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Rheological Images of Poly(vinyl chloride) Gels. 2. Divergence of Viscosity and the Scaling Law before the Sol−Gel Transition

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ABSTRACT: The zero shear viscosity η_0 of poly(vinyl chloride) (PVC)/bis(2-ethylhexyl) phthalate (DOP) pregels has been measured as a function of polymer concentration c as well as molecular weight. It was observed that the zero shear viscosity diverged as the gelling system approached the gel point. The establishment of the scaling law, $\eta_0 \propto \epsilon^{-\gamma}$, was examined where γ is the scaling exponent and ϵ the relative distance defined as $(c_g - c)/c_g$. Here c_g is the critical concentration for the sol−gel transition. Two methods were used to determine the scaling exponent γ. One is the direct determination of γ using the c_g obtained by means of the frequency independence of loss tangent. The other is called the Takigawa method that determines simultaneously γ and c_g by mathematically transforming the scaling law into $-\eta_0^{-1}(\mathrm{d}\eta_0^{-1}/\mathrm{d}c)^{-1} = (c_g - c)/\gamma$. Good agreement was obtained between the two methods. The scaling law, $\eta_0 \propto \epsilon^{-\gamma}$, was found to hold well for the PVC pregels, and the scaling exponent γ was a constant (=1.5 ± 0.1) and was independent of the PVC molecular weight. The results suggest that the gelation rate defined as $-\mathrm{d}\eta_0/\mathrm{d}\epsilon$ $(=\gamma\eta_0/\epsilon)$ is related to PVC molecular weight, and at the same ϵ increases with decreasing molecular weight. The errors in determining the scaling exponent γ were also discussed.

Introduction

Rheologically, the sol−gel transition for a chemically gelling material is defined as the instance at which the zero shear viscosity η_0 diverges. A scaling law

$$\eta_0 \propto \epsilon^{-\gamma} \qquad \text{for } p < p_g \tag{1}$$

is established for η_0 in the vicinity of the gel point. Here $\epsilon = (p_g - p)/p_g$ indicates the relative distance of a variable p departing from the sol−gel transition point p_g, and p can be, for example, the degree of cross-linking, gelation time, or temperature in a gelation process. γ is the critical exponent determining the critical characteristics in the vicinity of the sol−gel transition. Since the exponent γ is always positive, the zero shear viscosity diverges at the gel point ($p \rightarrow p_g$). In chemical gelation, a three-dimensional network forms through permanent covalent bonds, which cannot be dissolved in solvents and is also not thermoreversible. Since the molecular weight diverges at the gel point and a viscous flow is impossible in a permanent three-dimensional network of chemical gel, the zero shear viscosity must be infinitely high at and beyond the sol−gel transition.

A physically gelling material also forms a three-dimensional network. However, the junctions in physical gels are not composed of permanent chemical bonds, and they are of a thermoreversible nature. Depending on the feature of each gelling system, for example, the junctions may be hydrogen bonds, crystalline regions, ionic clusters, or phase-separated microdomains. In this case, the molecular weights are still constant at and beyond the gel point, and gels can be melted at elevated temperatures or dissolved in suitable solvents. Thermoreversibility is the most important characteristic of a physical gel, completely differing from chemical gels. The scaling law of eq 1 has also been applied to describe the critical behavior of physical gels.[1−3]

The scaling law of eq 1 is established only for pregels. A pregel is defined as the system in which the storage modulus G' is not zero and is frequency-dependent but the equilibrium modulus G_e is zero. For physically gelling materials, further dilution or enhancement of temperature may bring a pregel solution to enter the pure viscous region where $G' = 0$ and $\eta' =$ constant. The existence of PVC aggregates in solution has been experimentally examined by light scattering (Rayleigh scattering).[4] Abied et al.[5,25] presented the molecular models for the PVC aggregates formed in dilute solutions ($c < c_g$), which describe the PVC aggregate as a fibril-like structure comprising the syndiotactic crystallites and the bridging chains between the crystallites. However, the details about the structure of PVC aggregates have not been completely elucidated. Therefore, the important issue in studying PVC pregels (i.e. below the critical gel concentration) has to deal with how PVC forms aggregates and what is the molecular structure of PVC aggregates. Another question is whether the molecular structure of PVC aggregates has effect on the scaling law if the structure is changeable.

Theoretically, the value of the critical exponent γ in eq 1 has been predicted by many models.[1,6−10] The classic theory based on the Bethe lattice (the tree approximation) gives $\gamma = 0$,[6,7] while the models using percolation theory predict different values of γ depending on the model assumption.[8−10] For example, $\gamma = {}^4/_3$ has been reported for the case of hydrodynamic interactions.[10] However, the experiments gave various values of γ: (1.3−1.5) ± 0.2 for the silica gels,[11] 1.4 ± 0.2 for the epoxy resins,[10,12] (0.9−1.9) ±0.1 for the end-crosslinking hydroxyl-terminated polybutadienes,[13] 1.2 for the polybutadienes,[14] and 1.67 for the poly(vinyl alcohol) gels.[15] It seems that γ has values between 1 and 2 but no universal γ exists.

