7, we are able to obtain the gel strength S_g at the gel point by plotting $G'(\omega)$ and $G''(\omega)/\tan(n\pi/2)$ against polymer concentration c. An

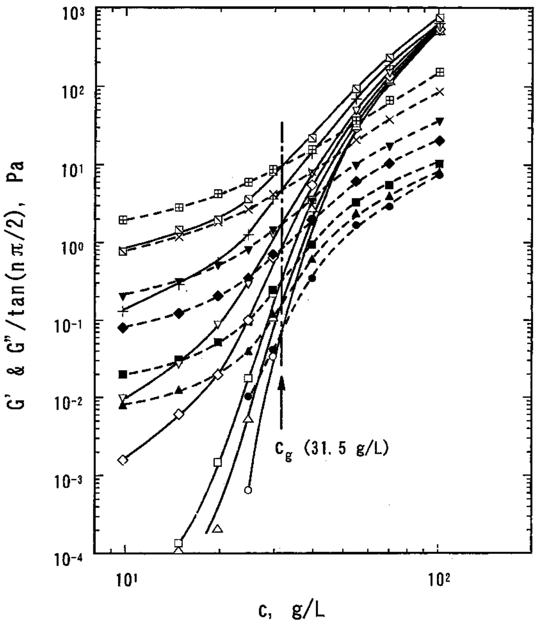

Figure 5. Plots of G' (solid lines) and $G''/\tan(n\pi/2)$ (dashed lines) against polymer concentration c for PVC3-1/DOP samples. The angular frequency ω was varied from 0.1 to 100 rad/s. $n = 0.75$ was used to calculate $G''/\tan(n\pi/2)$. The gel point c_g is indicated by the arrow. Values of G' and $G''/\tan(n\pi/2)$ are represented by the marks as shown below.

ω(rad/s)	0.1	0.398	1	3.98	10	39.8	100
G' (Pa)	○	△	□	◇	▽	+	⊞
$G''/\tan(n\pi/2)$ (Pa)	●	▲	■	◆	▼	×	■

example of this kind of plot is illustrated in Figure 5 for the PVC3-1/DOP samples. Since the gelling system at the gel point follows the frequency independence of tan δ, all crossover points excellently appear at the gel point of $c_g = 31.5$ g/L, which is consistent with that obtained using the frequency independence of tan δ. Using the value of $G'(\omega)$ at any crossover point and eq 7, we obtained the value of S_g. The values of S_g obtained in this way are presented in Table 2.

Discussion

Critical Behavior in the Vicinity of the Sol–Gel Transition. A universal value of the scaling exponent n (=0.75 or 3/4) has been found for our PVC/DOP gelling materials.[8] The important conclusion is that n is independent, not only of the PVC molecular weight but also of the molecular weight distribution. Rheologically, the meaning of n can be understood from the definition in eq 5. Since the phase angle δ varies from 0 to $\pi/2$ as n takes a value between 0 and 1, n measures the viscoelastic distance from a completely viscous liquid ($\delta = \pi/2$) or from a completely elastic solid ($\delta = 0$). In general, a lower value of n implies formation of a more highly elastic gel, and the same value of n means an equivalent viscoelasticity. But, it should be noted here that we do not take account of the absolute values of $G'(\omega)$ or $G''(\omega)$ for comparison of the viscoelasticity because n does not directly contain the information about the dynamic moduli. The universal value of n found for the PVC/DOP samples may suggest a similarity in the gel structure at the gel point.

To examine the effect of molecular weight on the critical concentration, c_g was plotted against the weight average molecular weight M_w in Figure 6 along with the data for the component PVCs. The other PVCs (PVC9, $M_w = 87\,400$, $M_w/M_n = 2.0$; PVC10, $M_w = 102\,000$, $M_w/M_n = 2.0$) studied previously[8-10] were also presented in the figure for comparison. The data in Figure 6 were able to be approximately expressed by the straight line to give a relation as

