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Stress relaxation and change in entanglement structure of polyisobutylene in large shearing deformations

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Simultaneous measurements of stress relaxation and differential dynamic modulus were made at 20°C for polyisobutylene in large shearing deformations on which intermittent small oscillations were superposed perpendicularly. Static shear strain varied from 0.1 to 1.0 while the frequency of the superposed oscillations was 0.1 Hz, which falls in the middle of the plateau zone of the polymer. The strain dependence of the differential dynamic modulus was found to coincide with the damping function in relaxation modulus which is well explained by the Doi–Edwards theory. It was concluded that non-linear behaviour in relaxation modulus results from a change in entanglement structure.

(Keywords: stress relaxation; non-linear viscoelasticity; differential dynamic modulus)

INTRODUCTION

In dense polymer liquids of high molecular weight, the polymer molecules are entangled with each other, forming a quasi-network structure[1–3]. The viscoelastic properties of such well entangled polymers can be expressed by two parameters, i.e. the plateau modulus and the maximum relaxation time[4]. The former is a measure of the entanglement structure. In linear viscoelasticity, it is a measure of mesh size of the entanglement network[5].

The entanglements may be dissolved and re-formed continuously. In the range of linear viscoelasticity, the dissolution and re-formation are balanced. Hence the density of entanglement remains constant[6–8]. In the non-linear range of viscoelasticity under large strain and/or high strain rate, however, not only is the polymer coil distorted but also the entanglement density may change due to imbalance of dissolution and re-formation of entanglements. For a large step strain, for example, the relaxation modulus depends on strain. However, the maximum relaxation time has been proved to be independent of strain even outside the range of linear viscoelasticity[4]. These facts imply that the height of the rubbery plateau changes in the non-linear range of viscoelasticity. Hence the change in entanglement structure due to external stimuli may be important in understanding non-linear viscoelasticity.

Such a change in entanglement structure can be monitored by measuring the differential dynamic modulus by means of oscillatory deformations superposed on a large deformation. In superposing small oscillatory shears on a large shearing deformation, we have two directions for superposition: parallel and perpendicular to the shearing plane of the large deformation. Adopting parallel superposition in previous works[7–10], it was found that the entanglement structure does indeed change with the strain given to the material.

In this work, we adopt perpendicular superposition. The purpose of this work is to study non-linear stress relaxation and change in entanglement structure using perpendicular differential dynamic modulus as a probe.

EXPERIMENTAL

A sample of commercial polyisobutylene, L-100, was generously offered by Exxon Chemicals Co. Viscosity-average molecular weight was determined[7] to be 1.2×10^6. The sample was used in the undiluted state.

In this work, a Pochetitino type and Couette type of shear deformation were adopted for large shearing and small oscillatory shearing, respectively. The special device for combination of the two types of deformation was the same as that used in previous work[8]. The device consists of an inner bob and an outer cup which can move independently. The Pochetitino-type and Couette-type shears can be obtained by their relative displacement along axis and relative rotation around axis, respectively.

Figure 1 shows a schematic diagram of the apparatus made by outselves in this work. Relative motion along axis was driven by an oil pressure servo-controlled piston (JT Toshi). Force and displacement along axis were detected by a load cell (Nihon Tokushu Sokki, LRM-50K) and a cantilever spring type displacement transducer (Tokyo Sokki, CE-10). Special air bearings were equipped to prevent rotation of the load cell axis. Relative rotation around axis was driven by a stepping motor equipped with harmonic gear of 1/100 gear ratio (Oriental motor, UPD556HG2-A2, 0.036°/step). Rotational oscil-

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latory torque and angle were detected by a non-rotational type torque meter (Nihon Tokushu Sokki, TCF-01K) and a non-contact type Laser Feed Monitor (Keyence, FC-2000).

Experiments were made for various step shears from 0.1 to 1.0. The strain amplitude of the superposed oscillations was less than 0.03. In this range of oscillatory amplitude, the differential dynamic modulus was found to be independent of the amplitude, even if the static shear along axis was high. The frequency was 0.1 Hz. All the measurements were made at 20°C.