Experimentally, if the critical point p_g is known, γ is directly obtained from the slope of the plot of η_0 against

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ϵ in a log−log scale. If the gel point p_g is unknown, it is efficient to use eq 1 to simultaneously determine p_g and the exponent γ. By mathematically transforming eq 1 into

$$-\eta_0^{-1}\,(\mathrm{d}\eta_0^{-1}/\mathrm{d}p)^{-1} = (p_g - p)/\gamma \qquad (2)$$

the values of p_g and γ are then obtained from the slope and intercept of the plot of $-\eta_0^{-1}(\mathrm{d}\eta_0^{-1}/\mathrm{d}p)^{-1}$ vs p. The experimental examination of this method can be viewed from the studies of poly(vinyl alcohol) gels carried out by Takigawa et al.[15] who first used this method to determine the gel point. In this study, we also use this method to determine the critical concentration, c_g, and the scaling exponent, γ, and then compare them with the c_g obtained by means of the frequency independence of loss tangent and the γ from the direct application of eq 1.

Our interests have been in exploring a whole rheological image of the physically gelling system: poly(vinyl chloride) (PVC) solutions and gels with different molecular weights of PVC.[16] In the previous report,[16] a constant value of the scaling exponent n is found (n = 0.75) to be independent of the molecular weight of PVC, even though the sol−gel transition is strongly molecular weight dependent. The polymer concentration c_g at the gel point as well as the gel strength S_g are inversely proportional to the PVC molecular weight. These results describe a unique structure of the PVC gelling system at the gel point. In this work, as the second part of our studies of the PVC solutions and gels, rheological studies have been conducted by focusing on how the zero shear viscosity diverges when the gelling system goes close to the gel point from dilute concentrations of PVC, what the scaling law is for these pregels, and whether the molecular weight of PVC affects the scaling law.

Experimental Section

Materials. The materials used in this study were three poly(vinyl chloride)s (PVC), designated as PVC4, PVC9, 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 weight-average molecular weight M_w: 3.94 × 10^4 for PVC4; 8.74 × 10^4 for PVC9; 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; $M_w = 2.54 \times 10^5$ 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; PVC17, syndio = 0.35, hetero = 0.49, iso = 0.16.

Three gelling systems of the purified PVCs in bis(2-ethylhexyl) phthalate (DOP) were prepared at room temperature from THF solutions (about 70 wt % of THF) of PVC and DOP. No stabilizers or additives were added. Since we have known the critical concentration c_g for each PVC from the previous study,[16] the polymer concentration was directly chosen to cover the pregel region of each series. The evaporation of THF from each solution proceeded at room temperature, and it took from 1 to 2 weeks, depending on the polymer concentration. After the THF evaporated completely, transparent liquids were obtained. Since a sufficiently long time (more than 2 weeks) was taken for the evaporation and the equilibrium of gelation prior to rheological measurements, each sample was considered to be stable with time. The rheological reproducibility was confirmed from some selected samples.

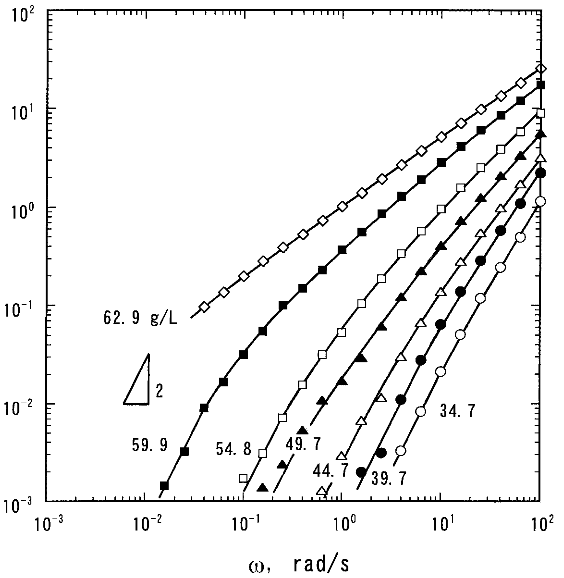

Figure 1. Storage modulus G' as a function of angular frequency ω for PVC4/DOP samples. The PVC concentration ranges from 34.7 to 62.9 g/L as indicated.

