

Rheological Images of Poly(vinyl chloride) Gels. 6. Effect of Temperature

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ABSTRACT: Dynamic viscoelastic properties of poly(vinyl chloride) (PVC)/bis(2-ethylhexyl) phthalate (DOP) gels with different molecular weights and various polymer concentrations have been studied as a function of temperature. These PVC gels exhibited an elastic solid at room temperature and gradually became liquid (sol) with increasing temperature. The sol–gel transition took place at a critical gel temperature at which the scaling law of $G'(\omega) \sim G''(\omega) \propto \omega^n$ held, allowing an accurate determination of the critical gel temperature by means of the frequency independence of the loss tangent. The scaling exponent n obtained was 0.75, independent of temperature as well as molecular weight. This is in good agreement with the previous results observed at 40 °C and suggests the formation of a similar fractal structure of the PVC gels. Furthermore, the molecular structure of the gel junctions was analyzed using the modified Eldridge–Ferry procedure developed by Tanaka and Nishinari. The junction structure was found to be almost independent of molecular weight and gelation temperature, giving a support to the similarity of the fractal structure in the PVC gels.

Introduction

We have recently conducted a series of rheological studies for poly(vinyl chloride) (PVC) in bis(2-ethylhexyl) phthalate (DOP).^{1–5} The following scaling laws have been found to hold well before, at, and beyond the sol–gel transition concentration at a constant temperature of 40 °C, respectively:^{1–3}

$$\eta_0 \propto \epsilon^{-\gamma} \quad \text{for} \quad c < c_g \quad (1)$$

$$G'(\omega) \sim G''(\omega) \propto \omega^n \quad \text{for} \quad c = c_g \quad (2)$$

$$G_e \propto \epsilon^z \quad \text{for} \quad c > c_g \quad (3)$$

where $\epsilon (=|c - c_g|/c_g)$ is defined as the relative distance to the gel point c_g , η_0 is the zero shear viscosity, G' and G'' the dynamic moduli as a function of angular frequency ω , and G_e the quasi-equilibrium modulus. We have found that $n = 0.75$, $\gamma = 1.5$, and $z = 2.6$. The scaling exponents in eqs 1–3 were independent of the PVC molecular weight, suggesting the similarity of the fractal structure of the PVC gels. However, it is unknown if the scaling laws of eqs 1–3 still remain the same or not at elevated temperatures, although they are well established for the critical concentration of the PVC gels at 40 °C.^{1–3,5} There are no theories dealing with the dependence of the scaling laws on temperature, and also we have not found any experimental results concerning the issue. One of the purposes of this paper is to study whether the scaling law of eq 2 is the same at high temperatures.

The junction structure of a physical gel is most important in reflecting information about the gel formation and in controlling the created molecular structure of the gel network.^{6–8} Since most physical gels are

composed of complex network junctions, however, it is not easy to elucidate the junction structure by experiments. For instance, a physical PVC gel is generally considered to have a network consisting of small crystallite domains as the junctions and flexible chains connecting the junctions,^{8,9} but the formation of the network structure through an array of fibrous crystals has also been proposed¹⁰ and partially examined by the experiments.^{6,11–16} However, details in the junction structure of PVC gels have not been completely understood.

Besides experimental examination of the junction structure, a theoretical model based on the junction multiplicity has been proposed to analyze the junction structure in thermoreversible gels.^{17,18} The method, termed as a modified Eldridge–Ferry procedure by Tanaka and Nishinari,¹⁹ deals with a gel junction structure composed of s chains and ζ monomers (repeat units) of each chain, as shown in Figure 1. The s is called the junction multiplicity, and ζ is the junction length. From the method, they derived an expression of the critical concentration c_g as a function of the gelation temperature T and molecular weight M :

$$\ln c_g = \zeta \Delta h / k_B T - (s - 1)^{-1} \ln M + \text{constant} \quad (4)$$

Here Δh is the enthalpy of bonding per mole of the repeat units taking part in the junction, and k_B is the Boltzmann constant. Using eq 4, the temperature dependence of a gel with a constant molecular weight M allows us to evaluate the junction length ζ . On the other hand, estimation of the junction multiplicity s is given from the dependence of c_g on M at a constant temperature of T . This method was applied to the experimental data on the gelation of polyethylene in toluene, atactic polystyrene in carbon disulfide, and poly(vinyl alcohol) (PVA) in water.¹⁹ For example, for the PVA/water system, the multiplicity s was estimated to increase from 2.1 at 71 °C to 3.6 at 91 °C, while the junction length ζ (=16.3) was independent of molecular weight. Another purpose of this paper is to examine whether the modified Eldridge–Ferry procedure can be

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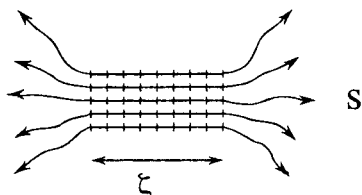


Figure 1. Model junction, proposed by Tanaka and Nishinari,¹⁹ comprises s chains and ζ repeat units (or monomers) of each chain.

applicable to PVC/DOP gels by analyzing the temperature dependence of dynamic viscoelastic properties of the PVC/DOP gels with various concentrations and molecular weights and to know information about junction structure.

