Chain Dynamics of Poly(but-1-ene) from Carbon-13 Nuclear Magnetic Relaxation Measurements

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ABSTRACT: Carbon-13 spin–lattice relaxation and nuclear Overhauser enhancement measurements have been carried out on poly(but-1-ene) in pentachloroethane solution over the temperature range −15 to 130 °C at 90.52 and 22.62 MHz. At the higher frequency, all spin–lattice relaxation times except those of the methyl group pass through a minimum as a function of temperature. The nuclear Overhauser enhancements increase monotonically with increasing temperature and approach their maximum value of 2.99 only above 40 °C at the lower frequency. The relaxation data for the chain backbone are interpreted in terms of isotropic motional models characterized by (i) a single correlation time and (ii) two correlation times. The latter model is more satisfactory.

The chain dynamics of a number of polymers in bulk and solution have been examined by ^{13}C relaxation measurements.[1–23] These include polystyrene,[1,3,8,16,18] poly(*m*-fluorostyrene),[10] poly(*p*-fluorostyrene),[10] poly(4-vinylpyridine),[6] poly(vinyl chloride),[5] polyacrylonitrile,[3,5] poly(vinyl alcohol),[5] polyisobutylene,[5,12,15] polyethylene,[4,23] polypropylene,[4,16,17] poly(methyl methacrylate),[16,21,22] poly(*n*-butyl methacrylate),[7] poly(methacrylic acid),[14] poly(vinylidene fluoride),[21] poly(styrene peroxide),[18] poly(styrene sulfide),[19] poly(styrene sulfone),[20] poly(but-1-ene sulfone),[20] poly(methylene oxide),[11] poly(ethylene oxide),[3] poly(propylene oxide),[12,16] poly(dimethylphenylene oxide),[13] poly(diphenylphenylene oxide),[13] *cis*- and *trans*-polyisoprene,[2,8] and *cis*-polybutadiene.[8,9]

Few ^{13}C dynamic experiments have been reported for polyolefins despite their importance and structural simplicity. Inoue et al.[4] observed isotactic and atactic polypropylene between 100 and 150 °C and could detect no dependence of the ^{13}C spin–lattice relaxation time T_1 on stereoisomerism, although Randall[17] has reported marginally longer T_1 values for isotactic sequences in an atactic polymer. The study of Inoue et al. was carried out at temperatures sufficiently high for the nuclear Overhauser enhancement (NOE) to have its theoretically maximum value of 2.99 for all carbons; the work of Randall did not include NOE data. In addition, these studies were performed at a single spectrometer frequency, so they do not furnish a basis for a critical evaluation of the motional autocorrelation function for the chain backbone.[16]

Poly(but-1-ene) was chosen for this study because it is one of the simplest polyolefins which is soluble at low temperatures. Experiments could be conducted over a wide temperature range (−15 to 130 °C). Two magnetic field strengths (8.46 and 2.11 T) were used to extend the data base. One objective was to observe the ^{13}C T_1 values as a function of temperature and obtain their minima, which provide a sensitive test of the motional model and its related parameters.[16] At the higher field strength T_1 minima were observed for all carbons except that of the methyl group. However, at the lower field strength, corresponding to a fourfold reduction of the ^{13}C resonance frequency to 22.62 MHz, the T_1 minima occur at temperatures so low that the resonances are too broad for reliable measurement.

The combined T_1 and η data are sufficient to demonstrate that the main-chain motional autocorrelation function is represented poorly by a simple exponential. A more reasonable and consistent interpretation of the backbone motions of poly(but-1-ene) is made in terms of a motional model invoking two discrete correlation times.

