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Rheological Images of Poly(vinyl chloride) Gels. 1. The Dependence of Sol−Gel Transition on Concentation

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ABSTRACT: Dynamic viscoelastic properties of poly(vinyl chloride) (PVC)/bis(2-ethylhexyl) phthalate (DOP) solutions and gels have been studied as a function of polymer concentration and molecular weight. All PVCs were linear polymers and had a similar distribution in molecular weight. Increasing the polymer concentration gradually from the liquid state to the solid state allowed the rheological observation of the sol−gel transition. The gel point c_g, which depends on the polymer concentration, was accurately determined by the frequency independence of loss tangent in the vicinity of the sol−gel transition and was found to be inversely proportional to the molecular weight as expressed by $c_g \propto M_w^{-1}$. The scaling exponent n obtained was constant ($n = 0.75$) and independent of the molecular weight of PVC. The gel strength S_g at the gel point decreased with increasing PVC molecular weight. A constant gel strength ($S_g/c_g = 1.27 \times 10^{-2}$ Pa s$^{0.75}$ g^{-1} L) was obtained by normalizing the gel strength S_g with c_g to eliminate the effects of M_w. These results suggest a unique character and structure at the gel point of the gelling system.

Introduction

Poly(vinyl chloride) (PVC) has been manufactured commercially for over 60 years.[1,2] Historically, PVC was first used to mix with plasticizers to produce flexible materials. One of the most remarkable characteristics of plasticized PVCs is that the addition of a high level (up to 99 wt % of plasticizers, depending on the PVC molecular weight) of the plasticizers to PVC still allows the system to remain a useful degree of mechanical strength and elasticity.[2] This surprising property is known to be due to the formation of a three-dimensional network of PVC molecules in the solvents (the plasticizers), which is called gelation. Unlike chemical gels where the junctions for the three-dimensional network are chemical bonds, which can not be released or created physically through heating or cooling, the plasticized PVCs form physical gels that are thermoreversible.[3−15]

PVC has been found to form gels in numerous solvents,[3−15] and the physical properties of the PVC gels have been widely studied as a function of temperature (or time),[6−8,10,14] concentration,[3,4] and types of plasticizers[6,7,9,15] for numerous interests. Since the mechanism of PVC gelation and the structure of the PVC gels have still not been fully elucidated, attention has been paid to the experimental analysis and the theoretical prediction of the molecular structure of the PVC gels.[5,7,9,11−13,15,16] A generally accepted model is the fringed-micelle structure model that describes a PVC gel where the network is composed of small crystallite domains, the junctions, and flexible chains connecting the junctions.[17] Furthermore, the small crystal junctions are generally visualized as tiny bundles or platelets that are formed by intermolecular and/or intramolecular aggregation.[17] However, a different schematic, proposed originally by Yang and Geil[18] and experimentally supported by Guenet et al.,[7,9,11,13,15,16] predicts formation of the network structure through an array of fibrous crystals. These fibrous crystals are expected to form through intermolecular aggregation.

Techniques such as X-ray diffraction,[5] light scattering (LS),[11,16] neutron diffraction,[13,15] small-angle neutron scattering (SANS),[15] and rheology[6,8,10,14] have been widely used to elucidate the mechanism of PVC gelation and the molecular structure of the PVC gels. Before and near the sol−gel transition, PVC clusters with sizes ranging from a few tens to hundreds of nanometers were observed in solution using light scattering,[11,16] which is evidence that the PVC clusters form first and then contribute to the subsequent crystal junctions of gels unlike the formation from a homogeneous solution through a percolation process. The X-ray diffraction measurements carried out by Lemstra et al.[5] confirmed the crystallinity of the stretched PVC gels, which showed patterns similar to those in the commercial bulk PVCs.[19] The commercial PVC usually possesses crystallinity within 10%.[19] The conclusion drawn from the SANS experiments that gives support to the model of fibrous crystal structure is that rodlike sections exist in the PVC gels.[15] Rheology provides one with a convenient tool to view the particular behavior of a gelling system from the liquid state to the solid state. For example, a novel way of defining the gel point was given and experimentally examined for the PVC solution that underwent a sol−gel transition with aging time.[6] The details of this method will be reviewed in the next section.

Most studies of physical gels provide one with just a partial image of the gelation behavior. It is of interest to have the entire rheological image of a physically gelling system as a function of concentration, temperature, molecular weight, and so on. For this purpose, a series of poly(vinyl chloride) (PVC) solutions and gels with different molecular weights of PVC have been prepared over a wide range of concentrations hopefully allowing us to observe their rheological behavior before, near, and beyond the sol−gel transition as a function of concentration, temperature, and molecular weight. The PVC systems have been chosen as the objective of our studies because, although it is a well-known physically gelling polymer and one of most long-used commercial polymers, its gelation mechanism and gel structure have not been fully understood.