Experimental Section

Materials. The polymers employed in this work were four commercial poly(vinyl chloride) (PVC)s produced through suspension polymerization. The details in the molecular characteristics of these PVCs have been given elsewhere.¹ Here we just repeat some of them for reader's convenience. The four PVCs were named as PVC4 ($M_w = 3.94 \times 10^4$, $M_w/M_n = 1.9$), PVC9 ($M_w = 8.74 \times 10^4$, $M_w/M_n = 2.0$), PVC10 ($M_w = 1.02 \times 10^5$, $M_w/M_n = 2.0$), and PVC17 ($M_w = 1.73 \times 10^5$, $M_w/M_n = 2.2$). ¹³C 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.

Prior to the sample preparation, all PVCs were purified by using tetrahydrofuran (THF)/methanol as the solvent/precipitant. Four series of the purified PVCs in bis(2-ethylhexyl) phthalate (DOP) were prepared at room temperature from THF solutions (about 70 to 90 wt % of THF) of PVC and DOP. A 2 wt % quantity of a tin-type stabilizer was added for the PVC/DOP samples with a PVC concentration higher than 7 wt %. Since we have known the critical concentration c_g at 40 °C for each PVC/DOP series from the previous study,¹ the polymer concentrations were directly selected to be higher than the c_g of each series. The evaporation of THF from each THF solution in a flat laboratory dish proceeded at room temperature, and it took longer than 3 weeks. After the THF evaporated completely, transparent soft/solid gels were obtained. Due to the sufficiently long time taken for the evaporation of THF and prior to rheological measurements, each sample was stable with time. The good reproducibility of the data was obtained, when a few samples were measured after 1 and 2 months.

Rheological Measurements. The dynamic rheometers (Rheometric Scientific, ARES 200FRTN1 and RDA II) were employed to measure the storage shear modulus G' and loss modulus G'' as a function of angular frequency ω at a certain temperature. Parallel plates (25 or 50 mm diameter) were used, depending on the viscoelastic properties of each sample. Then the PVC/DOP gel was transferred from the flat laboratory dish into the rheometer. All frequency sweep measurements were carried out by using a variable temperature step of 2–20 °C from room temperature or the lowest measurable temperature (choose the higher one) to the complete flow temperature or 190 °C (choose the lower one). Depending on the viscoelastic properties of each sample, the linearity of dynamic viscoelasticity was ensured by applying the suitable amplitude of shear strain. We did not measure the dynamic viscoelastic properties by a cooling procedure because one has to take the effect of gelation rate into account. It has been found by te Nijenhuis and Winter²² and confirmed in this work that the thermoreversible rate for the PVC gels from a once-melt sample (sol) to lower temperature was not instant and it might take over 100 h or even more. The data on the temperature dependence of the viscoelastic behavior were

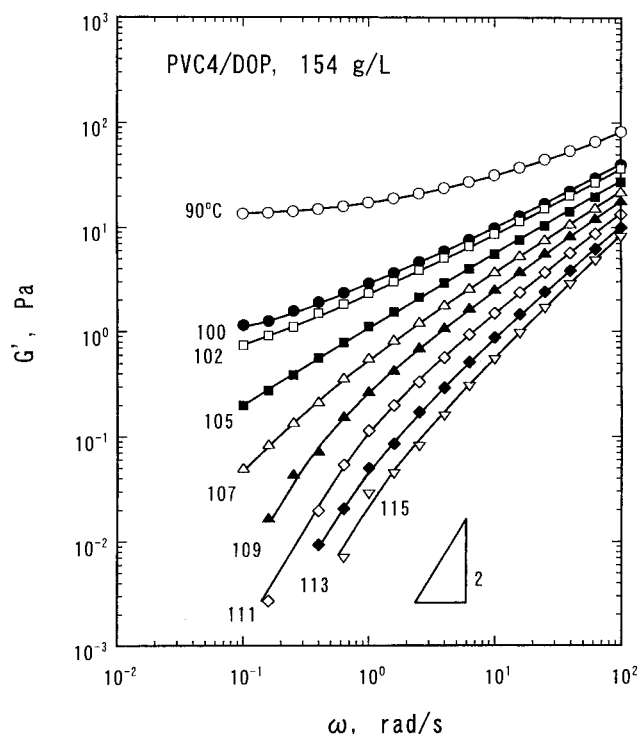


Figure 2. Storage modulus G' of the PVC4/DOP gel with $c = 154$ g/L as a function of angular frequency ω at various temperatures.

obtained from the frequency sweep data measured at various temperatures by a heating procedure.