Experimental Section

Material. The poly(but-1-ene) employed was prepared by Dr. R. H. Hansen (Bell Laboratories). It had an intrinsic viscosity in heptane at 60 °C of 0.33 dL/g, corresponding to a weight-average molecular weight of 69 500.[24] The appearance of the ^{13}C spectrum depends on temperature, as can be seen in Figure 1. At 85 °C, all peaks are narrow singlets which give no evidence of stereoisomerism. As the temperature is lowered the peaks broaden, partly because of the usual shortening of the spin–spin relaxation times, but also because structural irregularity becomes evident. It is likewise observed that all peaks except that of the methyl group move noticeably upfield; the principal resonance becomes more shielded by about 0.91 ppm over the temperature range 85 to 0 °C.

The side-chain methylene (sc-CH$_2$) resonance shows the greatest splitting as temperature is decreased. In the spectrum obtained at 0 °C, the peaks for this carbon are assigned to *mm, mr,* and *rr* triads (in order of increasing shielding) by analogy to the assignments established for the methyl group of polypropylene.[25,26] On this basis, the polymer is estimated to contain about 80% isotactic triads. It is unlikely that T_1 and NOE vary outside of experimental error with stereosequence.

Methods. The polymer solution was prepared at a concentration of 0.1 g/cm^3 in pentachloroethane and sealed under argon after it had been degassed on a vacuum line. The solution was contained in a tube of 8 mm outer diameter, which was placed concentrically in a 10 mm diameter tube. The annulus was filled with ethylene glycol-d_4, deuterium oxide, or acetone-d_6 to provide the deuterium lock signal for the spectrometer at high, medium, and low temperatures, respectively.

Measurements were made on Bruker HX-360 and WH-90 spectrometers with ^{13}C resonance frequencies of 90.52 and 22.62 MHz, respectively. Temperatures were measured with a calibrated thermocouple and a thermometer placed in a tube containing ethylene glycol. All T_1 values were derived from manual plots of the relaxation data obtained by the standard inversion-recovery method. Depending on temperature and the spectrometer, between 600 and 20 000 scans were required for each value of the delay time τ between the π inverting pulse and $\pi/2$ sampling pulse. Repetition times for the π pulses were greater than $5T_1$ in all cases, except for measurement of the methyl carbon relaxation at 130 °C and 90.52 MHz, for which it was $3.5T_1$. Between 7 and 11 τ values were used to obtain each T_1 value.

NOE measurements were made by direct comparison of peak areas obtained with broadband proton decoupling to the corresponding areas obtained when the decoupler was in the coherent mode and offset from the proton resonance frequency by 16 to 30 kHz in order to maintain constant sample temperature. Peak areas were measured by the computer integration routine included in the spectrometer software and by weighing cut out traces of the peaks; the two methods gave essentially equal results. Line widths in the proton-decoupled spectra at 90.52 MHz varied from a minimum of ca. 6 Hz at 130 °C to a maximum of ca. 24 Hz at −10 °C (we have seen that some of the broadening at the lower temperatures is attributable to chemical shift dispersion).

A spectral window of 10 000 Hz and 16K computer locations were used for data acquisition on the HX-360; the respective values on the

0024-9297/78/2211-0325$01.00/0

Table I
Effect of Temperature on the Carbon-13 Spin–Lattice Relaxation Times and Nuclear Overhauser Enhancements for Poly(but-1-ene) Observed at Two Magnetic Field Strengths in Pentachloroethane Solution (0.1 g/cm^3)

	Temp, °C												
	T_1, ms ± 5%						$\eta + 1$, NOE ± 10%						
Carbon	130	100	85	40	0	−15	130	100	85	40	20	0	−10
					Field Strength = 8.46 T								
α-CH	520		230	200	230		2.5	2.3	2.3	1.6	1.4	1.3	1.2
β-CH$_2$	290		160	120	160		2.6	2.4	2.1	1.6	1.4	1.2	1.2
sc-CH$_2$	410		190	140	150		2.3	2.3	2.1	1.7	1.5	1.4	1.3
-CH$_3$	2370		1240	770	580		2.3	2.3	2.3	1.9	1.6	1.6	1.5
					Field Strength = 2.11 T								
α-CH	450	310	230	110	60	60	2.6		2.8	2.8			
β-CH$_2$	260	190	150	60	35	27	2.7		2.6	2.5			
sc-CH$_2$	340	240	180	70	55	29							
-CH$_3$				590									

