Chain Contraction and Change in Entanglement Structure of Well-Entangled Polymer in Large Shearing Deformations

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Introduction. Viscoelastic properties of well-entangled polymers can be expressed by two parameters, i.e., the plateau modulus and the maximum relaxation time even outside the range of linear viscoelasticity.[1] The former, a measure of the entanglement structure, can be given by measurements of the differential dynamic modulus by means of oscillatory deformations superposed on a large deformation.[2−7]

In previous works, there was found correspondence between nonlinear viscoelastic response and change in the entanglement structure.[3−7] The entanglement structure shows no change in the range of linear viscoelasticity,[2,3,5,7] while it really changes with the strain given to the material in large shearing deformations.[3−7] The change in the entanglement structure was confirmed to be irreversible in reversing double-step large shearing where the second strain, γ_2, is separated from the first, γ_1, by an interval of time, t_1, which is equal to or longer than a characteristic time τ_k, after which so-called time-strain factorability holds in the relaxation modulus.[4] Such irreversibility is important in understanding the nonlinear viscoelasticity of well-entangled polymers, as has been discussed by Wagner.[8−11] Doi has explained that a nonlinear stress relaxation arises from chain contraction during the equilibration process.[12] The chain contraction is considered to finish at a time scale τ_k. Hence, the irreversible change in the entanglement structure may arise from the chain contraction. If this is true, the reversible change will be observed when the second reversing strain is given at $t \ll \tau_k$.

The purpose of this work is to test the idea of the effect of chain contraction on the irreversible change in the entanglement structure.

Experimental Section. The sample is a polybutadiene, PVB-48, prepared by an anionic polymerization technique. The values of weight-average molecular weight, $\bar{M}_w$, and the ratio of the weight-average to number-average molecular weights, $\bar{M}_w/\bar{M}_n$, were determined to be 4.8×10^5 and 1.1_3 by a light scattering method and gel permeation chromatography, respectively. The content of the 1,2-structure of the sample was 68%. Taking the molecular weight between entanglements, M_e, as 3600, the number of entanglements per molecule of the sample is 1.3×10^2. The sample was used at the undiluted state. Figure 1 shows the dynamic modulus and loss tangent master curves of the sample PVB-48 in linear viscoelasticity at −5 °C. The arrow denotes the frequency of the superposed small oscillations. We note that the present measurements of the differential dynamic modulus are made in the rubbery plateau.

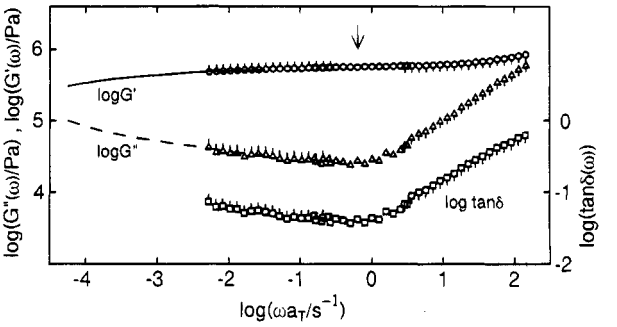

Figure 1. Dynamic modulus and loss tangent master curves for the undiluted 1,2-polybutadiene PVB-48 at −5 °C. Open circles denote the data at −5 °C. Circles with pip up obtained at −18.5 °C were shifted by log $a_T = -1.48$. Circles with pip down at −17 °C were shifted by log $a_T = 1.16$. The solid and broken lines denote the storage and loss moduli converted from the shear relaxation modulus for the same sample, respectively. The arrow denotes the frequency of the superposed small oscillations (log $\omega = -0.2$, $\nu = 0.1$ Hz).

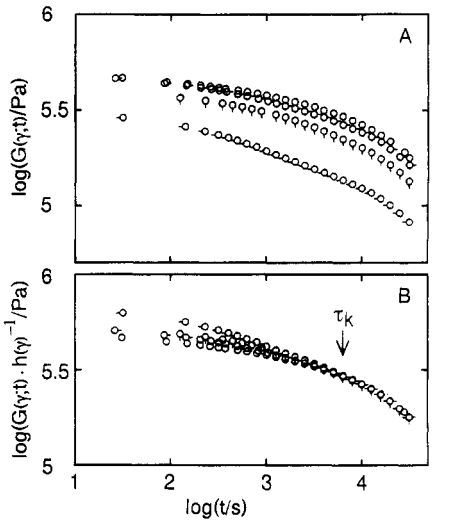

Figure 2. (A) Double-logarithmic plots of $G(\gamma,t)$ against t for four different strains: no pip, $\gamma = 0.1$; pip right, $\gamma = 0.5$; successive 90° rotations clockwise, 1.0 and 2.0. (B) Double-logarithmic plots of reduced relaxation modulus $G(\gamma,t)/h(\gamma)$ for the data in A against t.

