Viscoelastic Properties of Poly(vinyl chloride) Sols

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I. Introduction

Structures[1−10] and properties[2,3,11−16] of poly(vinyl chloride) (PVC) have been examined in various solvents. In rather poor solvents, PVC forms physical gels at low temperatures (T) and high concentrations (c). These gels are 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 elasticity are well related to this network structure, although uncertainties still remain for detailed structures of the cross-links (either fibrous crystals[2−4,6,9] or small crystallites)[10] and of the gel strands (either individual PVC chains or their fibrous aggregates).[7,8]

Recently, we began a series of studies[17−22] for PVC gels in bis(2-ethylhexyl) phthalate (DOP) to rheologically characterize this material. *Critical gels* are known to exhibit power-law-type frequency (ω) dependence of the storage and loss moduli G' and G'',[23,24]

$$G'(\omega) = g\omega^n, \quad G''(\omega) = \tan(n\pi/2)g\omega^n \qquad (1)$$

This dependence was observed for PVC's of various molecular weights M at respective gelation concentrations c_g.[17−22] Although c_g changed with M and molecular weight distribution (MWD), the exponent n was independent of M and MWD ($n \cong 0.75$).[17,21] Thus, the PVC/DOP critical gels of various M had a similar fractal structure[25−28] (a similar degree of branching/bifurcation). Corresponding to this fractal structure, the critical gel exhibited surprisingly weak nonlinearities in its rheological properties under large strain/fast flow.[20]

At $c > c_g$, well-developed, noncritical PVC/DOP gels are formed. For these gels in a vicinity of the gelation point, the equilibrium modulus G_e at constant T (40 °C) exhibited power-law behavior, $G_e \propto \epsilon^z$ with $\epsilon = |c - c_g|/c_g$ being a normalized distance from the gelation point.[19] The exponent z ($\cong$2.5) was independent of M,[19] suggesting a similarity of the gel network structure for various M.[29]

Thus, the rheological properties and underlying structures of the PVC/DOP gels ($c \geq c_g$) have been elucidated to a considerable depth. On the other hand, the properties and structures of the PVC/DOP sols ($c < c_g$) are not so clearly understood yet, although some limited information has been obtained for the c dependence of the zero-shear viscosity.[18]

Table 1. Characteristics of PVC Samples[a]

code	$10^{-3}M_w$[b]	M_w/M_n[c]
PVC4	39.4	1.89
PVC9	87.4	2.01
PVC17	173	2.24

[a] The samples have the triad tacticity of syndio:hetero:iso = 0.33:0.49:0.18 (determined from NMR).[17] [b] Determined from light scattering.[17] [c] Determined from GPC.[17]

Concerning this sol structure, we expect that the PVC crystal domains are not fully dissolved in DOP (unless at very high T), and the PVC chains are partially cross-linked at the surviving domains to form fragmented networks of finite sizes. In fact, Guenet and co-workers[30,31] observed a similar fragmented structure (PVC aggregates) in some solvents, e.g., diethyl malonate[30] and diethyl oxalate.[31]

Viscoelastically, this fragmented (or multibranched) structure in the sol should be most clearly reflected in the steady-state compliance: The compliance, being independent of the monomeric friction, can be utilized as a sensitive measure of the relaxation mode distribution,[32,33] and this mode distribution of the sols should reflect the multibranched structure therein. Considering this feature, we have examined the compliance of the PVC/DOP sols of different M at various c and T. We found that the compliance is essentially determined by ϵ, and thus the sol structure is universally dependent on ϵ. These findings are explained in this paper.

II. Experimental Section

Table 1 summarizes characteristics of the PVC samples. These samples were synthesized via suspension polymerization at Mitsubishi Chemical Co. GPC measurements revealed that the PVC chains have an approximately logarithmic-normal MWD.

