Rheological Images of Poly(vinyl chloride) Gels. 3. Elasticity Evolution and the Scaling Law beyond the Sol−Gel Transition

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Received October 2, 1997; Revised Manuscript Received November 26, 1997

ABSTRACT: The elasticity evolution of poly(vinyl chloride) (PVC)/bis(2-ethylhexyl) phthalate (DOP) gels beyond the gel point c_g has been studied as a function of polymer concentration c and molecular weight. The gel elasticity G_e, which was defined as the frequency-independent dynamic storage modulus G' at low frequencies, developed as a function of polymer concentration. The scaling law for the elasticity evolution, $G_e = k\epsilon^z$, was found to hold well for all the PVC gels with different molecular weights. Here, ϵ [$=(c - c_g)/c_g$] is defined as the relative distance, z the scaling exponent, and k the front constant. The z obtained was constant ($z = 2.6 \pm 0.1$), independent of the PVC molecular weight, being excellently consistent with the theoretical prediction ($z = {}^8/_3$) using the percolation model. Furthermore, the analysis of the front constant k provided information about the dependence of the gel elasticity on molecular weight. As a result, the gel elasticity could be described as $G_e = 10^{14} M_w^{-2.4}\epsilon^{8/3}$, allowing one to discuss separately the molecular weight contribution and the relative distance contribution. The ability of this relation to predict the elasticity evolution has also been examined.

Introduction

One of the most important characteristics of a gel is illustrated as its elasticity evolution as a function of the relative distance ϵ [$=(c - c_g)/c_g$], as is usually described by the scaling law[1−4]

$$G_e \propto \epsilon^z \tag{1}$$

where G_e is the quasi-equilibrium modulus, and z the scaling exponent. Here, c is the polymer concentration and c_g the critical concentration for the sol−gel transition. The term "quasi-equilibrium" refers to the difficulty (or even sometimes impossibility) of obtaining the thermodynamic equilibrium modulus of a physical gel.[5] This is because physical gels, unlike chemical gels consisting of permanent chemical cross-links, are of a thermoreversible nature with respect to the physical junctions. The physical junctions are formed by self-association, and reverse enhancement of temperature or dilution by a good solvent may make the junctions dissociate. The physical junctions are considered to be in the dynamic quasi-equilibrium state and are completely different from chemical bonds that are never released unless decomposition takes place. From the rheological viewpoint, any physical junctions will be able to release through a relaxation process if the observation time is sufficiently long. To avoid this kind of confusion in understanding physical gelation, we restrict our discussion in this study to the physical gels that are thermodynamically stable at a forming temperature after they form. In the other words, one may consider that this is a case of the infinite relaxation time. Under this assumption, we will examine whether the scaling law of eq 1 is established for the poly(vinyl chloride) (PVC) gels.

What the value of the scaling exponent z in eq 1 should be has always been interesting to researchers. The theories based on different assumptions have predicted different values of z. For example, the classical mean-field gelation theory based on the Bethe lattice (tree approximation) predicts $z = 3$.[1−3] Using the percolation model,[6] de Gennes[7] predicts a value of $z \approx 1.9$. And later, Martin et al.[8,9] also used the percolation theory to give the prediction of $z = {}^8/_3$ either for the Rouse behavior (without considering hydrodynamic interactions) or for the Zimm behavior (with considering hydrodynamic interactions).

Winter[10] applied an assumption, that the longest relaxation time τ_m in the vicinity of the gel point p_g takes the same scaling exponent α as $\tau_m \propto \epsilon^{-\alpha}$ before ($p < p_g$) and beyond ($p > p_g$) the gel point, where $\epsilon = |p - p_g|$, to describe the relaxation behavior of critical gels. If this is true, τ_m diverges symmetrically on both sides of the gel point and the symmetry of τ_m results in a relation, $n = z/(z + \gamma)$.[10a] Here n is the scaling exponent for $G(t) \sim t^{-n}$ at the gel point. The same expression has also been derived by Martin et al.[8,9] using the percolation model. However, the relation has never been directly proven directly by experiments.

Different values of z were experimentally obtained from different gels, but z usually varies between 1.9 and 3.5.[9] For example, Mours and Winter[10b] reported $z = 2.0−2.4$ for polybutadiene chemical gels, Koike et al.[11] obtained $z = 2.5 \pm 0.1$ for the end-cross-linked polybutadiene gels, and the experiments carried out by Lopez et al.[12] gave $z = 2.0$ for the poly(vinyl chloride) gels in diethyl oxalate and $z = 3.7$ for the poly(vinyl chloride) gels in dibutyl oxalate. The variation of the z value with the gel system suggests that z should be related to the gel structure.