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In this report, which is the first part of our studies of the PVC solutions and gels, the work focuses on how the sol−gel transition can be determined rheologically when the polymer concentration governs the physical gelation, what the scaling law is for the gellation in the stable gelling system, and how the molecular weight of PVC affects the critical behavior of gelation. Future studies will be continuously conducted on our other interests such as (1) how the rheological behavior and the scaling law before and beyond the gel point are controlled by polymer concentration, molecular weight, and temperature, (2) the thermal reversibility of the PVC gels, and (3) the relaxation patterns near the gel point. We believe that our rheological studies of the PVC gelling systems will be able to give a whole image of the physical gelation to readers.

Theoretical Description of Gelation Rheology

As is well-known, a polymeric gel is a three-dimensional network forming from flexible chains through either chemical cross-linking or physical phase transformation. The gelation is such a phenomenon that a polymeric liquid dramatically becomes solidlike at a critical point of time, temperature, polymer concentration, etc. The critical change from the liquid state to the solid state is known as the sol−gel transition at which rheologically the zero-viscosity and relaxation time of the system diverge. The sol−gel transition takes place in a thermodynamically nonequilibrium state like the glass transition where polymer chains are physically frozen from the melt. Even though studies of gels have lasted for more than 50 years and various theoretical models have been proposed to explain the formation and properties of gels,[20−25] gelation has not been satisfactorily described by any theories that are able to explain why the gelation occurs and how gel structures form, because gels are especially complex systems and each gel has its own complexities. The complexities of gels have long caused scientists to conduct a number of studies for chemical gels[25−32] and physical gels.[3−18,35−39]

The well-used experimental and theoretical methods for description of the gelation are based on the scaling law. Like many physical parameters of polymers, rheological behavior of a gelling polymeric system can be also approximately described by power laws. Various power laws have been proposed and examined to explain or predict rheological features of gelling systems, especially for the sol−gel transition.[20−34,38,39] In the vicinity of the gel point, the zero-viscosity, η_o, exhibits a power law

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

and the equilibrium modulus G_{eq} follows

$$G_{eq} \propto \epsilon^{z} \quad \text{for } p > p_g \tag{2}$$

Here $\epsilon = |p - p_g|/p_g$ indicates the relative distance of a variable p from the sol−gel transition point p_g, and p can be, for example, degree of cross-linking, concentration, time or temperature in a gelation process. γ and z are the critical exponents determining the critical characteristics in the vicinity of the sol−gel transition. Since the exponent γ is always positive, the zero-viscosity diverges at the gel point ($p \to p_g$). Theoretically, the values of the critical exponents γ and z have been predicted by many models.[20−25] The classic theory based on the Bethe lattice (the tree approximation) gives $\gamma = 0$ and $z = 3$,[20,21] while the models using percolation theory predict different values of γ and z depending on the model assumption.[22−25] For example, $\gamma = {}^4/_3$ and $z = {}^8/_3$ have been reported for the case of hydrodynamic interactions.[24]

Table 1. Molecular Characteristics of Poly(vinyl chloride)s

polymer	$M_w \times 10^{-3}$ [a]	$M_w \times 10^{-3}$ [b]	M_w/M_n [b]
PVC4	39.4	63.6	1.89
PVC9	87.4	137	2.01
PVC10	102	160	2.02
PVC17	173	254	2.24

[a] Measured by light scattering in THF at 25 °C. [b] Measured by GPC in THF at 25 °C, and polystyrenes were used as standards.

To study a gelling system, it is important to know how to determine its gel point. Traditionally, many researchers use the crossover of $G'(\omega)$ and $G''(\omega)$ as an indicator of the gel point. This method is simple and convenient, but not valid in general. A valuable contribution to this area is attributed to the studies of chemical and physical gelations in Winter's laboratory.[6,26−31,33,38] They[26] first experimentally found a scaling law of $G'(\omega) = G''(\omega) \sim \omega^{1/2}$ at the gel point and later generalized it to be

$$G'(\omega) \sim G''(\omega) \sim \omega^n \qquad 0 < n < 1 \tag{3}$$

or

$$G''(\omega)/G'(\omega) = \tan\delta = \tan(n\pi/2) \tag{4}$$

for all gelling systems.[27,28] The frequency independence of the loss tangent in the vicinity of the gel point has been widely examined for chemical and physical gels,[6,27−34,38,39] and also been employed 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 and the critical gelation temperature.[6,27−34, 38,39] It has not been reported how the gel point can be measured by this method as a function of concentration for a physical gel. Experimentally, n is found not to be constant, but it has a value between 0 and 1.[6,27−34,38,39] On the other hand, in the theoretical field, Martin et al. predict that n is between ${}^2/_3$ and 1.[24,25] Therefore, it seems that there is no universal value of n, probably because n is related to the specific nature of each gelling system.

