# Rheological Images of Poly(Vinyl Chloride) Gels. 4. Nonlinear Behavior in a Critical Gel State

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ABSTRACT: Nonlinear rheology was examined for a critical gel of poly(vinyl chloride) in dioctyl phthalate (PVC/DOP). PVC crystal domains worked as the cross-linking domains in this *physical* gel. In the linear regime, the gel exhibited power-law dependence of storage and loss moduli on frequency $\omega$, $G'(\omega) \propto G''(\omega) \propto \omega^n$ with $n \cong 0.7$. In stress relaxation experiments the gel exhibited nonlinear damping of the relaxation modulus $G(t,\gamma)$ with increasing step-strain $\gamma$, but the magnitude of damping was much smaller than that for homogeneous homopolymer liquids. In addition, for the gel, the $G(t,\gamma)$ data for the largest strain examined ($\gamma = 5$) were in close agreement with the linear $G(t)$ measured after imposition of this strain. On start-up of shear flow at a rate $\dot{\gamma}$, the viscosity growth function $\eta_+(t,\dot{\gamma})$ of the gel followed the linear $\eta_{+,L}(t)$ at a short time scale, deviated downward from $\eta_{+,L}(t)$ but still increased gradually at an intermediate time scale, exhibited an apparent plateau (pseudo-steady-flow behavior) over a long time scale and finally decreased with further increases of time. These features of $\eta_+(t,\dot{\gamma})$ and $G(t,\gamma)$ were discussed in relation to flow/strain-induced changes of the fractal structure in the gel.

## I. Introduction

Poly(vinyl chloride) (PVC) forms physical gels in various solvents, and the structures[1−10] and physical properties[2,3,11−16] of those gels have been extensively 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 are unequivocally related to this network structure: For example, for well-developed gels forming a densely connected network throughout the whole system, the equilibrium elasticity is related to orientation/deformation of the PVC gel strands. However, details of the structure of the cross-linking domains, either fibrous crystals[2−4,6,9] or small crystallites,[10] have not been elucidated completely. In addition, the structures of the gel strands, either individual PVC chains or their fibrous aggregates,[7,8] may change with various factors such as temperature, concentration, solvent quality, method of gel preparation, and so on. Furthermore, changes in the properties of the PVC gels with these factors and with externally applied strain/flow, which reflect changes in the gel structure, have not been fully understood. Thus, no general molecular picture has been established for the structure and properties of PVC gels, although some limited aspects of the structure and properties were elucidated from the studies[1−16] so far carried out.

In an attempt to rheologically approach this molecular picture, Li, Aoki, and co-workers[17−19] recently began a series of studies for PVC in dioctyl phthalate (DOP). For PVC samples of various molecular weights $M$, they examined the sol−gel transition concentration $c_g$ at a constant temperature (= 40 °C). They found a proportionality, $c_g \propto M^{-1}$, which suggests an important role of the PVC chain size in formation of continuous gel networks.[17] For *critical* gels (at $c = c_g$) exhibiting a power-law type relaxation modulus, $G(t) = S_g t^{-n}$, they also found that the exponent $n$ ($\cong 0.75$) was independent of $M$ (independent of $c_g$) while the gel strength $S_g$ was proportional to $c_g$.[17] This result suggests that the PVC gel strands of different $M$ have a similar fractal structure (similar magnitude of bifurcation). The other findings, the $M$-independence of power-law exponents that characterize divergence of zero-shear viscosity of PVC sols (pregels)[18] and development of equilibrium modulus of PVC gels[19] with increasing $c$, also suggest a similarity of structure in the PVC sols and/or gels of various $M$.

As an extension of the above series of studies, this paper focuses on nonlinear rheological properties of a critical PVC/DOP gel under large step-strains and continuous flow. In general, the nonlinearity of polymeric systems reflects changes in the chain conformation and/or higher order structures induced by the strain/flow. These changes are expected to be quite different for critical gels and homogeneous polymeric liquids: The latter have a well-defined maximum length scale $\xi$ (=chain dimension), while the former have a self-similar fractal structure with an infinitely large $\xi$. From this point of view, this paper discusses a role of the fractal structure in appearance of the nonlinearity, placing emphasis on a difference between the nonlinear features of the critical gel and the homogeneous polymers.