We have recently investigated the viscoelastic properties of poly(vinyl chloride) (PVC) gels both in the vicinity of the sol−gel transition and in the pregel state as a function of polymer concentration and molecular weight.[13,14] We have found that the exponent n for the relaxation modulus $G(t)$ at the gel point was 0.75 and the scaling exponent γ for the zero shear viscosity η_0 was 1.5. Both n and γ were independent of the PVC

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S0024-9297(97)01449-6 CCC: $15.00

molecular weight. If the relation, $n = z/(z + \gamma)$,[8-10] is applicable to the PVC gels, z is then predicted to be 4.5, which seems too large to be able to meet the theoretical prediction. Instead of discussing the theoretical prediction, however, here we report the viscoelastic behavior of the PVC postgels to discuss what the scaling law is for the elasticity evolution and how the PVC molecular weight influences the scaling law. Combining our previous studies of the PVC gels,[13,14] we hope to give readers the entire rheological images of the PVC/DOP gels throughout the range from the pregel state to the postgel state.

Experimental Section

Materials. As is described in the previous studies,[13,14] the materials used in this study were four poly(vinyl chloride)s (PVC), designated as PVC4, PVC9, PVC10, and PVC17, all of which were produced at about 50 °C by suspension polymerization. Prior to molecular characterization and sample preparation, all PVCs were purified by using THF/methanol as solvent/precipitant. Characterization by light scattering in tetrahydrofuran (THF) at 25 °C provided the following weight-average molecular weight M_w: 3.94×10^4 for PVC4; 8.74×10^4 for PVC9; 1.02×10^5 for PVC10; 1.73×10^5 for PVC17. GPC measurements in THF gave the following molecular characteristics: $M_w = 6.36 \times 10^4$ and $M_w/M_n = 1.89$ for PVC4; $M_w = 1.37 \times 10^5$ and $M_w/M_n = 2.01$ for PVC9; $M_w = 1.60 \times 10^5$ and $M_w/M_n = 2.02$ for PVC10; $M_w = 2.54 \times 10^5$ and $M_w/M_n = 2.24$ for PVC17. The narrow polystyrenes were used as standards for calibration of GPC. ^{13}C NMR experiments measured the tacticity of the polymers: PVC4, syndio = 0.33, hetero = 0.49, iso = 0.18; PVC9, syndio = 0.33, hetero = 0.50, iso = 0.17; PVC10, syndio = 0.33, hetero = 0.49, iso = 0.18; PVC17, syndio =0.35, hetero =0.50, iso = 0.15.

Four gelling series of the purified PVCs in bis(2-ethylhexyl) phthalate (DOP) were prepared at room temperature from THF solutions (about 70−90 wt % of THF) of PVC and DOP. Then 2 wt % of a tin-type stabilizer were added for the PVC/DOP samples with a PVC concentration higher than 7 wt %. Since we have known the critical concentration c_g for each PVC/DOP series from the previous study,[13] the polymer concentrations were directly selected to cover the postgel region of each series until the PVC concentration of 30 wt % (323 g/L). The evaporation of THF from each solution proceeded at room temperature, and it took longer than 2 weeks. After the THF evaporated completely, transparent and viscoelastic samples were obtained. Since a sufficiently long time was taken for the evaporation of THF and the equilibrium for gelation prior to rheological measurements, each sample was considered to be stable with time. The rheological reproducibility was confirmed for some selected samples.

Rheological Measurements. The PVC/DOP sample was transferred from the flat laboratory dish into the dynamic rheometer (Rheometric Scientific, ARES 100FRTN1 or RDA II). Then 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 the gel forming temperature (the room temperature of about 30 °C, which might change with the 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 the dynamic viscoelasticity was ensured by applying the suitable amplitude of shear strain.

Results and Discussion

Dynamic Viscoelastic Properties of PVC/DOP in the Postgel State. Figures 1−4 show the storage modulus G' as a function of angular frequency ω for the PVC4/DOP, PVC9/DOP, PVC10/DOP, and PVC17/DOP samples, respectively. All the polymer concentrations, as indicated in each figure, are beyond the corresponding critical gelation concentration, c_g.[13] In the observed frequency range, however, the samples (for example, c = 70.0, 72.1, 75.2, and 80.3 g/L for the PVC4 series; c = 35.7, 37.7, and 39.7 g/L for the PVC9 series; c = 29.7 g/L for the PVC 10 series; and c = 14.8, 15.8, and 16.7 g/L for the PVC17 series) near the gel point did not show the expected frequency-independent modulus G_e, the quasi-equilibrium modulus. It is unclear at present whether G_e can be observed at lower frequencies for these samples. However, it is believed that G_e should