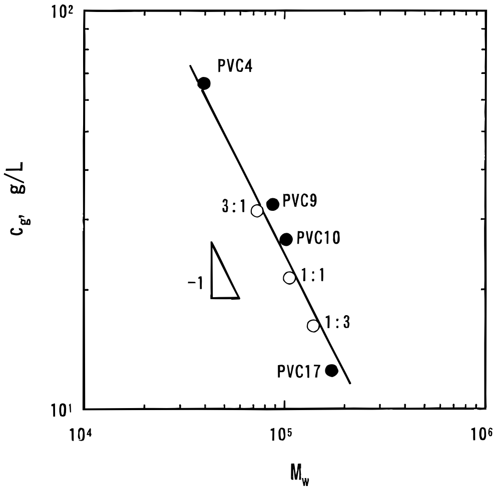

Figure 6. Dependence of the critical concentration c_g on the weight-average molecular weight M_w for the (PVC blend)/DOP samples (opened circles). M_w of PVC blends was calculated using M_w of component PVCs, PVC4 and PVC17. c_g versus M_w for PVC9 ($M_w = 87\,400$, $M_w/M_n = 2.0$)/DOP and PVC10 ($M_w = 102\,000$, $M_w/M_n = 2.0$)/DOP, studied previously,[8] is presented here for comparison. The solid straight line has a slope of −1.

$$c_g \propto M_w^{-1} \tag{8}$$

for the molecular weight dependence of the gel point. This is well consistent with the result obtained in the previous study.[8] This result demonstrates that, in the range of PVC molecular weights studied, the critical gelation concentration is related only to the weight-average molecular weight M_w of PVC and not influenced by changing the PVC molecular weight distribution.

In general, if PVC1/DOP and PVC2/DOP exhibit the critical concentrations c_{g1} and c_{g2}, respectively, and $c_{g1} \neq c_{g2}$, the c_g of a gelling system made from a PVC1/PVC2 blend would be expected to have a value between c_{g1} and c_{g2}. Furthermore, according to the relation $c_g \propto M_w^{-1}$ in eq 8, one can directly derive a relation of $1/c_g = w_1/c_{g1} + w_2/c_{g2}$ where w_i is the weight fraction of component polymer i. The direct calculation using this relation gives $c_g = 31.9$ g/L for PVC3-1/DOP, $c_g = 21.0$ g/L for PVC1-1/DOP, and $c_g = 15.7$ g/L for PVC1-3/DOP. All the calculated values of c_g are in good agreement with the experimental ones, as shown in Table 2, indicating establishment of the mixing rule

$$1/c_g = w_1/c_{g1} + w_2/c_{g2} \tag{9}$$

for (PVC blend)/DOP samples. Figure 7 shows the reciprocal of c_g for (PVC blend)/DOP as a function of PVC17 content (wt %), where the solid straight line was obtained using the rule $1/c_g = w_1/c_{g1} + w_2/c_{g2}$. A good consistency is given between the experimental values of c_g and the calculated ones.

Influence of Long Chains on the Gel Strength S_g. The gel strength S_g at the gel point does not exhibit the same dependence on M_w as c_g does. As shown in Figure 8, $S_g(M_w)$ deviates significantly from the solid line, which represents the relation, $S_g \propto M_w^{-1}$, found in the previous work.[8] All the S_g values from the blends

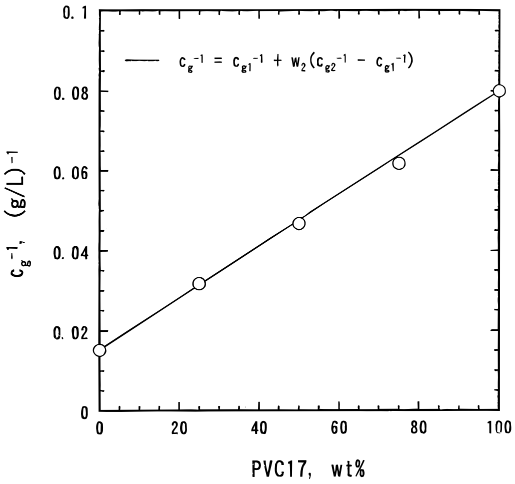

Figure 7. Critical concentration c_g of a (PVC blend)/DOP sample, prepared from PVC4 and PVC17, as a function of PVC17 content. The solid line indicates the blending law $c_g^{-1} = w_1c_{g1}^{-1} + w_2c_{g2}^{-1}$ or $c_g^{-1} = c_{g1}^{-1} + w_2(c_{g2}^{-1} - c_{g1}^{-1})$, where w_i is the weight fraction of the component PVC i, 1 = PVC4 and 2 = PVC17.