The systems examined were the sol/gel of the PVC samples in DOP at various PVC concentrations c. These systems were prepared from tetrahydrofuran (THF) solutions of PVC and DOP after slow evaporation of THF. Details of this preparation method were described elsewhere.[17]

For the PVC/DOP systems, the linear viscoelastic, storage and loss moduli G' and G'' were determined with a laboratory rheometer, ARES (Rheometrics). Parallel plate fixture (radius = 2.5 cm) was used. At high T, respective PVC/DOP systems behaved as the sol to exhibit the terminal relaxation tails, $G' \propto \omega^2$ and $G'' \propto \omega$ (ω = angular frequency). From these tails, the steady-state compliance of the PVC chains was determined.

III. Results and Discussion

III.1. *T* and *c* Dependence of Compliance. Figure 1 shows the linear viscoelastic behavior of a representative system, the PVC4/DOP system with $c = 66$ g L^{-1}. (The data at $T \leq 60$ °C were obtained previously,[20] and the reproducibility was confirmed in this study.) The critical gelation temperature, where the power-law behavior (eq 1) is observed, is $T^* = 49$ °C.[20] At $T \geq 60$ °C (well above T^*), the system becomes a rapidly relaxing sol and exhibits the terminal relaxation tails ($G' \propto \omega^2$ and $G'' \propto \omega$) in our experimental window. The steady-state compliance of the PVC chains in the sol, J_{pol} , was evaluated from these tails,[32,33]

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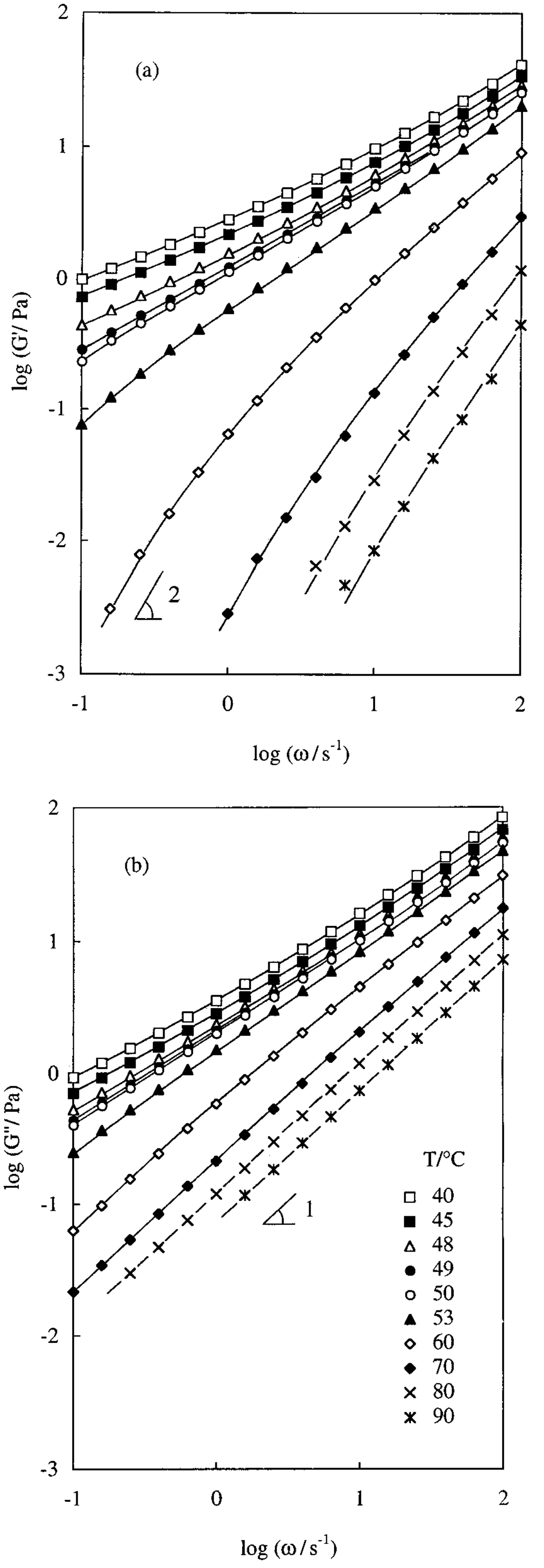

Figure 1. Linear viscoelastic behavior of the PVC4/DOP system ($c = 66$ g/L) at various temperatures as indicated. The critical gelation temperature is $T^* = 49$ °C.

$$J_{\mathrm{pol}} = \left(\frac{G'/\omega^2}{[(G''/\omega) - \eta_s]^2}\right)_{\omega\to 0} \tag{2}$$

Here, η_s is the viscosity of the solvent (DOP).