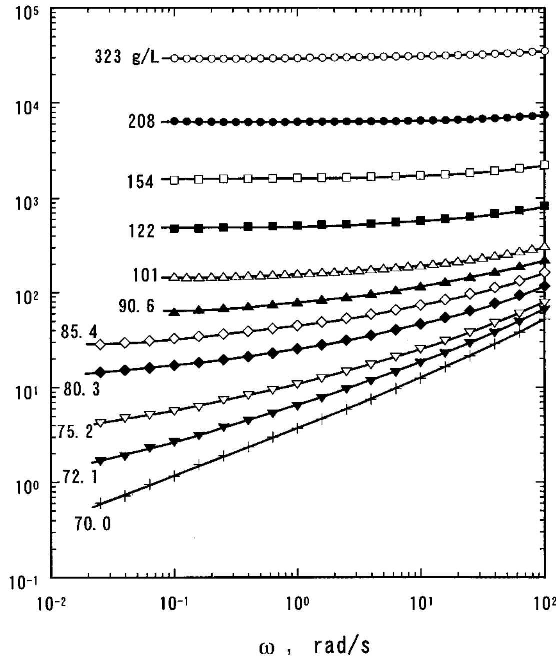

Figure 1. Storage modulus G' as a function of angular frequency for PVC4 /DOP gels. The PVC concentration ranges from 70.0 to 323 g/L as indicated. The critical concentration for the sol−gel transition is 66.0 g/L.[13]

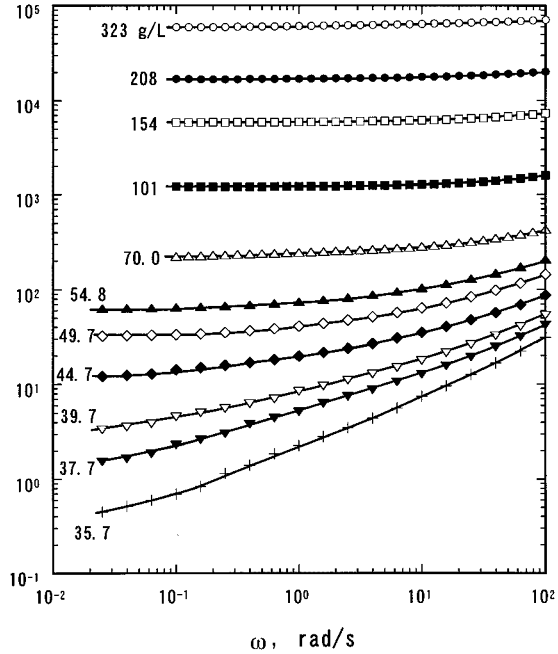

Figure 2. Storage modulus G' as a function of angular frequency for PVC9 /DOP gels. The PVC concentration ranges from 35.7 to 323 g/L as indicated. The critical concentration for the sol−gel transition is 32.7 g/L.[13]

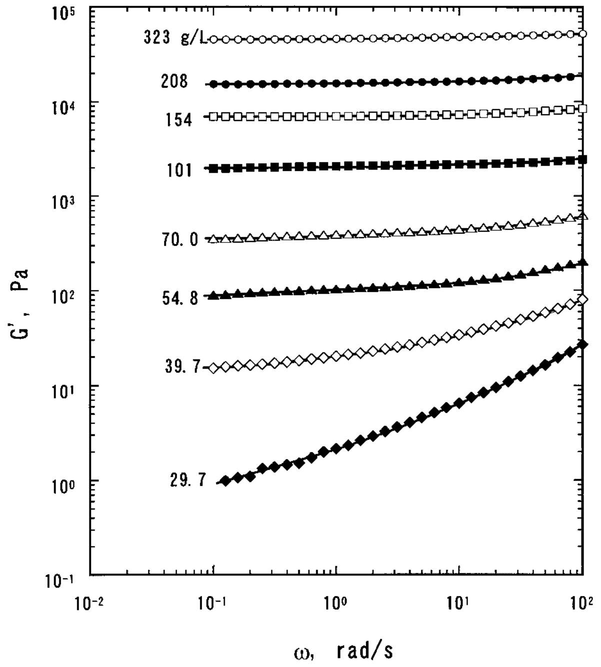

Figure 3. Storage modulus G' as a function of angular frequency for PVC10 /DOP gels. The PVC concentration ranges from 29.7 to 323 g/L as indicated. The critical concentration for the sol–gel transition is 26.7 g/L.[13]

