with silanol causes a lack of silanol in the polymerization system and decreases the catalyst activity.[3] In the case of (Al-I), the formation of the Si–O–Al linkage is presumed to be very small compared with the case of (Al-II) and (Al-III). Therefore, the decrease of silanol by reaction between the aluminum complex and silanol must be negligible. On the other hand, in the case of (Al-II) and (Al-III), a part of the silanol reacts with a part of the aluminum complex even in the dark, and the amount of the silanol that does not react with the aluminum complex is determined by the equilibrium constant. However, when UV light is used, presumably, there is a lack of silanol in the polymerization system because the reaction of silanol with (Al-II) or (Al-III) is promoted under UV radiation. We tried to find an increase in the ligand-exchange reaction after UV irradiation by use of ^{1}H NMR spectroscopy. However, there was no difference in the ratio before and after UV radiation. The ratio of the ligand exchange under UV irradiation might change immediately to that measured in the dark, even if the ligand-exchange reaction is promoted under UV irradiation. There is no evidence on ligand exchange under UV radiation; however, it might be possible under UV radiation if the aluminum complex is labile under UV radiation.[7]

In conclusion, this paper reports the fact that polymerization proceeds faster under UV radiation only when a catalyst with a definite structure is used. The difference in polymerization behavior supports the difference in initiation mechanism, which was already reported.

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Comparison of the Pure Reptational Times Calculated from Linear Viscoelasticity and Diffusion Motion Data of Nearly Monodisperse Polymers

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Received March 26, 1985

A recently proposed general linear viscoelastic theory[1] indicates that the primitive chain contour length fluctuation (the $\mu_B(t)$ process) is responsible for the most part for stress decline in the plateau region of a step strain–stress relaxation. In the terminal region, the observed reptational motion is modified because of the same chain length fluctuation effect. From an analysis of the linear viscoelastic relaxation data of nearly monodisperse polymers in terms of the general theory, it was shown that these effects due to chain contour length fluctuation are the major factors causing the difference between the observed molecular weight (MW) dependence of zero-shear viscosity ($\eta_0 \propto M^{3.4}$) and that predicted by the reptational chain model ($\eta_0 \propto M^3$). In the low-MW region ($M_w < 7M_e$) two additional fast dynamic processes, the Rouse chain motion between two cross-linked points and the chain slippage through entanglement links, need be included. Furthermore, it was concluded that the constraint release effect on the linear viscoelastic relaxation is negligible as far as a very narrow molecular weight distribution (MWD) is concerned.

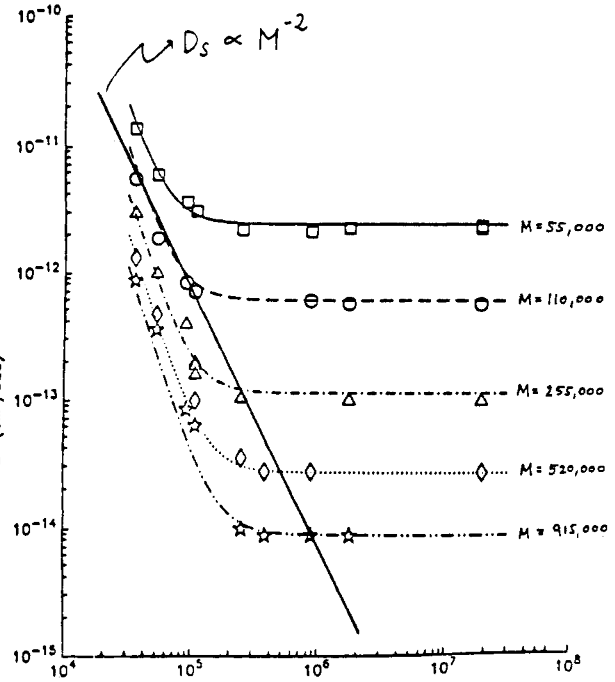

Figure 1. Tracer diffusion constant D of deuterated polystyrene of molecular weight M diffusing in polystyrene of molecular weight P vs. P (Reprinted with permission from ref 2. Copyright 1984 The American Physical Society). The straight line indicating the molecular weight dependence of the self-diffusion constant, D_S, has a slope of −2 (see text).

