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Viscoelastic Properties of Poly(vinyl chloride) Gels: Universality of Gel Elasticity

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ABSTRACT: The equilibrium modulus G_e of the poly(vinyl chloride) (PVC)/bis(2-ethylhexyl) phthalate (DOP) gels was examined at temperatures $T \geq 40$ °C. Near the sol−gel transition temperature, G_e decreased rapidly with increasing T. The normalized moduli G_eM/cRT of the gels at different M, T, and/or c were universally dependent on the relative distance from the gelation point, ϵ, with c and M being the PVC concentration and molecular weight, respectively, and R being the gas constant. This result suggested that the mesh size of the gel network near the gelation point was universally determined by ϵ and M. The normalized moduli were smaller than unity, i.e., $G_e < cRT/M$ at low ϵ. This result suggested that the average mesh size near the gelation point was larger than the PVC chain size. Thus, several PVC chains appeared to be connected at cross-linking crystal domains to form a larger, effective mesh strand.

I. Introduction

Poly(vinyl chloride) (PVC) forms physical gels in various plasticizers, and the structures[1−6] and physical properties[1,2,5,7−12] of those gels have been investigated. The gels are generally classified as randomly cross-linked networks of flexible PVC strands, and the PVC crystal domains work as the cross-linking domains. Some properties of the gels such as the equilibrium modulus are unequivocally related to this network structure. However, details of the structure of the cross-linking domains, either fibrous crystals[1−3] or small crystallites,[6] have not been elucidated completely, and the structures of the gel strands themselves (either individual PVC chains or their fibrous aggregates[4,5]) may change with temperature, concentration, solvent quality, and so on.

In attempt to rheologically characterize the PVC gels, we[13−20] recently began a series of studies for PVC gels. For the critical PVC gel at the sol−gel transition concentration (gelation point) c_g, the storage and loss moduli, G' and G'', exhibited the characteristic power-law dependence[21] on the angular frequency ω,[13,17,18]

$$G'(\omega) = G''(\omega)/\tan(n\pi/2) \propto \omega^n \quad \text{for} \quad c = c_g \tag{1}$$

The exponent, $n = 0.75$, was independent of the PVC molecular weight M,[13] the molecular weight distribution,[17] temperature T,[18] and the plasticizer solubility toward PVC,[19] suggesting that the PVC critical gels included a similar fractal network structure irrespective of these factors. c_g decreased in proportion to $M_w{}^{-1}$ and with decreasing plasticizer solubility[19] (and/or, equivalently, with decreasing T[18]). These results demonstrated an important role of the chain size and crystallizability in the critical gel formation.

For the PVC sols in bis(2-ethylhexyl) phthalate (DOP) at $c < c_g$, the zero shear viscosity η_0 at 40 °C exhibited a power-law (scaling) relationship[14]

$$\eta_0 \propto \epsilon^{-\gamma} (\gamma \cong 1.5) \quad \text{for} \quad c < c_g \tag{2}$$

Here, ϵ ($= |c - c_g|/c_g$) is the relative distance to the gelation point. Since η_0 is proportional to the monomeric friction ζ that changes with c and T in nontrivial ways, this relationship can be unequivocally related to the sol structure *only* in the close vicinity of the gelation point (where c and T vary only slightly and ζ remains constant).

To investigate the sol structure in wider ranges of c and T, we examined the steady-state compliance of PVC sols in DOP, $J_{pol} = [\omega^{-2}G'/(\omega^{-1}G'' - \eta_s)^2]_{\omega\to 0}$, with η_s being the DOP viscosity. J_{pol} is independent of ζ and can be directly related to the sol structure. The J_{pol} of the sols was larger than that of the homogeneous polymer solution, suggesting some heterogeneity (fragmented network structure) in the sols. Further analyses revealed that the normalized compliance $cRTJ_{pol}$ was universally dependent on ϵ irrespective of M, T and c:[20]

$$cRTJ_{pol} \propto \epsilon^{-\alpha} (\alpha \cong 3.1) \quad \text{for} \quad c < c_g \tag{3}$$

This result suggested that the fragmented sol network structure (e.g., network size and degree of branching) was universally determined by ϵ irrespective of M_w, c, and T.