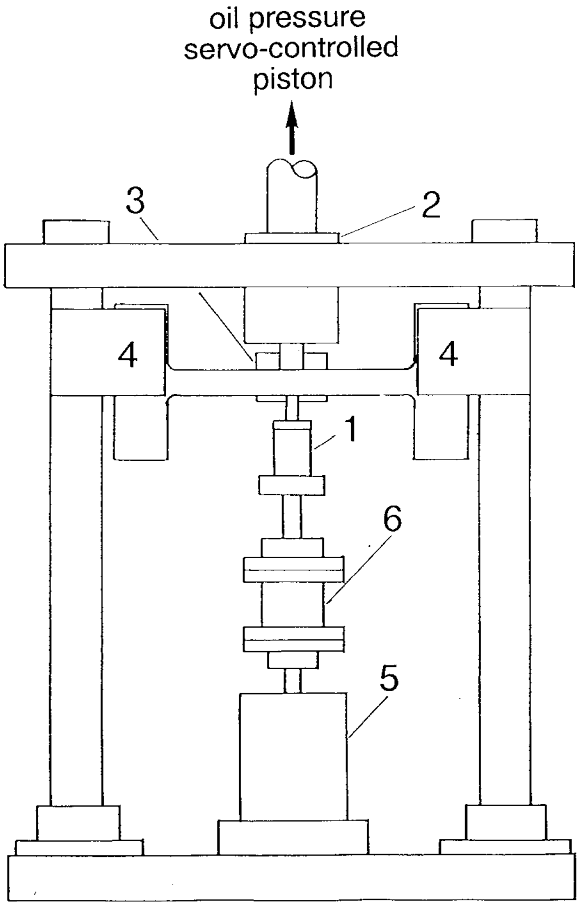

Figure 1 Schematic diagram of the apparatus for measurements of stress relaxation and perpendicular differential dynamic modulus: 1, sample cell; 2, load cell; 3, linear displacement transducer; 4, air bearing; 5, stepping motor; 6, torque meter

Figure 2 shows dynamic modulus and loss tangent master curves for the L-100 sample in the linear viscoelasticity range, where the data denoted by large symbols were obtained in this work and the data denoted by small symbols were obtained in the previous work[7]. The good agreement lends considerable confidence to the accuracy of the measurements. The present sample has a molecular weight distribution. The value $M_w/M_n = 2.2$ was estimated by gel permeation chromatography on the basis of a calibration curve of standard polystyrenes. However, a clear rubbery plateau was observed. The arrow in *Figure 2* denotes the frequency of the superposed oscillations. We note that the present measurements of differential dynamic modulus are made in the middle of the rubbery plateau zone.

RESULTS

The values of linear relaxation modulus, shown by circles, for the L-100 sample are plotted double logarithmically against time in the top panel of *Figure 3*. The solid line shows the data for the same sample in the linear viscoelasticity range obtained in the previous work[7] using another apparatus, a Weissenberg Rheogoniometer R-18, and another sample geometry, a hollow cylinder-shaped shell. We find excellent agreement between the solid line and the data at $\gamma = 0.1$, manifesting the accuracy of the measurements. The values of non-linear relaxation modulus, $G(\gamma; t)$, for various strains are also plotted in the top panel. The curves can be shifted vertically to be superposed at a long-time region as shown in *Figure 4*. Hence $G(\gamma; t)$ can be factored into strain-dependent and time-dependent terms as expected[4,11-18]:

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

The experimental values of $h(\gamma)$ are plotted in *Figure 5A*. The broken line denotes the theoretical values by Doi

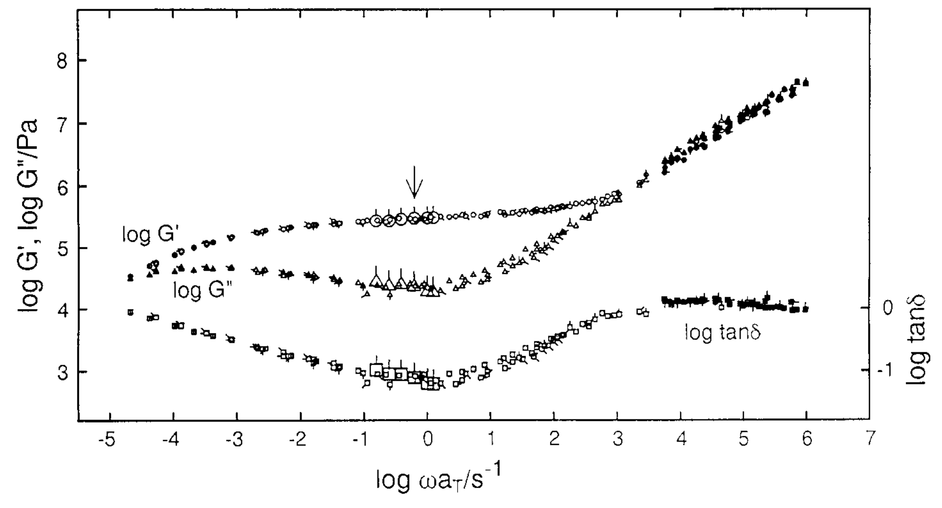

Figure 2 Dynamic modulus and loss tangent master curves for the undiluted polyisobutylene L-100 at 20°C. Large symbols show the data obtained in this work; small symbols show the data obtained previously[7]. The arrow denotes the frequency of the superposed small oscillations (log $\omega = -0.2$, $\nu = 0.1$ Hz)

and Edwatds[19-22] without use of the independent alignment approximation. Experimental values agree with the theory.