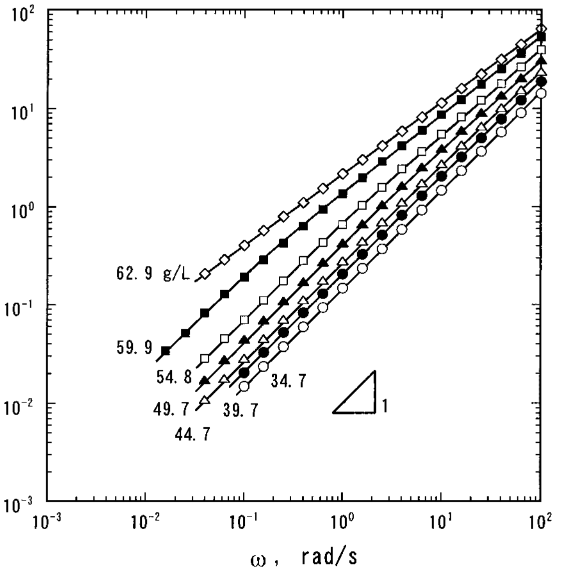

Figure 2. Loss modulus G'' as a function of angular frequency ω for PVC4/DOP samples. The PVC concentration ranges from 34.7 to 62.9 g/L as indicated.

Rheological Measurements. The PVC/DOP sample was transferred from the flat laboratory dish into the rheometer (Rheometric Scientific, ARES 100FRTN1). The rheometer was equiped with a force transducer allowing the torque measurement ranging from 0.004 to 100 g cm. Then 25 mm or 50 mm diameter parallel plates were used for the dynamic measurements. The shear storage modulus G', loss modulus G'', and complex viscosity η^* were measured as a function of angular frequency ω at 40 °C. Depending on the viscoelastic properties of each sample, the linearity of dynamic viscoelasticity was ensured by applying the suitable amplitude of shear.

Results and Discussion

Dynamic Viscoelastic Properties of PVC/DOP in the Pregel State. The shear storage moduli G' and loss moduli G'' are illustrated in Figures 1 and 2 as a function of angular frequency for the PVC4/DOP samples. The polymer concentration ranges from 34.7 to 62.9 g/L as indicated. The dynamic mechanical behavior of the pregel samples follows the liquidlike terminal behavior at very low frequencies:[17,18]

$$G'(\omega) \propto \omega^2 \qquad G''(\omega) \propto \omega \quad (\text{at } \omega \rightarrow 0) \tag{3}$$

The establishment of the above relations indicates the existence of the zero shear viscosity η_0. A similar behavior was also observed for the PVC9 and PVC17 pregels.

The zero shear viscosity η_0 can be directly obtained from the complex viscosity $\eta^*(\omega)$ at $\omega \rightarrow 0$. Figures 3−5 present the complex viscosity η^* as a function of angular frequency ω for PVC4, PVC9, and PVC17 systems. The PVC concentrations are indicated in the figures. In each figure, the frequency-independent behavior of η^* is observed at low frequencies. The range of the frequency-independence of η^* shifts to lower frequencies as the polymer concentration increases. Simultaneously, the value of η^* increases as a function of polymer concentration. We define the value of η^* in the range of frequency-independence as the zero shear viscosity, η_0. Our discussion in this report will be concentrated on the nature of η_0. η^* of samples with PVC concentrations close to the critical points c_g (for example, 62.9 g/L for PVC4 and 29.7 g/L for PVC9) do not show the frequency-independence in the observed range of frequency, and they tend to have a much higher zero shear viscosity at low frequencies than the others. Here, we exclude them from discussion of the nature of zero shear viscosity. When the polymer concentration is increased to reach to the gel point, the zero shear viscosity becomes infinite and immeasurable.

Some theories have been derived for describing the rheological behavior of a gelling system evolving towards the gel point. Theoretically, the application of the Boltzmann's superposition principle to the complex modulus G^* gives the expression of $\eta^*(\omega)$ by the stress relaxation modulus $G(t)$:[18]

$$\eta^*(\omega) = \int_0^\infty G(t)\, \exp(-i\omega t)\, \mathrm{d}t \tag{4}$$

To fit $\eta^*(\omega)$ data to this equation, the form of $G(t)$ has to be known in advance. Friedrich et al.[19] proposed

$$G(t) = St^{-k} \exp(-t/\tau_0) \tag{5}$$

to represent the relaxation function prior to the sol−gel transition. Here S is the quality related to the stiffness of a pregel, k the parameter, and τ_0 the relaxation time, all of which are determined by the physical nature of a gelling material. The calculation of eq 4 by substituting eq 5 gives

$$\eta^*(\omega) = S\, \Gamma(1 - \mathrm{k})/(i\omega + \tau_0^{\ -1})^{1-\mathrm{k}} \tag{6}$$

where Γ is the gamma function. The three parameters, S, k, and τ_0 are then determined by a nonlinear fitting of $\eta^*(\omega)$ data. Equation 6 is identical with the Davidson−Cole relationship proposed in 1951[20]

$$\eta^*(\omega) = \eta_p/(1 + i\omega\tau_0)^\sigma \tag{7}$$

by letting $\eta_p = S\Gamma(1 - k)\, \tau_0^{1-k}$ and $\sigma = 1 - k$.