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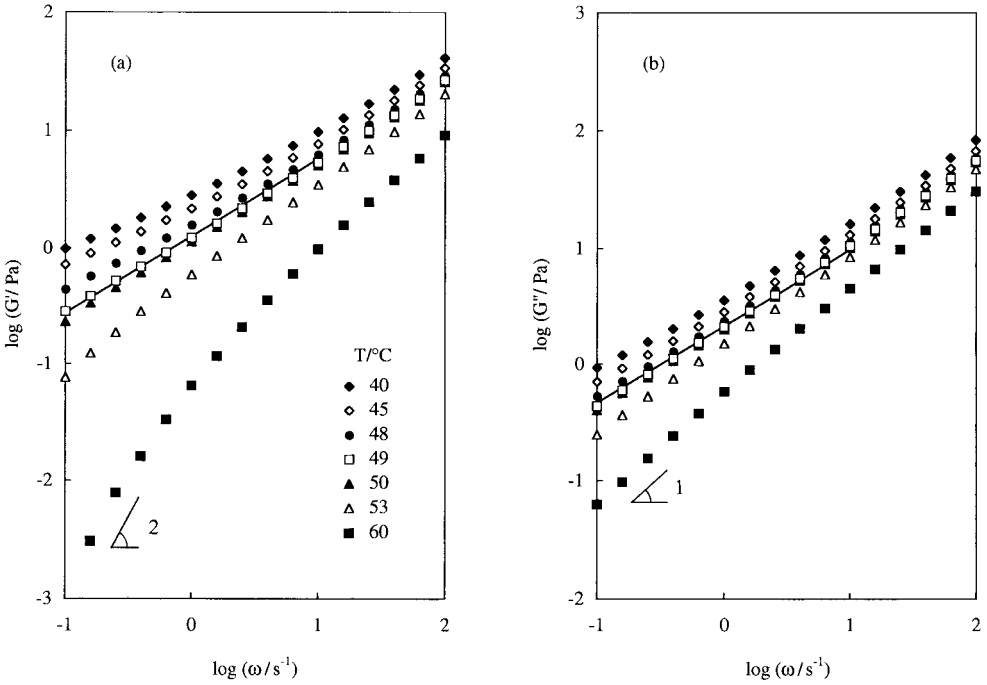


**Figure 1.** Linear viscoelastic behavior of the PVC4/DOP system ($c$ = 66 g/L) at various temperatures as indicated. The storage and loss moduli, $G'$ (part a) and $G''$ (part b), were measured for the freshly prepared system in the order of increasing temperature. The solid lines indicate the power-law type $\omega$ dependence of $G'$ and $G''$ for the critical gel at $T^*$ = 49 °C.

## II. Experimental Section

**II.1. Material.** A PVC sample, coded as PVC4 in the previous studies,[17−19] was used. This sample was synthesized via suspension polymerization at Mitsubishi Chemical Co. and had a weight-average molecular weight of 39.4 × 10$^3$ (determined from light scattering), a heterogeneity of $M_w/M_n$ = 1.89 (determined from GPC), and a triad tacticity of syndio:hetero:iso = 0.33:0.49:0.18 (determined from NMR).[17]

A system subjected to rheological tests was a sol/gel of PVC4 in DOP. The PVC4 concentration $c$ was 66 g/L. As in the previous work,[17] the sample was prepared by the following method: Prescribed amounts of PVC4 and DOP were first dissolved in excess tetrahydrofurane (THF, a good solvent for PVC) at room temperature to make a homogeneous solution (of ≅70 wt % THF). Then, at this temperature, THF was allowed to evaporate from the solution placed in a shallow glass dish. Within 3 weeks, the weight of the system became constant and the evaporation of THF was completed. The PVC4 concentration was determined from this constant weight.

The PVC4 chains began to form crystal domains at some point during the above evaporation procedure, and a soft but well-developed PVC4/DOP gel system was recovered on completion of this procedure. This gel was highly deformable at $T \geq$ 40 °C (where rheological measurements were conducted), reflecting the flexibility of the gel strands at those $T$.

**II.2. Measurements.** Rheological measurements were carried out with a laboratory rheometer, ARES (Rheometrics) with a cone-plate fixture (radius = 2.5 cm, cone angle = 0.04 rad). The PVC4/DOP system was soft even at room temperature that was well below the critical gelation temperature $T^*$. Thus a transducer covering a low torque range, 0.002−100 g cm, was used to accurately measure the rheological properties of this soft system.

Here, we have to add a statement concerning the gel structure in the PVC4/DOP system prepared with the above method. A memory of the initial structure (formed during the evaporation of THF) was partially preserved in the system even after the nonlinear rheological tests at 49 °C. This memory was erased when the system was heated above 100 °C. However, for the system once heated to $T$ > 100 °C and then cooled to the experimental temperature $T_{exp}$ (=40−60 °C), the interesting nonlinear features explained in this paper were not found. For the clearest observation of these features, we carried out rheological measurements for the freshly prepared PVC4/DOP system that was charged in the rheometer at 40 °C and heated to $T_{exp}$ (without experiencing higher temperatures).

Linear viscoelastic measurements were carried out at various $T_{exp}$ to determine the critical gelation temperature $T^*$. The measurements were conducted in the order of increasing $T_{exp}$ (so that the memory of the initial structure was best preserved). With this experimental procedure, good reproducibility of the data was obtained. As explained later for Figure 1, the $T^*$ thus determined was 49 °C.

For the PVC4/DOP *critical gel* at this $T^*$, the nonlinear relaxation modulus $G(t,\gamma)$ and growing stress $\sigma_+(t,\dot\gamma)$ were measured under step-strains of $\gamma$ = 0.2−5 and shear flow at $\dot\gamma$ = 0.05−5 s$^{-1}$, respectively. Rheological behavior of this gel turned out to be rather sensitive to a history of applied strain. Thus, $G(t,\gamma)$ was determined in the order of increasing $\gamma$ so as to minimize mechanical disturbance prior to the measurement at each $\gamma$. The measurements of $\sigma_+(t,\dot\gamma)$ were conducted after application of the step-strain of $\gamma$ = 5 so as to fix the initial condition for the stress growth under flow. The $\sigma_+(t,\dot\gamma)$ data thus obtained were summarized as a viscosity growth function, $\eta_+(t,\dot\gamma) = \sigma_+(t,\dot\gamma)/\dot\gamma$.