Experimental Section

Materials. The polymers used in this work were four commercial poly(vinyl chloride) (PVC)s made through suspension polymerization by Mitsubishi Chemical Co. Prior to the molecular characterization, all PVCs were purified by using tetrahydrofuran (THF)/methanol as solvent/precipitant. GPC measurements were carried out at 40 °C on a TOSOH HPLC system equipped with a differential refractometer. THF was used as an eluent, and polystyrenes with a narrow molecular weight distribution were used as standards for calibration of GPC. The weight-average molecular weights were also measured using light scattering (LS) (Otsuka Electronics DLS-700) in THF at 25 °C with a polarized light of 633 nm in wavelength. The GPC and LS results are given in Table 1, showing that all of the PVCs have a polydispersity index (M_w/M_n) of about 2.

^{13}C-NMR measurements were performed at 50 °C on a 10% solution of each PVC in THF-d_8 to determine the tacticity of the polymers. The following results are given for the triads: PVC4, syndio = 0.33, hetero = 0.49, iso = 0.18; PVC9, syndio

Table 2. Poly(vinyl chloride)/DOP Solutions and Gels[a]

	c (g/L)											
system	5.40	6.87	9.83	14.8	19.7	24.7	29.7	39.7	54.8	70.0	101	154
PVC4			○	○	○	○	○	○	○	△	□	□
PVC9	○	○	○	○	○	○	△	□	□			
PVC10	○	○	○	○	○	△	□	□				
PVC17	○	○	○	△	□	□						

[a] Key: (○) solution, (△) near the sol−gel transition; (□) gel.

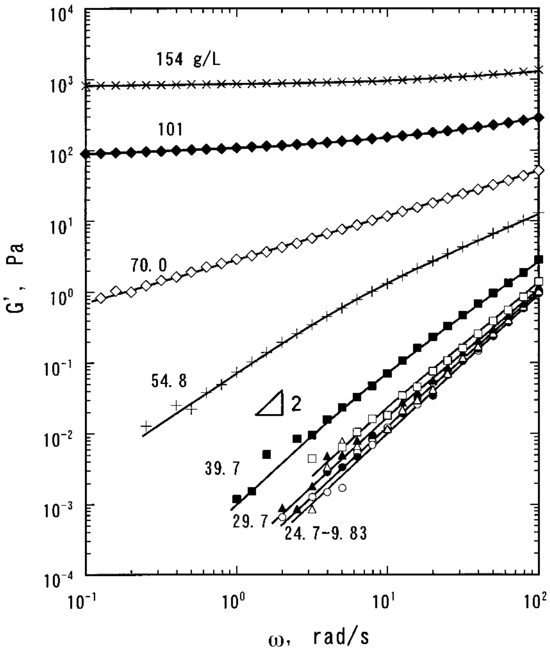


Figure 1. Storage modulus G' of PVC/DOP as a function of angular frequency ω for various concentrations of PVC4 as indicated.

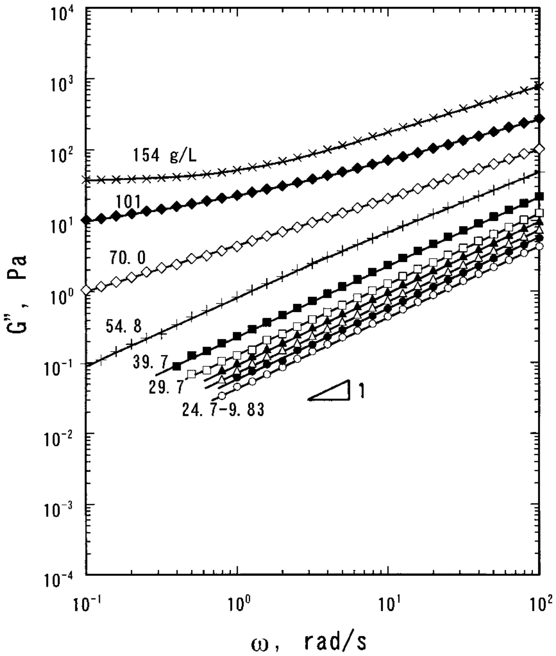


Figure 2. Loss modulus G'' of PVC/DOP as a function of angular frequency ω for various concentrations of PVC4 as indicated.

= 0.33, hetero = 0.50, iso = 0.18; PVC10, syndio = 0.33, hetero = 0.49, iso = 0.18; PVC17, syndio = 0.35, hetero = 0.50, iso = 0.16. Hexamethyldisiloxane was used as an internal reference standard.