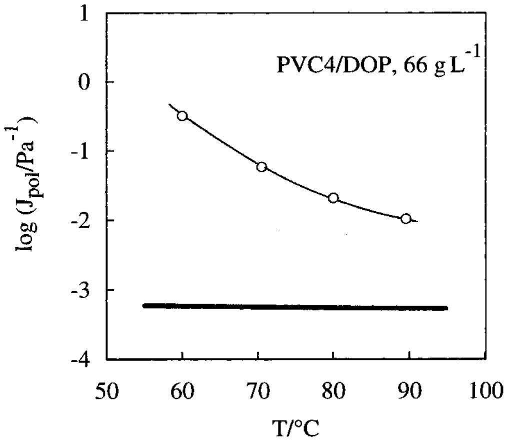

Figure 2. Temperature dependence of the steady-state compliance J_{pol} of the PVC4 sols in DOP ($c = 66$ g/L). Thick solid line indicates the Rouse compliance of molecularly dissolved PVC4 chains (forming no fragmented network structure).

This J_{pol}, having no contribution from the solvent, is related to the relaxation spectrum $H(\tau)$ of the PVC chains as[32,33]

$$J_{\mathrm{pol}} = \frac{\int_{-\infty}^{\infty} \tau^2 H(\tau)\,\mathrm{d}\ln\tau}{[\int_{-\infty}^{\infty} \tau H(\tau)\,\mathrm{d}\ln\tau]^2} \tag{3}$$

Usually, the relaxation times τ of slow viscoelastic modes have a common monomeric friction ζ ($\tau \propto \zeta$), but the intensities H of these modes are independent of ζ.[32,33] Thus, J_{pol} is independent of ζ (as noted from eq 3) and exclusively represents the relative distribution of slow modes; the larger the J_{pol} value at a given c, the broader the mode distribution. For the PVC sols, J_{pol} reflects the sol structure that determines this distribution.

Figure 2 shows T dependence of J_{pol} of the PVC4/DOP sol (at $T \geq 60$ °C) examined in Figure 1. As judged from M_w ($= 39.4 \times 10^3$) and c ($= 66$ g L^{-1}) of the PVC4 chains in this sol, the chains are nonentangled *if* they are molecularly dissolved in DOP without forming the cross-linking crystal domains. For this case, J_{pol} should be close to the Rouse compliance J_{Rouse} (as established for nonentangled, homogeneous solutions),[32,33]

$$J_{\mathrm{Rouse}} = Q\left(\frac{2M_w}{5cRT}\right) \quad \text{with } Q = \frac{M_z M_{z+1}}{M_w^2} \tag{4}$$

Here, Q is a correction factor for the molecular weight distribution (MWD). For the PVC4 chains having approximately logarithmic-normal MWD, this factor can be evaluated as $Q \cong (M_w/M_n)^3$.

In Figure 2, the thick solid line indicates the J_{Rouse} calculated from this approximate Q (with the M_w/M_n ratio being given in Table 1). The measured J_{pol} is orders of magnitude larger than this J_{Rouse}. More importantly, the measured J_{pol} decreases significantly, by a factor of ~100, with a rather small increase of T (from 60 to 90 °C). This strong decrease is never observed for molecularly dissolved chains.