The $G(t,\gamma)$ and $\eta_+(t,\dot\gamma)$ data at very short $t$ may include some uncertainty due to limited performance in the strain/shear rate control of the rheometer. Thus, we used the data only at $t$ > 0.1 s where the performance was confirmed by monitoring developments of the strain/shear rate with time.

## III. Results and Discussion

**III.1. Determination of $T^*$.** For the freshly prepared PVC4/DOP system subjected to no strain (except a small, unavoidable strain when mounting the sample in the rheometer at 40 °C), Figure 1 shows dependence of linear viscoelastic, storage and loss moduli $G'(\omega)$ and $G''(\omega)$ on the angular frequency $\omega$. The moduli were measured from low temperature to high temperature. At the lowest and highest temperatures, the system behaves as a well-developed gel (for which $G'(\omega)$ tends to level off with decreasing $\omega$) and a sol (exhibiting the terminal flow behavior $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$),

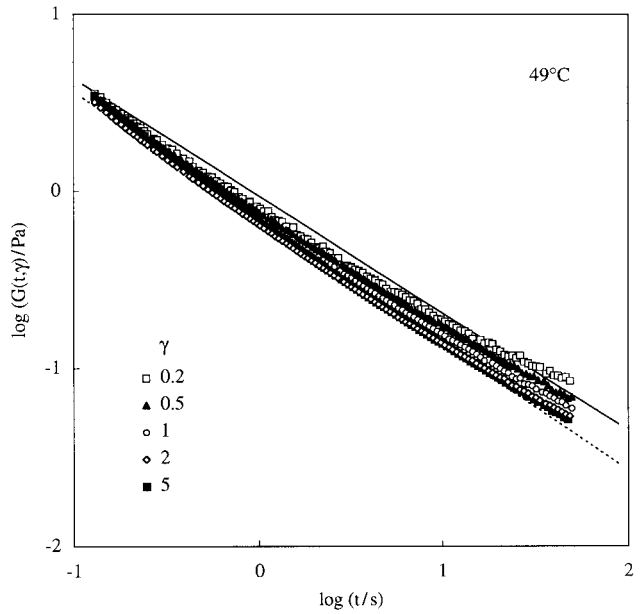


**Figure 2.** Nonlinear relaxation modulus $G(t,\gamma)$ for the PVC4/DOP critical gel ($c = 66$ g/L; $T^* = 49$ °C). The $G(t,\gamma)$ data were measured for the fresh gel in the order of increasing $\gamma$ so as to minimize mechanical disturbance prior to the measurement at respective $\gamma$. The solid and dotted lines, respectively, indicate the linear $G(t)$ for the fresh gel and the gel once subjected to the step-strain of $\gamma = 5$.

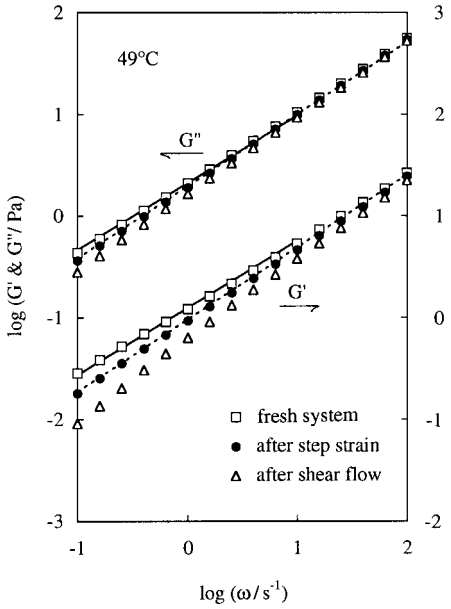


**Figure 3.** Linear viscoelastic moduli obtained for the critical PVC4/DOP gel in the fresh state (squares), after imposition of the step strain at $\gamma = 5$ (circles), and after subjected to shear flow at $\dot{\gamma} = 5$ s$^{-1}$ up to $\dot{\gamma}t = 40$ (triangles). The solid and dotted lines indicate the power-law type $\omega$ dependence of $G'$ and $G''$ for the first two cases.

respectively. Those data enable us to determine the critical gelation temperature $T^*$.

As demonstrated through extensive studies,[13,17,20−30] a critical gel generally exhibits a characteristic power-law relationship over a wide range of $\omega$

$$G'(\omega) = g\omega^n, \quad G''(\omega) = \tan(n\pi/2)\, g\omega^n \ (0 < n < 1) \quad (1)$$

Through a linear viscoelastic relationship,[31] the linear relaxation modulus $G(t)$ corresponding to eq 1 is given by

$$G(t) = S_g t^{-n}, \quad S_g = g/[\Gamma(1 - n)\cos(n\pi/2)] \quad (2)$$

Here, $\Gamma(x)$ is the $\Gamma$ function of $x$. The power-law type behavior of $G'(\omega)$, $G''(\omega)$ and $G(t)$ can be related with the self-similar fractal structure in the critical gel, i.e., the scale invariance of a magnitude of bifurcation (or a functionality of branching) of the gel network coarse-grained at various length scales.[27−30] The power-law index $n$ characterizes the fractal dimension reflecting this magnitude.[27−30]

