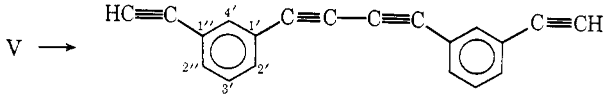
demonstrated by conversion of compound V to the bis-monsubstituted acetylene VII by an alkali cleavage reaction. The ^{13}C spectrum of VII did display two sets of equally intense peaks. One pair corresponding to C-1′ and C-1″ differed in chemical shifts by 0.24 ppm while the C-2′ and C-2″ pair differed by 0.20 ppm. This further confirmed the spectral data for the higher polymer.



VII

Polymer Characterization. The ratio of trimethylsilyl protons to aromatic protons in the ^1H nmr spectrum of the lower molecular weight polymer corresponded to a number-average molecular weight (M_n) for the polymer of 1110. This value is in agreement with elemental silicon analysis for which $\overline{M}_n = 1080$ and with the initial stoichiometric ratios of monofunctional to difunctional acetylenes after correcting for fractionation of the lowest oligomers during isolation. In addition, both the gel permeation chromatographic behavior and the intrinsic viscosity are in accord with a molecular weight near 1000 when compared with phenylethynyl-terminated polymers which were prepared predominantly from *m*-diethynylbenzene.[5] For the higher molecular weight polymer the spectral, elemental, and solution analyses were also consistent with the calculated molecular weight.

All of the peaks in the ^{13}C nmr spectrum of the lower polymer can be assigned to the carbon atoms in structure IV. Weak peaks due to end group nuclei are present at approximately the intensities which are suggested by the molecular weight. Variations in the observed intensities can be accounted for by relaxation phenomena and the Overhauser effect which can cause up to a threefold enhancement in signal where a proton is attached to or near the carbon undergoing resonance. Since all of the observed peaks can be assigned to structure IV, there is no evidence for abnormal linkages or moieties in the polymer. This is also the case for the ^1H spectrum where vinyl protons, for example, would be discernible. Thus, the polymer does not appear to be highly branched or to have undergone reactions other than the normal oxidative coupling. Additional reactions as the "Strauss coupling" reaction[16]

$$2R—C{\equiv}CH \longrightarrow R—C{\equiv}C—CH{=}CH—R$$

are copper catalyzed and can occur at elevated temperatures, but normally require acidic conditions. This reaction would lead to disubstituted vinyl groups in the backbone, but would not result in branching. Not only is there no evidence for these groups in the ^{13}C and ^1H spectra, but also there are no characteristic olefinic absorptions in the infrared spectra of either polymer.

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Shear Creep Studies of Narrow-Distribution Poly(*cis*-isoprene). II. Extension to Low Molecular Weights[1]

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ABSTRACT: Shear creep measurements have been made on six poly(*cis*-isoprene) samples of narrow molecular weight distribution with the molecular weights ranging from 3100 to 43,000. The viscosity η, the steady-state compliance J_e, and the maximum relaxation time τ_m are calculated from the creep curves. The critical molecular weight M_c at which the logarithmic plot of η against M exhibits an abrupt change in slope from 1.0 to 3.7 is found to be about 10,000. The molecular weight dependence of J_e also undergoes a rapid change near $M_b = 50,000$. At low molecular weights, J_e is approximately linearly dependent on M, in agreement with the prediction of the Rouse theory, while at high molecular weights, it is nearly independent of M. The maximum relaxation time τ_m varies as the 3.7 power of M over a wide range of molecular weight, from 6000 to 1,120,000. The entanglement compliance J_{eN} is found to be about 1.6×10^{-7} cm²/dyn for samples having $M > M_b$, which is merely one-eighth to one-tenth of J_e. The average molecular weight M_e between entanglement coupling points is about 3000, as evaluated from J_{eN}.