Results and Discussion

Dynamic Viscoelastic Properties of PVC/DOP Gels Passing through the Sol–Gel Transition Temperature. An example is illustrated here in Figures 2 and 3 to show how a PVC gel changes from the gel state to the sol state by passing through the sol–gel transition temperature in a heating process. In the two figures, the storage modulus G' and loss modulus G'' are presented as a function of angular frequency ω for the PVC4/DOP gel with a polymer concentration of 154 g/L. The measuring temperature was varied from 90 to 115 °C. At 90 °C, a gel plateau of G' is exhibited at low frequencies. The G' decreases significantly with increasing temperature. Finally, at high temperatures, the terminal behavior of $G' \propto \omega^2$ is observed at low frequencies, indicating that the sample has been in the sol state. Simultaneously, G'' exhibits a weaker dependence on temperature than G' , reflecting a change (0 to 1) in the slope of G'' vs ω curves at low ω . We can understand that the sol–gel transition occurred at a certain temperature during the heating process. We show how to determine the sol–gel transition temperature in the next section.

The same measurements were also carried out for all the other PVC gels with four molecular weights and various concentrations in order to determine the sol–gel transition as a function of temperature and molecular weight. Since there are huge amounts of similar data, we just select some of them in this report to discuss the features of temperature-dependent viscoelasticity of the PVC gels.

Figures 4 and 5 show G' and G'' at the frequency of 1 rad/s as a function of temperature for the PVC/DOP samples, respectively. The polymer concentration was

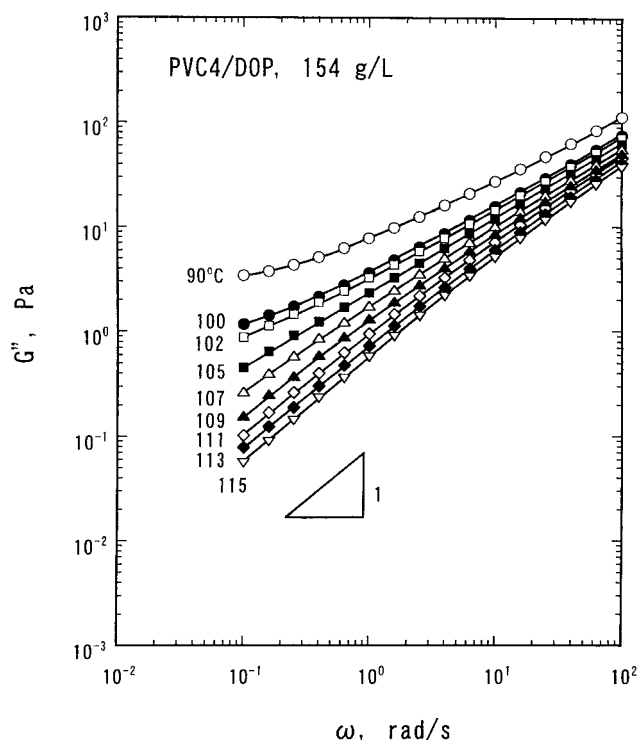


Figure 3. Loss modulus G'' of the PVC4/DOP gel with $c = 154$ g/L as a function of angular frequency ω at various temperatures.

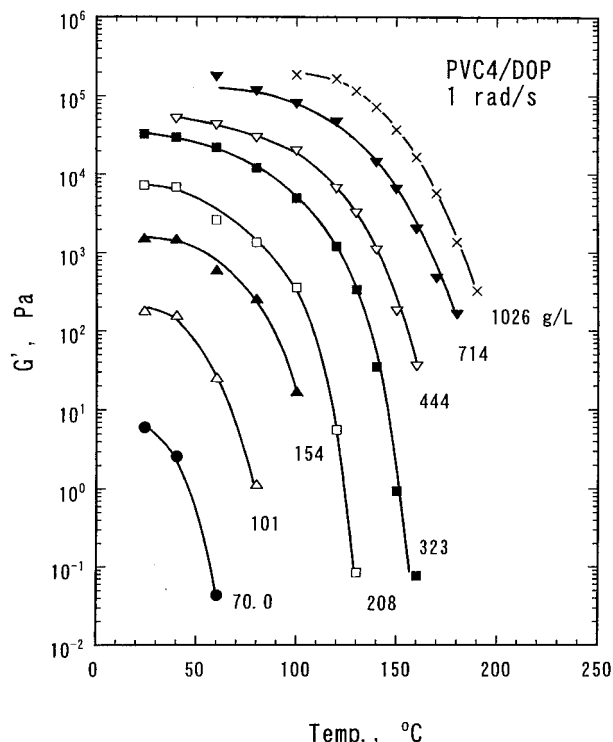


Figure 4. Storage modulus G' of PVC4/DOP gels as a function of temperature at an angular frequency ω of 1 rad/s. The polymer concentration c ranges from 70.0 to 1026 g/L.

