Shear Creep Studies of Narrow-Distribution Poly(*cis*-isoprene)[1]

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ABSTRACT: Shear creep measurements were made at temperatures between −68.6 and 98.0° on six narrow-distribution poly(*cis*-isoprene) samples with molecular weights of 57,600–1,120,000. The time–temperature reduction method was used for constructing master curves at a reference temperature of −30°. The curves for two low molecular weight samples (M_w = 57,600 and 103,000) showed deviations in the transition zone from those for other samples with higher molecular weights. Also, a corresponding effect of low molecular weight was observed on the shift factor a_T. It was found that these effects were avoided by the use of a lower value for the reference temperature of the samples. The viscosity η and the steady-state compliance J_e were determined by the extrapolation method of Ninomiya. Also the maximum relaxation time, τ_m, was evaluated by procedure X. It was found that η and τ_m varied as a power of the molecular weight, $M^{3.4}$, and J_e was independent of M. These results were in qualitative agreement with Hayashi's theory and also with Graessley's theory for entanglements. The entanglement spacing M_e was about 3500 and was nearly independent of M determined from the inflection in the $J(t)$ curves.

It has been widely recognized in recent years that the study of molecular weight dependence of the steady-state compliance J_e would furnish the key to an understanding of the molecular mechanism of polymer chain entanglements. Its counterpart, the molecular weight dependence of the viscosity η, has long been known to obey the relationship, $\eta \propto M^{3.4}$, for molecular weights M higher than a critical value M_c. For polydisperse polymers, M stands for the weight-average molecular weight M_w. On the other hand, the quantity J_e is quite sensitive to the molecular weight distribution, and this makes it difficult to deduce the correct molecular weight dependence from measurements on polydisperse samples. Use of a polymer with very narrow distribution of molecular weight is essential for the study.

Recently, several groups of investigators have measured the steady-state compliance of narrow-distribution polystyrene[2–5] and poly(α-methylstyrene)[6,7] by various methods, and found that J_e of these polymers are almost independent of M, or much less dependent on M than the first power. This is in contrast with the earlier results on a carefully fractionated poly(vinyl acetate)[8] and also with the recent results on an anionically prepared poly(methyl methacrylate).[9] In these cases, J_e was roughly proportional to M. Thus, it is questionable whether the above discrepancy originates from a difference in polydispersity or, more intrinsically, from a difference in the nature of polymer chains. In other words, the existence of a universal relationship between J_e and M is questioned.

Under the circumstances, we find it essential to study the problem by using another polymer with a very narrow distribution, which is preferably quite different in structure and properties from polystyrene and poly(α-methylstyrene). Poly(*cis*-isoprene) is thus selected as the working material in the present study. This paper presents the results of shear creep measurements on a series of six narrow-distribution poly(*cis*-isoprene) samples whose molecular weights are in the range from 57,600 to 1,120,000. The viscosity η, steady-state compliance J_e, and maximum relaxation time τ_m are evaluated from the shear creep compliance, and their dependence on molecular weight is studied in relation to the entanglement problem.

Experimental Section

Materials. The poly(*cis*-isoprene) samples were prepared by anionic polymerization *in vacuo* at 30° with *sec*-butyllithium as the initiator and *n*-hexane as the solvent. The apparatus and the technique used for the preparation were similar to those described by Morton, *et al.*,[10] and Fujimoto, *et al.*[11] Since the rate of initiation for polymerization in hydrocarbon solvents is much lower than the rate of propagation,[12] the seeding technique was employed for obtaining samples with sharp molecular weight distribution.[13] That is, the seeding was accomplished by mixing the initiator and a portion of monomers in the solvent and allowing the polymerization to proceed. The resulting active polymer with a molecular weight of about 5000–10,000 was used as the seed on which additional monomers were polymerized. A small amount of the low molecular weight fraction of the polymer was removed by elution at 35.0° using a large scale column with benzene–methanol mixtures.

