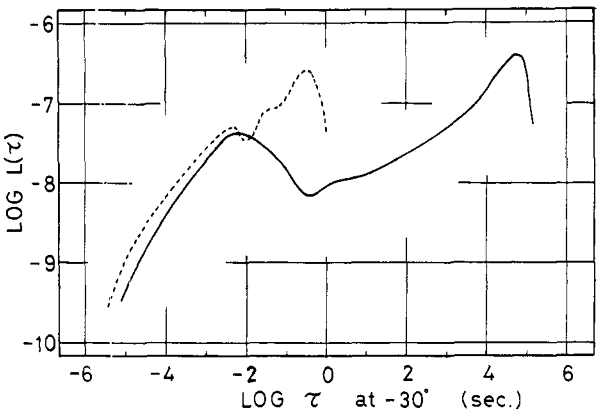

Figure 5. Two examples of the retardation spectrum: (—) I-31, (- - -) I-20.

which appeared at the end of the transition zone. Actually, the lower limit a was extended to $-\infty$, 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

$$J_{eN} = M_e/\rho RT \qquad (5)$$

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.

Acknowledgment. The authors are greatly indebted to Mr. T. Ogawa for his assistance in creep measurements.

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

---

(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.

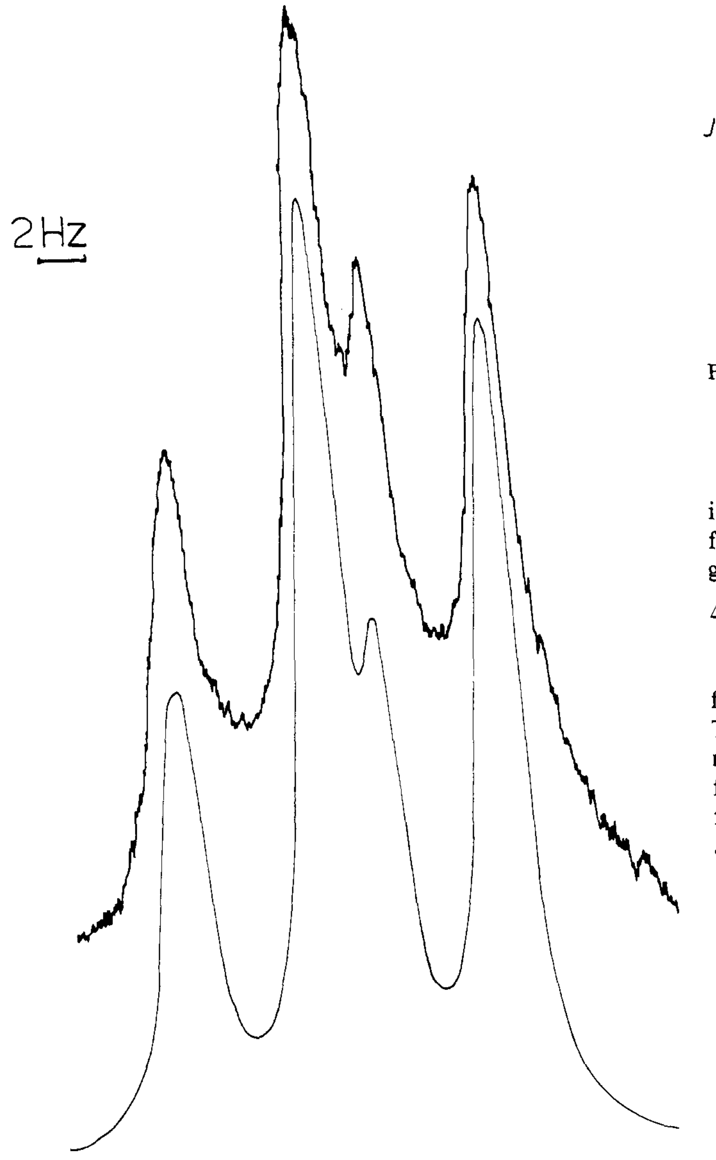

Figure 1. ^{13}C satellite pmr spectrum of poly(perdeuterioethylene-*co*-1-^{13}C-enriched ethylene) (upper trace, observed; lower trace, calculated).

$K = -26$ Hz,[2] $N = 14.8$ Hz, and different values of L, and, by comparison with the experimental spectrum, we got the best fit for $L = -2.9 \pm 0.3$ Hz. This gives $J = 5.95 \pm 0.16$ and $J' = 8.75 \pm 0.16$. Of course the sign of L is not given by this procedure.