Following the same strategy, we have investigated the gel structure in wide ranges of c and T. For this purpose, we focused our attention to the equilibrium modulus G_e, a ζ-independent quantity reflecting this structure, and looked for a universal relationship between G_e and ϵ (that corresponds to eq 3). In fact, we found the universal relationship for a normalized modulus G_eM/cRT and discussed the gel structure on the basis of this

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Table 1. Characteristics of PVC Samples

code	$10^{-3}M_w$[a]	M_w/M_n[b]	syndio/hetero/iso[c]
PVC4	39.4	1.89	0.33/0.49/0.18
PVC9	87.4	2.01	0.33/0.50/0.17
PVC17	173	2.24	0.35/0.50/0.15

[a] Determined from light scattering. [b] Determined from GPC. [c] Determined from ^{13}C NMR.

relationship. These results are summarized in this paper.

II. Experimental Section

II.1. Material. Three commercial poly(vinyl chloride)s (PVC)s, produced through suspension polymerization and fully characterized in the previous work,[13] were used. Table 1 summarizes their characteristics.

Prior to the sample preparation, all PVC samples were purified through precipitation from a tetrahydrofuran (THF)/methanol mixture. For preparation of the PVC/DOP gels, prescribed amounts of the purified PVC sample and DOP were dissolved in THF (70−90% in weight), and then THF was allowed to thoroughly evaporate from a shallow container (glass dish) at room temperature. During a long evaporation period (>3 weeks), the PVC/DOP gels were well-stabilized/equilibrated. Thus, no detectable change was observed for the rheological data obtained from repeated measurements with intervals of 1 and 2 months. The reproducibility of the data reported in this paper was confirmed in this way.

II.2. Measurements. For the well-stabilized PVC/DOP gels, dynamic measurements were conducted with a rheometer (ARES, Rheometrics) to measure the storage and loss moduli, G' and G''. A parallel plate fixture with a diameter of 25 mm was used. The oscillatory strain amplitude was kept small (<0.2) so that linear responses were detected.

The PVC/DOP gels, mounted in the rheometer at room temperature, were slowly heated from 40 °C up to respective flow temperatures (above the gelation points). During this heating procedure, the temperature T was kept constant at several selected points where the moduli were measured. Prior to the measurements, the gels were annealed at the selected T at least for 20 min.

On cooling from the flow temperature, the gelation was completed after slow transient changes (over a period ≥100 h) attributable to completion of crystal domain formation at respective T. Because of such slow changes (noted also by Nijenhuis and Winter[8]), the moduli obtained on cooling may reflect nonequilibrium gel structures at respective T. For this reason, only the moduli measured on heating are used in this paper; the gels were equilibrated (stabilized) at room temperature (~25 °C) during the sample preparation process, and the melting of crystal domains on heating occurred rapidly without significant delay.

III. Results and Discussion

Dynamic Behavior of PVC/DOP Systems at $T \geq$ 40 °C. Figure 1 shows the storage modulus G' of a PVC17/DOP system (c = 101 g/L) at respective T. The PVC gel is well developed at 40 °C to exhibit ω-independent G' (and much smaller G''; not shown). This G' is utilized as the equilibrium modulus G_e. G_e decreases with increasing T, first slowly and then rapidly as T approaches the sol−gel transition temperature.

At the sol−gel transition temperature T_{gel}, the Winter−Chambon relationship[21] (eq 1) is valid and the loss tangent (tan δ) is independent of ω. This ω-independence at the gelation point, confirmed for various chemical and physical gels,[8,13,17,18,21−26] was used to determine T_{gel} of our PVC systems.