The microstructure of the polymers was determined by high-resolution nuclear magnetic resonance[14] and infrared spectroscopic methods.[15] The results were 84.5, 8.5, and 7.0% for cis-1,4, trans-1,4, and vinyl structures, respectively, and were approximately constant for all polymers prepared. The weight-average molecular weight M_w was estimated from the intrinsic viscosity by using the relationship $[\eta] = 2.00 \times 10^{-4} \times M_w^{0.728}$ in toluene at 30°.[16] The number-average molecular weight M_n was determined by osmometry in toluene at 35° using a high-speed membrane osmometer (Mechrolab Model 502). The values of M_w and M_n are given in Table I. The ratios of M_w to M_n were less than 1.1

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TABLE I
NARROW-DISTRIBUTION POLY(*cis*-ISOPRENE)

Sample	M_w	M_n
I-21	5.76×10^4	6.06×10^4
I-23	1.03×10^5	1.14×10^5
I-25	1.59×10^5	1.76×10^5
I-31	3.95×10^5	3.70×10^5
I-32	6.20×10^5	6.20×10^5
I-34[a]	1.12×10^6	

[a] The ratio M_w/M_n determined from the sedimentation velocity boundary curves was 1.01.

for all samples. For the sample I-34, the ratio was 1.01 as determined directly from the sedimentation velocity boundary curves.

In order to avoid oxidation and/or decomposition of the samples, they were stored at about 0° in an argon atmosphere with an addition of 1% of 2,2-methylenebis(4-methyl-6-*tert*-butylphenol) as an antioxidant.

Methods. The shear creep measurements were made with a torsion pendulum of the Plazek, Vrancken, and Berge type.[17] A modification was introduced to measure the deformation of a sample by a linear variable differential transformer. This enabled us to detect an angular deformation as small as 2×10^{-4} deg. The temperature was regulated to within ±0.2° in the whole range studied, *i.e.*, from −68.6 to 98.0°.

Disk-shaped samples for shear creep measurements were molded under pressure at room temperature. The size of samples varied from 1.0 to 2.0 cm in diameter and from 0.3 to 0.5 cm in thickness. Samples were fixed tightly between two parallel metal disks by using α-cyanoacrylate as an adhesive. Absence of the effect of adhesive on the creep behavior of the sample was confirmed experimentally.

The density and the volume–temperature coefficient of the samples were determined by dilatometry. The dilatometers were made of Pyrex glass, and each consisted merely of a bulb with a capillary tube sealed to it. Changes in volume of a sample were determined from changes in the height of mercury in a capillary. Samples of about 1 g were used in all dilatometric measurements. The crystallization behavior of the polymer was also studied using a mercury-filled dilatometer.

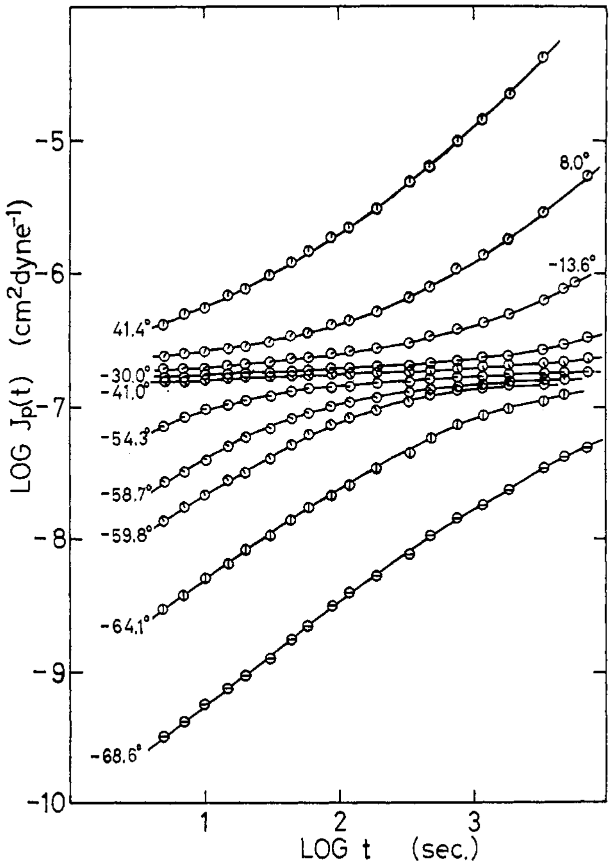

Figure 1. Shear creep compliance of sample I-32, plotted logarithmically against time at ten temperatures as indicated. The subscript p denotes multiplication by $T\rho/T_0\rho_0$.