Li and Aoki[17] defined $c_g$ for the PVC/DOP critical gel as a concentration where eq 1 holds. Following their definition, we determined $T^*$ of our PVC4/DOP gel to be 49 °C where the $G'(\omega)$ and $G''(\omega)$ data at $\omega < 10$ s$^{-1}$ are well described by eq 1 (solid lines in Figure 1) with the parameters

$$n = 0.66, \quad g = 1.26 \text{ Pa s}^{0.66} \quad \text{(for fresh PVC4/DOP gel at } T^*) \quad (3)$$

**III.2. Nonlinear Stress Relaxation at $T^*$. Overview.** Figure 2 shows the nonlinear relaxation modulus $G(t,\gamma)$ of the critical PVC4/DOP gel. The solid line indicates the linear $G(t)$ of the fresh gel calculated from eqs 2 and 3, and the dotted line represents $G(t)$ for an once-strained gel explained later for Figure 3.

A brief statement is necessary for these $G(t)$'s. For the fresh gel, $G'(\omega)$ and $G''(\omega)$ are described by the power-law relationship (eq 1) in a wide range of frequencies $\omega$, $0.1 \le \omega/\text{s}^{-1} \le 10$; see Figure 1. As explained later for Figure 3, the strained gel obeys this relationship even in a wider range, $0.1 \le \omega/\text{s}^{-1} \le 100$. Correspondingly, the $G(t)$'s of the fresh and strained gels are described by eq 2 in the range of $t$ examined in Figure 2. However, the PVC4/DOP gel should have the minimum size of its strands between the cross-linking domains (crystal domains), and the self-similarity in its fractal structure should vanish at length scales smaller than this size. This leads to the break down of the power-law behavior of $G(t)$ at short times below a cutoff time $t_0$: As judged from the above $\omega$ ranges where $G'$ and $G''$ exhibit a power-law dependence on $\omega$, we may estimate $t_0$ to be less than 0.1 and 0.01 s for the fresh and once-strained gels, respectively. These $t_0$ values are later utilized in analyses of the viscosity growth behavior.

As noted in Figure 2, the gel exhibits almost $\gamma$-independent $G(t,\gamma)$ at short $t$ (<0.5 s). On the other hand, at larger $t$, $G(t,\gamma)$ decreases a little with increasing $\gamma$, and a weak nonlinearity is observed. For the largest step-strain examined ($\gamma = 5$), the $G(t,\gamma)$ data were reproduced on successive application of this strain after an interval of 1 h.

To examine the nature of this damping behavior, we carried out linear viscoelastic measurements for the gel after the stress relaxation experiment at $\gamma = 5$. Figure 3 shows the $G'$ and $G''$ values obtained for this *once-strained* gel (filled circles). These moduli remained the same at least for 1 h after the stress relaxation experiment. For comparison, $G'$ and $G''$ are shown also for the fresh gel (subjected to no step-strain) and for the same gel subjected to shear flow (explained later for Figure 6).

In Figure 3, we first note that $G'$ and $G''$ are a little decreased after imposition of the large step-strain, $\gamma =$

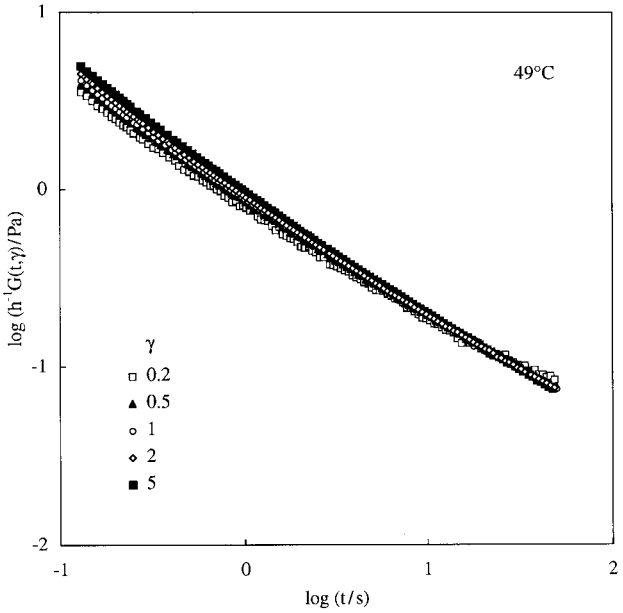


**Figure 4.** Reduced modulus $h(\gamma)^{-1}\,G(t,\gamma)$ for the critical PVC4/DOP gel ($c$ = 66 g/L; $T^*$ = 49 °C). The damping function $h(\gamma)$ was determined as a $G(t,\gamma)/G(t,0.2)$ ratio at an arbitrary chosen reference time, $t$ = 20 s. This $h(\gamma)$ enables excellent superposition of the reduced moduli for various $\gamma$ over a wide range of $t$ (>5 s).