In a previous paper,[2] the shear creep behavior of undiluted poly(*cis*-isoprene) of narrow molecular weight distribution (MWD) was studied with samples of molecular weight ranging from 57,000 to 1,120,000. It was found that the steady-state compliance J_e was nearly independent of molecular weight M and that the viscosity η, as well as the maximum relaxation time τ_m, varied as the 3.4 power of M. These properties of the viscoelastic functions agreed with those observed for other species of narrow MWD polymer, polystyrene,[3-10] poly(α-methylstyrene),[11-12] and poly(dimethyl-

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Table I
The Experimental Results for Poly(*cis*-isoprene) at −55°

Sample	M_w	η, P	J_e, cm²/dyn	τ_m, sec
I-29	3.1×10^3	1.62×10^6	2.57×10^{-8}	5.12×10^{-1}
I-28	5.7×10^3	1.07×10^7	1.66×10^{-7}	1.17×10^1
I-27	6.8×10^3	1.57×10^7	2.09×10^{-7}	1.95×10^1
I-20	1.75×10^4	9.43×10^8	8.50×10^{-7}	2.24×10^3
I-17	2.52×10^4	2.05×10^9	1.13×10^{-6}	7.35×10^3
I-14	4.32×10^4	1.41×10^{10}	1.76×10^{-6}	8.99×10^4

siloxane),[13] and they have recently been accepted as the characteristic properties of high molecular weight polymers or of polymers in the highly entangled state.[14]

In the range of low molecular weights, both η and J_e are approximately linearly dependent on M, in agreement with the predictions by the Rouse–Bueche theory[15,16] or its modified version.[17] As is familiar, the transition from this low molecular weight property of η to the high molecular weight one occurs abruptly at a characteristic value of molecular weight M_c, which is often referred to as the critical molecular weight for entanglement. The corresponding transition in the behavior of J_e, however, has not fully been clarified as yet. Graessley and Segal[18] have reported on concentrated solutions of narrow MWD polystyrenes that J_e varies as

$$J_e = [\alpha_1/(1 + \alpha_2 cM)]J_{eR} \tag{1}$$

with

$$J_{eR} = (2/5)(M/cRT) \tag{2}$$

Here α_1 and α_2 are constants, independent of polymer concentration c and molecular weight M, and the product RT has its usual meaning. In this case, the transition from the low molecular weight property, $J_e = \alpha_1 J_{eR}$, to the high molecular weight one, $J_e \propto 1/c^2RT$, occurs rather gradually over a wide range of molecular weight. On the other hand, Onogi, *et al.*,[5] have reported on undiluted samples of narrow MWD polystyrene that J_e displays a sharper transition between two types of property at a value of molecular weight near M_c, *i.e.*, 30,000–40,000. Still other groups of investigators[8,9,19] have found for the same polymer that J_e retains the low molecular weight property up to a certain molecular weight M_b between 100,000 and 200,000, which is considerably higher than M_c.

These facts caused our interest in extending the shear creep study of narrow MWD poly(*cis*-isoprene) of part I to the region of lower molecular weights and in clarifying the behavior of J_e and of other viscoelastic functions in the critical region of entanglement formation.

Experimental Section

Materials. The poly(*cis*-isoprene) samples used in this study were prepared by anionic polymerization as described previously,[2] and designated as I-14, -17, -20, -27, -28, and -29. The seeding technique[20] was used in the preparation of all the samples but I-29, having the lowest molecular weight. Since the molecular weight distribution of these samples was not very sharp as examined by the sedimentation velocity profiles, each sample was fractionated into five fractions in a Desreux column using benzene and methanol as the solvent and precipitant, respectively, and the fourth fraction, having the second highest molecular weight, was employed as the test sample. The weight-average molecular weight M_w was determined by the sedimentation equilibrium method using a Spinco-E ultracentrifuge. The values of M_w are given in Table I. No direct measurement was made on the number-average molecular weight M_n, but the ratio of M_w to M_n was roughly estimated to be less than 1.1 for three samples, I-14, -17, and -20, and less than 1.2 for the remaining three samples, I-27, -28, and -29, respectively, from the sedimentation velocity boundary curves.

The microstructure of the samples was estimated by high-resolution nuclear magnetic resonance[21] and infrared spectroscopic methods.[22] The contents of cis-1,4, trans-1,4, and vinyl structures were 84.5, 8.5, and 7.0%, respectively, for all the samples prepared. These values are also in agreement with those of the samples of higher molecular weights used in part I.