In this report, the pure reptational times at different MW's are calculated from the polymer diffusion constants obtained recently by Kramer's group at Cornell University using forward recoil spectrometry[2] and compared with those calculated from the linear viscoelastic results analyzed and reported previously.[1] Very good agreement has been obtained between these two different types of measurements, which were done independently. In the comparison, the physical significance of the relaxation times, especially as related to the possible role played by the constraint release in different conditions, is described.

Kramer et al. have measured the diffusion motion of a thin layer of a deuterated polystyrene (the labeled molecules) into a hydrogenated polystyrene base (the matrix). In their thorough study, they have varied both the MW of the labeled polymer and the matrix polymer. For a labeled polymer, if the MW of the matrix polymer is higher than a certain value (P_c), the measured diffusion constant is independent of the matrix MW. In other words, in such

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Table I
Comparison of $\tau_C{}^0$ and T_d Calculated from the Linear Viscoelasticity and Diffusion Motion Data, Respectively, and Ratios of $\tau_C{}^0$ and the Actually Observed Reptation Time τ_C (Containing the Chain-Length Fluctuation Effect) at Different Molecular Weights

MW	τ_C	$\tau_C{}^0$	$\tau_C{}^0/\tau_C$	D_G	T_d	$T_d/\tau_C{}^0$
55 000	6.96×10^{-3}	2.71×10^{-2}	3.9	2.5×10^{-12}	3.42×10^{-2}	1.26
110 000	0.092	0.217	2.35	5.9×10^{-13}	0.29	1.33
255 000	1.6	2.7	1.68	1.1×10^{-13}	3.6	1.33
520 000	16.1	22.9	1.42	3×10^{-14}	26.9	1.17
915 000	96.6	125	1.29	9×10^{-15}	158	1.26

a case, constraint release does not affect the diffusion motion of the labeled polymer. If the MW of the labeled polymer is high, P_c is lower than its value. In the low-MW region (M_w <100 000), P_c is higher than the M_w of the labeled polymer. A figure showing their results is reproduced here (Figure 1). Except for the labeled polymer of lowest M_w, the self-diffusion constant, D_S (i.e., for the case that the MW's of the labeled and the matrix polymers are identical), follows the scaling law

$$D_S \propto M^{-2} \tag{1}$$

predicted by the reptational chain model.[3-6] A straight line (passing through the points where matrix MW = labeled MW) showing the scaling law is drawn in Figure 1.

In a recent line shape analysis of stress relaxation moduli of samples in the MW range 422 000–16 700 ($31M_e$–$1.24M_e$) of polystyrene,[7,8] it was shown that the ratio ζ'/ζ (i.e., the ratio of the friction coefficients for a segment to move in the direction perpendicular to the chain contour (ζ') vs. along the chain contour (ζ)) decreases from a plateau value of 3.3 to another plateau value of 1 with decreasing MW, while ζ is independent of MW. The decrease of the ζ' value with decreasing MW is associated with the concentration of chain ends that possess extra local free volume.

As shown in Figure 1, it appears that constraint release affects the D_S value at the lowest MW ($M_w \approx 55 000$) of the studied samples. Since constraint release allows the polymer chain to move in the direction perpendicular to the chain contour, the correction for iso-free-volume should make the D_S value of the low-MW sample much closer to the $D_S \propto M^{-2}$ line.

In the Doi–Edwards model,[3-6] the polymer chain undergoing the reptation motion has a constant primitive chain length, and the MW dependence of the pure reptation time is given as

$$\tau_C{}^0 = KM^3/M_e \tag{2}$$

with K being independent of MW and given as

$$K = \zeta b^2 N_0{}^2/kT\pi^2 M^2 \tag{3}$$

where ζ, b, and M/N_0 are the friction constant, length, and mass associated with each Kuhn segment.