Four gelling systems of the PVCs in bis(2-ethylhexyl) phthalate (DOP) were prepared at room temperature (about 30 °C) from THF solutions (about 70 wt % of THF) of PVC and DOP. No stabilizers were added to the solutions. The evaporation of THF from each solution proceeded at room temperature, and it took a time period ranging from 1 to 2 weeks, depending on the polymer concentration. After THF evaporated completely, transparent liquids or solid films were obtained. After about 2 weeks, the weight of each sample became constant. Since a sufficiently long time 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 for some selected samples. The samples prepared in the present work are listed in Table 2. Since the phase state in each sample at room temperature is also indicated in Table 2, the table can be used as a phase diagram for the gelling system.

Rheological Measurements. The PVC/DOP liquid or solid sample was transferred from the flat laboratory dish into the dynamic rheometer (ARES 100FRTN1, Rheometric Scientific). The rheometer was equiped with two force transducers allowing the torque measurement to range from 0.004 to 100 gcm. Then 25 or 50 mm diameter parallel plates were used for the dynamic measurements. The shear storage modulus G' and loss modulus G'' were measured as a function of angular frequency ω at 40 °C. The measuring temperature (40 °C) 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, a suitable shear amplitude, γ, was used to ensure the linearity of dynamic viscoelasticity.

Results and Discussion

Dynamic Viscoelastic Properties through the Sol−Gel Transition. 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 series. The polymer concentration ranges from 9.8 to 154 g/L as indicated. The dynamic mechanical behavior of the PVC solutions follows the liquidlike terminal behavior at very low concentrations:

$$G'(\omega) \propto \omega^2 \qquad G''(\omega) \propto \omega \quad (\text{at } \omega \to 0) \tag{5}$$

while the deviation from the above relations becomes more pronounced for the higher concentrations of PVC. The behavior, $G'(\omega)$ = constant at $\omega \to 0$, is consistent with the results reported by Nijenhuis and Winter,[6] indicating the formation of a gel plateau. The slope of the $G'(\omega)$ vs ω curve (at $\omega \to 0$) on the log−log scale undergoes a change from 2 to 0, while that of the $G''(\omega)$ vs ω curve (at $\omega \to 0$) varies from 1 to 0. Therefore, it is reasonable to consider that the liquid−solid transition should take place at some value of the slope between 0 and 2 for the $G'(\omega)$ curves or at a slope between 0 and 1 for the $G''(\omega)$ curves. Furthermore, it is obvious at the gel point that both slopes take a common value between 0 and 1.

The similar viscoelastic behavior was observed for the other systems, PVC9, -10, and -17. The range of polymer concentration c where the sol−gel transition is observed was dependent on the molecular weight of PVC.

Determination of the Gel Point. One may prefer to use the crossover of $G'(\omega)$ and $G''(\omega)$ to determine the gel point by comparing the $G'(\omega)$ in Figure 1 with the $G''(\omega)$ in Figure 2. However, it is impossible to find where the gel point is because there is no crossover of $G'(\omega)$ and $G''(\omega)$ in the frequency range for all concentrations. The plots of $G'(\omega)$ and $G''(\omega)$ against polymer

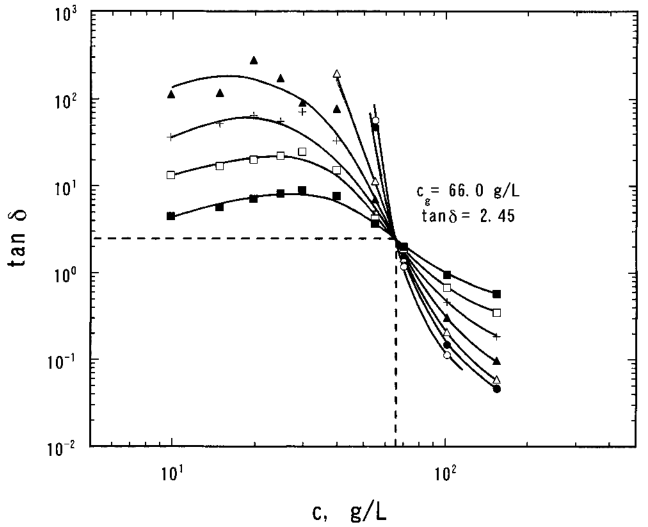


Figure 3. Loss tangent tan δ as a function of polymer concentration c for the PVC4 system at various angular frequencies (0.1, 0.316, 1, 3.16, 10, 31.6, 100 rad/s). c_g is the gel point.