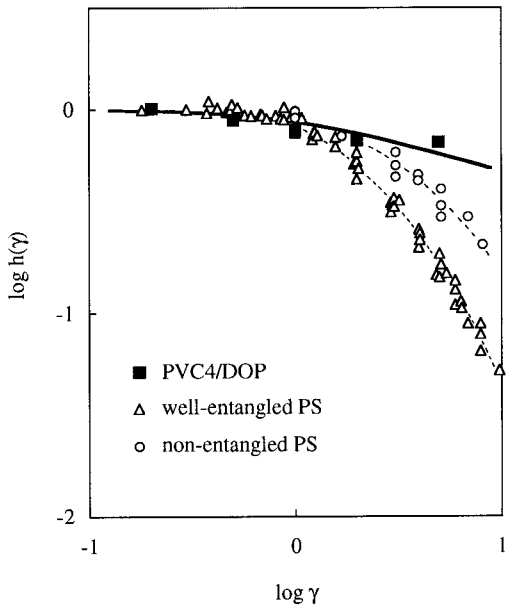


**Figure 5.** Comparison of damping functions $h(\gamma)$ for the critical PVC4/DOP gel (filled squares), well-entangled linear/star-branched polystyrene chains (with $M/M_e$ = 5−50; triangles),[32−34] and nonentangled linear polystyrene chains (with $M/M_e$ = 1 and 2; circles).[35] These polystyrene chains are in semidilute solutions.

5. In the entire range of $\omega$ examined, the $G'$ and $G''$ values of the once-strained gel are well described by the dotted lines that represent the power-law relationship (eq 1) with the parameters

$$n = 0.71, \quad g = 0.97 \text{ Pa s}^{0.71} \quad \text{(for once-strained PVC4/DOP gel at } T^*\text{)} \quad (4)$$

These results indicate that the large step-strain ($\gamma$ = 5) induces a small but definite change in the gel structure. This change, characterized by the difference between the parameters given in eqs 3 and 4, would correspond to a strain-induced change in the fractal dimension (magnitude of bifurcation of the gel strands). Concerning this point, the validity of eq 1 for the once-strained gel strongly suggests that the fractal nature of the gel structure itself is still preserved after imposition of the step-strain.

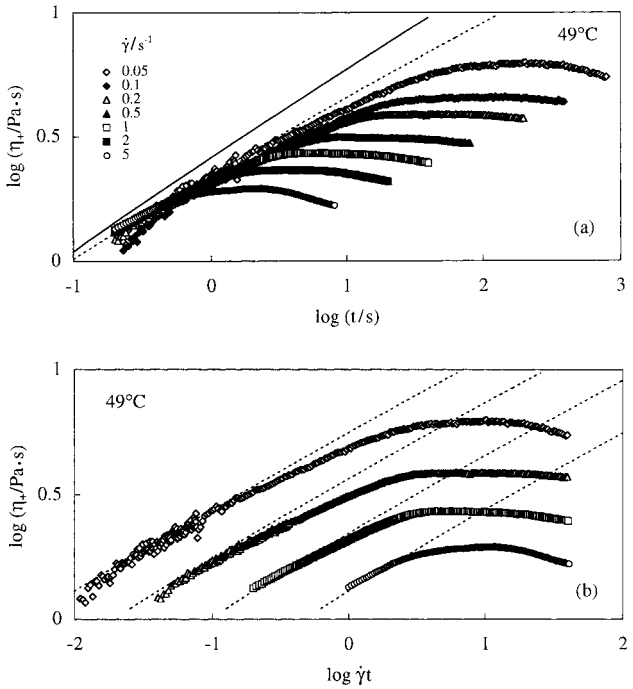


**Figure 6.** Viscosity growth function $\eta_+(t,\dot\gamma)$ for the critical PVC4/DOP gel ($c$ = 66 g/L; $T^*$ = 49 °C). In parts a and b, respectively, the $\eta_+(t,\dot\gamma)$ data are plotted against the time and strain ($\dot\gamma t$) after startup of shear flow. At all shear rates, the flow was applied up to a strain of $\dot\gamma t$ = 40. The $\eta_+(t,\dot\gamma)$ data were measured in the order of increasing $\dot\gamma$ for the gel once subjected to the step-strain of $\gamma$ = 5. The dotted and solid curves indicate the viscosity growth functions in the linear regime calculated for this once-strained gel and fresh gel, respectively.

For the once-strained gel, the linear $G(t)$ calculated from eqs 2 and 4 is shown in Figure 2 (dotted line). The $G(t,\gamma)$ data for $\gamma$ = 5 (filled squares) are very close to this $G(t)$. This fact strongly suggests that the damping of $G(t,\gamma)$ simply reflects strain-induced changes in the fractal structure. In other words, *the gel essentially exhibits linear behavior according to the structure at the respective* $\gamma$ values. This origin of damping is quite different from that for homogeneous polymeric liquids. This difference is quantified below.

**Damping Function.** As revealed from extensive experiments,[32−34] the terminal relaxation intensity of $G(t,\gamma)$ for entangled homopolymer chains is decreased but the relaxation time is not affected by large step-strains. This experimental fact is summarized as the time−strain separability

$$G(t,\gamma) = h(\gamma)G(t) \quad \text{for large } t \qquad (5)$$

Here, $G(t)$ is the linear relaxation modulus and $h(\gamma)$ is a damping function. For well-entangled chains having $M/M_e$ = 5−50 ($M_e$ = entanglement spacing), $h(\gamma)$ is universally dependent on $\gamma$ irrespective of the chain concentration and the topological structure (linear and/or star-branched). For nonentangled chains (with $M/M_e$

$< 2$), the time−strain separability still holds but the $\gamma$ dependence of $h(\gamma)$ becomes weaker and less universal.[32,35]