Figure 2 shows tan δ vs T plots at various ω for the PVC17/DOP gel examined in Figure 1. All curves pass through a common point at T_{gel} (=147.5 ± 2.5 °C for this gel). For the gels of various c and M, Figure 3 shows c dependence of T_{gel} determined in this way. These T_{gel} data agree with the previous data.[18]

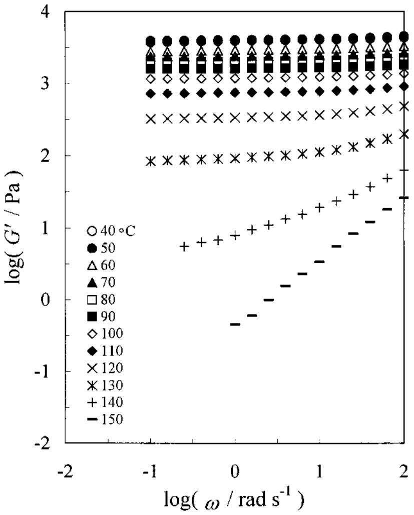

Figure 1. Plots of storage modulus G' against angular frequency ω for the PVC17/DOP gel (c = 101 g/L) at various temperatures as indicated.

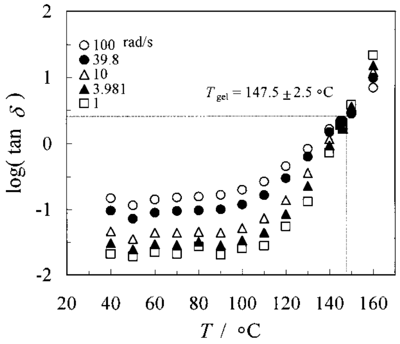

Figure 2. Plots of loss tangents tan δ against temperature T for the PVC17/DOP gel (c = 101 g/L) at various angular frequencies, ω = 1, 3.98, 10, 39.8, 100 rad s^{-1}. T_{gel} is the sol−gel transition temperature.

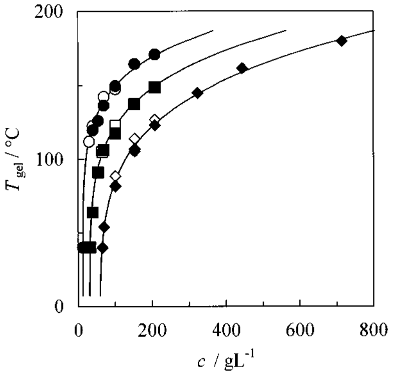

Figure 3. Variation of the sol−gel transition temperature T_{gel} with PVC concentration c. The unfilled diamonds, squares, and circles, respectively, indicate T_{gel} of the PVC4/DOP, PVC9/DOP, and PVC17/DOP systems obtained in this study. The filled diamonds, squares, and circles are for the T_{gel} of the same systems obtained in the previous study.[18]

Concentration Dependence of G_e of PVC/DOP Systems. For the PVC17 gels at various T, Figure 4 shows plots of G_e against c. The c dependence of G_e becomes weaker for larger c. However, if the G_e data are approximately fitted with a power-law relationship, $G_e \propto c^a$, the exponent a increased from 3.4 (at 40 °C) to

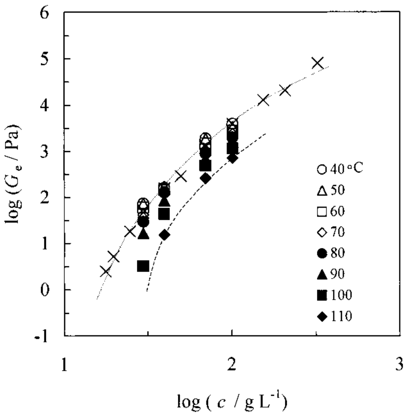

Figure 4. Plots of equilibrium modulus G_e of the PVC17/DOP gels against the PVC concentration c at various temperatures T as indicated. The cross indicates the G_e data at the 40 °C obtained in the previous study.[15]