Martin et al.[10] presented a modified form of $G(t)$ by adding the fourth parameter β to the exponential term:

$$G(t) = St^{-k} \exp(-(t/\tau_0)^\beta) \tag{8}$$

This may allow a better fitting of data to eq 4. However, the physical meaning of β would be difficult to interpret. To get the four parameters in eq 8 requires a nonlinear regression program. An experimental examination of eq 8 has been conducted by Peyrelasse et al.[3] who studied the gelation of gelatin solutions and found that β was nearly constant ($\beta \approx 0.44$) and the others were gelation-dependent. We are now studying what kind of relaxation function can be applied to the PVC pregels.

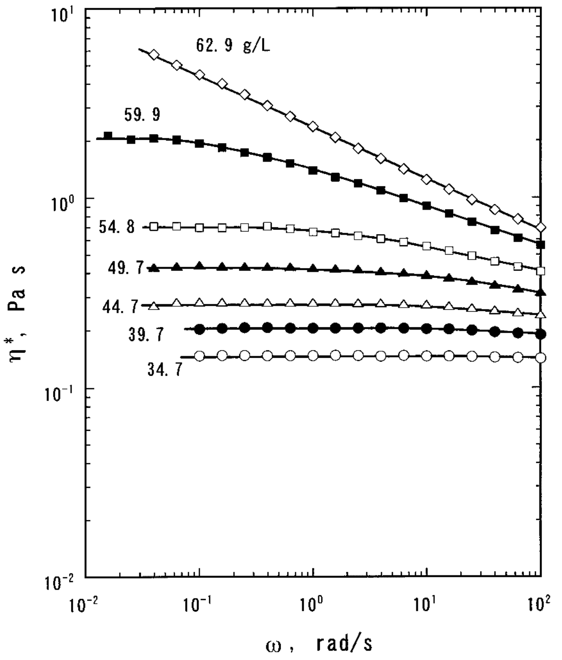

Figure 3. Complex viscosity η^* as a function of angular frequency ω for PVC4/DOP samples. The PVC concentration ranges from 34.7 to 62.9 g/L as indicated.

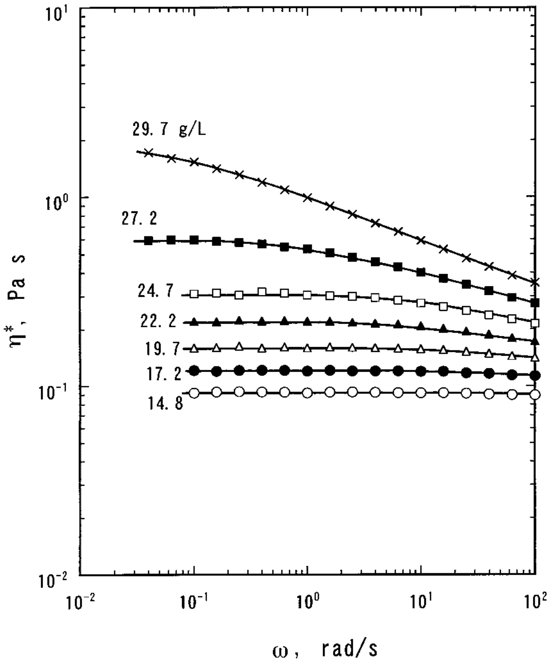

Figure 4. Complex viscosity η^* as a function of angular frequency ω for PVC9/DOP samples. The PVC concentration ranges from 14.8 to 29.7 g/L as indicated.

As a gelling system approaches to its gel point at which the relaxation time τ_0 is infinite, either eq 5 or eq 8 takes the same form

$$G(t) = St^{-\mathrm{k}} \tag{9}$$

the relaxation function at the gel point where S is the gel strength (usually rewritten as S_g) and k is the