These results confirm that the PVC chains in the sol are partially cross-linked at their crystal domains to form fragmented networks of finite sizes: The broad relaxation mode distribution (specified by $J_{\mathrm{pol}} \gg J_{\mathrm{Rouse}}$) reflects the distributions in the size and degree of branching of these networks. The significant decrease

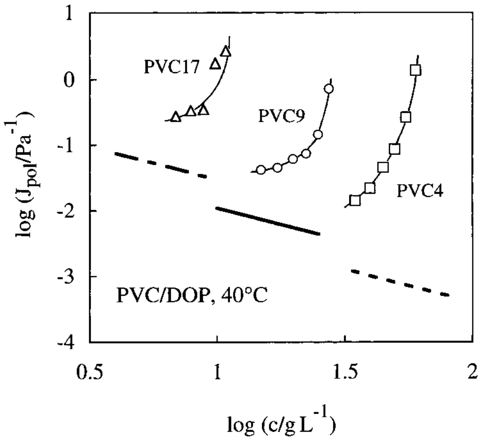

Figure 3. Concentration dependence of the steady-state compliance J_{pol} of the PVC4, PVC9, and PVC17 sols in DOP at 40 °C. Thick dotted, solid, and dashed lines respectively indicate the Rouse compliance of molecularly dissolved PVC4, PVC9, and PVC17 chains.

of J_{pol} with T is attributable to decreases of the network size and degree of branching due to partial dissolution of the crystal domains. This partial dissolution was noted also in a recent dielectric study of the PVC sol.[34]

The above features of the PVC sols in DOP are similar to the features of the sols in other solvents.[30,31] Guenet and co-workers[30] reported that the sols in diethyl malonate included two types (weak- and strong-type) of physical cross-links, and the weak-type cross-links are easily dissolved with increasing T. The partial dissolution of the crystal domains (physical cross-links) in our PVC/DOP sols may be related to similar, weak domains.

Figure 3 shows c dependence of J_{pol} of the PVC4, PVC9, and PVC17 sols at 40 °C. The thick dotted, solid, and dashed lines respectively indicate the J_{Rouse} (eq 4 with $Q \cong (M_{\mathrm{w}}/M_{\mathrm{n}})^3$) calculated for the PVC4, PVC9, and PVC17 sols. The measured J_{pol} is again much larger than J_{Rouse} and strongly increases with increasing c (toward c_{g}). This increase of J_{pol}, never observed for molecularly dissolved chains, suggests that the fragmented network in the PVC sol becomes larger and more complicatedly branched with increasing c.

III.2. Universality of Compliance. For *molecularly dissolved* linear polymers, J_{pol} scales as[32,33]

$$\frac{cRT}{M} J_{\mathrm{pol}} = \begin{cases} \tilde{J}_{\mathrm{d}} & \text{for } cM < M_{\mathrm{c}}' \text{ (in nonentangled regime)} \quad (5a) \\ \dfrac{1}{cM}\tilde{J}_{\mathrm{N}} & \text{for } cM < M_{\mathrm{c}}' \text{ (in entangled regime)} \quad (5b) \end{cases}$$

Here, M_{c}' is a characteristic molecular weight for appearance of entanglement effects on J_{pol} of bulk polymer. $\tilde{J}_{\mathrm{d}}$ and $\tilde{J}_{\mathrm{N}}$ are constants independent of c, M, and T. (For narrow MWD linear polymers, $\tilde{J}_{\mathrm{d}} \cong 0.4$ and $\tilde{J}_{\mathrm{N}} = (2 - 3)\rho M_{\mathrm{e}}°$ with ρ and $M_{\mathrm{e}}°$ being the density and entanglement spacing of bulk polymer.) Equation 5 indicates that the reduced compliance $cRTJ_{\mathrm{pol}}/M$ is universally dependent on a product, cM, irrespective of the c, M, and T values.

As can be noted from Figures 2 and 3, eq 5 fails completely for the J_{pol} data of the PVC sols because of the changes in the fragmented network structure with c and T. However, eq 5 is still useful to provide us with a clue for discussing the sol structure, as explained below.