Results

Time–Temperature Superposition. In Figure 1, the shear creep compliance $J_p(t)$ of the sample I-32 is plotted logarithmically against time t at ten different temperatures from −68.6 to 41.4°. For clarity in distinguishing the curves, the data obtained at −56.6, −50.9, −48.2, and −42.9° have been omitted from the figure. The subscript p signifies that the shear creep compliance $J(t)$ has been multiplied by a 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 latter has been chosen arbitrarily as −30.0° for the present system. The density ρ was calculated from eq 1 derived from dilatometry. Families of creep curves similar to those shown

$$1/\rho = 1.0990 - 7.79 \times 10^{-4}(15 - T) \qquad (1)$$

in Figure 1 were obtained for all other samples, though not reproduced here.

Dilatometry on unvulcanized rubbers often indicates that crystallization occurs at temperatures between −40 and +10°.[18] But, this was not the case for our poly(*cis*-isoprene) samples; that is, no appreciable volume change was observed in the above temperature region within the time required for attaining the thermal equilibrium and performing the creep measurements. Evidently crystallization of the poly(*cis*-isoprene) samples is inhibited due to their limited cis-1,4 contents even at temperatures where the rate of crystallization of natural rubbers is high.

In the absence of a crystallization effect, it may be expected that the time–temperature superposition principle is applicable in the whole temperature range studied, and that a master curve can be constructed from a family of creep curves in Figure 1 by horizontal shifting alone. Figure 2 shows the master curve thus obtained for the sample I-32. It is evident in the figure that the superposition has been successfully achieved and the experimental points lie mostly within 2% of

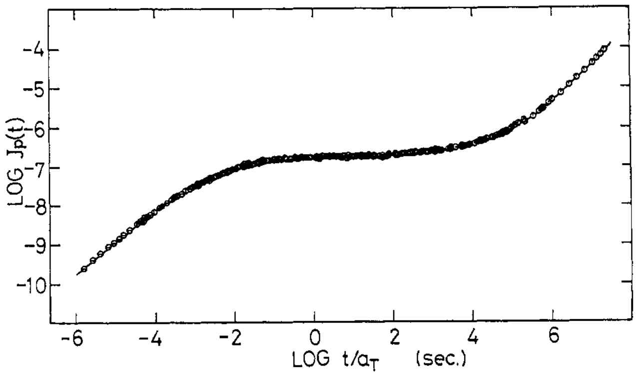

Figure 2. The master curve of I-32, obtained by plotting the data of Figure 1 by the method of reduced variables, indicates that superposition has been successfully achieved.

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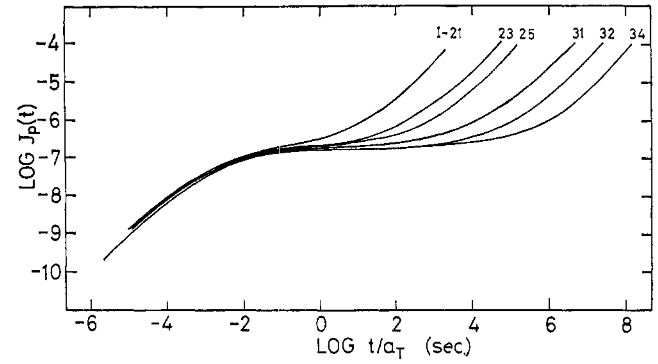

Figure 3. The master curve of six poly(*cis*-isoprene) samples as indicated.

the master curve. The errors are mainly due to uncertainty involved in the determination of sample dimensions. The master curves obtained for all samples with $T_0 = -30°$ are summarized in Figure 3. It is notable that in the transition zone, the master curves for low molecular weight samples, I-21 with $M_w = 5.76 \times 10^4$ and I-23 with $M_w = 1.03 \times 10^5$, are slightly displaced to the left of the common curve for higher molecular weight samples by factors of about 0.25 and 0.10, respectively, in the logarithmic time scale.