In the proposed general linear viscoelastic theory,[1] by taking the chain-length fluctuation effect into account, the observed reptation time, τ_C, in the linear viscoelastic relaxation is derived as

$$\tau_C = (KM^3/M_e)[1 - (M_e/M)^{1/2}]^2 \tag{4}$$

The chain-length fluctuation is an intramolecular motion and in self-diffusion should have no effect on the movement of the center of mass of the polymer. For this reason, the diffusion constant is totally insensitive to chain-length fluctuation and is related to the pure reptation time $\tau_C{}^0$ by the equation

$$D_G = R^2/3\pi^2\tau_C{}^0 \tag{5}$$

from the Doi–Edwards theory, where R is the end-to-end distance of the polymer and D_G is the polymer diffusion constant free from the constraint release effect. As shown in Figure 1, the plateaus are the D_G values at the specified MW's. As explained above, $D_G = D_S$ for the labeled polymers of high MW. With the R^2 value known ($R^2 = 0.46 \times 10^{-16} M$),[9,10] the measured D_G values can be used to calculate the pure reptation time $\tau_C{}^0$ (denoted as T_d below for the values calculated from D_G values at different MW's.)

Although we observe the modified reptational process (eq 4) in a linear viscoelastic relaxation, the obtained K and M_e values from the stress relaxation line shape analysis[1] can be used to calculate the pure reptation time $\tau_C{}^0$ for comparison with T_d calculated from D_G.

The K and M_e values have been obtained at 154 and 185 °C as listed in Tables I and II of ref 1. From the obtained K and M_e values, the $\tau_C{}^0$ values at the MW's of the labeled polymers used in the diffusion measurement are calculated according to eq 2. The obtained $\tau_C{}^0$ values at the two temperatures are then used to calculate the $\tau_C{}^0$ values at 170 °C (the temperature at which the diffusion measurements were made) by interpolation through a WLF plot with $T_\infty = 69$ °C.[11] As listed in Table I, the calculated $\tau_C{}^0$ and T_d values are in very good agreement. The choice of the T_∞ value has a very small effect on the obtained $\tau_C{}^0$ values. Using an Arrhenius interpolation (equivalent to $T_\infty = 0$ K), the average $T_d/\tau_C{}^0$ ratio is about 1.1.

In the high-MW regions (M_w > 100 000), the self-diffusion constant D_S is free from any constraint release effect. The analysis of the linear viscoelastic data also indicates that the constraint release effect is negligible for nearly monodisperse MWD as assumed in the Doi–Edwards and the general linear viscoelastic theories. The good agreement between $\tau_C{}^0$ and T_d further confirms this conclusion. In addition, this is not contradicted but rather supported by only a small constraint release effect on the D_S values at low MW's.

As we know now, in linear viscoelastic relaxation we observe the modified reptational relaxation process characterized by the relaxation time τ_C. The ratio $\tau_C{}^0/\tau_C$ becomes quite large at low MW. Also listed in Table I are the values of τ_C and $\tau_C{}^0/\tau_C$. At M_w = 55 000, the $\tau_C{}^0/\tau_C$ value is as large as 3.9. On the other hand, if we make the correction for iso-free-volume to the D_S value at MW = 55 000 by a factor of 0.55 (i.e., the ratio of the ζ'/ζ value at MW = 55 000 and $\zeta'/\zeta = 3.3$ at high MW),[7,8] the D_S data point becomes only slightly higher (~30%) than the $D_S \propto M^{-2}$ line in Figure 1. As a result, the observed linear viscoelastic relaxation should still be free from the constraint release effect in the low-MW region (see the note in ref 21 in ref 7). This conclusion has also been reached directly from the stress relaxation line shape analysis for samples in the low-MW region.[7,8]

It is important to emphasize the differences in physical properties probed by the two methods. In linear viscoelastic relaxation, what is measured is the extent of relaxation of the stress on the tube (of the reptational chain model). The stress can be totally relaxed, mostly through chain-length fluctuation, even though the center of mass of the polymer has not diffused more than a fraction of its end-to-end distance.