The apparatus, a Weissenberg Rheogoniometer R-18 (Sangamo Controls Ltd.), and the geometry of deformation were the same as in the previous works.[3,4,6] All the measurements were made at −5 °C. Not only single-step but also double-step finite shear deformations were applied to the sample. In the single-step experiments, the static shear strain varied from 0.1 to 2.0. In the reversing double-step experiments, the first strain, $\gamma_1 = 1.0$, was applied at a time $-t_1$, followed by the second strain, $\gamma_2 = -1.0$, at time zero. The times t_1 selected were 500 and 7000 s.

Results and Discussion. Figure 2A shows the double-logarithmic plots of the relaxation modulus, $G(\gamma,t)$, against time for various strains. The curves can be shifted vertically to be superposed at a long-time region as shown in Figure 2B. Hence, $G(\gamma,t)$ can be factored into strain-dependent and time-dependent terms at the long-time region as expected.[3,14−20]

$$G(\gamma,t) = h(\gamma)\, G(0,t) \qquad (1)$$

The values of log $h(\gamma)$ at $\gamma = 0.1$, 0.5, 1, and 2 were 0, −0.04, −0.11, and −0.33, respectively. These values

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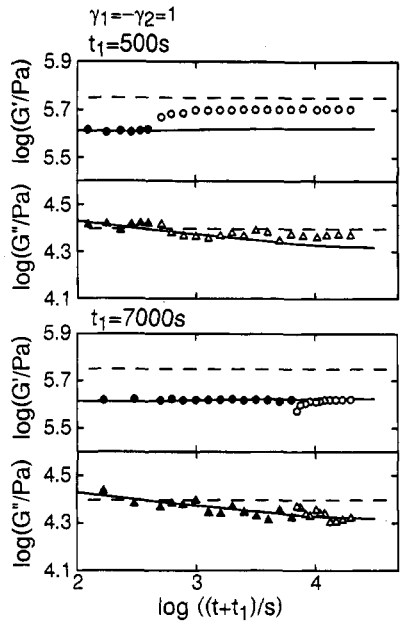

Figure 3. Double-logarithmic plots for differential dynamic moduli against $t + t_1$ for $t_1 = 500$ s (upper panels) and $t_1 = 7000$ s (lower panels). $\gamma_1 = -\gamma_2 = 1.0$. Filled circles and filled triangles denote $G'(\omega,\gamma_1;t+t_1)$ and $G''(\omega,\gamma_1;t+t_1)$, respectively. Open circles and open triangles denote $G'(\omega,\gamma_1,\gamma_2;t_1,t)$ and $G''(\omega,\gamma_1,\gamma_2;t_1,t)$, respectively. The solid lines denote differential storage and loss moduli data in a single-step deformation of $\gamma = 1.0$ observed in this work. The broken lines denote $G'(\omega,0)$ and $G''(\omega,0)$ measured before shearing.

obtained are very close to the theoretical values predicted by Doi and Edwards without the use of the independent alignment approximation.[13] Such agreement was also observed for polydisperse polyisobutylenes of $N (=CM/M_e) > 130$.[3,6,7] Our data on $h(\gamma)$ for the sample of $N > 130$ contrast with those observed by Osaki et al.,[15,18] Vrentas and Graessley,[19] and Larson et al.[20] They have reported that the experimentally observed $h(\gamma)$ is much smaller than the theoretical prediction, if $N > 50$, despite the fact that the Doi–Edwards theory should be more valid in the higher molecular weight sample. The data on $h(\gamma)$ for polybutadienes having various molecular weights will be reported elsewhere.

From Figure 2B, the characteristic time, τ_k, after which the strain-dependent relaxation modulus can be written by eq 1, is found to be around 6300 s ($\log \tau_k \sim 3.8$). Hence, chain contraction may have finished after 6300 s.

An experimental comparison between differential dynamic moduli after imposition of the second and first strains for two different time intervals is shown in Figure 3. The time intervals, t_1, were 500 and 7000 s in the upper and lower panels, respectively. The values of differential dynamic moduli after imposition of the first and second strains are denoted by filled and open symbols, respectively. The former data (filled symbols) were in good agreement with the data of the differential dynamic modulus in a single-step deformation of $\gamma = 1.0$ shown by the solid lines, which were observed in the additional experiment.

When $t_1 = 7000$ s, which corresponds to the time scale τ_k, the G' curve in the second strain is lower than or coincides with the curve in a single-step deformation of $\gamma = 1.0$. The differential loss modulus changed in a similar way to the differential storage modulus, though the data on G'' were somewhat less precise. The feature of the result in the lower panel is consistent with the previous result for polyisobutylene having high molecular weight in the case of $t_1 \sim \tau_k$.[4] Furthermore, such irreversibility in the entanglement structure change was observed in the case of $t_1 \gg \tau_k$ too.[4]

In the case of $t_1 = 500$ s ($\ll\tau_k$), however, both the G' and the G'' curves in the second strain are higher than the solid lines. The results mean that the entanglement structure recovers by the second strain γ_2 imposed with time interval $t_1 \ll \tau_k$ in the opposite direction to the first strain γ_1 but does not recover by γ_2 imposed with $t_1 \sim \tau_k$ or $t_1 > \tau_k$.

It may be concluded that the irreversible change in the entanglement structure in a large step-shear arises from chain contraction.

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