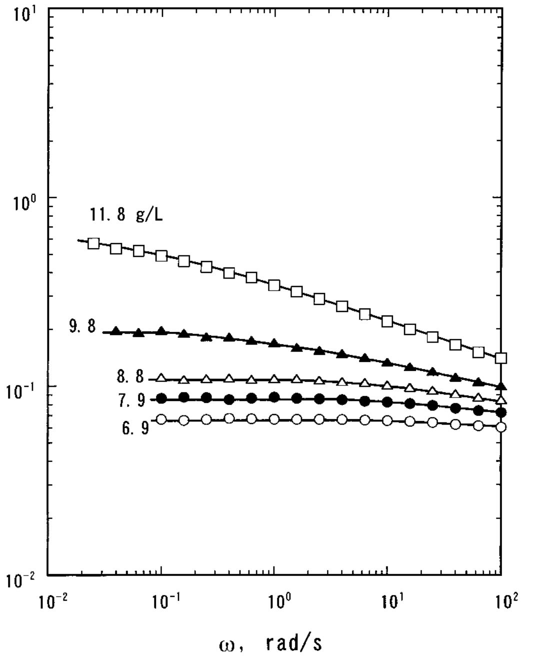

Figure 5. Complex viscosity η^* as a function of angular frequency ω for PVC17/DOP samples. The PVC concentration ranges from 6.9 to 11.8 g/L as indicated.

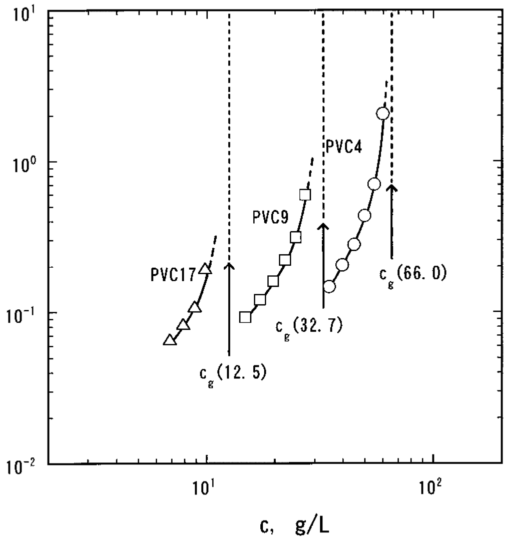

Figure 6. Zero shear viscosity η_0 as a function of polymer concentration c for PVC4, PVC9, and PVC17 systems. c_g indicates each position of the gel point (polymer concentration, g/L) obtained in the previous study.[16]

scaling exponent (usually expressed by n). As we have found,[16] n has a value of 0.75 for the PVC/DOP gelling system and is independent of PVC molecular weight.

Divergence of Zero Shear Viscosity near the Sol−Gel Transition. The zero shear viscosity η_0 was obtained by $|\eta^*|_{\omega\to 0}$ and plotted against polymer concentration c in Figure 6. The gel point c_g of each gelling system is indicated in the figure. η_0 of each system tends to diverge near its gel point. The divergence of the zero shear viscosity can also be theoretically expressed from eq 4. The calculation of η^* by substituting $G(t) = S_g t^{-n}$ into eq 4 gives

$$\eta^*(\omega) = S_g \Gamma(1 - n)/(i\omega)^{1-n} \tag{10}$$

at the gel point, where S_g is a constant for a given gelling material and $n = 0.75$ for the PVC/DOP systems.

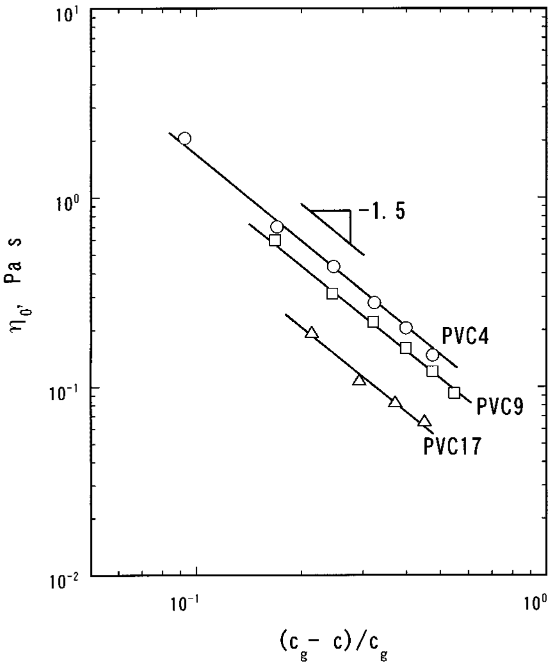

Figure 7. Zero shear viscosity η_0 as a function of the relative distance $(c_g - c)/c_g$ for PVC4, PVC9, and PVC17 systems.

Therefore, the zero shear viscosity must diverge at the gel point under the limit of $\omega \to 0$.

Determination of the Scaling Exponent γ. The scaling exponent γ given in eq 1 governs how fast the gelation proceeds, and γ also describes the divergence of zero shear viscosity. In most cases, γ is not experimentally given if the critical point for the sol−gel transition is unknown. Although many theories have predicted the value of γ, the experiments did not give a universal γ as mentioned in the Introduction. γ seems to be a parameter dependent on the gelling system but most likely ranges between 1 and 2. In this work, as shown below, we examine two methods for the determination of γ and discuss the errors in determining γ.