Measurements. The shear creep measurements were made with a torsional pendulum of the Plazek–Vrancken–Berge type.[23] The details of the apparatus and measurements have been described previously.[2,24] The present samples having low molecular weights were essentially viscous liquids at room temperature, and it was hard to mold a cylindrical specimen fitting into the gap between two circular plates of the apparatus. Thus, in the present measurements, we spread an appropriate amount of sample on the lower circular plate and raised the plate to a suitable height to allow the sample to take a cylindrical shape between two plates. Then, the sample was cooled in a housing down to the temperature of measurement. During the process of cooling, we monitored the shape of the sample through a window of the sample housing and manipulated the height of the lower plate to compensate the volume contraction due to cooling and so as to retain the cylindrical shape of the sample. The surface tension of the sample and the adhesion to the stainless plates enable us to follow these procedures. The diameter of the sample was varied from 0.6 to 2.0 cm by using various sets of the circular plates. The thickness of the sample was varied from 0.15 to 0.25 cm, which was measured by a traveling microscope with a precision of ±0.005 cm.

The shear creep measurements were made at various temperatures between −72.7 and −29.1°. The temperature was regulated to within ±0.2° over the whole temperature range studied.

Results and Discussion

Shear Creep Master Curves at Constant Temperature. The master curve of each sample was constructed from a family of creep curves obtained at more than six different temperatures by the usual procedure based on the time–temperature superposition principle. Figure 1 shows the master curves of six samples of low molecular weight poly(*cis*-isoprene), where a_T represents the shift factor for the time–temperature reduction. The subscript p signifies that the shear creep compliance $J(t)$ has been multiplied by the eleasticity factor, $T\rho/T_0\rho_0$. Here ρ and ρ_0 represent the densities at temperature T and a reference temperature T_0, respectively. The reference temperature was chosen arbitrarily as −55° in this figure. The value of the thermal expansion coefficient of the polymer was taken as 7.13×10^{-4} irrespective of the molecular weights of the samples.

The viscosity η and the steady-state compliance J_e were evaluated from the master curves by the extrapolation method of Ninomiya.[25] The results are shown in Table I. The errors involved in these values of J_e are estimated to be less than

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(24) N. Nemoto, Ph.D. Thesis, Kyoto University, 1970. See also ref 2.

(25) K. Ninomiya, *J. Phys. Chem.*, **67**, 1152 (1963).

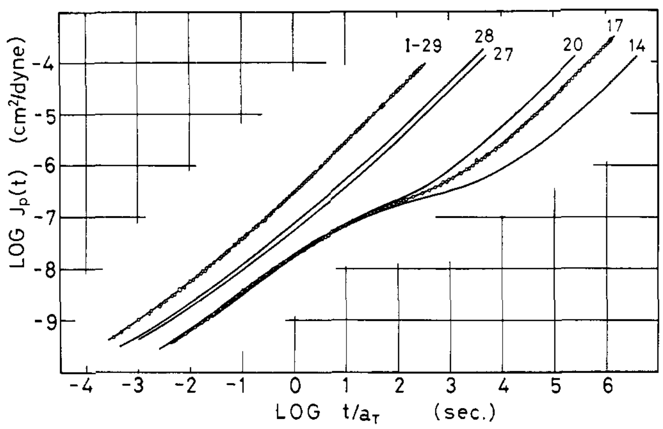

Figure 1. The creep master curves of six poly(*cis*-isoprene) samples at −55° Original data points are shown for samples I-29 and I-17.

10%. This limit of error is somewhat larger than the corresponding limit, 5%, for the higher molecular weight samples studied in part I, reflecting the increased difficulty in determination of the sample dimensions of soft materials as the present.

Recently Plazek and O'Rourke have demonstrated from creep and creep recovery measurements on narrow MWD polystyrenes that the temperature dependence of the viscosity is different from that of the recoverable compliance.[8,26] They have concluded that the time–temperature equivalence is not applicable to the total creep compliance, especially when the temperature is close to the glass-transition temperature. They have also shown that the steady-state compliance J_e of low molecular weight polystyrene decreases appreciably with decreasing temperature as the glass-transition temperature is approached. In the present study, however, no measurement was made on the creep recovery. Consequently, we were not able to confirm any of these low molecular weight or low-temperature effects. In other words, any significant failure of the conventional time–temperature reduction has not been recognized in the construction of the creep master curves shown in Figure 1.