The value of the characteristic time, τ_k, after which the strain-dependent relaxation modulus can be written by equation (1), was estimated to be 8.5×10^2 s for the L-100 sample in the previous work[7]. The value, shown by the arrow in *Figure 4*, agrees with the present data.

The perpendicular differential dynamic storage and loss moduli, $G'_{\perp}(\omega,\gamma;t)$ and $G''_{\perp}(\omega,\gamma;t)$, for the L-100 sample are plotted double logarithmically against time in the bottom two panels of *Figure 3*. The initial values of $G'(\omega,0)$ and $G''(\omega,0)$, measured before the sample was strained in each experiment, are shown at the left of each panel. For the smallest strain, both $G'_{\perp}(\omega,\gamma;t)$ and $G''_{\perp}(\omega,\gamma;t)$ remain practically equal to $G'(\omega,0)$ and $G''(\omega,0)$, respectively, throughout the relaxation process, although $G''_{\perp}(\omega,\gamma;t)$ data are less precise. This is consistent with the previous result obtained by parallel differential dynamic modulus[6-8], confirming that the total density of entanglement remains constant in the linear region.

For the higher strains in *Figure 3*, the values of $G'_{\perp}(\omega,\gamma;t)$ are smaller than $G'(\omega,0)$. The degree of decrement is more prominent with the increase of static strain. The first values of $G'_{\perp}(\omega,\gamma;t)$ recover very gradually with time. In $G''_{\perp}(\omega,\gamma;t)$, too, a similar tendency can be seen, although the data are much scattered. The features on perpendicular differential dynamic modulus are consistent with the previous results by parallel differential dynamic modulus[7].

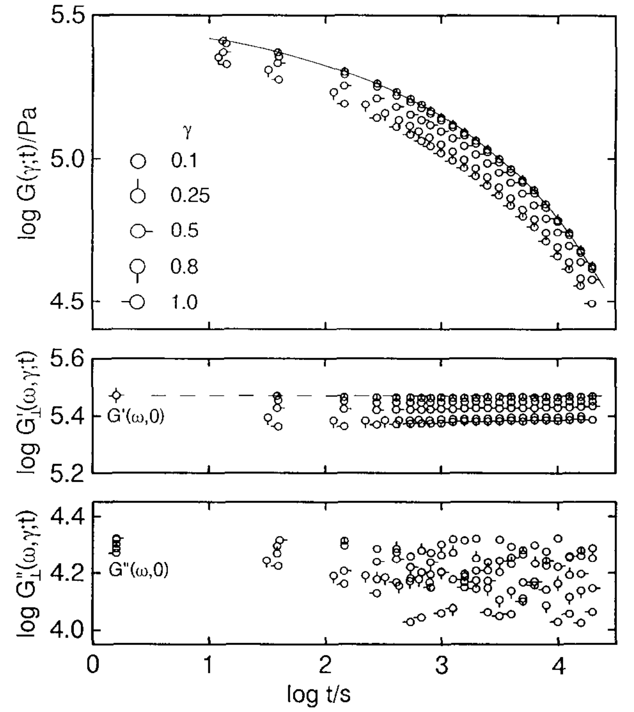

Figure 3 Double logarithmic plots of $G(\gamma;t)$, $G'_{\perp}(\omega,\gamma;t)$ and $G''_{\perp}(\omega,\gamma;t)$ against t for five different shear strains denoted in the top panel. $G'(\omega,0)$ and $G''(\omega,0)$ denote measurements before imposition of strain. The value of $G'(\omega,0)$ is extended by the broken line in the middle panel