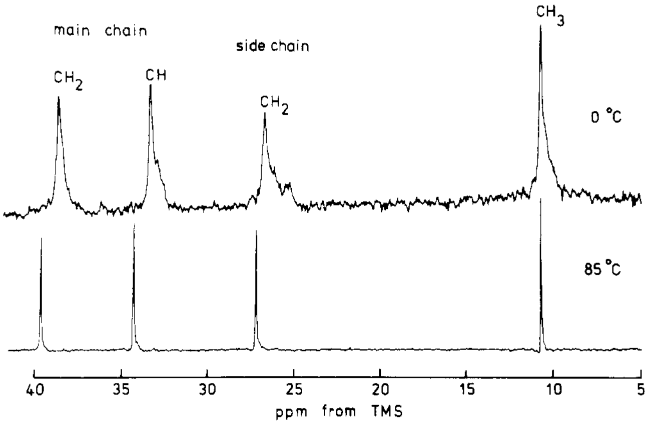

Figure 1. Carbon-13 NMR spectra of poly(but-1-ene) at 90.52 MHz. Stereoirregularity only becomes apparent at the lower temperature (0 °C). Experimental details as follows: The 0 °C spectrum represents 6000 transients accumulated with a repetition time of 0.6 s in 8K computer points with a window of 10 000 Hz. The 85 °C spectrum represents 400 transients accumulated with a repetition rate of 3.0 s in 32 K computer points with a window of 10 000 Hz.

WH-90 were 3012 Hz and 8K. The T_1 values were reproducible to ±5%. The relative error in the NOE values was substantially greater (±10%), owing to the difficulty in obtaining a reasonable signal-to-noise ratio in the proton-coupled spectra. This difficulty, compounded by line broadening, made it impractical to obtain NOE values below 40 °C at 22.62 MHz.

Results and Discussion

I. General Features of the T_1 and NOE Relationships to Temperature. The relaxation data are given in Table I. At 90.52 MHz all T_1 values except that of the methyl group pass through a minimum between 40 and 0 °C. It was not possible to observe any T_1 minima at 22.62 MHz. The NOE values are not as sensitive to temperature as the T_1 values. Within experimental error, the NOE for the backbone carbons approaches the maximum value 2.99 above 40 °C at 22.62 MHz. This is not the case at 90.52 MHz, where all NOE values are less than maximum even at 130 °C and decrease monotonically with decreasing temperature.

At any given temperature the C–H bonds of the side chain carbons are reorientating more rapidly in the laboratory frame than those of the backbone carbons. The dipolar relaxation (next section) of the side chain carbons is therefore less efficient with the present field strengths and temperature range, resulting in longer relaxation times. This is particularly marked for the methyl group, which is able to rotate very rapidly. A quantitative evaluation of side chain motion will not be presented here.

II. Quantitative Treatment of Relaxation Data. Under the present conditions all ^{13}C nuclei in poly(but-1-ene) relax exclusively by a dipolar mechanism with N directly bonded protons at distance $r_{\text{C-H}}$. Therefore the following relations apply:[27]

$$\frac{1}{NT_1} = \frac{1}{10}\frac{\gamma_H^2\gamma_C^2\hbar^2}{r_{\text{C-H}}^6} \times \{J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)\} \quad (1)$$

$$\eta = \frac{\gamma_H}{\gamma_C}\left\{\frac{6J_2(\omega_H + \omega_C) - J_0(\omega_H - \omega_C)}{J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)}\right\} = \text{NOE-1} \quad (2)$$

where the $J_n(\omega)$ terms are the spectral density functions which prescribe the components of the motional frequency spectrum at $(\omega_H - \omega_C)$, ω_C, and $(\omega_H + \omega_C)$. These spectral densities are the Fourier transforms of the autocorrelation functions for the orientation angle of the C–H bond vector in the laboratory frame, expressed as second-order spherical harmonics.