In this connection, we note that the lowest limits of molecular weight and temperature in our measurements were still not so low as those in the study of Plazek, *et al.* For example, the lowest molecular weight is 3100 for sample I-29, which is to be compared with 1100 for the lowest molecular weight polystyrene of Plazek and O'Rourke. The molecular weight 3000 of poly(*cis*-isoprene) roughly corresponds to a value of 7000 or more of polystyrene if comparison is made for the number of skeletal atoms in a molecule. The lowest temperature studied, −72.7°, is also 15–20° higher than the glass-transition temperature of I-29. Under these conditions, it is unlikely that a serious error is introduced in the estimates of η and J_e by the use of the time–temperature superposition. Of course, the values of J_e obtained by the Ninomiya method may be regarded as the high-temperature asymptotes in the sense of Plazek and O'Rourke.[8]

Viscosity at Constant Friction Factor as a Function of Molecular Weight. The viscosity $\eta_{-55°}$ of a sample evaluated at −55° may be converted to the viscosity $\eta_{\zeta'}$ at a constant friction factor ζ' by adding an amount $\Delta \log t$, which is equal to the horizontal distance between two master curves in the transition region, one being of the sample in question and the other of a reference sample, I-14: *i.e.*, $\log \eta_{\zeta'} = \log \eta_{-55°} + \Delta \log t$. Here ζ' represents the friction factor which characterizes the segment mobility in the sample I-14 at −55°. In part I, however, the viscosity at constant friction factor, η_ζ, has been evaluated at a different standard ζ_0 of the friction factor, by using the viscosity of a sample with sufficiently high molecular weight at −30°, actually of I-34, as the reference. Thus, we readjusted the viscosity values $\eta_{\zeta'}$ to the latter standard of friction factor ζ_0 by subtracting 3.18 from $\log \eta_{\zeta'}$; *i.e.*,

$$\log \eta_\zeta = \log \eta_{-55°} + \Delta \log t - 3.18 \tag{3}$$

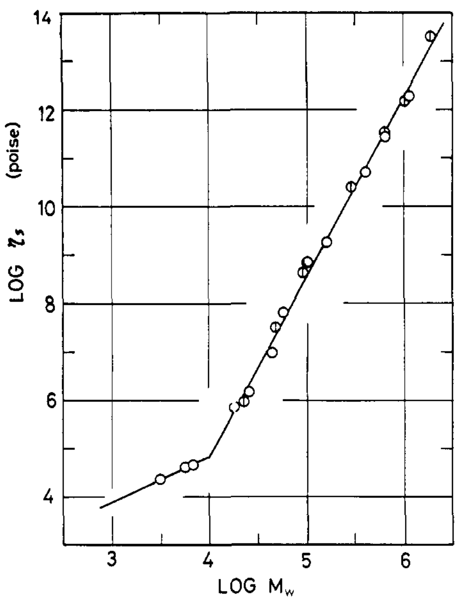

Figure 2. The logarithmic plot of η_ζ at constant friction factor against M_w: (O) present data and those reported in part I, (⦶) data of Holden. The two straight lines have slopes of 1.0 and 3.7.

The values of η_ζ thus obtained are shown in Figure 2 by open circles, together with the values for the samples of higher molecular weights given in part I. For the sake of comparison, this figure also shows the zero-shear viscosity data of Holden.[27] The original data of Holden were obtained for undiluted samples of narrow MWD poly(*cis*-isoprene) at four temperatures, 27, 50, 57, and 75°. Therefore, their data were reduced to −30° with the aid of the shift factor a_T given by eq 2 in part I, and then to the state of constant friction factor ζ_0 by applying a low molecular weight correction to the samples with $M < 90{,}000$. It is seen in Figure 2 that the viscosity data of Holden thus corrected are in good agreement with ours.

The logarithmic plot of η_ζ against M_w is well represented by two straight lines[28] with slopes of 1.0 and 3.7, which mutually intersect at the point corresponding to $M_c = 10{,}000 \pm 1000$. This value of M_c is slightly lower than the previous estimate 14,000 which was derived from the solution data of Fetters by extrapolation to the undiluted state.[29] In part I, it was reported that η_ζ varies as the 3.4 power of molecular weight in the range of M between 57,600 and 1,120,000. Now, a slightly higher power, 3.7 ± 0.1, seems to be more appropriate for representing the molecular weight dependence of η_ζ in the extended range of M.