varied from 70.0 to 1026 g/L. All the samples shown in Figures 4 and 5 were in the gel state at room temperature. For each concentration of PVC, there appears a gel plateau of G' at low temperatures and G' decreases with increasing temperature. As a result, the sol-gel transition took place at a temperature for each concentration. On the other hand, the dependence of the gel

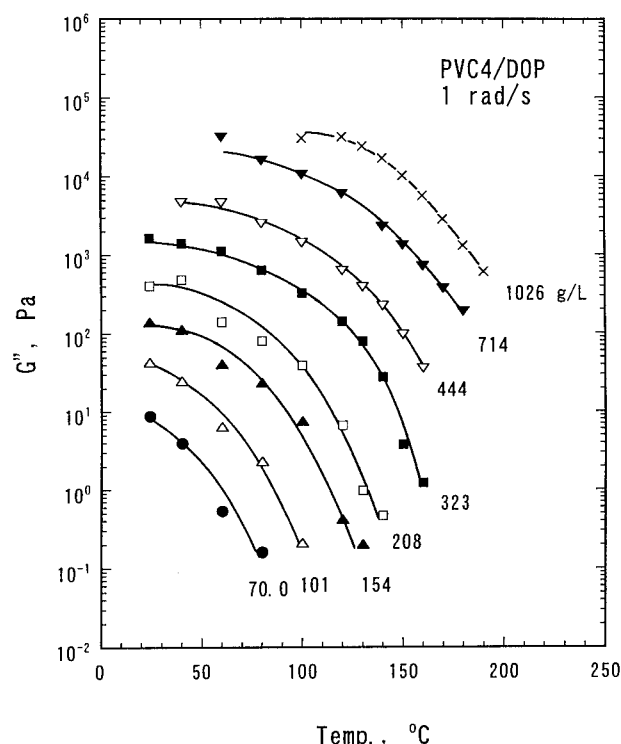


Figure 5. Loss modulus G'' of PVC4/DOP gels as a function of temperature at an angular frequency ω of 1 rad/s. The polymer concentration c ranges from 70.0 to 1026 g/L.

modulus on polymer concentration can be simultaneously observed in the following way. The gel plateau at low temperatures, which represents the gel elasticity G_e , increases with concentration by complying with the scaling law of $G_e \propto c^z$, where z is the scaling exponent, as reported previously.³ The sol-gel transition shifts to high temperatures with increasing PVC concentration.

Determination of the Sol-Gel Transition Temperature. The comparison of G' with G'' in the same scale, as shown in Figures 4 and 5, allows one to see a crossover point of G' and G'' curves for each PVC concentration. Traditionally, many people use the crossover temperature of G' and G'' at a constant frequency as a measure of the gel point. Since the crossover is frequency-dependent, however, we do not use this way to determine the sol-gel transition temperature. As confirmed by a number of experiments,²⁰⁻²⁷ the method, called the frequency independence of loss tangent, is able to give an accurate determination of the gel point. In this work, we also examine this method for determining the sol-gel transition temperatures of the PVC gels. Since $\tan \delta$ loses its dependence on frequency and converges at the gel point, the gel point is determined from a multifrequency plot of $\tan \delta$ vs gelation time, cross-linking degree, concentration, or temperature, depending on which variable governs the gelation process. We have used the method to determine the sol-gel transition concentration c_g for the PVC/DOP gels.^{1,5} In this work, since the gelation variable was temperature, we plotted $\tan \delta$ against temperature in order to decide the critical temperatures by the method. An example for this kind of plot is presented in Figure 6 for the PVC4/DOP of 154 g/L. In this figure, each kind of symbol represents the $\tan \delta$ measured at a certain angular frequency ω . The angular frequency ranged from 0.1 to 100 rad/s. One can observe the convergent point of all $\tan \delta$ vs temperature curves, which is then