Method 1. Since we have known the critical concentration of each gelling system,[16] it is convenient to directly determine γ by plotting the zero shear viscosity against the relative distance ϵ $(=(c_g - c)/c_g)$. The direct determination of γ using ϵ is illustrated in Figure 7. The values of c_g were measured by means of the frequency-independence of loss tangent.[21−23] In the log−log scale, the data were well fitted by the straight lines. To our surprise, each straight line has the same slope of −1.5. And then one can directly obtain the value of γ, 1.5, which is independent of the PVC molecular weight.

Method 2. To use eq 2 to determine γ and p_g (in this work, $p_g = c_g$), one needs to first calculate the reciprocal of the zero shear viscosity, η_0, and then compute the derivative of η_0^{-1} against c, i.e., $d\eta_0^{-1}/dc$, by fitting η_0^{-1} vs c to the best curve. η_0^{-1} was plotted against c in Figure 8 for PVC4, PVC9, and PVC17 samples and the data were mathematically fitted by the solid curves. The following relations were obtained from the fitting:

$$\eta_0^{-1} = 47.1 - 26.3 \log c \qquad \text{for PVC4} \tag{11a}$$

$$\eta_0^{-1} = 50.4 - 34.0 \log c \qquad \text{for PVC9} \tag{11b}$$

$$\eta_0^{-1} = 64.3 - 58.7 \log c \qquad \text{for PVC17} \tag{11c}$$

By taking $\eta_0^{-1} = 0$ at the gel point, one gets $c_g = 61.8$,

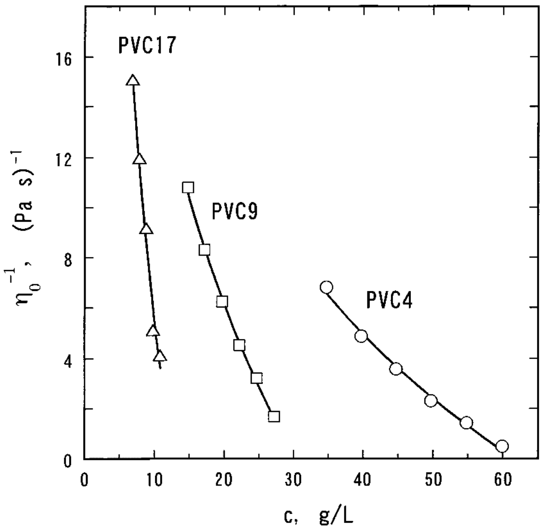

Figure 8. Reciprocal of zero shear viscosity η_0 as a function of polymer concentration c for PVC4, PVC9, and PVC17 systems. The solid lines are obtained by fitting and expressed by eq 11a-c.

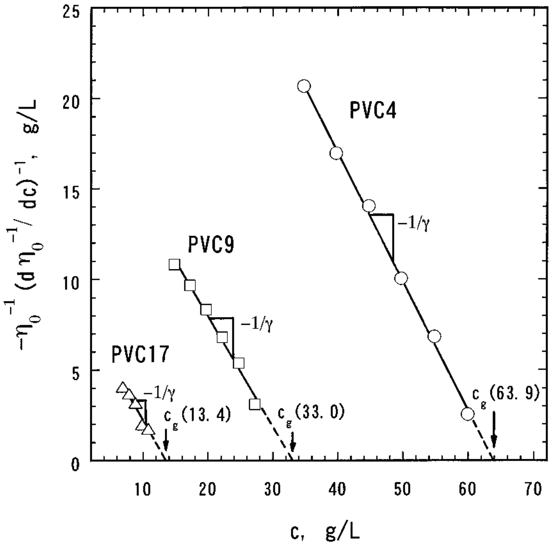

Figure 9. Plots of $-\eta_0^{-1}(d\eta_0^{-1}/dc)^{-1}$ vs polymer concentration c for PVC4, PVC9, and PVC17 systems. For each gelling system, a linear fitting of the data gives simultaneously the value of exponent γ and the critical concentration c_g. The results are presented in Table 1.

Table 1. Comparison of the Critical Concentration, c_g, and the Scaling Exponent, γ, Obtained Using Two Methods, the Frequency Independence of Loss Tangent[16] and the Takigawa Method[15]

system	c_g,[a] g/L	c_g,[b] g/L	γ[c]	γ[b]
PVC4	66.0	63.9	1.5	1.4
PVC9	32.7	33.0	1.5	1.6
PVC17	12.5	13.4	1.5	1.5

[a] Determined using the frequency independence of loss tangent.[16] [b] Determined using the Taklgawa method.[15] [c] Slopes of straight lines of η_0 vs $(c_g - c)/c_g$ in log–log scale. c_g[a] was used.