Steady-State Compliance as a Function of Molecular Weight. The values of J_e obtained at −55° are reduced to

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(26) D. J. Plazek, *ibid.*, **69**, 3480 (1965).

(27) G. Holden, *J. Appl. Polym. Sci.*, **9**, 2911 (1965).

(28) See, for example, G. C. Berry and T. G Fox, *Advan. Polym. Sci.*, **5**, 261 (1968).

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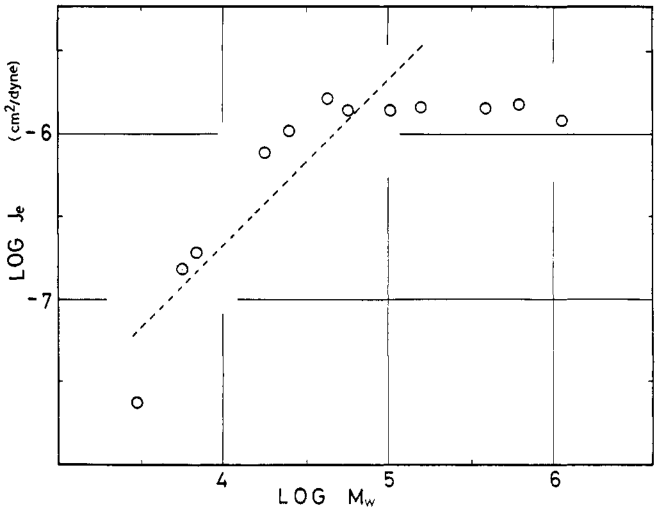

Figure 3. The logarithmic plot of J_e against M_w at −30°. The dotted line represents the Rouse prediction, $J_{eR} = {}^2/_5(M/\rho RT)$.

the values at −30° by multiplying a factor of $^{218}/_{243}$, the ratio of two temperatures. These values of J_e are plotted logarithmically against M_w in Figure 3, along with those of the samples of higher molecular weights reported in the previous paper. The prediction of the Rouse theory,[15,16] $J_{eR} = {}^2/_5 \times (M/\rho RT)$, is also indicated by the dotted line for the sake of comparison. In the region of molecular weights lower than about 40,000–50,000, the observed values of J_e are roughly in agreement with the prediction of the Rouse theory. Closer inspection, however, reveals that J_e of the lowest molecular weight sample, I-29, is slightly lower than the theoretical value, while those of the remaining five samples, from I-28 to I-14, are slightly higher. The former type of departure of J_e from the Rouse theory may be regarded as the same anomaly as that recently observed for low molecular weight polystyrenes by several investigators.[8,9,30] On the other hand, the significance of the latter type of departure is not clear as yet.

At high molecular weights, J_e is nearly independent of M, as already been pointed out in part I. Now, it may be seen from the figure that the transition from the low molecular weight behavior of J_e to the high molecular weight one occurs rather abruptly at a certain value of molecular weight, $M_b \simeq 50{,}000$, in contrast to the prediction of eq 1. This value of M_b is appreciably higher than the value, $M_c = 10{,}000$, in the logarithmic plot of η_ζ against M. This result is in accord with the recent observations by O'Reilly, Prest,[7] and others[8,9] that the viscoelastic properties of narrow MWD polystyrenes as represented by η_ζ and J_e obey the predictions of the so-called modified Rouse theory[17] up to $M_b \simeq 100{,}000$, which obviously exceeds $M_c \simeq 35{,}000$.

Maximum Relaxation Time as a Function of Molecular Weight. The maximum relaxation time τ_m was calculated by using procedure X,[31] after the creep compliance $J(t)$ was converted to the relaxation modulus $G(t)$.[32] The values of τ_m at −55° are listed in Table I. These values are then converted to the values $\tau_{m\zeta}$ at constant friction factor at −30°, and the latter are plotted logarithmically against M in Figure 4. It is remarkable that the log $\tau_{m\zeta}$ *vs.* log M_w plot exhibits no distinct break at M_b and supports a straight line with the slope of 3.7 over almost the whole range of M studied, as indicated by the solid line. It is, however, difficult to decide whether or not there exists a break at M_c in the plot. To give an answer to the question, the experimental error involved in $\tau_{m\zeta}$ seems too large in the region of low molecular weight, and the number of data points insufficient. In this interpretation, the lower end of the straight line in Figure 4 is represented by the dotted line.