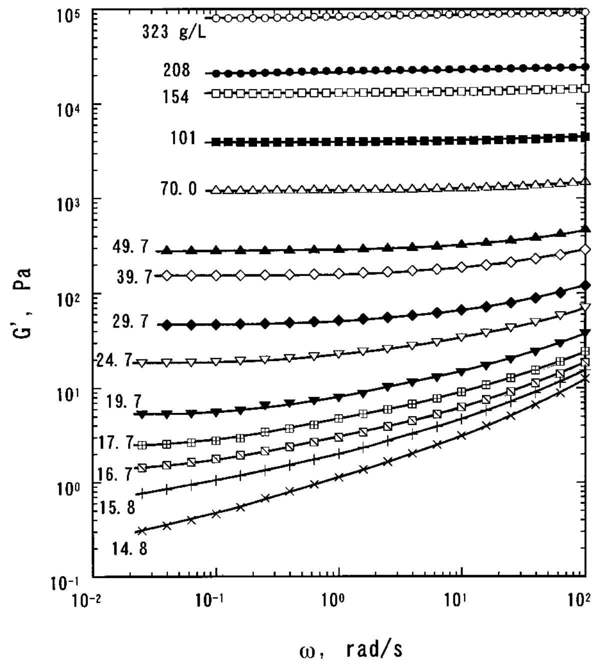

Figure 4. Storage modulus G' as a function of angular frequency for PVC17 /DOP gels. The PVC concentration ranges from 14.8 to 323 g/L as indicated. The critical concentration for the sol–gel transition is 12.5 g/L.[13]

Table 1. Quasi-Equilibrium Modulus G_e as a Function of Polymer Concentration c or the Relative Distance ϵ ($=(c - c_g)/c_g$) for PVC4, PVC9, PVC10, and PVC17 Series[a]

series	c (g/L)	ϵ	G_e (Pa)
PVC4	85.4	0.294	2.84×10
	90.6	0.373	6.25×10
	101	0.530	1.46×10^2
	122	0.849	4.82×10^2
	154	1.33	1.58×10^3
	208	2.15	6.29×10^3
	323	3.89	2.92×10^4
PVC9	44.7	0.367	1.21×10
	49.7	0.520	3.23×10
	54.8	0.676	6.34×10
	70.0	1.14	2.25×10^2
	101	2.09	1.21×10^3
	154	3.71	5.84×10^3
	208	5.36	1.69×10^4
	323	8.88	5.99×10^4
PVC10	39.7	0.487	1.51×10
	54.8	1.05	8.97×10
	70.0	1.62	3.52×10^2
	101	2.78	1.97×10^3
	154	4.77	6.91×10^3
	208	6.79	1.52×10^4
	323	11.1	4.52×10^4
PVC17	17.7	0.416	2.50×10^0
	19.7	0.576	5.24×10^0
	24.7	0.976	1.84×10
	29.7	1.38	4.66×10
	39.7	2.18	1.54×10^2
	49.7	2.98	2.88×10^2
	70.0	4.60	1.24×10^3
	101	7.08	3.93×10^3
	154	11.3	1.29×10^4
	208	15.6	2.09×10^4
	323	24.8	8.04×10^4

[a] Here the critical concentration c_g is 66.0, 32.7, 26.7, and 12.5 g/L for the PVC4, PVC9, PVC10, and PVC17 series, respectively.[13]

exist beyond the gel point if a permanently strong (it is equivalent to an infinite relaxation time) network forms. The range of polymer concentration in which G_e was not clearly observed may be more interesting because the gel network structure would be expected to develop in the concentration range.

On the other hand, as the PVC concentration increased, the G_e was clearly observed in the low-frequency region as an increasing function of polymer concentration. The quasi-equilibrium modulus G_e was obtained from the G' in the frequency independent range, and presented in Table 1. Table 1 excluded the samples which did not exhibit the frequency independent G' in the observed frequency range. We are now going to examine the elasticity evolution and the scaling law based on the data given in Table 1.

Elasticity Evolution. The gel elasticity characterized by the quasi-equilibrium modulus G_e is illustrated as a function of polymer concentration c in Figure 5. For each molecular weight of PVC, G_e increases with c, but the gradient of the G_e vs c curve becomes mild as c increases, indicating a slow of the elasticity evolution rate. On the other hand, the effect of PVC molecular weight on elasticity evolution can be observed in the following way:

(1) To obtain the same value of G_e, one needs to prepare a more concentrated gel from a lower molecular weight of PVC but the difference in concentration goes down for more concentrated gels. (2) At the same concentration, c, G_e is increased significantly by increasing PVC molecular weight, but (3) the effect of PVC molecular weight on G_e becomes weak with increasing polymer concentration c. As a result, the superposition by shifting the $G_e(c)$ curves along the c axis seems not to hold for these gels. Also one may observe that the $G_e(c)$ curves tend to converge as c approaches to 100% (about 1390 g/L) PVC (bulk). But this is beyond the scope of our studies of the PVC gels.