In general, J_{pol} is inversely proportional to the polymer mass per unit volume (c) and to the thermal energy (RT per mole). If a characteristic length scale ξ corresponding to the terminal relaxation is determined by M of the chain, the reduced compliance $cRTJ_{\mathrm{pol}}/M$ is universally dependent on the structure-controlling parameter in the system. An example of this situation is found for the homogeneous, molecularly dissolved solutions: In such solutions, ξ is given by the dimension of respective chains, and the product cM works as the parameter controlling the entanglement mesh structure; the entanglement number per chain is given by $cM/\rho M_e°$.[32,33] On the other hand, if ξ is independent of M, the other type of reduced compliance, $cRTJ_{\mathrm{pol}}$, is expected to be universally dependent on the structure-controlling parameter.

For the PVC sols at various c and T, the fragmented network structure would be determined according to the normalized distance from the gelation point, $\epsilon = |c - c_{\mathrm{g}}|/c_{\mathrm{g}}$. Thus, ϵ can be utilized as the structure-controlling parameter in the sols. For the PVC4, PVC9, and PVC17 chains in DOP, the c_{g} data at various T were obtained in the previous study.[22] From these c_{g} data, the ϵ values for the PVC4, PVC9, and PVC17 sols were evaluated with uncertainties less than ±15%.

In Figure 4a, the raw J_{pol} data of the PVC sols are plotted against ϵ thus evaluated. Since the dependencies of J_{pol} on the thermal energy and polymer mass are not corrected in this plot, the data points are largely scattered.

In Figure 4b, the reduced compliance $cRTJ_{\mathrm{pol}}/M_{\mathrm{w}}$ is plotted against ϵ. The scatter in this plot is less significant than that seen in Figure 4a. However, the data points in Figure 4b systematically shift upward with decreasing M_{w}, and the quantity $cRTJ_{\mathrm{pol}}/M_{\mathrm{w}}$ is not universally dependent on ϵ.

Finally, the other type of reduced compliance $cRTJ_{\mathrm{pol}}$ is plotted against ϵ in Figure 4c. The data points are collapsed around the dashed line that represents a relationship,[35]

$$cRTJ_{\mathrm{pol}} \propto \epsilon^{-3.1} \quad \text{(for PVC/DOP sols at various } c, T, M) \quad (6)$$

Differing from the feature seen in Figure 4b, the increase of M_{w} results in no systematic deviation from this relationship. This result suggests that the fragmented network structure in the PVC sols is universally determined according to the ϵ value and that the network size, i.e., the length scale corresponding to the *terminal* relaxation, decreases with increasing ϵ. (For well-developed PVC/DOP gels, a corresponding universality of the gel mesh size was suggested from the equilibrium modulus data, $M_{\mathrm{w}}G_{\mathrm{e}}/cRT \sim \epsilon^{1.8}$ in a wide range of ϵ. Further details will be presented in our next paper.[36]).

Here, it should be emphasized that the PVC/DOP sols exhibit the universal ϵ dependence of $cRTJ_{\mathrm{pol}}$, not of $cRTJ_{\mathrm{pol}}/M_{\mathrm{w}}$ (cf. parts b and c of Figure 4). This result leads us to speculate that the size and degree of branching of the fragmented sol network are uniquely determined by ϵ and insensitive to M_{w}. This speculation seems to be reasonable because, for a given ϵ, the crystal domains would be formed with nearly the same prob-