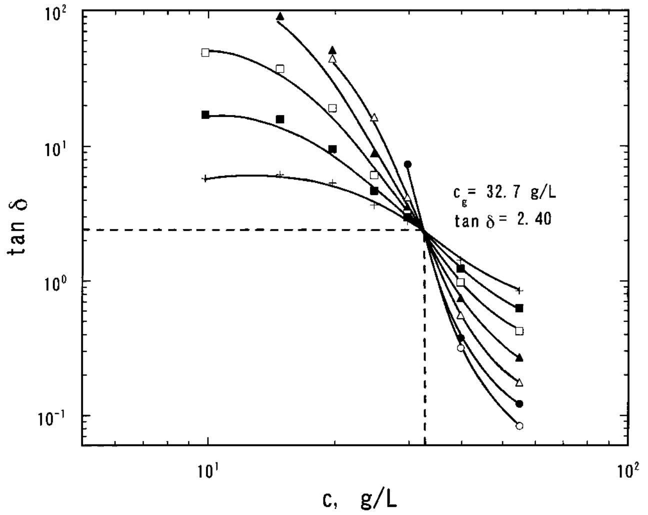


Figure 4. Loss tangent tan δ as a function of polymer concentration c for the PVC9 system at various angular frequencies (0.1, 0.316, 1, 3.16, 10, 31.6, 100 rad/s). c_g is the gel point.

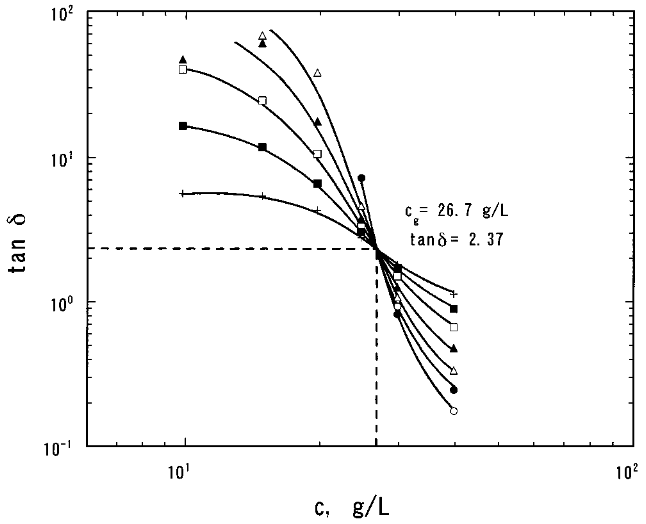


Figure 5. Loss tangent tan δ as a function of polymer concentration c for the PVC10 system at various angular frequencies (0.1, 0.316, 1, 3.16, 10, 31.6, 100 rad/s). c_g is the gel point.

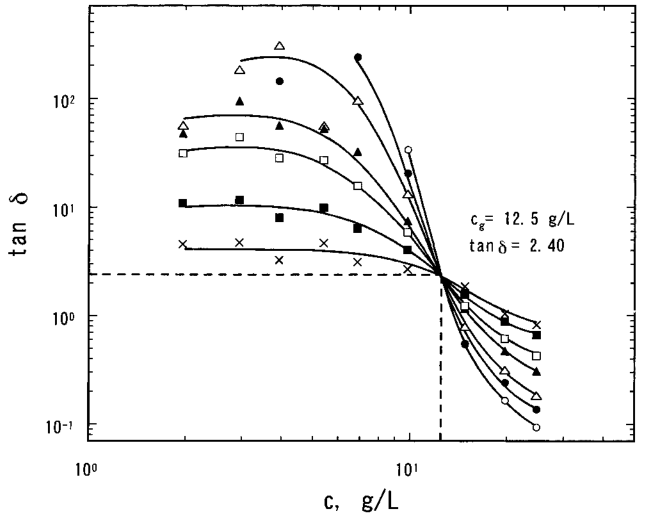


Figure 6. Loss tangent tan δ as a function of polymer concentration c for the PVC17 system at various angular frequencies (0.1, 0.398, 1, 3.98,10, 39.8, 100 rad/s). c_g is the gel point.

Table 3. Critical Concentration c_g for the Sol–Gel Transition and Scaling Exponent n, Determined in This Work

system	c_g (g/L)	S_g (Pa s^n)	n
PVC4	66.0	0.835	0.753
PVC9	32.7	0.424	0.749
PVC10	26.7	0.344	0.746
PVC17	12.5	0.154	0.749

concentration c will give a crossover point. Since the crossover point is dependent on frequency, however, the definition of the gel point by this method is not available. We have to consider other methods to determine the gel point. The method described in eqs 3 and 4 has been examined for determination of the gel point for the physically gelling systems prepared in this work.