For the PVC4/DOP critical gel, the large step-strain changes the linear $G(t)$; cf. Figure 2. Thus the gel does not obey the time−strain separability in the usual sense. However, for the $G(t)$'s of the fresh and once-strained gel, the difference in the power-law indices $n$ is rather small; cf. eqs 3 and 4. Correspondingly, the relaxation rate of $G(t,\gamma)$ changes with $\gamma$ only slightly (cf. Figure 2). Thus, for the critical PVC4/DOP gel, we define $h(\gamma)$ as

$$h(\gamma) = G(t,\gamma)/G(t,0.2) \quad \text{at } t = 20 \text{ s} \tag{6}$$

where the $G(t,0.2)$ data for the smallest $\gamma$ examined ($=0.2$) are used as the reference data for evaluation of $h(\gamma)$, and $t = 20$ s is an arbitrarily chosen reference time.

Utilizing the $h(\gamma)$ thus obtained, Figure 4 compares the reduced $h(\gamma)^{-1}G(t,\gamma)$ data of the PVC4/DOP gel for $\gamma = 0.2-5$. Those data are well superimposed with each other over a considerably wide range of time, $t > 5$ s. This result indicates that the time−strain separability is *formally* valid for the critical PVC4/DOP gel to a very good approximation. At the same time, we have to again emphasize that the separability is not valid *in the usual sense*: The damping of the gel reflects the strain-induced changes in the linear $G(t)$; cf. Figure 3.

Figure 5 shows the $\gamma$ dependence of $h(\gamma)$ for the PVC4/DOP critical gel. For comparison, representative $h(\gamma)$ data are also shown for well-entangled linear and star-branched polystyrenes[32−34] and for nonentangled linear polystyrenes,[35] both in semidilute solutions. Clearly, the gel exhibits a much weaker $\gamma$ dependence of $h(\gamma)$ than the polystyrene solutions, even compared to the nonentangled solutions that exhibit just a modest damping.

**Origin of Weak Damping for the Critical Gel.** In general, polymer chains subjected to large step-strains exhibit the damping of their $G(t,\gamma)$ whenever the shrinkage (recovery of equilibrium length) is faster than the rotation (orientational relaxation). For the entangled linear/star-branched polymers, the difference between the shrinkage and rotation is well described by the tube model.[36] In fact, $h(\gamma)$ of this model, reflecting the decrease of stress due to the abandonment of some entanglement points and release of tension along the chain contour on the shrinkage in the tube, is in close agreement with the data (including those shown in Figure 5).[32−34,36] The damping seen for the nonentangled chains[32,35] strongly suggests that the shrinkage is faster than the rotation also for those chains, although no theory is available for quantitative description for this damping behavior.

In relation to the above molecular mechanism, the very weak damping of the critical PVC4/DOP gel (Figure 5) can be attributed to close coincidence of the shrinkage and rotational rates for the gel strands.[37] This coincidence can be related with the fractal structure in the critical gel. The gel strands sustaining the stress at long time scales are incorporated in the fractal network. For such a strand having both ends attached to cross-linking domains, the shrinkage and rotation (at length scales larger than the minimum strand size) would simultaneously occur at essentially the same rate. The very weak damping of the PVC4/DOP gel appears to be a natural consequence of this coincidence of the shrinkage and rotation rates.

Concerning this molecular picture, we have to remember the distinct feature of $G(t,\gamma)$ found in Figure 2. At long $t$, e.g., in a range of $t > 5$ s where the excellent superposition of the $h(\gamma)^{-1}G(t,\gamma)$ data is observed, the $G(t,\gamma)$ data for the largest step-strain ($\gamma = 5$) are in close agreement with the linear $G(t)$ obtained after imposition of this strain. This fact leads us to attribute the weak damping of the gel to the strain-induced changes in the fractal structure that possibly results from partial rupture of the PVC crystal domains (cross-linking domains). The $h(\gamma)$ merely reflects this structural change. If the shrinkage and rotation rates of the gels strands were significantly different, there could also be a contribution to $h(\gamma)$ from this difference. However, the $h(\gamma)$ data do not have this contribution and thus the shrinkage and rotation rates appear to be essentially the same. This result is in harmony with the above molecular picture.

In relation to these arguments, it would be of particular interest to examine the nonlinear damping of chemically cross-linked critical gels. In these gels, the cross-linking domains would not be ruptured and the fractal network structure would not change. Thus comparison of the $h(\gamma)$ data of the chemical and physical gels would enable us to further examine the origin of the damping for these gels. This is considered as important future work.

**III.3. Viscosity Growth Behavior. Overview.** For the PVC4/DOP critical gel, Figure 6 shows the viscosity growth function $\eta_+(t,\dot\gamma)$ at various $\dot\gamma$. All $\eta_+(t,\dot\gamma)$ data were obtained after the stress relaxation experiment at $\gamma = 5$. At respective $\dot\gamma$, $\eta_+(t,\dot\gamma)$ was measured up to a strain of $\dot\gamma t = 40$. In parts a and b, respectively, $\eta_+(t,\dot\gamma)$ are plotted against the time and strain after the startup of flow. For clarity of the figure, only representative data are shown in part b.