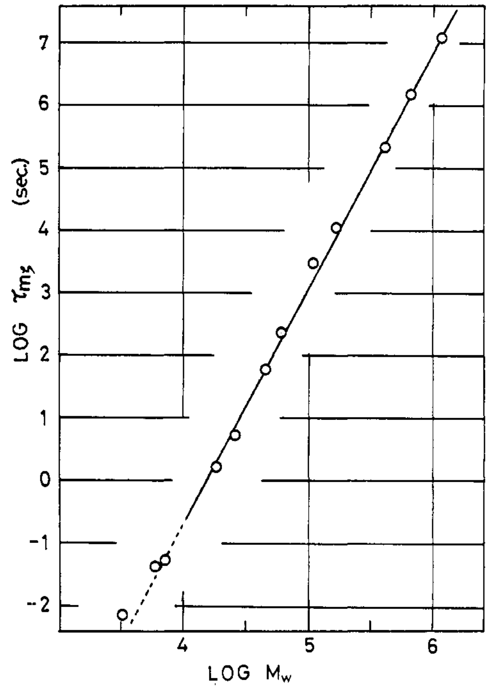

Figure 4. The logarithmic plot of $\tau_{m\zeta}$ at constant friction factor against M_w. The straight lines has a slope of 3.7.

Table II

Entanglement Compliance J_{eN} and Average Molecular Weight between Entanglement Coupling Points M_e

Sample	M_w	$10^7 J_{eN}$, cm²/dyn	J_e/J_{eN}	$10^{-3}M_e$ From J_{eN}	$10^{-3}M_e$ From J_{inf}
I-20	1.75×10^4	1.59	5.3	3.02	3.15
I-21	5.76×10^4	1.42	9.7	2.71	3.34
I-31	3.95×10^5	1.58	8.9	3.00	3.50
I-34	1.12×10^6	1.57	7.6	2.98	3.13

Entanglement Compliance and Entanglement Spacing. The shear compliance associated with entanglement network, J_{eN}, can be given by

$$J_{eN} = \int_a^b L(\tau)\mathrm{d}\ln\tau \qquad (4)$$

where $L(\tau)$ is the retardation spectrum.[33] We calculated $L(\tau)$ from the creep master curves given in Figure 1 by using the second approximation of Schwarzl and Staverman.[34] The retardation spectra $L(\tau)$ thus obtained for samples I-31 and I-20 are shown as examples in Figure 5 by the solid line and the dotted line, respectively. The integral limits, a and b, in eq 4 were taken to encompass the maximum of $L(\tau)$

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(30) L. A. Holmes, S. Kusamizu, K. Osaki, and J. D. Ferry, *J. Polym. Sci., Part A-2*, 9, 2009 (1971).

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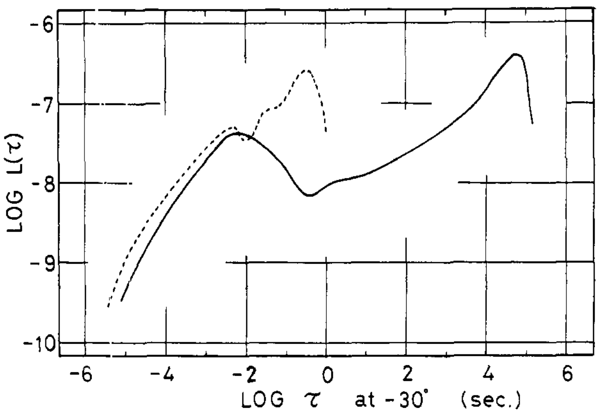

Figure 5. Two examples of the retardation spectrum: (—) I-31, (- - -) I-20.

which appeared at the end of the transition zone. Actually, the lower limit *a* was extended to − ∞, because the value of the glassy compliance was negligible in comparison with that of J_{eN}. The higher limit *b* was chosen so as to eliminate the contribution from the slippage of entanglement at longer times. The values of J_{en} thus evaluated are given in Table II. They are nearly independent of molecular weight not only for the samples with $M > M_b$ but also for the sample I-20 having M between M_c and M_b. The ratio J_e/J_{eN} is about 8–10 for samples with $M > M_b$, which is larger by a factor of 4–5 than the corresponding values, about 2, for polystyrenes[33,5] and poly(α-methylstyrene).[11]

The average molecular weight M_e between entanglement coupling points can be calculated from J_{eN} by

$$J_{eN} = M_e/\rho RT \tag{5}$$

Here the front factor is assumed to be unity. The values of M_e obtained by eq 5 are also shown in Table II.