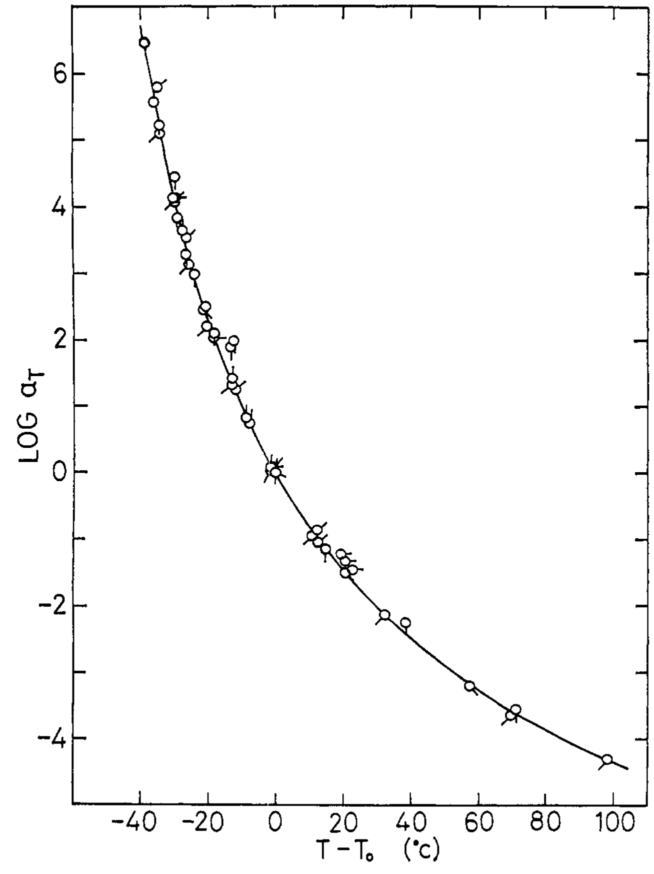

Figure 4. The semilogarithmic plot of a_T against $T - T_0$, with each sample reduced to its own T_0 as $T_0 = -32.8°$ for I-21, $-31.1°$ for I-23, $-30°$ for the others: pip up, I-21; succesive 45° rotation clockwise, I-23, I-25, I-31, I-32, and I-34.

Except for these two samples, the shift factors a_T obtained in the time–temperature reduction are well represented by the WLF-type equation[19]

$$\log a_T = -\frac{8.20(T - T_0)}{89.5 + T - T_0} \qquad (2)$$

with $T_0 = -30°$. On the other hand, slightly different constants are obtained for the samples I-21 and I-23, provided that T_0 is fixed at $-30°$. This, of course, is closely related to the above-mentioned shift of the master curves in the transition zone. Since neither crystallization nor substantial variation of the microstructure of chains has been observed, these effects are attributable to the molecular weight dependent nature of the free volume, or in other words to the effect of chain ends. Accordingly, the displacement, Δ log *t*, of the master curve of a low molecular weight sample from that of I-34, which was chosen as the reference sample with $T_0 = -30°$, may be put equal to the difference in log a_T for the former sample at two temperatures: at $-30°$ and at the temperature at which the former sample is in the iso-free-volume state with I-34 at $-30°$. The temperature difference can be readily read from the plot of log a_T *vs.* *T* for the test sample. The values of T_0 thus obtained were -32.8 and $-31.1°$ for samples I-21 and I-23, respectively.