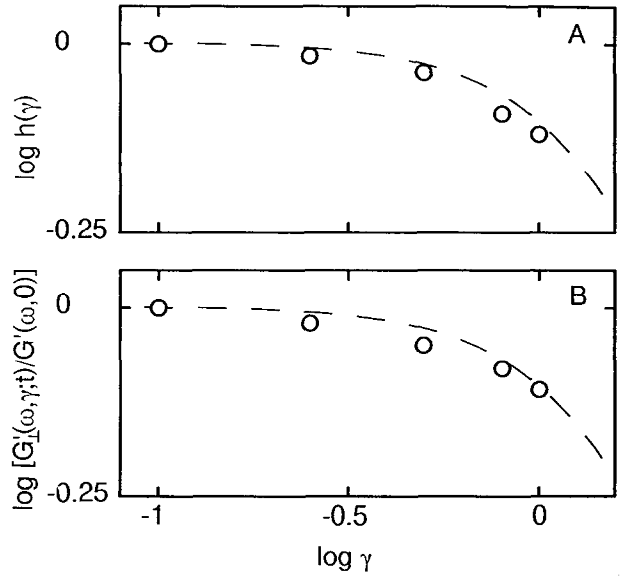

Figure 5 Static shear strain dependences of (A) $h(\gamma)$, determined in *Figure 4*, and (B) $G'_{\perp}(\omega,\gamma;t)/G'(\omega,0)$ at $t = 100$ s. The broken line denotes theoretical values by Doi and Edwards without use of the independent alignment approximation

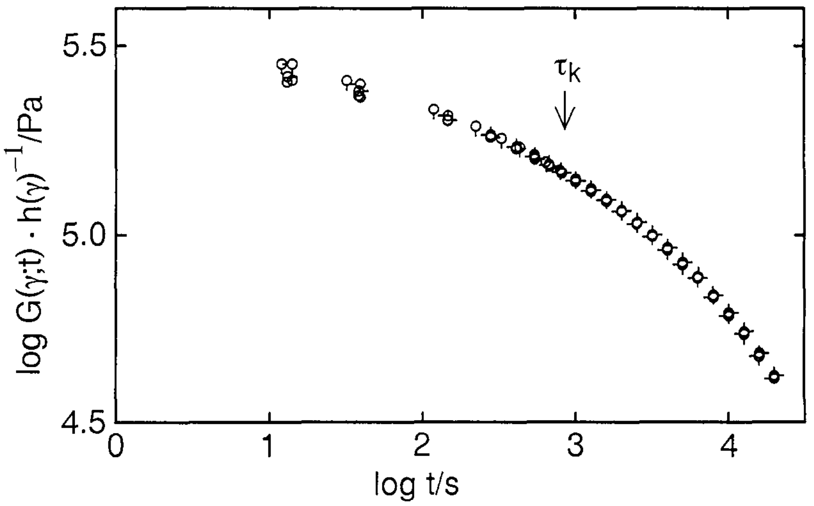

Figure 4 Double logarithmic plots of reduced relaxation modulus $G(\gamma;t)/h(\gamma)$ against t. Symbols as in *Figure 3*

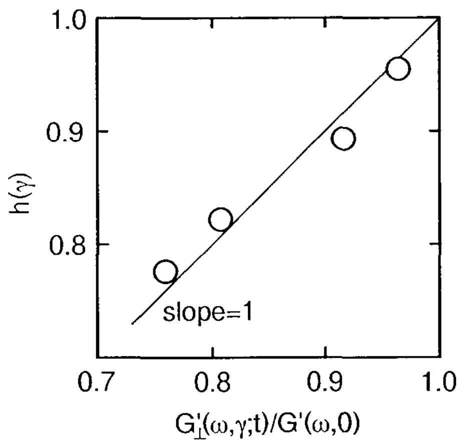

Figure 6 Comparison between experimental values of $h(\gamma)$ and those of $G'_\perp(\omega,\gamma;t)/G'(\omega,0)$ at $t=100$ s for four different static shear strains. The solid line is drawn with a slope of unity

Thus it is certain that the entanglement structure of the polymer changes with strain.

DISCUSSION

As discussed in previous papers[6,7], one may postulate that a change in entanglement structure arises from an anisotropic configuration of the chain molecule and a change in entanglement density through chain contraction in the equilibration process. Such an idea can be tested by comparing the damping observed in $G'_\perp(\omega,\gamma;t)$ with the Doi–Edwards theory[19–22] as shown in *Figure 5B*, where data of $G'_\perp(\omega,\gamma;t)$ at $t=100$ s were used. It is clear that the shear strain dependence of the ratio of $G'_\perp(\omega,\gamma;t)$ to $G'(\omega,0)$ at a short-time region is as well explained by the Doi–Edwards theory[19–22] as that of $h(\gamma)$.

Figure 6 shows the direct comparison between experimental values of $h(\gamma)$ and those of the ratio $G'_\perp(\omega,\gamma;t)/G'(\omega,0)$ at $t=100$ s. The slope is unity within experimental error, showing the equivalence of $h(\gamma)$ and $G'_\perp(\omega,\gamma;t)/G'(\omega,0)$.

Hence it may be concluded that the non-linear behaviour in relaxation modulus results from the change in entanglement structure.

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