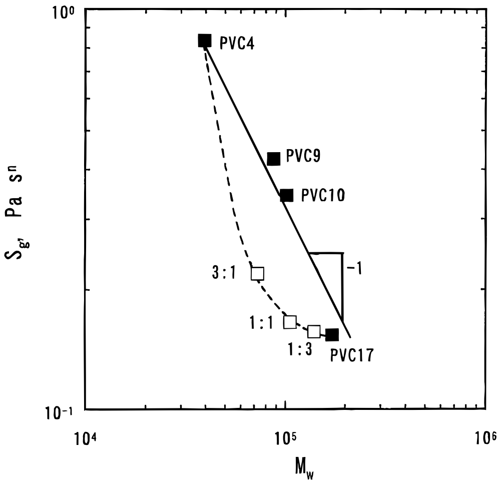

Figure 8. Dependence of the gel strength S_g on the weight-average molecular weight M_w for the (PVC blend)/DOP samples (opened squares) and the PVC/DOP samples (filled squares). $n = 0.75$ was used to obtain S_g.

are much lower than the corresponding values of the solid line when compared at the same M_w. As a result, the relation $S_g \propto M_w^{-1}$ no longer holds for the (PVC blend)/DOP samples. The reason for the deviation from the relation is considered to be due to long chains of PVC in the system, which have a crucial contribution to the gel strength. The fact that the gelling system prepared from the high molecular weight of PVC (PVC17) has only 18.4% of the gel strength of the system from the low molecular weight of PVC (PVC4), implies that the gel strength is dominated by the long chains. As shown in Table 2, the addition of 25 wt % PVC17 to PVC4 was able to make the gel strength drop by about 74% while the addition of 25 wt % PVC4 to PVC17 resulted only in a slight increase in the gel strength from 0.154 to 0.157 Pa $s^{0.75}$. The results in the present study support the above hypothesis that the long chains govern the gel strength at the gel point.

As well-known, the average molecular weights, M_n, M_w, and M_z are separately defined as ratios of differently sensitive portions of molecular weight distribution. In other words, the contribution of short chains to the average molecular weight is reflected in M_n while the contribution of long chains appears in M_z. M_w has an average level between M_n and M_z. The plots of S_g against the z-average molecular weight M_z are presented in Figure 9 in order to examine if S_g of a (PVC blend)/DOP system can be expressed by a relation of $S_g \propto M_z^{-k}$ where the exponent k is a constant. M_z values of the component PVCs and PVC were determined using GPC with a universal calibration by polystyrene standards and are shown in Table 1. Being consistent with the discussion in the last paragraph, the dependence of S_g on molecular weight distribution results in a new relation: $S_g \propto M_z^{-1}$. This relation is not inconsistent with the previous relation $S_g \propto M_w^{-1}$. Because M_z/M_w is almost constant for PVC4, -9, -10, and -17.

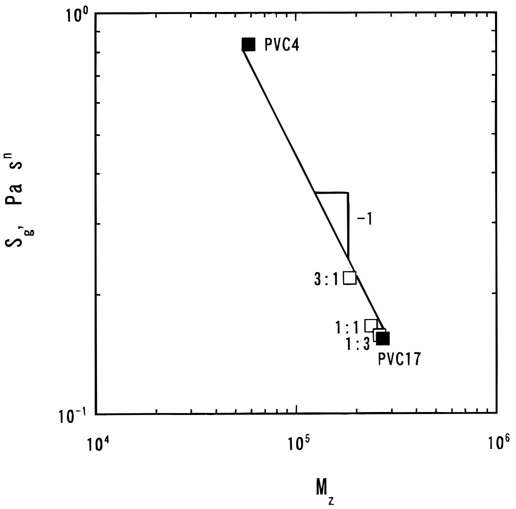

Figure 9. Dependence of the gel strength S_g on the z-average molecular weight M_z for the (PVC blend)/DOP samples (opened squares) and the component PVC/DOP samples (filled squares). n was 0.75.