30.3, and 12.5 g/L for the PVC4, PVC9, and PVC17 systems, respectively, from the above equations. These values of c_g are almost consistent with those (66.0 g/L for PVC4, 32.7 g/L for PVC9, and 12.5 g/L for PVC17) obtained by means of the frequency independence of loss tangent at the gel point.[16] However, it is unclear whether η_0^{-1} should take the above form to be a function of c until the gel point. Since, in the case of method 2, we are just interested in the slope of η_0^{-1} vs c curve for the calculation of $-\eta_0^{-1}(d\eta_0^{-1}/dc)^{-1}$, the mathematical formulation of $\eta_0^{-1}(c)$ is not important in the present work. We will take account of what should be the expressing form of $\eta_0^{-1}(c)$ in future work.

The derivative of η_0^{-1} against c, i.e., $d\eta_0^{-1}/dc$, was directly obtained using eq 11a–c, and then $-\eta_0^{-1}(d\eta_0^{-1}/dc)^{-1}$ was calculated. Figure 9 shows that $-\eta_0^{-1}(d\eta^{-1}/dc)^{-1}$ is a linear function of c for each system. The values of c_g and γ were directly calculated from the intercept and slope of each straight line. The results were presented in Table 1. In this report, method 2 is also termed as the Takigawa method since Takigawa et al.[15] first used the method to determine the exponents c_g and γ. As compared to c_g obtained by means of the frequency independence of loss tangent and γ from method 1, both c_g and γ values from method 2 vary within a deviation of about ±7%. It can be concluded that method 2 is also a useful method for determination of c_g and γ although more points of data may be expected to give better results. The biggest advantage of method 2 is the simultaneous determination of c_g and γ by knowing the zero shear viscosity. The disadvantage of this method, however, is illustrated as the possible enhancement of the error level during the calculation of $d\eta_0^{-1}/dc$. As we have found, the fitting of $\eta_0^{-1}(c)$ using different mathematical functions could give different formulations and then the value of γ varied, but c_g remained almost the same. This indicates that γ is a more sensitive parameter than c_g.

Errors in Determining γ. Except for experimental errors in preparing samples and determining the viscoelastic functions, further errors may be deduced by the data analysis. Since the determination of c_g and γ by means of method 2 needs more steps of mathematical calculation than using method 1, more errors would be expected to remain in the former case. Fortunately, the frequency independence of loss tangent provides one with an accurate method for determination of the critical concentration c_g.[21–23] This method is considered to be able to minimize the error in determining c_g better than the other methods (for example, method 2) because of the excellent convergence of tan δ at the gel point.[16,22,23]

We give an example to show how γ can be varied by c_g. Figure 10 presents the zero shear viscosity η_0 as a function of the relative distance ϵ $(=(c_g - c)/c_g)$ for PVC4 samples, where three values (62.7, 66.0, and 69.7 g/L) of c_g were used to calculate ϵ. The value 66.0 g/L was determined by means of the frequency independence of tan δ in our previous report.[16] As shown in Figure 7, this value (66.0 g/L) of c_g results in a good linear relation between η_0 and ϵ by giving the slope of -1.5. If c_g (66.0 g/L) is allowed to vary from $0.95c_g$ (= 62.7 g/L) to $1.05c_g$ (= 69.7 g/L), the best fitting of $\eta_0(\epsilon)$ to the straight line gives a slope of -1.1 for $c_g = 62.7$ g/L as well as a slope of -2.0 for $c_g = 69.3$ g/L. Then, one gets $\gamma = 1.1$ for $c_g = 62.7$ g/L and $\gamma = 2.0$ for $c_g = 69.3$ g/L. Therefore, it is clear that the variation of c_g to $c_g \pm 5\%c_g$ leads to the serious deviation of γ from the value 1.5. Also, it should be noted from Figure 10 that the linearity of fitting becomes worse as c_g deviates from 66.0 g/L, and the data may prefer to be fitted by the dashed curves. This clearly suggests that the accurate determination of c_g is necessary for the determination of γ. Otherwise, the value of γ will be meaningless.