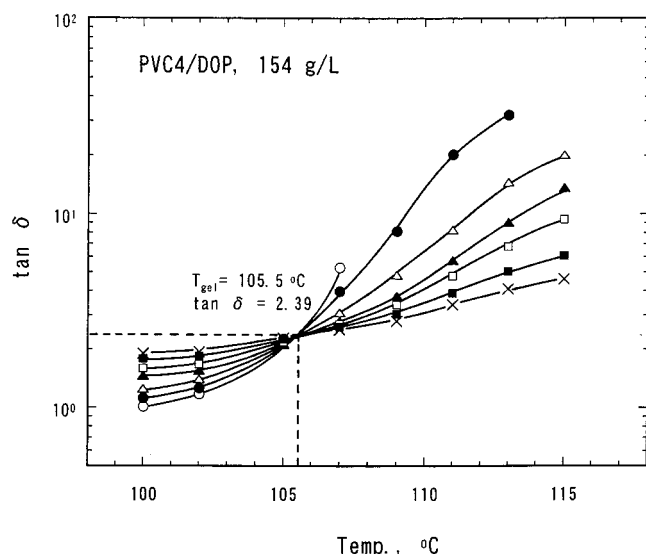


Figure 6. Loss tangent $\tan \delta$ as a function of temperature for the PVC4/DOP with $c = 154$ g/L at various angular frequencies (above T_{gel} , from top to bottom, $\omega = 0.1, 0.398, 1, 3.98, 10, 39.8$, and 100 rad/s). T_{gel} is the gel point.

defined as the sol–gel transition temperature T_{gel} ($=105.5$ °C in this case). Simultaneously, the value of $\tan \delta$ at the gel point provides the information about the scaling exponent n of eq 2, and then we directly obtained $n = 0.75$ by using the relation of $\tan \delta = \tan(n\pi/2)$ at the gel point. In the same way, we also obtained $T_{\text{gel}} = 54.0$ °C and $n = 0.75$ for the PVC4/DOP of 70.0 g/L as well as $T_{\text{gel}} = 81.5$ °C and $n = 0.74$ for the PVC4/DOP of 101 g/L. These results indicate that the scaling exponent n is independent of the sol–gel transition temperature. The same value of n ($=0.75$) has been found to be established well for all the critical PVC/DOP gels at 40 °C. The above results in this work are surprisingly consistent with the previous conclusion.^{1,5} The universal value of n ($=0.75$), which is independent of the sol–gel transition concentration and temperature, suggests that the critical PVC gels have the similarity in the fractal structure.

We believe that the way used in Figure 6 to determine the gel point is the best. However, one has to deal with a number of data in order to get such plots. To avoid huge amounts of data treatment, we applied here the method in the another way for the other PVC/DOP gels prepared in this work. As we have proved that the scaling exponent n is universal for the PVC/DOP gels, we go to examine the method and to determine the sol–gel transition temperatures, as follows. From the scaling law of eq 2, a relation of $G'(\omega)/G''(\omega) = \tan(n\pi/2)$ is derived at the gel point. This relation means that $G'(\omega)$ is equal to $G''(\omega)/\tan(n\pi/2)$ at the gel point. We have examined the establishment of this relation when the gelation variable was the polymer concentration.^{1,5} Two examples of this kind of plot are given in Figures 7 and 8. Here, $n = 0.75$ was used to calculate $\tan(n\pi/2)$ and the frequency was varied from 0.1 to 100 rad/s. One can observe a crossover of $G'(\omega)$ and $G''(\omega)/\tan(n\pi/2)$ at each frequency and the temperature corresponding to the crossover, which is independent of frequency. Therefore, the results are equivalent to the frequency independence of loss tangent and also prove that the scaling exponent n of 0.75 is universal for the PVC/DOP gels. For the other samples, we were able to accurately determine their sol–gel transition temperatures in this way within

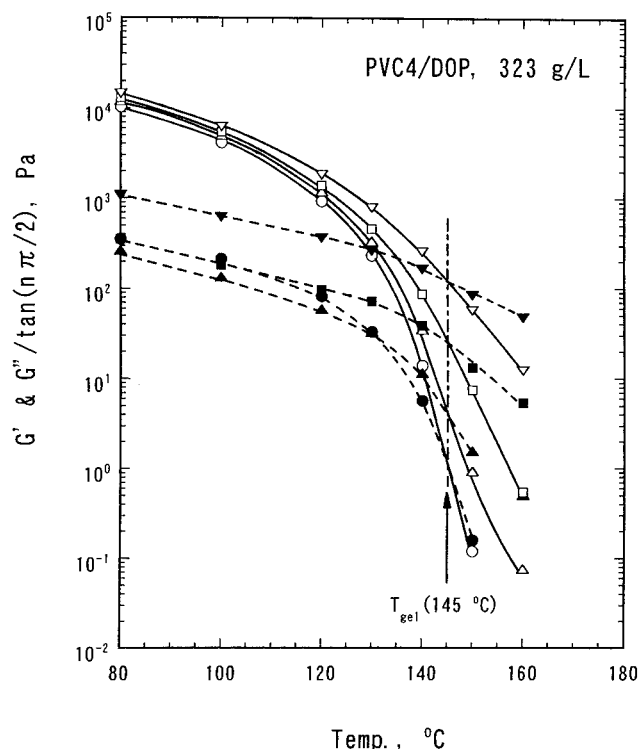


Figure 7. Plots of G' (open symbols) and $G''/\tan(n\pi/2)$ (filled symbols) against temperature for the PVC4/DOP with $c = 323$ g/L. Angular frequency ω was varied from 0.1 to 100 rad/s (\circ and \bullet for 0.1 rad/s; \triangle and \blacktriangle for 1 rad/s; \square and \blacksquare for 10 rad/s; ∇ and \blacktriangledown for 100 rad/s). $n = 0.75$ was used to calculate $G''/\tan(n\pi/2)$. The gel point $T_{\text{gel}} (=145$ °C) is indicated by the arrow.

reasonable experimental error. The results are shown in Table 1.