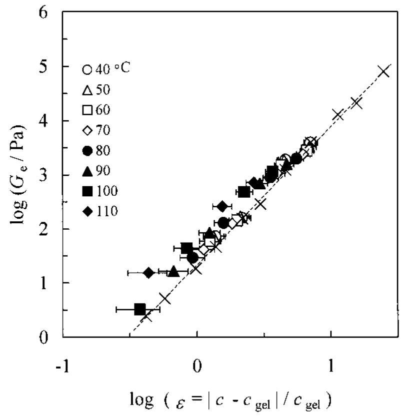

Figure 5. Equilibrium modulus G_e of the PVC17/DOP gels at various temperatures T plotted against the relative distance from the gelation point, $\epsilon = |c - c_g(T)|/c_g(T)$. The symbols are the same as in Figure 4. The dotted line indicates the fit for the data at 40 °C obtained previously.[15]

4.7 (at 100 °C). This exponent is much larger than the exponent for the entanglement plateau modulus G_N of homogeneous polymer solutions;[27] $G_N \propto c^{\beta}$ with $\beta = 2-2.5$. Similar results were found for all gels examined.

The large, apparent exponent a of the gels is related to a structural change in the gels with c and T. This structural change is in turn reflected in the change of c_g with T; for example, c_g of the PVC17 gel increases from 12.5 g/L (at 40 °C) to 21.6 g/L (at 100 °C).

In Figure 5, G_e of the PVC17 gels is plotted against the relative distance from the gelation point, $\epsilon = |c - c_g(T)|/c_g(T)$. The ϵ values utilized in this plot were obtained from the c_g data (Figure 3) with a satisfactory accuracy; the error bars in Figure 5 correspond to ±10% uncertainty in c_g. At respective T, G_e can be (approximately) described by a power-law relationship, $G_e \propto \epsilon^z$, over a wide range of ϵ (and of c), and the exponent z (= 2.6 ± 0.3) is roughly the same for all gels examined. This power-law relationship, found also in the previous study,[15] suggests that the gel structure (reflected in G_e) is determined by ϵ, not by c. (Note that ϵ includes the effect of T on c_g.)

More importantly, Figure 5 demonstrates that the magnitude of G_e is not uniquely determined by ϵ; for a given ϵ, G_e is larger for higher T. This change of G_e, not noted in the previous measurements at constant T (40 °C),[15] provides us with a clue for further discussing the gel structure, as explained below.

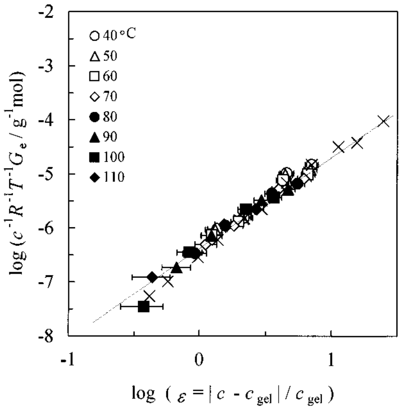

Figure 6. Normalized equilibrium modulus $c^{-1}R^{-1}T^{-1}G_e$ of the PVC17/DOP gels at various temperatures T plotted against the relative distance from the gelation point, $\epsilon = |c - c_g(T)|/c_g(T)$. The symbols are the same as in Figure 4.

Universality of G_e. In a discussion of G_e, we first remember the fact that the modulus of polymer network systems is generally proportional to the polymer mass per unit volume (i.e., to c) and thermal energy (RT per mole) as well as to a factor specifying the network structure. A good example of this fact is noted for G_e of a chemically cross-linked, homogeneous polymer network (not gelling systems); $G_e = cRT/M_x$ with M_x being an average molecular weight of the network strand between cross-links. Thus, the structural parameter of this network, $1/M_x$, is most clearly examined for a normalized modulus, G_e/cRT, not for G_e itself.

The same argument applies to PVC gels, and the gel network structure is examined more directly for G_e/cRT than for G_e. Figure 6 shows plots of G_e/cRT against ϵ for the PVC17 gels ($M = 173 \times 10^3$) at various T as indicated. The scatter of the data at different T seen in Figure 5 is largely reduced in Figure 6. Thus, for the PVC17 gels, the normalized modulus G_e/cRT appears to be universally determined by ϵ irrespective of c and T. The same type of universality was found for the PVC4 and PVC9 gels having different M.