Figure 4 shows the plots of log a_T against $T - T_0$, where the corrected values of T_0 are used for the two samples, while the original value, $-30.0°$, is used for the other four samples. It is evident in the figure that all data support a single WLF-type equation, eq 2, indicated by the solid line. The relation between the molecular weight dependence of T_0 and that of T_g will be investigated in detail over an extended range of molecular weight in a later communication.

Viscosity and Steady-State Shear Compliance. The shear viscosity η and the steady-state shear compliance J_e, which characterize the viscoelastic behavior in the terminal zone, were calculated by the extrapolation method of Ninomiya.[20] The values of η were also calculated from the deformation rate after apparent steady-state flow was reached. Both estimates of η were in excellent agreement with each other to an accuracy of 1%. As is seen in Figures 2 and 3, a sufficient number of experimental points were available in the present measurements in the region where the value of d log $J(t)$/d log *t* exceeded 0.95, and in this region, the plot of $J(t)/t$ *vs.* $1/t$ was approximately linear. Accordingly, the extrapolation method led to reasonably accurate estimates of η and J_e. Errors involved were estimated to be less than 5% in the case of J_e and much smaller in the case of η.[21] The values of η and J_e thus obtained are summarized in Table II.

Since the dependence of η on *M* should be discussed at a constant friction factor ζ_0, or, in other words, at the iso-free-volume state, the values of η for the low molecular weight samples, I-21 and I-23, were multiplied by factors of 1.80 and 1.25, respectively, which were derived from the shift of the master curves of these samples in the transition zone. Correction due to the variation of ρT was also applied, though it

Table II
The Experimental Results for Poly(*cis*-isoprene) at −30 °

Sample	η, P	J_e, cm²/dyn	τ_m, sec	M_e
I-21	5.98×10^7	1.38×10^{-6}	2.37×10^2	3.34×10^3
I-23	6.70×10^8	1.38×10^{-6}	3.01×10^3	3.50×10^3
I-25	1.78×10^9	1.43×10^{-6}	1.11×10^4	3.50×10^3
I-31	5.03×10^{10}	1.40×10^{-6}	2.13×10^5	3.50×10^3
I-32	2.70×10^{11}	1.50×10^{-6}	1.49×10^6	3.09×10^3
I-34	1.77×10^{12}	1.20×10^{-6}	1.16×10^7	3.13×10^3

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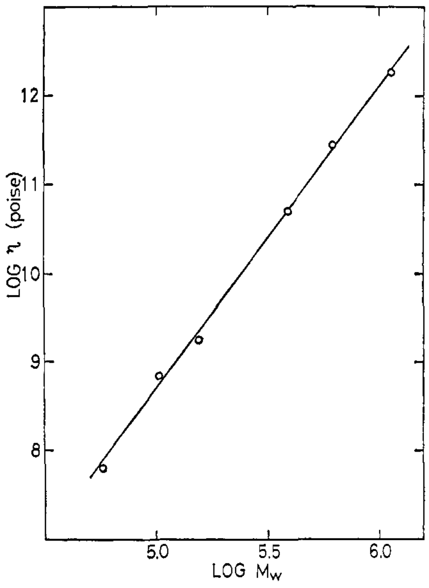

Figure 5. The logarithmic plot of η at constant friction factor against M_w.

was negligibly small in all cases. In Figure 5, the values η at constant ζ_0 are plotted against M_w on the double logarithmic scale. It is seen that the plots are well represented by a straight line with a slope of 3.4. The same slope has been obtained by Fetters for the solution viscosity of narrow-distribution poly(*cis*-isoprene) in decane.[22]

Figure 6, the logarithmic plot of J_e against M_w, shows that J_e is nearly independent of M_w over the entire range studied. This behavior is the same as that observed for two other narrow-distribution polymers, polystyrene[2-5] and poly(α-methylstyrene) having high molecular weights.[6,7]

In order to study the molecular weight dependence of the maximum relaxation time τ_m, the creep master curves given in Figure 3 were converted, through the use of the well-known approximate formula,[23] to the relaxation moduli. τ_m was calculated from the latter with the aid of the procedure of Tobolsky and Murakami.[24] The values of τ_m at $-30°$ are given in Table II and plotted logarithmically against M_w in Figure 7. Here the values for I-21 and I-23 have been multiplied by the same factors as those used for the viscosity. τ_m varies as the 3.4th power of M_w, though some scattering of the data is observed.