It is necessary to have some dynamic model to interpret the observed T_1 and η values. The simplest model (model I) views the macromolecule as a rigid sphere immersed in a viscous continuum and randomly reoriented by a series of small-angle diffusive steps. For such isotropic rotatory diffusion the angular orientational autocorrelation function decays exponentially with time constant τ_c (the motional correlation time), leading to the familiar spectral density term:

$$J_n(\omega) = \frac{\tau_c}{1 + \omega^2\tau_c^2} \quad (3)$$

Thus the chain motion is characterized by a single discrete correlation time τ_c.

An alternative model (model II) is one originally developed by Hunt and Powles[28] to describe the proton relaxation of glycerol and isobutyl bromide in the viscous and glassy states. Their model was based on the defect-diffusion model proposed by Glarum[29] and included an extra term to account for molecular tumbling. Valeur and co-workers[30] formulated a model of localized conformational jumps of chain segments on a tetrahedral lattice, involving three and four bond motions without conformational bias. Their spectral density function was identical to that of Hunt and Powles provided that a term was included for large-scale tumbling motion.[31] The appropriate spectral density term for backbone motions is:[16]

$$J_n(\omega) = \frac{\tau_0\tau_D(\tau_0 - \tau_D)}{(\tau_0 - \tau_D)^2 + \omega^2\tau_0^2\tau_D^2}\left\{\left(\frac{\tau_0}{2\tau_D}\right)^{1/2}\right.$$

Table II
Parameters for the Motional Models to Describe the Carbon-13 NMR Relaxation of Poly(but-1-ene) at Various Temperatures

Temp °C	Model I log (τ_cS)	Model II log (τ_DS)	 τ_D/τ_0
130	−10.00	−10.25	0.10
100	−9.79	(−9.78)[a]	(0.20)
85	−9.67	−9.67	0.25
40	−9.25	−9.27	0.33
20	−9.03	(−8.92)	(0.50)
0	−8.77	−8.67	0.70
−10	−8.62	(−8.45)	(0.80)
−15	−8.55	(−8.33)	(0.90)

[a] Values in parentheses were chosen partly with regard to maintaining a consistent trend with temperature (see text).

$$\times\left[\frac{(1+\omega^2\tau_0{}^2)^{1/2}+1}{1+\omega^2\tau_0{}^2}\right]^{1/2}+\left(\frac{\tau_0}{2\tau_D}\right)^{1/2}$$
$$\times\frac{\omega\tau_0\tau_D}{(\tau_0-\tau_D)}\left[\frac{(1+\omega^2\tau_0{}^2)^{1/2}-1}{1+\omega^2\tau_0{}^2}\right]^{1/2}-1\bigg\} \quad (4)$$

Here, τ_0 characterizes large-scale tumbling motions and τ_D characterizes local segmental motions.

Evaluation of model I (eq 1, 2, and 3) and model II (eq 1, 2, and 4) was done by computer. A C–H bond distance of 0.11 nm was chosen. For model II a series of T_1 and η values were calculated with log τ_D in the range from −6.0 to −12.0 (incremented by steps of 0.01) for a variety of τ_D/τ_0 ratios R from 0.001 to 10.0. These computed values allowed a family of relaxation curves (NT_1 and η vs. log τ_D for each R) to be constructed at both magnetic field strengths. At each temperature the most appropriate curve set (and hence τ_D and τ_0 values) was selected by obtaining the most consistent match to the eight independent observables (NT_1 and η for the α and β carbons at two field strengths). The number of observables was insufficient at 100, 20, −10, and −15 °C to allow an unambiguous choice of τ_D and τ_0. In these cases the reasonable assumption that the correlation times varied consistently with temperature provided an additional criterion for selection.