Here, we further examine the universality for these gels of *different M*. Figure 7a shows the plots of G_e against ϵ for the PVC4, PVC9, and PVC17 gels at various c and T. A large scatter of the plots is noted even for respective series of gels (having the same M) because G_e is not corrected for c and T.

Figure 7b shows the plots of G_e/cRT against ϵ for the PVC4, PVC9, and PVC17 gels. For respective series of gels, the normalized modulus G_e/cRT is dependent only on ϵ, as already noted in Figure 6. However, for the gels having different M, G_e/cRT is not uniquely determined by ϵ; see three dashed lines for the three series of gels. For a given ϵ, the magnitude of G_e/cRT is almost inversely proportion to M.

Considering this result, Figure 7c shows plots of the other type of normalized modulus G_eM/cRT against ϵ. This modulus is almost universally determined by ϵ irrespective of the c, T, and M values. This universality suggests that the effective mesh size M_g of the randomly cross-linked PVC gel network (not very far from the gelation point $c_g(T)$) is determined by ϵ and M. Thus, we find the expression

$$G_e = cRT/M_g \quad \text{with} \quad M_g = Mf(\epsilon) \qquad (4)$$

Here, $f(\epsilon)$ is a function of only ϵ. The data in Figure 7c

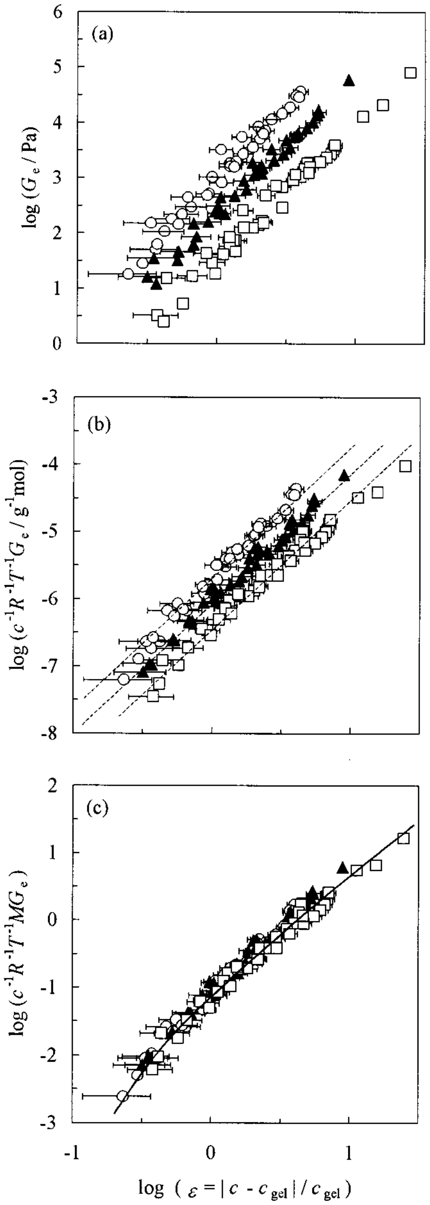

Figure 7. (a) Equilibrium modulus G_e, (b) normalized equilibrium modulus $c^{-1}R^{-1}T^{-1}G_e$, (c) the other type of normalized equilibrium modulus $c^{-1}R^{-1}T^{-1}MG_e$ of the PVC/DOP gels plotted against the relative distance from the gelation point, $\epsilon = |c - c_g(T)|/c_g(T)$: circles, triangles, and squares are for the PVC4, PVC9, and PVC17 gels. The solid curve in part c, representing a relationship $G_e \propto cRT\epsilon^{1.8}/M$ for large ϵ, is drawn as a guide for eye.

suggest that $f(\epsilon)$ is approximately proportional to $\epsilon^{-1.8}$ in the range of ϵ examined, although $f(\epsilon)$ tends to depend more strongly on ϵ in the close vicinity of the gelation point (for small ϵ).