The approximate value of J_{eN} can also be obtained as the value of $J(t)$ at the inflection point of the log $J(t)$ *vs.* log t curve. The entanglement compliance thus obtained is designated as J_{inf}. Then, M_e is obtainable again by eq 5 with the assumption that $J_{eN} = J_{inf}$. The values of M_e obtained are also included in Table II, which are in good agreement with the previous estimates by eq 4 and 5. In spite of the large value of J_e/J_{eN}, the value of M_c/M_e is about 3, which is not very different from the value, about 2, obtained for other polymers.[33]

Conclusions

The shear creep behavior of narrow MWD poly(*cis*-isoprenes) reported in parts I and II of this series may be summarized as follows.

The viscosity at constant friction factor η_ζ is proportional to the first power of M in the region $M < M_c$, while it is proportional to the 3.7 power of M in the region $M > M_c$. The critical molecular weight M_c is about 10,000.

The steady-state compliance J_e increases with increasing M, roughly in agreement with the Rouse prediction, $J_R = {}^2/_5(M/\rho RT)$, in the region $M < 50,000$. At higher molecular weights, J_e is nearly independent of M. The transition between these two types of behavior of J_e occurs rapidly at about $M_b = 50{,}000$.

The maximum relaxation time $\tau_{m\zeta}$ is proportional to the 3.7 power of M over almost the whole range of M studied. No appreciable departure from this behavior has been observed in the region $M > 6{,}000$.

The ratio of the steady-state compliance to the entanglement compliance, J_e/J_{eN}, is about 8–10 in the region $M > M_b$, which is larger by a factor of 4–5 than the corresponding values for polystyrene and poly(α-methylstyrene). The ratio between the entanglement spacing and the critical molecular weight for entanglement, M_c/M_e, is about 3, which is not very different from the values for other polymers.

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Communications to the Editor

Conformation of Polyethylene by Nuclear Magnetic Resonance

The determination of polymer structure using nmr spectra is a very widely used technique which has been applied to a large number both of synthetic and natural macromolecules. Nevertheless polyethylene has not received much attention, the main reason being the extreme simplicity of its spectrum. However, if one could measure in some way the interproton vicinal coupling constants of the CH_2–CH_2 fragment of this macromolecule, it would be possible to obtain information about the conformation of the C–C bond.

This possibility prompted us to synthesize an isotopically substituted polyethylene suitable for this kind of investigation. The synthesis was performed by copolymerizing perdeuterioethylene and 1-^{13}C-enriched ethylene (60% enrichment) (ratio 9:1 in the feeding gas) using a catalyst consisting of $AlEt_3$ and VCl_4. The resulting copolymer can be described in first approximation as a sequence of CD_2CD_2 monomeric units among which are embedded at intervals $^{13}CH_2CH_2$ units, as shown in the schematic formula $-(CD_2)_x{}^{13}CH_2CH_2(CD_2)_y-$.

The pmr spectrum of the above copolymer dissolved in *o*-dichlorobenzene (150 mg/ml) was obtained at 100° under deuterium decoupling using an HFX-Bruker spectrometer operating at 90 MHz. A Fabri-tek-1070 computer of average transients was used to accumulate the spectrum.

According to the above formula we should expect a satellite spectrum of the AA′BB′X type, X being the ^{13}C nucleus, so that the analysis for determining J and J' can be carried out by considering the subspectrum as aa′bb′ (Figure 1). Following the usual symbolism, the parameters of this spectrum are $K = 2J_{gem}$, $M = J_{gem} - J_{gem} = 0$, $N = J_{vic} + J'_{vic}$, and $L = J_{vic} - J'_{vic}$. Considering that $N = 14.8 \pm 0.1$ Hz is explicity given by the splitting of transitions 1 and 3 (*i.e.*, by the separation of the outer lines),[1] the problem of determining L remains. For this purpose we have simulated, with the aid of a computer program and using a plotter, different spectra with

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(1) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution nuclear magnetic resonance," McGraw-Hill, New York, N. Y., 1959, p 147.