Scaling Law below the Sol–Gel Transition. As shown above, the use of either method 1 or method 2 gives a molecular weight independent exponent γ of 1.5 ± 0.1, indicating establishment of the scaling law for

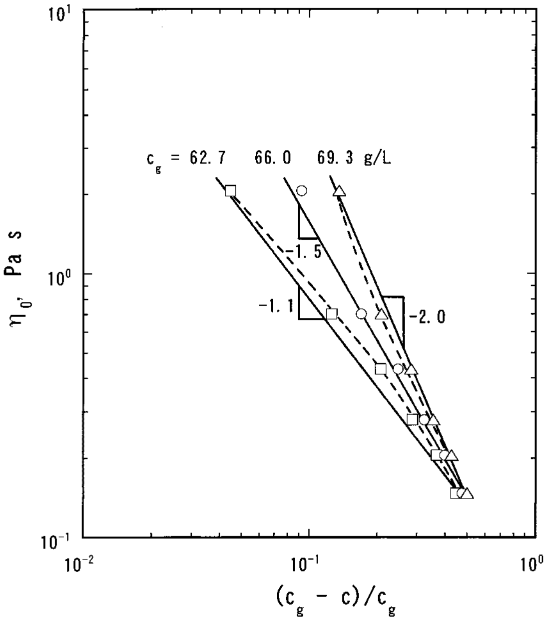

Figure 10. Example of variation of the slope of η_0 vs $(c_g - c)/c_g$ with three c_g for PVC4/DOP samples.

the PVC/DOP pregels. This γ value is somewhat larger than that (1.3) predicted by the three-dimensional percolation theory.[9,10] The definition of γ by eq 1 clearly gives γ the meaning that it is a parameter governing the gelation rate. That is, the larger the γ, the faster the gelation rate. In another way, the gelation rate is defined as the increment of zero shear viscosity η_0 per unit relative distance ϵ. By taking the derivative of η_0 against ϵ and rearranging the equation, one obtains the gelation rate

$$d\eta_0/d\epsilon = -\gamma\eta_0/\epsilon \qquad (12)$$

By this definition of gelation rate, however, the same value of γ does not mean the same rate of gelation. For this study, furthermore, the definition leads to a conclusion that the smaller the PVC molecular weight, the faster the gelation rate, because polymers with lower molecular weights have higher values of η_0 at the same ϵ than those with higher molecular weights as shown in Figure 7. In the other words, the capability of gelation is governed not only by the exponent γ but also by the zero shear viscosity η_0 that is a function of molecular weight.

Although various values of γ have been reported from many experiments,[10-15] the physical meaning of γ is still unclear at present. The comparison of physical gels with chemical gels may help one to consider the physical meaning of γ. For example, unlike the physical gels in this study, the γ for the chemical gels did not take a constant value but monotonously increased from 0.9 to 1.9 with increasing polymer concentration c in the end-crosslinking gelling system while the scaling exponent n at the gel point had a constant value of 0.67 in the range of polymer concentration studied.[13] This comparison may suggest that γ is related to the molecular structure of pregels. The fact that a more concentrated chemical end-crosslinking system exhibits a higher value of γ than the others may reflect a higher probability for the formation of a network through the chemical gelation because there are more end-reactive groups in the concentrated systems.[13] On the other hand, the independence of γ of the molecular weight for the physical gels in this study may suggest the formation of clusters with a similar molecular structure.

The formation of PVC aggregates during gelation has been experimentally examined by light scattering and neutron scattering experiments.[4,5,25] On the basis of neutron scattering data, a group of European researchers[5,25-29] have proposed the fiberlike model to describe the molecular structure of PVC aggregates, that fibrous crystals arise from the crystallization of rigid or semirigid chains and there are no fold chains in the crystals. The fiberlike morphology has also been experimentally observed for the PVC/(good solvent) gels[30] and also for the PVC/(bad solvent) gels.[25] The fiberlike model is totally different from the traditional description of the PVC gel structure where the junctions for the gel network are small bundle crystals (containing fold chains) being connected by flexible intermolecular chains.[24] Although studies of PVC gels have lasted for more than 60 years, the mechanism for the formation of PVC aggregates or clusters and the molecular structure of the PVC pregels have not been fully elucidated. But it is believed that the scaling law for pregels should be controlled by the mechanism of cluster formation and further by the molecular structure of pregels.

Conclusions

Poly(vinyl chloride) (PVC) pregels were prepared from THF solutions. Bis(2-ethylhexyl) phthalate (DOP) was used as the solvent or plasticizer for the pregels. Dynamic measurements were conducted to allow to observe the zero shear viscosity of the pregels as a function of polymer concentration and molecular weight. Below the gel point c_g at which the zero shear viscosity diverged, the zero shear viscosity η_0 varied following the scaling law of $\eta_0 \propto \epsilon^{-\gamma}$, where γ is the scaling exponent and ϵ $(=(c_g - c)/c_g)$ is the relative distance. γ was found to be 1.5 ± 0.1 and independent of molecular weight. The results may suggest that (1) similar molecular structures of pregels are formed and (2) at the same relative distance ϵ, the gelling system with a high molecular weight of PVC has a higher capability for gelation than the system with low molecular weight.

Two methods were used to determine the scaling value of γ, and good agreements were obtained. By discussing the errors in determining γ, we found that an incorrect value of c_g may cause significant deviation of γ.

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