The relation between the scaling exponent n and the gel strength S_g have been reported and discussed especially for the chemical gels[14,16,17] in which increasing the cross-linking density led to a reduction of n. However, in this study, since n is constant for the PVC/DOP gels and S_g varies with M_z, the S_g cannot be directly considered to be a function of n.

To further understand the meaning of S_g, S_g was normalized by the corresponding gelation concentration c_g to give the result shown in Figure 10. If S_g is only related to the total mass of polymer in the system, the gel strength per unit of mass should be independent of molecular weight. Although the normalized gel strength S_g/c_g was found to be almost constant ($S_g/c_g \approx 0.0127$) for PVC4, -9, -10, and -17/DOP systems,[8] the (PVC blend)/DOP samples prepared from the two polymers do not like to follow this rule by showing the strong dependence of S_g/c_g on molecular weight M_w. For example, the PVC3-1/DOP system exhibits a S_g/c_g value of about half of that of the PVC4/DOP system. It is not been clear at present why the normalized gel strength S_g/c_g can be significantly lowered by adding a second PVC.

Scaling Law for Elasticity Evolution beyond the Gel Point and the Contribution of Long Chains. One of the most important characteristics of a gel is illustrated as its elasticity evolution as a function of the relative distance ϵ defined as $\epsilon = (c - c_g)/c_g$, as usually described by $G_e \propto \epsilon^z$, eq 3. The term "quasi-equilibrium" refers to the difficulty (or even sometimes the impos-

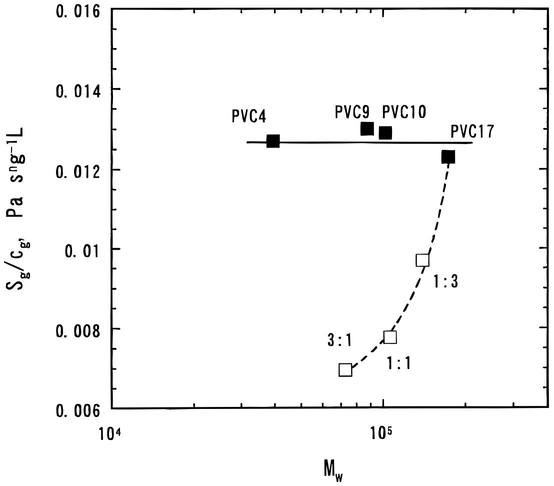

Figure 10. Normalized gel strength S_g/c_g as a function of weight-average molecular weight M_w for the (PVC blend)/DOP samples (opened squares) and the PVC/DOP samples (filled squares).

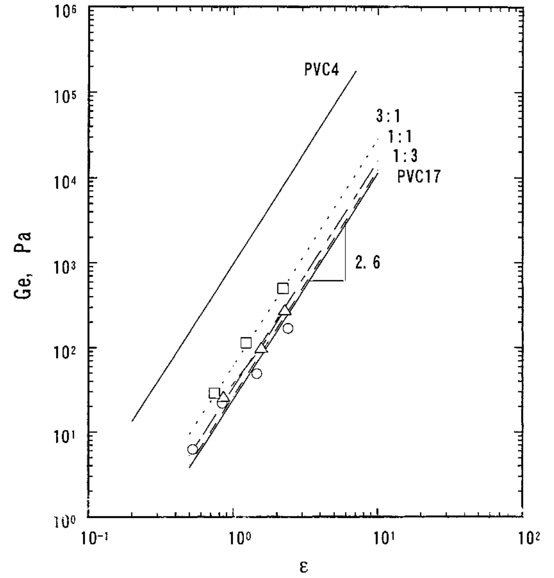

Figure 11. Quasi-equilibrium modulus G_e as a function of the relative distance ϵ for PVC4/DOP (the solid line), PVC3-1/DOP (□), PVC1-1/DOP (△), PVC1-3/DOP (○), and PVC17/DOP (the other solid line) samples. The broken lines were obtained by calculating G_e from the PVC4 and PVC17 lines based on an assumption that G_e for a (PVC blend)/DOP sample follows the relation $G_e = 10^{14}(M_z/1.5)^{-2.4}\epsilon^{2.6}$.

sibility) of obtaining the thermodynamic equilibrium modulus of a physical gel.[19] In the previous study,[10] we found that the scaling law for the elasticity evolution, $G_e = k\epsilon^z$, held well for all the PVC gels with various molecular weights, where $z = 2.6$, being excellently consistent with the theoretical prediction ($z = 8/3$) using the percolation model.[3,4] In this work, we also examine whether the scaling law of eq 3 still holds for the (PVC blend)/DOP systems.