The Scaling Law for the Gel Elasticity. The scaling law of eq 1 was examined by plotting the equilibrium modulus G_e against the relative distance ϵ in the double logarithmic scale as shown in Figure 6. To

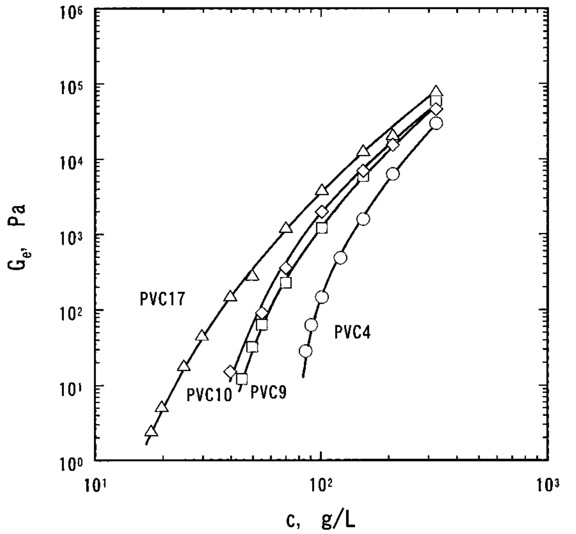

Figure 5. Quasi-equilibrium modulus G_e as a function of polymer concentration c for PVC4, PVC9, PVC10, and PVC17 series.

obtain the scaling exponent z, linear fitting to the data was performed separately for each series to give the following relations:

$$\log G_e = 2.89 + 2.66 \log \epsilon \quad \text{for PVC4 series} \tag{2a}$$

$$\log G_e = 2.24 + 2.67 \log \epsilon \quad \text{for PVC9 series} \tag{2b}$$

$$\log G_e = 2.00 + 2.63 \log \epsilon \quad \text{for PVC10 series} \tag{2c}$$

$$\log G_e = 1.33 + 2.57 \log \epsilon \quad \text{for PVC17 series} \tag{2d}$$

Here $\epsilon = (c - c_g)/c_g$. The correlation coefficient, which was used to evaluate the goodness of each fitting to the above relation, was higher than 0.998. The average value of the slopes is 2.63 ± 0.04 so that we are able to regard reasonably the scaling exponent z as a constant which is independent of the PVC molecular weight. By taking account of the experimental errors in determining the scaling exponent, we prefer to use 2.6 ± 0.1 to express the z in this work. This is also consistent with the expression of the exponent γ ($=1.5 \pm 0.1$) for $\eta_0 \propto \epsilon^{-\gamma}$.[14]

As mentioned in the Introduction, the application of the percolation theory to prediction of the scaling law has given different values of z.[1,3,7–9] But the theoretical z seems to be a value between about 2 and 3. Interestingly, the same value of z ($={}^8/_3$) has also been theoretically predicted with and without considering hydrodynamic interactions.[8,9] However, the experiments have never exactly met the prediction.[9–12] Surprisingly, however, the z values obtained in this study are excellently close to the theoretical prediction of $z = {}^8/_3$.

The relation, $n = z/(z + \gamma)$, presented first by Winter[10a] and rederived by Martin et al.[8] using a percolation model, describes the symmetry of the longest relaxation time τ_m on both sides of the gel point. The application of the relation, $n = z/(z + \gamma)$, to the PVC/DOP gels in this work gives a prediction of $z = 4.5 \pm 0.3$, where $n = 0.75$ and $\gamma = 1.5 \pm 0.1$ were used.[13,14] It is apparent that this relation fails to predict the scaling behavior of the PVC gels studied. In the other words, the symmetric scaling law before and beyond the gel point is not verified by this work. The experimental examination of the symmetry has also been carried out by Mours and Winter[10b] who interestingly obtained a much larger scaling exponent α (α = 2.5−2.4) for $\tau_m \propto \epsilon^{-\alpha}$ before the gel point than that (α = 1.2−1.4) beyond the gel point for the chemical gels of polybutadienes. Using $\alpha = \gamma/(1 - n)$ for $c < c_g$ and $\alpha = z/n$ for $c > c_g$ to calculate the exponents α,[10] one obtains α = 6.0 and α = 3.5 before and beyond the gel point, respectively, for the PVC/DOP gels. This is phenomenally in good agreement with Mours et al.'s experimental results:[10b] α before the gel point is much larger than α beyond the gel point. The above results seem to prove that the approach to the gel point from the side of $p < p_g$ is faster than from the other side ($p > p_g$).