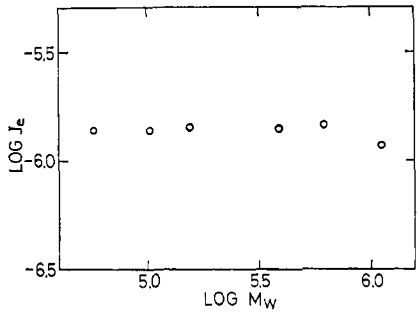

Figure 6. The logarithmic plot of J_e against M_w.

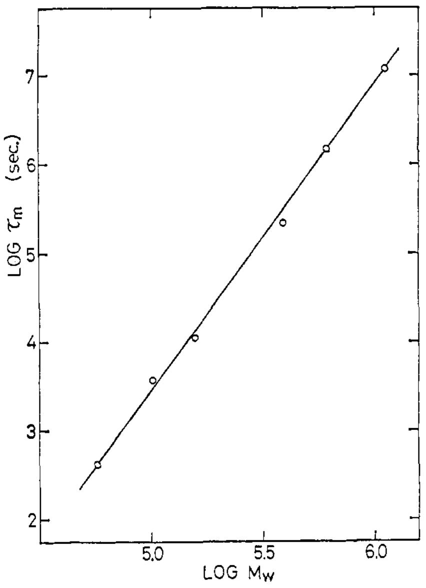

Figure 7. The logarithmic plot of τ_m against M_w.

Discussion

Because of a lack of low molecular weight data, we could not locate the value of the critical entanglement molecular weight M_c. All the polymers investigated have molecular weights higher than M_c, and accordingly we must confine ourselves to discussions of the properties of bulk polymers in the entangled state.

Two different predictions concerning the molecular weight dependences of J_e and τ_m of the entangled systems have been presented theoretically. The first, which is due to Ferry, *et al.*,[25] predicts J_e to be proportional to M and τ_m to $M^{4.4}$. The basic assumption in this theory is that the effect of entanglements is equivalent to the effect of the increased friction constant on the chain motion, with nodes spaced farther apart than $2M_e$. Here M_e is the molecular weight between entanglement coupling points. The recent theory of Chompff, *et al.*, also predicts similar dependences of J_e and τ_m on M.[26] On the other hand, Hayashi has assumed that the entanglement affects not only the friction constant but also the elastic force constant of polymer chains.[27] Then, based on a temporarily cross-linked network model, he has shown that J_e is nearly independent of M, while τ_m is proportional to $M^{3.5}$. The present results are in agreement with these predictions.

The average molecular weight between entanglement coupling points, M_e, can be evaluated from the inflection point in the log $J(t)$ *vs.* log t curve of each sample in the plateau zone with the aid of the theory of rubberlike elasticity.[28] As shown in Table II, the entanglement spacing M_e determined by that method is nearly independent of M_w. Its magnitude is somewhat smaller than the selected average of published results (*ca.* 5000) of Porter and Johnson.[29] The value of the critical entanglement molecular weight M_c for bulk poly(*cis*-isoprene) has not been determined yet. However, if an extrapolation is made from the solution data of Fetters, M_c is

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(28) A front factor of 1 was assumed here: see P. J. Flory, *Chem. Rev.*, **35,** 51 (1944).

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14,000.[22] A rather large value of about 4 is obtained for the ratio of M_c/M_e, but this, of course, is no more than a tentative estimate. In order to locate M_c of bulk polymers, the shear creep study extending to a molecular weight of 2000 is now in progress in our laboratory.