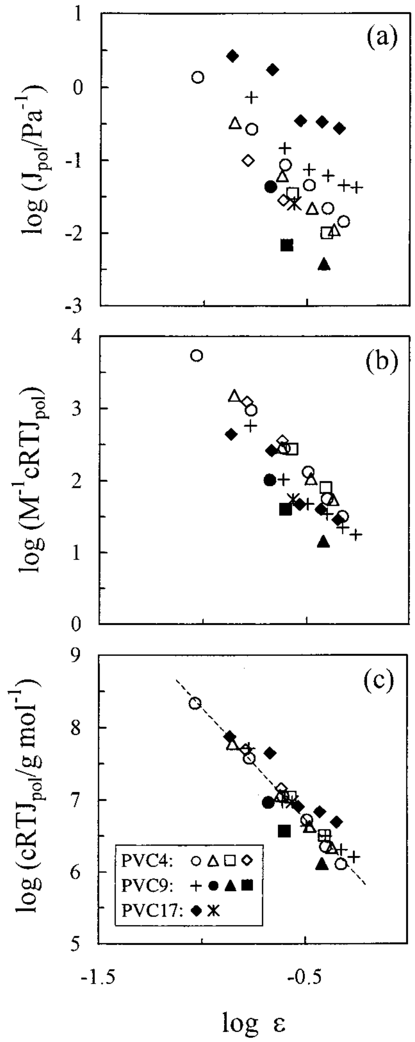

Figure 4. Plots of (a) raw J_{pol} data, (b) reduced compliance $cRTJ_{\mathrm{pol}}/M_w$, and (c) the other type of reduced compliance $cRTJ_{\mathrm{pol}}$ of various PVC sols against the normalized distance ϵ from the gelation point. The symbols are common in parts a–c.

ability at various portions along the PVC chain backbone (except in the close vicinity of the chain ends). No structural data supporting/disproving this speculation are available, and a structural study of the PVC/DOP sols is desirable.

Finally, a comment needs to be made for the viscosity of the PVC sols examined in Figure 4. For each sol at constant T, changes of the PVC viscosity $\eta_{\mathrm{pol}} = \eta_0 - \eta_s$ with c were roughly described by a power-law relationship, $\eta_{\mathrm{pol}} \propto \epsilon^{-1.7\pm0.1}$ (for $\epsilon = 0.1-0.5$), and the viscosity normalized for the polymer mass and thermal energy roughly obeyed a similar relationship, $\eta_{\mathrm{pol}}/cRT \propto \epsilon^{-1.4\pm0.1}$. These relationships, found for relatively large c (and thus for $\eta_{\mathrm{pol}} \cong \eta_0$), correspond to the previously reported power law,[18] $\eta_0 \propto \epsilon^{-1.5\pm0.1}$ at constant T and M_w.[35] However, on changes of T and M_w, none of the η_0, η_{pol}, and η_{pol}/cRT data exhibited universal dependence on ϵ, which is different from the behavior of compliance (cf. Figure 4c). This difference is attributed to a fact that the viscosity is not uniquely determined by the sol structure but is proportional to the monomeric friction ζ; ζ changes with c and T and thus with $\epsilon = |c - c_g(T,M_w)|/c_g(T,M_w)$ in a nontrivial way, thereby resulting in the nonuniversal feature of the viscosity. This result in turn indicates that the sol structure is most clearly examined for the ζ-independent compliance, as demonstrated in this paper.

IV. Concluding Remarks

For the PVC/DOP sols, we have examined changes of the steady-state compliance J_{pol} with c, T, and M. The J_{pol} was significantly larger than the compliance expected for molecularly dissolved PVC chains, suggesting that the PVC chains in the sol formed fragmented networks of finite sizes (physically cross-linked at the PVC crystal domains). The reduced compliance $cRTJ_{\mathrm{pol}}$ was found to be universally dependent on the normalized distance from the gelation point, $\epsilon = |c - c_g|/c_g$, irrespective of the c, T, and M_w values. This result suggests that the fragmented network structure in the sols, characterized by the network size and degree of branching, is uniquely determined by ϵ.

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(29) (a) The PVC gel structure quite possibly changes with the solvent quality (solubility toward PVC), as suggested from the G_e data of the gels in various solvents.[29b] (b) Kakiuchi, M.; Aoki, Y.; Watanabe, H.; Osaki, K. *J. Soc. Rheol. Jpn.*, in press.
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(35) Equation 6, being valid in a wide range of ϵ (between 0.1 and 0.5), should not be regarded as a scaling law associated to the critical gelation phenomenon. (This scaling law is conceptually valid only for $\epsilon \rightarrow 0$.) Instead, eq 6 simply indicates that the sol structure is universally determined by ϵ. Similarly, the previously reported relationship for the viscosity,[18] $\eta_0 \propto \epsilon^{-1.5\pm0.1}$ for $\epsilon = 0.1-0.5$, does not necessarily represent the critical scaling behavior.
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