The scaling law of eq 2 describes the critical behavior of a PVC/DOP gel at the gel point. Being in good agreement with the previous studies of the PVC gels^{1,5} at a constant temperature of 40 °C, the scaling exponent n has been further found in this work to be independent of the sol–gel transition temperature. Now we know that the n is a universal exponent for the PVC/DOP gels. This result is very significant because it suggests an important feature of the critical PVC gels, that the sol–gel transition takes place at the same viscoelastic distance from a completely viscous liquid ($n = 1$) or from a completely elastic solid ($n = 0$). Although the gel strength at the gel point is dependent on molecular weight, polymer concentration, and temperature, the same value of n suggests an equivalent viscoelasticity at the gel point and may also mean the formation of the similar fractal structure.

Estimation of the Junction Structure Using the Modified Eldridge–Ferry Procedure by Tanaka and Nishinari. It is of interest to know the junction structure of a gel network because the junction structure should be related to both the gelation mechanism and the final network structure. Experimentally, it is quite difficult to measure the junction structure because of the complexities in gel networks. The modified Eldridge–Ferry procedure¹⁹ provides us with a simple schematic for the junction structure shown in Figure 1. Although a real junction structure may not be as simple as that described by this model, the relation (eq 4) derived from the model is still of value as a measure for estimation of the junction structure, especially for the case where the junction structure is invariable with concentration, temperature, and molecular weight.

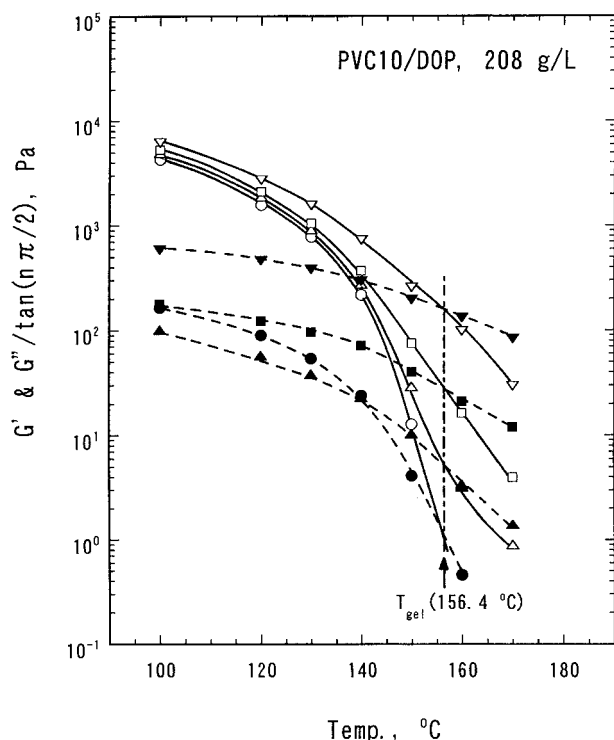


Figure 8. Plots of G' (opened symbols) and $G''/\tan(n\pi/2)$ (filled symbols) against temperature for the PVC10/DOP with $c = 208$ g/L. Angular frequency ω was varied from 0.1 to 100 rad/s (\circ and \bullet for 0.1 rad/s; \triangle and \blacktriangle for 1 rad/s; \square and \blacksquare for 10 rad/s; ∇ and \blacktriangledown for 100 rad/s). $n = 0.75$ was used to calculate $G''/\tan(n\pi/2)$. The gel point $T_{\text{gel}} (=156.4^\circ\text{C})$ is indicated by the arrow.

Table 1. Sol–Gel Transition Temperature T_{gel} as a Function of PVC Concentration c for PVC4, -9, -10, and -17 Series, Determined by the Method Shown in Figures 7 and 8

c , g/L	T_{gel} , $^\circ\text{C}$			
	PVC4	PVC9	PVC10	PVC17
39.7		63.8 ± 1.7	87.4 ± 2.0	119.6 ± 3.6
54.8		91.0 ± 0.5	105.0 ± 0.9	126.0 ± 1.1
70.0	54.0^a	106.1 ± 2.4	112.3 ± 1.0	136.5 ± 0.5
101	82.0 ± 1.0	117.4 ± 0.5	126.0 ± 0.0	149.6 ± 0.9
101	81.5^a			
154	107.0 ± 1.0	137.2 ± 0.1	144.2 ± 0.6	164.5 ± 1.1
154	105.5^a			
208	123.4 ± 0.7	148.6 ± 0.4	156.4 ± 0.8	170.9 ± 2.1
323	145.0 ± 1.0	165.9 ± 1.4	171.9 ± 0.6	188.0 ± 3.5
444	161.6 ± 2.7			
714	180.7 ± 3.0			

^a Measured directly using the frequency independence of loss tangent.