The method is known as the frequency-independence of tan δ. The gel point is determined from a multifrequency plot of tan δ vs gelation time, temperature, or concentration, depending on which parameter governs the gelation process.[6,27,28,30–34,38,39] The gel point has been well determined using this method when the gelation time[6,27–34,38] or temperature[39] was a controlling variable for the gelation processes. In this work, this type of plot is the tan δ vs polymer concentration for different frequencies, as shown in Figures 3–6 for the four systems of PVC4, -9, -10, and -17, respectively. All curves in each figure pass through the common point at the 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 using this method. The critical exponent n was simply calculated from the gel point using the relation in eq 4. The value of n was found to be constant, independent of the systems. Values of c_g and n determined are given in Table 3. The discussion about the molecular weight dependence of c_g and n will be given in the next section.

This method, the frequency-independence of tan δ, can be also applied in an alternative way to determine the gel point as shown below. Since the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ at low frequencies ($\omega \rightarrow 0$) can be approximately expressed by the scaling law $G'(\omega) \propto \omega^{n_1}$ and $G''(\omega) \propto \omega^{n_2}$, respectively, a crossover at $n_1 = n_2 = n$ will be observed as an indicator of the gel point. The experimental examination of this

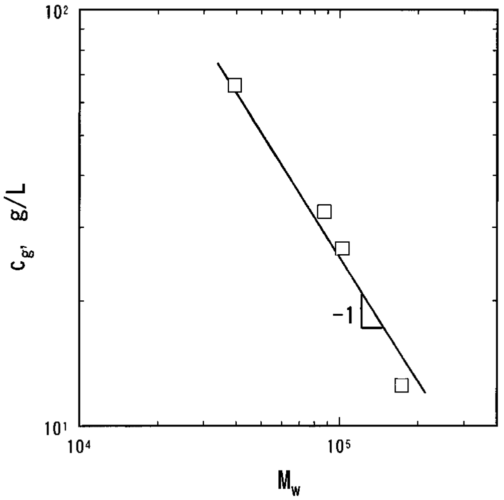


Figure 7. c_g as a function of weight average molecular weight M_w measured by light scattering.

way can be viewed from the ref 32. We prefer to directly use the frequency independence of loss tangent to determine the gel point because of its accuracy.

Dependence of the Gel Point on Molecular Weight. The gel points c_g obtained from Figures 3–6 were plotted against the weight-average molecular weight M_w in Figure 7. The molecular weight M_w used here was determined using a light scattering technique. Through a linear fitting to the data, we obtained an approximate power law

$$c_g \propto M_w^{-1} \tag{6}$$

for the molecular weight dependence of the gel point. Thus, c_g is inversely proportional to the molecular weight. So far, we have not found any theories that predict this kind of power law.

The effect of molecular weight has been experimentally examined by Yang and Geil,[18] who observed that the larger the molecular weight, the higher the gel melting point. The results are explained to be due to the different crystallinities of PVCs with different molecular weights. In general, the longer the molecular weight of PVC, the higher the degree of syndiotacticity. In this study, we have selected the PVC samples with as similar tacticities as possible in order to make a gelling system which is influenced only by the molecular weight. The distribution of tacticity along the chain may have effects on gelation.[18,41] If the junctions for the gel network form only from the syndiotactic crystals, the distributions of syndiotacticity along the chains with different molecular weights have to be taken into account. Since the molecular structure of the junctions for the PVC gels have not been fully elucidated, further works are needed to answer the issues.

On the other hand, if PVC aggregates or clusters are necessarily formed before and near the sol–gel transition,[11,16,30] the sol–gel transition will correspond to a percolation of the polymer chains that connect the clusters across the solution volume. In this way, the longer chain should provide the higher probability of percolation. And also, the end effects of shorter chains can be considered to be larger than longer chains. As a combined result, the gelation of the higher molecular weight polymer takes place at the lower concentration.

Exponent *n* and Gel Strength S_g. The power laws in eqs 1 and 2 describe the critical behavior of a gelling system before and beyond the sol–gel transition respectively, and no power laws are able to predict the whole range covering before and beyond the gel point. The well-used scaling law for the rheological behavior of a gelling system in the vicinity of the gel point is the relation in eq 3 and the deduced descriptions from eq 3, such as eq 4. For example, the shear relaxation modulus $G(t)$ is predicted to obey a power law relaxation at the gel point:[27–34]

$$G(t) = S_g t^{-n} \tag{7}$$

Here S_g is the gel strength and has an unusual unit of Pa s^n. n is named the critical relaxation exponent because n determines the stress relaxation rate at the gel point. The physical meaning of S_g may be somewhat abstract due to its unusual dimensions. One may simply understand that S_g is the relaxation modulus at the gel point when the relaxation time t is 1 s. The expression of S_g as $S_g = G(t)t^n$ may help one to understand the physical meaning of S_g. $n = 0$ gives $S_g = G_0$, the elastic modulus, that describes the rigidity of the system, while S_g represents the viscosity for $n = 1$.