Recently, Graessley and Segal have presented a semiempirical equation which expresses J_e in terms of the entanglement density E.[30] For highly entangled systems, the equation is simplified as

$$J_{eR}/J_e = (1/5)E \tag{3}$$

in which J_{eR} represents the steady-state compliance for a monodisperse collection of Rouse chains, *i.e.*

$$J_{eR} = (2/5)(M/\rho RT) \tag{4}$$

Here ρ is the density and RT has its usual meaning. Since E is given by M/M_e, the above equation (3) shows the independence of J_e on M, in agreement with the present result. However, the values of J_e and M_e given in Table II yield

$$J_{eR}/J_e = 0.052E \tag{5}$$

The numerical coefficient is smaller by a factor of about 4 than that in eq 3.

In conclusion, the present results seem to be favorable to the view that the independent nature of J_e on M first observed on polystyrene and poly(α-methylstyrene) is common to a wider class of narrow-distribution polymers, at least of nonpolar polymers.

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Configurational Statistics of 1,4-Polybutadiene Chains

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ABSTRACT: 1,4-Polybutadiene chains are treated in terms of structural units CH—CH$_2$—CH$_2$–CH═ consisting of three single bonds bounded by double bonds. Although conformational interactions differ markedly depending on the steric configuration, cis or trans, of the adjoining double bonds, those within a given unit are essentially independent of the conformations of neighboring units in all cases. The units thus defined may be treated, therefore, as statistically independent. The present scheme as applied to the stereoregular polymers in which all double bonds are either cis or trans is virtually equivalent to that of Mark. It offers the advantage of being readily applicable to polymers comprising both cis and trans residues CH$_2$—CH═CH—CH$_2$ in any specified proportion and succession. Statistical weight parameters are chosen in the light of conformational energy calculations and newer results of spectroscopic investigations on low molecular analogs. Average chain dimensions and their temperature coefficients, strain-birefringence coefficients, average bond conformations, coefficients of rotational isomerization by stretching, and strain-induced dichroic effects are calculated as functions of the stereochemical composition. The properties of predominantly trans polymers are much more sensitive to stereoirregularity (*i.e.*, to cis residues) than are those of predominantly cis polymers.

Rotational isomeric state schemes for the statistical treatment of *cis*-1,4- and *trans*-1,4-polybutadiene chains and of the corresponding polyisoprenes were formulated by Mark.[1-3] He succeeded in giving a coherent account of the characteristic ratio $C_\infty = (\langle r^2\rangle_0/nl^2)_{n\to\infty}$ and of the temperature coefficient d ln $\langle r^2\rangle_0/\mathrm{d}T$ of the mean-square end-to-end distance $\langle r^2\rangle_0$ for each of these four polymers. His analysis is in satisfactory accord with results of experiments. Ishikawa and Nagai[4,5] applied the same scheme to the treatment of the strain birefringence of the polydienes.

In this paper we present a comprehensive treatment of the properties of poly-1,4-butadiene (PBD). In addition to revised calculations on the characteristic ratio, its temperature coefficient, and the strain birefringence,[3,6-8] we have investigated average bond conformations,[3,9] rotational isomerization with stretching,[10] and preferential orientations[11] of *cis-* and *trans*-C—CH═CH—C *residues* according to methods developed recently. Mark's[1,2] rotational isomeric scheme for PBD chains is reexamined and minor modifications are introduced. It is reformulated in terms of *structural units* CHCH$_2$CH$_2$CH═ embracing three single bonds and bounded by successive double bonds of the chain. Inasmuch as these may be either cis or trans, four kinds of structural units are distinguished. Through analysis of the interactions dependent upon rotations about the sequence of three single bonds comprising each kind of structural unit, a basis is established for treating chains containing both cis and trans double bonds (*i.e.*, both cis and trans residues) in any proportion and any order of succession. Calculations of the properties of PBD chains are carried out as a function of the fraction f_{cis} of cis residues throughout the range $0 \leq f_{cis} \leq 1$. We thus explore the effects of stereoirregularity.

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