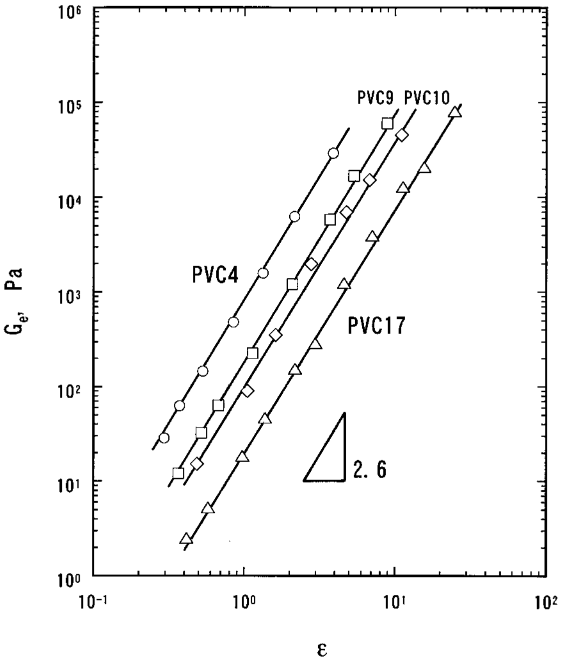

Figure 6. Quasi-equilibrium modulus G_e as a function of the relative distance ϵ for the PVC4, PVC9, PVC10, and PVC17 series. The linear fitting gives the solid straight lines.

Since the scaling exponent z is a molecular weight independent parameter (in the other words, it does not contain the information about the effect of molecular weight), it is believed that such the information on molecular weight must be involved in the intercept term of each relation (eq 2a−d), which is the front constant k for the scaling law, $G_e = k\epsilon^z$. From eq 2a−d, the front constant k was directly obtained to be 776 ($=10^{2.89}$), 174 ($=10^{2.24}$), 100 ($=10^{2.00}$) and 21.4 ($=10^{1.33}$) for the PVC4, PVC9, PVC10, and PVC17 series, respectively. Now we are ready to examine the effect of PVC molecular weight on the gel elasticity expressed by G_e.

The front constant k was plotted in Figure 7 against the weight-average molecular weight M_w. In the log−log scale, the data were able to be approximately expressed by the straight line. The straight line had a fitting goodness of correlation coefficient 0.99. The slope and the intercept are −2.4 and +14, respectively, which are what we need to discuss the molecular weight effect on the gel elasticity. Now we obtain the relation

$$G_e = 10^{14} M_w^{\ -2.4} \epsilon^{8/3} \tag{3}$$

where $\epsilon = (c - c_g)/c_g$ and G_e takes units of pascals. The scaling exponent $z = {}^8/_3$ is used because this theoretical value is almost consistent with our experimental results. Now, it becomes clear that the gel elasticity G_e is

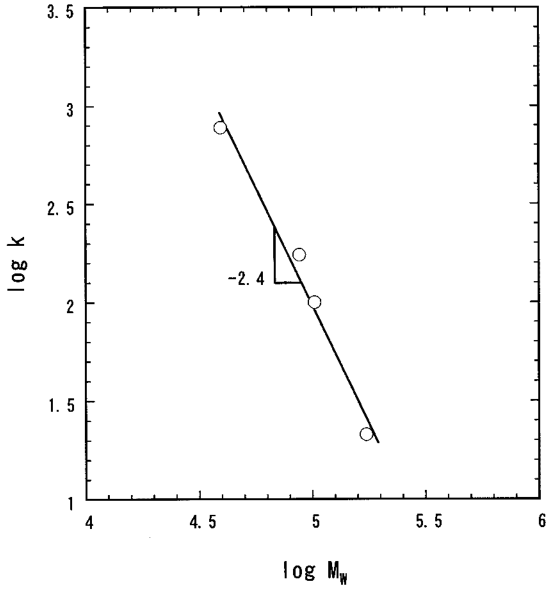

Figure 7. Front constant k in the relation of $G_e = k\epsilon^z$ as a function of weight-average molecular weight. The linear fitting gives a slope of -2.4 and intercept of 14.0.

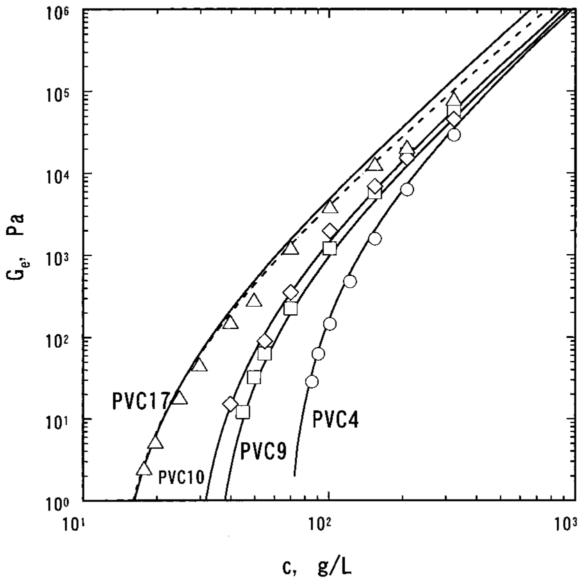

Figure 8. Calculated quasi-equilibrium modulus G_e (solid lines) using the relation $G_e = 10^{14} M_w^{-2.4}\epsilon^{8/3}$ for the PVC4, PVC9, PVC10, and PVC17 series. $z = {}^8/_3$ was used for the calculation. The dashed line was calculated using $z = 2.57$ for the PVC17 series. The same experimental data in Figure 5 are presented again in this figure.