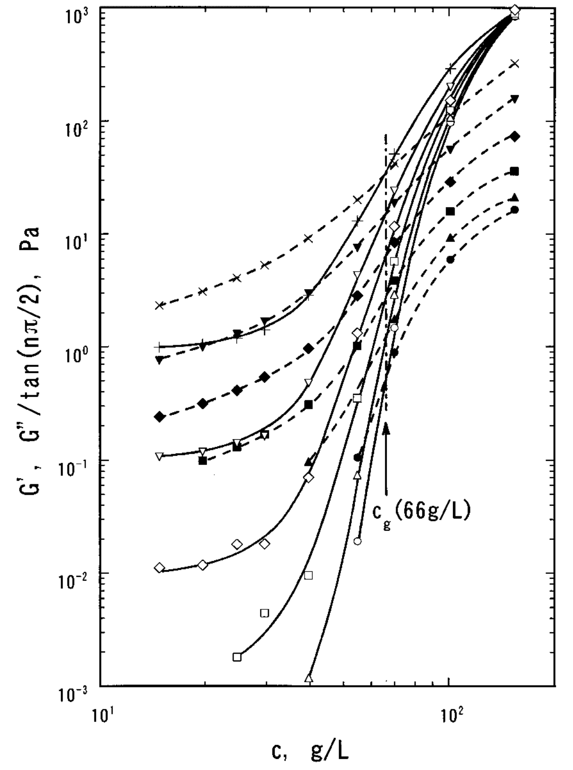
A similar expression can also be applied for dynamic moduli G' and G'' [27–34]

$$G'(\omega) = G''(\omega)/\tan(n\pi/2) = S_g \omega^n \Gamma(1 - n) \cos(n\pi/2) \tag{8}$$

at the gel point. Here $\Gamma(1 - n)$ is the Γ function. By knowing n, one can calculate S_g from $G'(\omega)$ or $G''(\omega)$ at the gel point using eq 8.

Using the method in eq 4, we first obtained a constant value of $n = 0.75$ from the gel points shown in Figures 3–6. Although the gel point c_g varies with change in the molecular weight of PVC, values of the critical exponent n are the same, implying a unique feature of the gelling system at the gel point. A number of studies have showed that n is not universal and varies with the gelling systems. For the chemical gels, the values of n were reported to be 0.5–1,[26–28] 0.2–0.7,[30] 0.31–0.91,[31] 0.45–0.65,[32] 0.45–0.5,[33] and 0.67.[34] On the other hand, relatively high values of n were observed for the physical gels: 0.77–0.83,[6] 0.78,[38] 0.62,[39] and 0.75 in this work. It was also experimentally found that increasing the cross-linking density led to a reduction of n in the case of chemical gels[30,32,34] and that n remained the same when the polymer concentration was varied for the physical gelation during a temperature sweep.[39] As the gelation theories predict the value of n to be between $^2/_3$ and 1,[20–25] it is almost consistent with the experimental values of n for the physical gels. However, a detailed discussion about the relation between n and the gel structure has not been made yet.

Rheologically, the meaning of n can be understood from the original relation of eq 4. Since the phase angle δ varies from 0 to $\pi/2$ as n takes a value between 0 and 1, n measures the rheological distance from a complete viscous liquid or from a complete elastic solid. Considering that an elastic network forms at the gel point, it will be impossible for n to have a value of 1 to meet $\delta = \pi/2$. On the other hand, since a completely (ideally) elastic state is also infeasible at the gel point, n will not take a value of 0. It is experimentally difficult to distinguish between a Newtonian fluid and a system with $n \cong 1$ at the gel point. 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. Note here that we do not take account of the absolute



ω (rad/s)	0.316	1	3.16	10	31.6	100
G' (Pa)	○	△	□	◇	▽	+
G"/tan(nπ/2) (Pa)	●	▲	■	◆	▼	×

Figure 8. Plots of G' and $G''/\tan(n\pi/2)$ against polymer concentration c for the PVC4 system. The angular frequency ω was varied from 0.316 to 100 rad/s. $n = 0.75$ was used to calculate $G''/\tan(n\pi/2)$. The gel point is indicated by the arrow.

values of $G'(\omega)$ or $G''(\omega)$ for comparison of the viscoelasticity because n does not directly contain the information about the dynamic moduli. Some relations between n and the gel strength have been reported and discussed especially for the chemical gels[30,34] but it cannot be a necessary condition to draw a conclusion that the gel strength must be a function of n.