The relaxation of the tube stress through either reptation or chain-length fluctuation cannot happen without disentanglement of a neighboring chain. The unimportance of the constraint release in a linear viscoelastic relaxation of a monodisperse polymer indicates that such a disentanglement mainly occurring in a middle section of a chain does not cause immediate relaxation of stress or randomization of orientation in this part of tube (i.e., other than the tube ends). In other words the relaxation of stress in the middle part of a chain through disentanglement of a neighboring molecule is not as effective as through its own reptation or chain-length fluctuation at both ends of the tube. In the study of linear viscoelasticity of blend systems consisting of two nearly monodisperse components, the same effect was observed.[12]

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Communications to the Editor

Phase Transition of a Cationic Gel

First referred to by Flory,[1] the tremendous swelling behavior of ionic gels has been studied by Tanaka and other researchers and led our attention to the phase transition of ionic gels. Nowadays, the phase transition has gained wider acceptance with the various findings of novel phenomena and theories.[1–13] Tanaka et al. have demonstrated that ionized polyacrylamide gels, under certain conditions, undergo discrete, reversible transitions in equilibrium volume with changes in solvent composition (acetone–water mixtures),[4–6] temperature,[7–10] pH,[10] salt concentration and species,[6] and electric field.[11] The above behavior can be taken as a phase transition between the swollen gel and the shrunken gel. The phase transition is governed by the sum of three terms: the osmotic pressure, which arises from the elasticity of the gel, the interaction between gel polymer networks, and the thermal motion of counterions in the ionic gel.[9]

Ilavsky et al.[5] reported a similar phase transition in acetone–water mixtures, using diethylacrylamide–sodium methacrylate copolymer gels. However, these conventional approaches to the phase transition of ionic gels were all limited to anionic, or negatively charged, gels. Therefore, whether cationic, or positively charged, gels undergo the same phase transition as anionic gels is one of the important current questions in this field. We report here the phase transition of a cationic gel in acetone–water mixtures, having examined temperature and solvent composition dependencies.

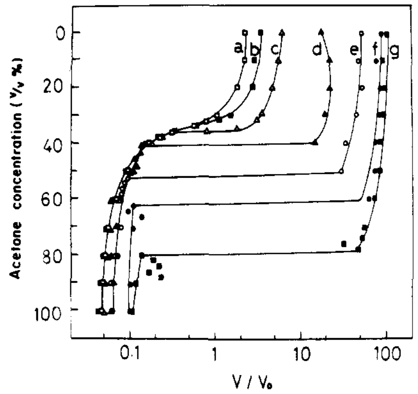

Figure 1. Equilibrium degree of swelling of cationic gels consisting of acrylamide (1 g), *N*,*N*′-methylenebisacrylamide (26.6 mg), and various amounts of trimethyl(*N*-acryloyl-3-aminopropyl)ammonium iodide: (a) 0 mg; (b) 3.2 mg; (c) 12.7 mg; (d) 50.7 mg; (e) 101.4 mg; (f) 405.8 mg; (g) 1902.1 mg.

Cationic gel samples used in the present experiment were prepared in the following way. Acrylamide (1 g) (the linear constituent), trimethyl(*N*-acryloyl-3-aminopropyl)ammonium iodide (TMAAPAI, 3.2–1902.1 mg) (the ionic component), *N*,*N*′-methylenebisacrylamide (BIS, 26.6 mg) (the cross-linking consitutent), and 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50, 80 mg) (the initiator) were dissolved in distilled water to a final volume of 20 mL. Gel samples with the desired ion density were obtained after gelation of the solutions at 60 °C for 1 h. TMAAPAI was made by reacting ((dimethylamino)propyl)acrylamide (DMAPAA) with methyl iodide. DMAPAA was obtained from Kojin Co. Ltd.

The sample preparation procedure is mostly the same as in previous works.[6,8–13] The prepared gels were washed in water and placed in acetone–water mixtures of various compositions. After the gels had reached equilibrium, the diameters of each cylindrical gel were measured.

Figure 1 shows the relationship of acetone concentration to the swelling ratio, V/V_0. The quantity V/V_0 represents the ratio of the final network volume to initial network volume for the cationic gels. The ratio is given by $(d/d_0)^3$, where d_0 and d are the initial and final equilibrium diameters of the gel, respectively. For swollen gels $V/V_0 > 1$,

0024-9297/85/2218-2781$01.50/0