We can extract some information from the above expression, $M_g = Mf(\epsilon)$. The factor M included in M_g suggests that individual PVC chains work as a fundamental unit sustaining the gel elasticity. Concerning this point, we note that G_eM/cRT is smaller than unity and thus $M_g = cRT/G_e$ is larger than M for $\epsilon < 3$; see Figure 7c. This result strongly suggests that several PVC chains associate each other (at the cross-linking crystal domains) to together behave as an independent network strand of the size M_g. $f(\epsilon)$ gives this association number. This argument is consistent with an expected similarity of the bifurcated network structures in the gels of various c and M: The degree of bifurcation would be determined by ϵ and a characteristic length between effective bifurcation points (for a given ϵ) would be proportional to the length of the constituent chain, i.e., to M. (Note that M specifies the concentration of the chain ends that locally disrupt the connectivity of the gel network.)

The relative distance ϵ utilized in the master plot (Figure 7c) represents the effects of c, T, and M on c_g in unified way. Thus, the dependencies of G_e on c ($> c_g$) and T($< T_{gel}$) are summarized as the universal dependence on this ϵ (cf. eq 4). This universality may reflect a wide distribution of the size of crystal domains (physical cross-links for the gels): Smaller crystal domains would be dissolved earlier on the increase of T/decrease of c and larger domains remaining at respective T and c may have a similarly broad, relative distribution of the size, possibly resulting in the observed universality of G_e on this dissolution. In this sense, our PVC gels are similar to a crystallizing copolymer of ethene and 1-butene examined by Horst and Winter.[28,29] The critical gelation behavior of this bulk copolymer is related to the broad melting on heating (that corresponds to the broad dissolution in our PVC gels).

Comments on the Power-Law Relationship between G_e and ϵ. At constant T, G_e of the gels having various c and M are almost proportional to ϵ^z with $z \cong 2.6$.[15] This z value is close to the critical exponent deduced from the percolation model.[30]

The above power-law relationship, $G_e \propto \epsilon^z$, captures some limited aspects of the gel structure discussed in the previous section. In fact, at constant T, c_g is determined only by M and the empirical equation found in this study, eq 4, reduces approximately to this power-law relationship.

However, we should emphasize that the gel elasticity (and underlying structure) in *wide* ranges of c, M, and T can be more comprehensively described by eq 4 than by the previously reported[15] power law, $G_e \propto \epsilon^z$ with $z = 2.6$: In a rigorous sense, this power law and the corresponding critical percolation picture are valid only in the close vicinity of the gelation point (i.e., for $\epsilon \to 0$) where the gelation can be regarded as a critical phenomenon. In constant, eq 4 simply indicates that the gel mesh size is determined by M and ϵ and is not limited in that vicinity. Thus, eq 4 holds in a much wider range of ϵ, e.g., in the range examined in Figure 7 ($0.2 < \epsilon < 20$).

IV. Conclusion

We have examined the equilibrium modulus G_e of PVC/DOP gels at $T \geq 40$ °C. Near the gelation point, G_e decreases rapidly with increasing T. In attempt to universally describe this decrease for the gels of various c and M, we have examined the dependence of G_e on the distance ϵ from the gelation point in several normalized forms. It turned out that the normalized equilibrium modulus G_eM/cRT of various gels is universally dependent on ϵ. This result suggests that the mesh size of the randomly cross-linked network in the gels near the gelation point is universally determined by ϵ and M. More specifically, an effective gel network strand appears to be composed of several PVC chains (associating with each other at the cross-linking crystal domains) to have the size $M_g = Mf(\epsilon)$, where $f(\epsilon)$ gives the association number. This molecular picture, derived from the observation that G_eM/cRT is universally dependent on ϵ and has the value smaller than unity (for $\epsilon < 3$), is consistent with the expected similarity of the bifurcated gel network structure for various c and M.

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