composed of two contributions: the molecular weight M_w and the relative distance ϵ. The G_e varies following both the molecular weight scaling and the relative distance scaling. It is convenient to use eq 3 to predict evolution of the equilibrium modulus G_e of a PVC gel as a function of the relative distance ϵ if M_w is known. To examine the goodness of eq 3 for fitting the experimental results in this study, we calculated G_e for all the PVC gels using eq 3. The results are presented in Figure 8, where the solid lines indicate the calculated G_e. To compare the experimental results with the calculation, the experimental values of G_e in Figure 5 or Table 1 have been presented again in the figure. As seen, except for the PVC17 series, the others are excellently fitted by the solid lines. The solid line for the PVC17 series fits well the data of low concentrations but deviates gradually as the polymer concentration increases. This result may imply a poorer fitting for the high molecular weight side. If $z = 2.57$ (see eq 2d) is used, instead of $z = {}^8/_3$, to calculate G_e, one obtains the dashed line as shown in Figure 8, which seems better to fit the data.

Here, it should be noted that in eq 3 the exponent z is independent of molecular weight, but the relative distance ϵ is not independent of molecular weight because ϵ contains the critical concentration c_g, which is a molecular weight dependent parameter.[13] In the other words, the same polymer concentration c does not give the same value of the relative distance if molecular weight is different.

Now, it can be concluded that the elasticity evolution in the PVC gels is well described by eq 3, although there is still a small deviation for the high molecular weight of PVC. The excellent consistency between the theoretical prediction and the experimental results may suggest that the development of elastic network beyond the gel point follows the percolation theory, even though the prediction given by the same theory did not fit the zero shear viscosity of PVC/DOP in the pregel state well.[14] Further work is needed for more detailed explanation of the mechanism of elasticity evolution.

The scaling law for the evolution of gel elasticity should be related to the molecular structure of gels, especially the structure of junctions. The percolation model[6] deals with the three-dimensional connection of clusters (or aggregates) for the formation of a network, but does not tell the molecular structure of clusters or junctions. For PVC gelling materials, there have been many works focusing on the molecular structure of gels.[15−21] For example, the molecular structure of PVC thermoreversible gels has been often modeled as the fringed-micelles, which are small crystallites connected by flexible chains.[18] However, the experiments carried out by a group of European researchers[15−17,19,20] have supported the model that the PVC gels take the fibrous crystal structure. The fiberlike morphology of the PVC gel in a good solvent (bromobenzene) has been identified by means of electron microscopy.[15] The samples were prepared using the freeze-etching technique and the gel network was observed to have a mesh size of about 0.1 μm.[15] The gelation of PVC can also been achieved in poor solvents. A poor solvent may help PVC to form a network with larger mesh sizes than those in good solvents. For example, Mutin and Guenet[16] reported the fibrous network of PVC in a poor solvent (cyclohexanone /hexanol = 60/40), which had a mesh size of about 10 μm, much larger than those (about 0.1 μm) formed in good solvents. This implies that the interaction between PVC and a solvent influences formation of the gel structure. Since there are few experiments showing the fiberlike network, further experimental examination of the PVC network would be necessary and is also of interest for studies of the scaling law, which may be expected to be affected by the gel network structure.

On the other hand, the efforts have been made to analyze or model the gel structure. For example, the cascade model has been applied to describe the elasticity (modulus) of PVC gels.[21, 22] The model gives an expression for G_e[21−23]

$$G_e = aRT[Nf\alpha(1 - \nu)^2(1 - \beta)/2] \qquad (4)$$

by modifying the classical theory of rubberlike elasticity describing G_e (=νRT),[5] where ν is the fraction of elastically effective chains. Here the front factor a is a parameter measuring the deviation from the ideal rubberlike elasticity, R the gas constant, T the absolute temperature, N the number of moles of polymer per unit volume ($N = c/M$), f the functionality (number of sites per polymer chain potentially available for cross-linking), α the fraction of cross-linking sites, and v (the extinction probability), and β are functions of f and α. The key parameter is the front factor a. The increase in the value of a from 1 will indicate a gradual shift from entropic elasticity to enthalpic elasticity. Lopez et al.[21] and Garcia et al.[22] used an evaluated functionality of f to calculate the other parameters in eq 4 for the PVC physical gels (including the chemically modified PVCs), and they obtained the relatively high values ($>$ 1) of a, reflecting enthalpic contributions to the gel modulus.