Within the hypothesis of rotational isomerism, let us assume that the CH_2CH_2 fragment conformation is an equilibrium between the forms of Figure 2, where P indicates the polymer chain. The energy difference $\Delta E° = E_g° - E_t°$ is given by the expression

$$\Delta E° = RT \ln 2 \frac{n_t}{n_g} \qquad (1)$$

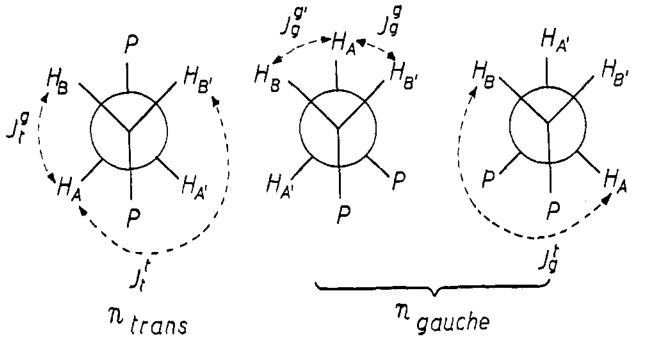

Figure 2. Rotational isomers of CH_2–CH_2 fragment.

where $E_t°$, $E_g°$, and n_t, n_g are the energies and molar fractions respectively, of the trans and gauche rotamers, and $n_t + n_g = 1$. The vicinal interproton coupling constants J and J' are the molar average of the individual couplings[3] (Figure 2). Superscripts indicate the orientation of the protons involved in the coupling, and subscripts indicate the conformers.

$$J = n_t J_t^g + n_g(J_g^t + J_g^{g'})/2 \qquad (2)$$

$$J' = n_t J_t^t + n_g J_g^g \qquad (3)$$

Combining the relationships 1 and 2 or 1 and 3 gives, respectively:

$$\Delta E° = RT \ln 2\,(J' - J_g^g)/(J_t^t - J') = RT \ln\,(J_t^g + J_g^{g'} - 2J)/(J - J_t^g))$$

from which is possible to calculate $\Delta E°$ in two different ways. The individual conformer parameters were obtained from model compounds: 1,2-di-*tert*-butylethane[3] for the trans form and 1,1,4-tetradeuteriocyclohexane[2] for the gauche form: $J_t^g = 12.94$; $J_t^g = 4.30$; $J_g^t = J_{aa} = 13.12$; $J_g^g = J_{ae} = 3.65$; and $J_g^{g'} = J_{ee} = 2.96$.

The values of $\Delta E°$ obtained using the above relations and parameters were 0.70 ± 0.05 and 0.72 ± 0.15 kcal/mole, respectively, from J' and J. In view of the approximation used in obtaining the L parameter, we also have calculated the $\Delta E°$ value on the basis of the measurement of N only. For this purpose we recall[3] that the sum of the vicinal coupling is again a molar average of N_g and N_t where $N_t = J_t^g + J_t^t$ and

$$N = n_t N_t + n_g N_g \qquad (4)$$

$N_g = [(J_g^t + J_g^{g'})/2] + J_g^g$. Combining relations 1 and 4 gives $\Delta E° = [RT \ln 2](N - N_g)/(N_t - N)$, from which a value of $\Delta E° = 0.68 \pm 0.06$ kcal/mole has been obtained, in fairly good agreement with the above values. Although this fact does not prove that the analysis is exact, it shows that it is not obviously wrong.

We can conclude that a reasonable value of $\Delta E°$ is 0.7 ± 0.15 kcal/mole where the quoted error is a combination of the experimental accuracy and of the approximation of taking the values of the individual J's from the model compounds.

The obtained value is a measure of the ratio of trans and gauche monomeric units of the polymer and, of course, does not give any information about the conformation of larger units. However, as far as we are aware, it is the first experimental determination of the average conformational energy of polyethylene.

L. Zetta,* G. Gatti
Istituto di Chimica delle Macromolecole, C.N.R.
20133 Milan, Italy

Received December 14, 1971

Evidence for the Occurrence of Flexible Sugar Ring Conformers in Cellulosic Chains

Several workers have attempted recently to provide an interpretation of the observed unperturbed polymer coil

---

(2) E. W. Garbisch and M. C. Griffith, *J. Amer. Chem. Soc.*, **90**, 6543 (1968).

(3) R. J. Abraham and G. Gatti, *J. Chem. Soc.*, 961 (1969).