The application of eq 4 requires one to analyze separately the dependences of the critical concentration c_g on temperature T and molecular weight M . Let us first examine the dependence of c_g on T . Using the data in Table 1, $\ln c_g$ was plotted against $10^3/T$ in Figure 9. Here, the T_{gel} data below 85°C were excluded from the plots since they deviated from the linear relation between $\ln c_g$ and $10^3/T$, probably due to some unknown effects, which we will study in future work. The solid straight lines were given by a linear fitting to the data of each M and then one directly obtained the slope of each line: -3.8 for PVC4, PVC9, and PVC10 and -5.4 for PVC17.

According to eq 4, the slope of the line at a constant M gives the calculation of the junction length ζ (number

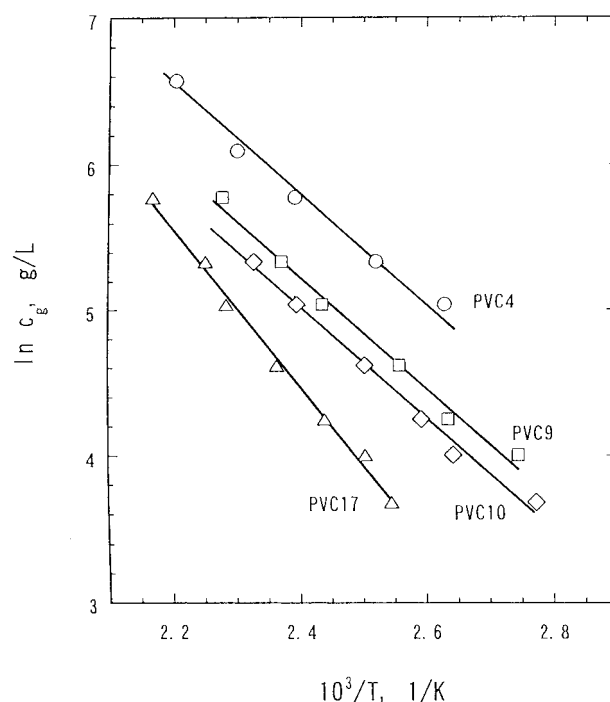


Figure 9. Plots of $\ln c_g$ against $10^3/T$ for the PVC/DOP gels.

of repeat units or monomers of each chain bound in the junction)

$$\zeta = |\text{slope}| 10^3 R / \Delta h \quad (5)$$

where R is the gas constant [$10^3 R = 8.3145$ kJ/(mol K)] and Δh has a unit of kJ/mol. To calculate ζ using eq 5, one needs to know Δh , the enthalpy of bonding per mole of the repeat units taking part in the junction. In this work, like what Tanaka and Nishinari did,¹⁹ we also assumed that Δh was the same as the heat of fusion in the bulk PVC crystal. This assumption is of meaning because the gel junction can be considered to be a dense crystallite domain in which the solvent (DOP in this case) is excluded. According to the literature,^{28–33} the heat of fusion for PVC was reported to be the values between 2.76 and 11.3 kJ/mol. Here, we use 3.28 kJ/mol²⁸ as Δh , because this value is thought to be most probable. Then, we can obtain $\zeta = 10$ for PVC4, -9, and -10 and 14 for PVC17, respectively. This increased tendency of ζ for PVC17 may be attributed to the increased syndiotacticity, as reported in the Experimental Section, because small variations of the syndiotacticity have a significant influence on the crystallinity. The junction length was found to be about 10, almost independent of the molecular weight. The invariability of ζ with M may also suggest the similarity of the fractal structure in the PVC gels.