In another way, Tanaka et al.[24] modeled the junction structure of physical gels by simply assuming that a physical junction is composed of s chains and ξ segments. This model may be used to deal with fringed-micellar crystallites of the junction structure if there is no chain folding involved in the junction. Although the recent examination of this model for the polyethylene, polystyrene, and poly(vinyl alcohol) gels (all of which were physical gels) gave some meaningful evaluations of the junction structure, the prediction by use of the model is still crude for at least three reasons: (1) the model will fail to deal with the physical gels without fringed-micellar junctions, especially for the gels with the fibrous network structure; (2) the model does not take account of the free energy of chain folding that is probably involved in the junction; (3) the polydispersity of the junction structure has not been considered.

As stated above, there are still many unsolved problems remaining in studies of PVC gels even though PVC has been known to form gels in numerous solvents for more than 50 years and a number of theoretical and experimental studies have been conducted during the period. The most interesting issue in future studies would be the relationship between the gel molecular structure and the scaling law.

Conclusions

Poly(vinyl chloride) (PVC) gels were prepared from THF solutions. Bis(2-ethylhexyl) phthalate (DOP) was used as the solvent or plasticizer for the gels. Dynamic viscoelastic measurements were carried out to allow us to observe the elasticity evolution of the PVC gels as a function of polymer concentration and molecular weight. It was found that the evolution of gel elasticity defined as the quasi-equilibrium modulus G_e followed the scaling law $G_e \propto \epsilon^z$, and the scaling exponent z (=2.6 ± 0.1) was independent of molecular weight. This result is consistent with the theoretical prediction ($z = {}^8/_3$) using the percolation model. We further examined the dependence of G_e on molecular weight by considering the front constant k of the relation $G_e = k\epsilon^z$ to be a function of molecular weight. As a result, G_e could be well expressed by $G_e = 10^{14} M_w^{-2.4}\epsilon^{8/3}$ to allow one to discuss separately the molecular weight contribution and the relative distance contribution. In the vicinity of the gel point, however, the frequency independent equilibrium modulus was not experimentally observed in the frequency range studied.

Acknowledgment. The authors gratefully thank Dr. Ming Long Yao of the Rheometric Scientific F. E. Ltd. (Japan) for his assistance in the rheological measurements.

References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083.
(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(3) Stockmayer, W. H. *J. Chem. Phys.* (a) **1943**, *11*, 45; (b) **1944**, *12*, 125.
(4) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, and London, 1979.
(5) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley & Sons: New York, 1980.
(6) Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.
(7) de Gennes, P. G. *J. Phys. (Paris) Lett.* **1976**, *37L*, 61.
(8) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 2620.
(9) Martin, J. E.; Adolf, D. *Annu. Rev. Phys. Chem.* **1991**, *42*, 311.
(10) (a) Winter, H. H. *Prog. Colloid Polym. Sci.* **1987**, *71*, 104. (b) Mours, M.; Winter, H. H. *Macromolecules* **1996**, *29*, 7221.
(11) Koike, A.; Nemoto, N.; Watanabe, Y.; Osaki, K. *Polym. J.* **1996**, *28*, 942.
(12) Lopez, D.; Mijangos, C.; Munoz, M. E.; Santamaria, A. *Macromolecules* **1996**, *29*, 7108.
(13) Li, L.; Aoki, Y. *Macromolecules* **1997**, *30*, 7835.
(14) Li, L.; Uchida, H.; Aoki, Y.; Yao, M. L. *Macromolecules* **1997**, *30*, 7842.
(15) Yang, Y. C.; Geil, P. H. *J. Macromol. Sci.* **1983**, *B22*, 463.
(16) Mutin, P. H.; Guenet, J. M. *Macromolecules* **1989**, *22*, 843
(17) Guenet, J. M. *Thermoreversible Gelation of Polymers and Biopolymers*; Academic Press: New York, 1992.
(18) Keller, A. *Faraday Discuss.* **1995**, *101*, 1.
(19) Reinecke, H.; Mijangos, C.; Brulet, A.; Guenet, J. M. *Macromolecules* **1997**, *30*, 959.
(20) Dahmani, M.; Fazel, N.; Munch, J. P.; Guenet, J. M. *Macromolecules* **1997**, *30*, 1463.
(21) Lopez, D.; Mijangos, C.; Munoz, M. E.; Santamaria, A. *Macromolecules* **1996**, *29*, 7108.
(22) Garcia, A.; Munoz, M. E.; Pena, J. J.; Santamaria, A. *Macromolecules* **1990**, *23*, 5251.
(23) Clark, A. H.; Farrer, D. B. *J. Rheol.* **1995**, *39*, 1429.
(24) Tanaka, F.; Nishinari, K. *Macromolecules* **1996**, *29*, 3625.

MA971449O