The viscosity growth function in the linear regime, $\eta_{+,\mathrm{L}}(t)$, is calculated from $G(t)$[31]

$$\eta_{+,\mathrm{L}}(t) = \int_0^t G(t')\,\mathrm{d}t' \tag{7}$$

As explained earlier, $G(t)$ of the PVC4/DOP gel should have the short time cutoff $t_0$ below which the power-law relationship (eq 2) is invalid. Thus we used eq 7 and calculated $\eta_{+,\mathrm{L}}(t)$, assuming that $G(t)$ has the following functional form:

$$G(t) = S_g t^{-n} \quad \text{for } t > t_0, \quad G(t) = S_g t_0^{-n} \quad \text{for } 0 \le t \le t_0 \tag{8}$$

The range of $t_0$ estimated earlier is $t_0 < 0.1$ s and $t_0 < 0.01$ s for the fresh and once-strained gels, respectively. In Figure 6, the solid and dotted curves indicate the $\eta_{+,\mathrm{L}}(t)$ for the fresh and once-strained gels calculated for $t_0 = 10^{-3}$ s. At $t = 1$ s, a difference between this $\eta_{+,\mathrm{L}}(t)$ and those calculated for any $t_0$ value in the above range was less than $\pm$ 25% and $\pm$ 10% for the fresh and strained gels. This difference rapidly decreases at longer $t$. Thus, at $t \ge 1$ s, the curves give a reliable basis for comparison of the $\eta_+(t,\dot\gamma)$ data with the linear $\eta_{+,\mathrm{L}}(t)$, in particular for the once-strained gel.

In part a of Figure 6, we note the linear viscosity growth behavior at short t: $\eta_+(t,\dot\gamma)$ for all $\dot\gamma$ commonly follow the linear $\eta_{+,\mathrm{L}}(t)$ for the once-strained gel and grow with time. (Since $\eta_+(t,\dot\gamma)$ were measured for the gel once subjected to the step-strain of $\gamma = 5$, $\eta_+(t,\dot\gamma)$ does not grow along the $\eta_{+,\mathrm{L}}(t)$ for the fresh gel.) At

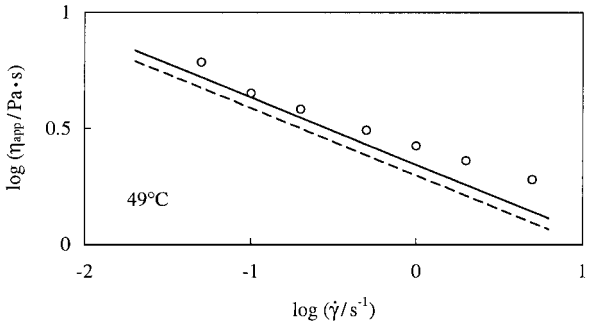


**Figure 7.** $\dot{\gamma}$ dependence of the apparent viscosity $\eta_{app}$ evaluated in the pseudo-steady regime for the critical PVC4/DOP gel ($c$ = 66 g/L; $T^*$ = 49 °C). The dashed and solid lines, respectively, show the $\omega$ dependence of $\eta'(\omega)$ and $|\eta^*(\omega)|$ (both proportional to $\omega^{-0.29}$) for the gel once subjected to the step-strain of $\gamma = 5$.

longer $t$, we clearly observe the nonlinear behavior: $\eta_+(t,\dot{\gamma})$ becomes dependent on $\dot{\gamma}$ and deviate downward from the linear $\eta_{+,L}(t)$. In this nonlinear regime, $\eta_+(t,\dot{\gamma})$ first keeps increasing gradually and then exhibits an apparent plateau (pseudo-steady-flow behavior) over a wide range of $t$ (e.g., for $t = 50-200$ s at $\dot{\gamma} = 0.1$ s$^{-1}$), but finally decreases with a further increase of $t$. Thus, no real steady flow is achieved for the gel at the long time end where the strain $\dot{\gamma}t$ reached 40. This behavior is qualitatively different from that seen for homogeneous homopolymer liquids.

Here, we examine the behavior of $\eta_+(t,\dot{\gamma})$ of the gel in the pseudo-steady regime. In Figure 7, an apparent viscosity $\eta_{app}(\dot{\gamma})$ ($=\eta_+(t,\dot{\gamma})$ in this regime) is plotted against $\dot{\gamma}$. The dashed and solid lines, respectively, represent the $\omega$ dependence of the dynamic viscosity and the magnitude of the complex viscosity, $\eta'(\omega) = G''(\omega)/\omega$ and $|\eta^*(\omega)| = [G'(\omega)^2 + G''(\omega)^2]^{1/2}/\omega$, determined from the linear viscoelastic measurements for the once-strained gel (cf. Figure 3). At low $\dot{\gamma}$ ($\leq$0.2 s$^{-1}$), $\eta_{app}(\dot{\gamma})$ is pretty close to $|\eta^*(\omega)|_{\omega=\dot{\gamma}}$ and the empirical Cox−Merz rule[38] is superficially valid. This result might suggest some similarity between the gel in the pseudo-steady regime at such low $\dot{\gamma}$ and homogeneous homopolymer liquids, the latter obeying this rule in the real steady state up to considerably large $\dot{\gamma}$. However, the gel exhibits a systematic deviation from the Cox−Merz rule at larger $\dot{\gamma}$, again demonstrating a difference from the behavior of those liquids.