The physical nature of a gelling system at the gel point can be described by the gel strength S_g defined by eq 7. The studies of chemical gels have showed that, the gel strength S_g rose while the exponent n decreased, as the cross-linking density increased.[31,32,34] This result implies that S_g is related to the physical strength of the gel network at the gel point. It is difficult to prepare a gelling system that is exactly located at the gel point to allow us to determine the gel strength S_g. Fortunately, however, we are able to take the advantage of eq 8 that suggests the existence of a crossover of $G'(\omega)$ and $G''(\omega)/\tan(n\pi/2)$ at the gel point: the value of $G'(\omega)$ at the gel point should be obtained by plotting $G'(\omega)$ and $G''(\omega)/\tan(n\pi/2)$ against polymer concentration c, and then S_g would be easily calculated. An example of this kind of plot is illustrated in Figure 8 for the PVC4 system. Since the system at the gel point obeys the frequency independence of tan δ, all crossover points appear quite well at the gel point of $c_g = 66.0$ 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 8, we obtained the value of S_g. It was also confirmed that, within the experimental errors, the value of S_g was constant and independent of which point of crossover was used. However, we preferred to use an averaged value from the six points as S_g to avoid any unreliability. Similarly, the values of S_g were obtained for the other systems, PVC9, -10, and -17. The results of S_g are given in Table 3. Although n is the same, S_g varies with the system to exhibit a molecular weight dependence of the sol−gel transition.

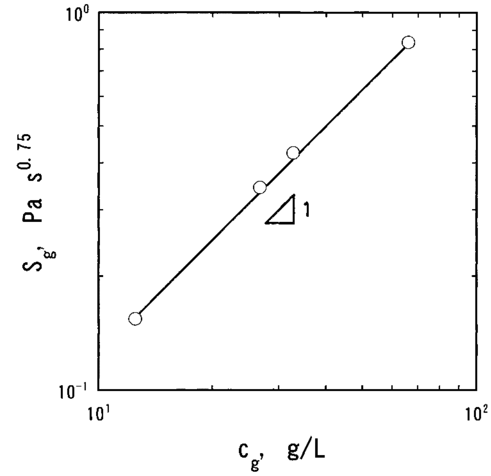


Figure 9. Relation between S_g and c_g.

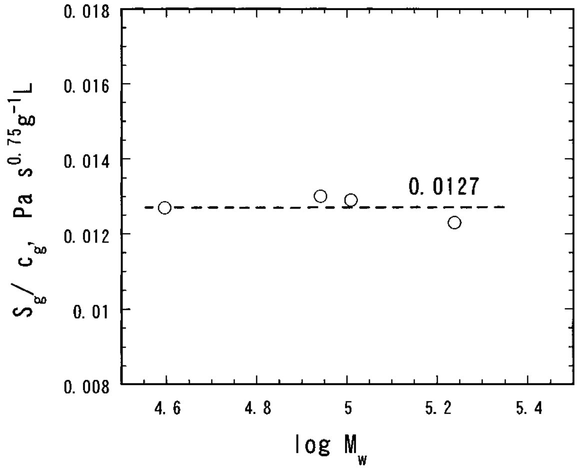


Figure 10. Normalized gel strength S_g/c_g as a function of M_w.

The values of S_g were plotted against the gelation concentration c_g in Figure 9. Surprisingly, we obtained a linear relation between S_g and c_g. This indicates that S_g is related to the total mass of polymer in the system. For a constant n, increasing the cross-link density of a chemical gel usually leads to an increase in the gel strength, as reported by many scientists.[30,31] The decrease of S_g with increasing M_w may be considered to be due to the reduction of the network density at the gel point. On the other hand, an endeavor has been made here to try to understand the meaning of S_g: S_g was normalized by the corresponding gelation concentration c_g to give the result in Figure 10. If the S_g is only related to the total mass in the system, the gel strength per unit of mass should be the same. As expected, S_g/c_g is almost constant ($S_g/c_g \approx 0.0127$), independent of the molecular weight of PVC. However, this conclusion would be affected by the molecular weight distribution (MWD) of PVC, and a broader MWD may result in a decrease in S_g/c_g. We will discuss this kind of gelation behavior in our future reports soon.

By summarizing the above results, three power laws can be built among c_g, S_g, and M_w: $c_g \propto M_w^{-1}$, $S_g \propto c_g$, and $S_g \propto M_w^{-1}$.

Conclusions

Four series of poly(vinyl chloride)/DOP gelling samples were prepared from THF solutions. A stable state in each sample was achieved after a sufficiently long time of evaporation for equlibrium. We conducted dynamic viscoelastic studies on these stable samples as a function of polymer concentration as well as molecular weight. Increasing the polymer concentration gradually from the liquid state to the solid state allowed us to observe rheologically the sol–gel transition. The gel point c_g was accurately determined by the frequency-independence of loss tangent in the vicinity of the sol–gel transition relying on polymer concentration, and was found to be inversely proportional to the molecular weight as scale as $c_g \propto M_w^{-1}$. The scaling exponent n (=0.75) obtained was constant, independent of the molecular weight. The gel strength S_g was a linear function of the gelation concentration c_g and S_g/c_g was independent of the molecular weight of PVC.

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