The gel elasticity characterized by the quasi-equilibrium modulus G_e is presented in Figure 11 as a function of the relative distance ϵ to allow examination of the scaling law, eq 3. In this figure, two solid straight lines with a slope of 2.6 represent G_e versus ϵ for PVC4/DOP and PVC17/DOP obtained in the previous work.[10] There are two features observed from Figure 11: (1) The quasi-equilibrium modulus G_e of (PVC blend)/DOP grows according to the same scaling law, $G_e \propto \epsilon^{2.6}$, but (2) the G_e value is not in proportion to the ratio of PVC4 to PVC17 in the blend. As discussed below, the second feature is the most interesting for us to elucidate the effect of long chains on the gel structure.

In the previous study, we found a general relation $G_e = 10^{14}M_w^{-2.4}\epsilon^{2.6}$, which could be used to describe the gel elasticity evolution as a function of molecular weight M_w and the relative distance ϵ. The application of this relation to fitting the data was largely successful for the PVCs having a polydispersity index (M_w/M_n) of about 2. However, this relation failed to predict the elasticity evolution for the (PVC blend)/DOP systems. All the G_e data for the (PVC blend)/DOP samples in Figure 11 tend to approach the straight line for PVC17. This result implies that G_e is governed by long chains in the system, very similarly to the gel strength S_g at the gel point, as we have discussed in the last section. In other words, the long chains of PVC make more contribution to the reduction of elasticity than the short chains when compared at the same relative distance ϵ to the gel point. Then, we would like to propose another but consistent relation $G_e = 10^{14}(M_z/1.5)^{-2.4}\epsilon^{2.6}$ instead of $G_e = 10^{14}M_w^{-2.4}\epsilon^{2.6}$. Because M_z/M_w is about 1.5 for PVC4, -9, -10, and -17 studied previously. The experimental data are consistent with the calculated values of G_e using the above relation, which are presented in Figure 11 with the broken lines as a function of the relative distance ϵ to correspond to three ratios of PVC4:PVC17 = 3:1, 1:1, and 1:3. Therefore, we believe that the quasi-equilibrium modulus G_e of PVC/DOP gels is a function of M_z as well as the gel strength at the gel point S_g.

Conclusions

Poly(vinyl chloride) (PVC) gels prepared from THF solutions were composed of a blend of two PVCs [a low molecular weight (MW) PVC and a high MW PVC] and bis(2-ethylhexyl) phthalate (DOP). The gelling samples were prepared to cover a wide range of PVC concentration to allow the rheological observation of the sol−gel transition as well as the elasticity evolution beyond the sol−gel transition. By analyzing the dynamic viscoelastic properties of the (PVC blend)/DOP gelling samples, we found (1) the scaling exponent n for eq 2 was 0.75, independent of the molecular weight distribution (MWD); (2) the gel point c_g obeyed the relation $c_g \propto M_w^{-1}$, where M_w is the weight-average molecular weight and c_g was well expressed by the mixing rule $1/c_g = w_1/c_{g1} + w_2/c_{g2}$, where w_i is the weight fraction of the component polymer i; (3) the gel strength at the gel point S_g did not scale with the weight-average molecular weight M_w and dropped as a function of the blend composition, but S_g followed $S_g \propto M_z^{-1}$, where M_z is the z-average molecular weight; and (4) the elasticity evolution beyond the sol−gel transition still followed the scaling law, $G_e \propto \epsilon^{2.6}$, as observed in the PVC gelling systems with the narrower MWDs of PVC, and the G_e at the same relative distance ϵ was controlled by M_z of PVC.

Acknowledgment. Authors thank Rheometric Scientific F. E. Ltd. (Japan) for access to the ARES rheometer.

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MA971889F