**Characteristic Nonlinear Features in Viscosity Growth.** Characteristic features of $\eta_+(t,\dot{\gamma})$ can be found in part b of Figure 6. For $\eta_+(t,\dot{\gamma})$ under slow flow ($\dot{\gamma} \leq$ 0.2 s$^{-1}$), the onset of nonlinearity (deviation from $\eta_{+,L}$), the onset of the pseudo-steady behavior, and the onset of decrease are characterized with $\dot{\gamma}$-insensitive strains $\gamma_n$ ($\cong$ 0.2), $\gamma_p$ ($\cong$ 3), and $\gamma_d$ ($\cong$ 15), respectively. Thus the nonlinearity under the slow flow is governed by the strain. In this sense, $\eta_+(t,\dot{\gamma})$ for small $\dot{\gamma}$ exhibits a qualitative similarity with $G(t,\gamma)$. The damping for $G(t,\gamma)$ is related to changes in the fractal gel structure that possibly result from partial rupture of the cross-linking domains (PVC crystal domains) due to the step-strains. Similarly, the nonlinearity of $\eta_+(t,\dot{\gamma})$ under the slow flow would reflect flow-induced structural changes in the gel (once strained at $\gamma = 5$ prior to the flow), and these changes appear to be determined by the strain $\dot{\gamma}t$. From this point of view, $\gamma_n$ can be assigned as a strain required for rupture of the cross-linking domains in this gel.

The situation is somewhat different under fast flow ($\dot{\gamma} \geq 1$ s$^{-1}$). Although $\gamma_p$ and $\gamma_d$ are nearly the same under the fast and slow flow, $\gamma_n$ increases with increasing $\dot{\gamma}$ under the fast flow; $\gamma_n \cong 0.5$ and 2 for $\dot{\gamma} = 1$ and 5 s$^{-1}$ (see squares and circles in part b of Figure 6). A time $t_n$ corresponding to these $\gamma_n$ does not change much with $\dot{\gamma}$; $t_n = \gamma_n/\dot{\gamma} \cong 0.5$ and 0.4 s for $\dot{\gamma} = 1$ and 5 s$^{-1}$, respectively. These results suggest that the cross-linking domains begin to be disrupted when *both* strain and time exceed the critical values $\gamma_n \cong 0.2$ and $t_n \cong$ 0.5 s.

On the basis of this molecular picture, we may explain features for the onset of nonlinearity under the flow and step-strains from a common point of view: Under the fast flow, $\dot{\gamma}t$ already exceeds $\gamma_n$ when $t$ reaches $t_n$ so that the onset of nonlinearity for $\eta_+(t,\dot{\gamma})$ is characterized with the time $t_n$. Similarly, the nonlinearity against large step-strains ($\gamma \geq \gamma_n$) is considered to emerge only when $t$ exceeds $t_n$: Interestingly, the $G(t,\gamma)$ data actually exhibit the nonlinear damping only at $t$ well above $t_n \cong$ 0.5 s; see Figure 2. In contrast, under the slow flow, $t$ already exceeds $t_n$ when $\dot{\gamma}t$ reaches $\gamma_n$. For this case, the strain $\gamma_n$ characterizes the onset of nonlinearity for $\eta_+(t,\dot{\gamma})$.

Concerning the flow-induced rupture of the crystal domains discussed above, we note in Figure 3 that the fast flow at $\dot{\gamma} = 5$ s$^{-1}$ applied up to the strain of $\dot{\gamma}t = 40$ results in decreases of linear viscoelastic moduli; see the circles and triangles. This decrease is comparable in magnitude with that induced by the step-strain of $\gamma =$ 5 (see the squares and circles), despite a fact that $\eta_+(t,\dot{\gamma})$ decreases for $\dot{\gamma}t > \gamma_d$ ($\cong$15) and the crystal domains appear to be rather massively disrupted under the fast flow at those $\dot{\gamma}t$. This result suggests that the domains are recovered to some extent after cessation of the flow. This recovery is an interesting subject for future work.

## IV. Concluding Remarks

For the PVC4/DOP critical gel, we have found weak damping of $G(t,\gamma)$ that is attributable to modest changes in the fractal structure of the gel due to strain-induced partial rupture of the PVC crystal domains. This damping mechanism is quite different from that for homogeneous polymeric liquids, the recovery of equilibrium contour length occurring faster than the orientational relaxation. This difference can be naturally related with the heavily bifurcated fractal structure of the critical gel network.

Under flow, the gel exhibits nonlinearities of $\eta_+(t,\dot{\gamma})$ attributable to flow-induced rupture of the crystal domains. Specifically, the onset of nonlinearity for $\eta_+(t,\dot{\gamma})$ is characterized with both strain ($\gamma_n \cong 0.2$) and time ($t_n \cong$ 0.5 s) that possibly correspond to the minimum strain and time required for the rupture of those domains. This feature of $\eta_+(t,\dot{\gamma})$ is in harmony with that of $G(t,\gamma)$.

It is of interest to further study the nonlinear nature of the gels in relation to these strain/flow effects on the gel structure. Of particular interest is the comparison of the nonlinear behavior of chemical and physical gels, the former having very stable cross-linking domains, and thus flow/strain should have negligible effects on the fractal structure. This comparison is considered as important future work.

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