Next, we analyze the dependence of the critical concentration c_g on M in order to evaluate the junction multiplicity s defined by the modified Eldridge–Ferry procedure. For the dependence of c_g on M at a constant temperature, we have obtained a relation of $c_g \propto M_w^{-1}$ for the PVC/DOP samples at 40°C .^{1,5} In this work, we did not directly measure c_g at constant temperatures, unlike what was carried out previously,¹ but we can estimate the c_g at various temperatures using the data in Table 1. By this way, we are able to examine the M dependence of c_g at any temperature from 40 to about 180°C . At five temperatures (80, 100, 120, 140, and 160°C), $\ln c_g$ was plotted against $\ln M_w$ in Figure 10. The

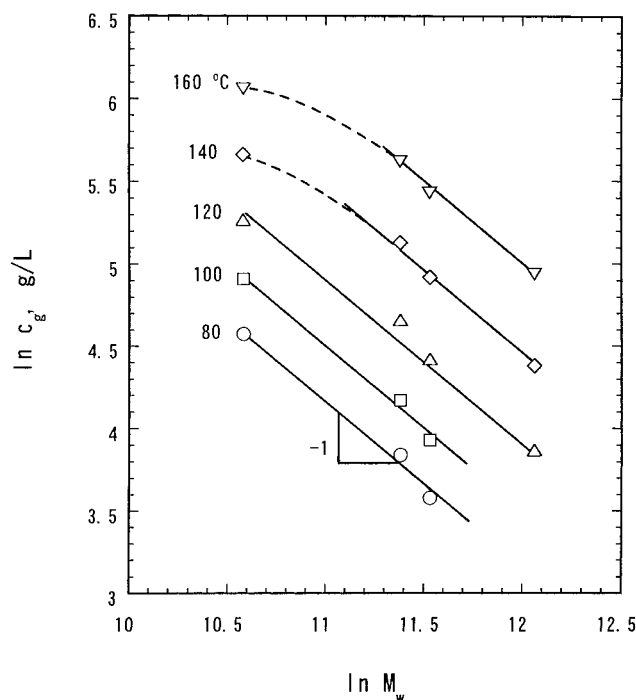


Figure 10. c_g as a function of weight average molecular weight M_w in log-log scale for the PVC/DOP gels at various temperatures.

slope of -1.0 was obtained except for high concentration points of PVC4. Below $120\text{ }^{\circ}\text{C}$, the dependence of c_g on M is completely consistent with the result obtained at $40\text{ }^{\circ}\text{C}$.^{1,5} The calculation by $s = 1 + 1/|\text{slope}|$ gives $s = 2.0$, almost independent of temperature. The previous result^{1,5} of $c_g \propto M_w^{-1}$ for the PVC/DOP samples at $40\text{ }^{\circ}\text{C}$ also gives $s = 2.0$, in nice agreement with the above conclusion.

Finally, we discuss the application of the modified Eldridge-Ferry procedure for the PVC gels. The results obtained by the procedure show that the junction structure comprises about two polymer chains having a length of about 10 repeat units or monomers. It would be physically impossible that the single network junction of the PVC gels consists of two polymer chains or simple pairwise cross-links. Therefore, one may think that the procedure is not applicable for the PVC gels because the junction structures are different from the fringed micellar model. However, if the junction involves chain folding instead of fringed-micelle, even two polymer chains can form a crystallite. In this case, we can apply the modified Eldridge-Ferry procedure for the PVC gels. On the other hand, Guenet and co-workers have proposed a fibrillar model based on the formation of a polymer-solvent complex.^{6,11-16} The model consists of three types of domain: syndiotactic crystals, organized domains of PVC-solvent complex, and disorganized domains. If the critical gel points, c_g and T_{gel} , are determined by melting of syndiotactic crystals, numerical values (ζ and s) for the junction size may be meaningful for the PVC gels. But, if not, these values become meaningless. Using the fibrillar model, we can speculate the reason why the critical gel concentration c_g is inversely proportional to molecular weight. When the PVC gels are composed of an array of straight or nearly-straight fibers, the percolation due to such fibers may be inversely proportional to the molecular weight. Since we have not completely elucidated the molecular

structure of the junction, further works are needed to answer the issues. The most important conclusion in this section is that the junction structure in the PVC gels is almost independent of temperature and molecular weight. This suggests the similarity in the gel network structure of the PVC gels and it may help us to explain why the scaling exponents are irrespective of molecular weight.

Conclusions

Four commercial poly(vinyl chloride) (PVC)s were used to prepare the physical gels in bis(2-ethylhexyl) phthalate (DOP) from the THF solutions at room temperature. These gels covered a wide range of polymer concentration, and then the studies of the dynamic viscoelastic properties were conducted as a function of temperature for these PVC/DOP gels. The sol-gel transition temperatures were able to be accurately determined by the frequency independence of loss tangent. The scaling exponent n ($=0.75$) at the gel point was confirmed to be universal for the PVC/DOP gels, which was independent of both temperature and molecular weight, suggesting the similarity of the fractal structure in the critical PVC gels. The modified Eldridge-Ferry procedure by Tanaka and Nishinari¹⁹ was applied to evaluate the junction structure in the gels by analyzing separately the dependences of the critical concentration c_g on temperature as well as molecular weight. It was found that the junction structure in the PVC gels was almost independent of both temperature and molecular weight, indicating again the similarity of the fractal structure in the critical PVC gels.

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