A satisfactory match of the experimental data over the entire temperature range could not be obtained with model I. However, for the purpose of comparison, two reasonable assumptions were made. First the model was considered to be valid at the highest observation temperature (130 °C) so that τ_c could be obtained from NT_1. Second it was assumed that τ_c varied with temperature according to an Arrhenius type expression with an apparent activation energy of 20 kJ/mol (a typical value for the potential barrier to conformational transitions in polymers of the present type). Then τ_c could be calculated at the lower temperatures, from which NT_1 and η could be predicted according to the model.

The correlation times for the two models at various temperatures are shown in Table II. The correspondong NT_1 and η values lie on the dashed curves for model I and on the solid curves for model II in Figure 2. Neither model fits all the data within experimental error over the entire temperature range. The reliability of the NOE data is poor compared to the T_1 data. The latter are also more sensitive and provide a more stringent test of the models at the temperature extremes.

It is clear from Figure 2 that model II is the more satisfactory. The NT_1 minima predicted by model I are too low (37.5 and 150 ms at 2.11 and 8.46 T, respectively) compared to the experimental data. Further, whereas this model fits the NT_1 data at the higher temperatures, it then predicts η values which are greater than those observed at 8.46 T.

A significant deviation of the observed data from model II occurs at 8.46 T for the lowest temperatures. Here the predicted η values are too high and the predicted NT_1 values are too low. Model I can reproduce the low-temperature η values at 8.46 T (but, as we have seen, the correspondence to NT_1 is then particularly poor). It is significant that the experimental NT_1 values for the α and β carbons are not equal at these low temperatures, particularly at 8.46 T. This suggests that eq 1 is not strictly correct and its deficiency is most likely due to the assumption of isotropic motion. Similar results have been reported for poly(propylene oxide) in bulk[8] and solution,[12] being particularly marked in the former state.

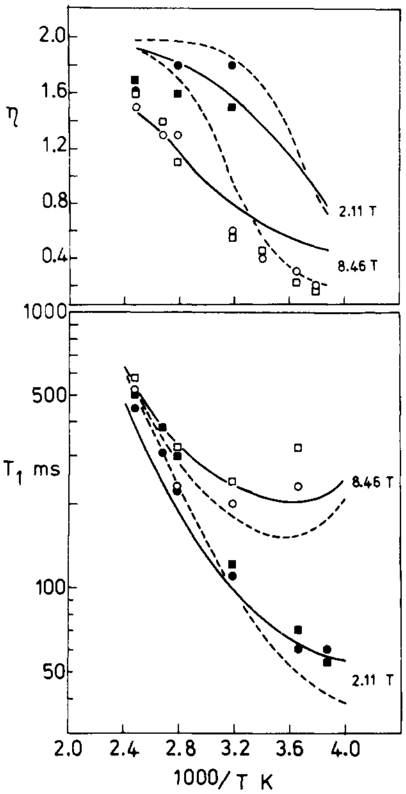

Figure 2. Comparison of the relaxation curves computed from model I (dashed curves) and model II (solid curves) with the observed data for the chain backbone of poly(but-1-ene): Circles, α carbon; squares, β carbon; open points, data obtained at 8.46 T; closed points, data obtained at 2.11 T.

From Table II we note that the τ_D/τ_0 ratio for model II increases with decreasing temperature, indicating a larger activation energy for local segmental jumps than for long-range tumbling-type motions. This behavior has been observed for polystyrene and poly(propylene oxide).[16] The values of the apparent activation energies derived from Arrhenius plots are 22 kJ/mol for segmental jumps and 12 kJ/mol for tumbling. The former value approximates the backbone torsional potential barrier and the latter is nearly identical to the viscosity activation energy for the solvent, which is 13 kJ/mol.[32]

The activation energies are quite reasonable and lend support to model II. However, as pointed out by Heatley,[16] the conformity to reasonable physical behavior may be coincidental, as the two adjustable parameters (τ_D and τ_0) allow a fair latitude in the model.

Our results reinforce the findings by others that model I is not generally satisfactory in its description of polymer NMR relaxation data.[8,16] It is conceiveable that a motional model involving a suitable distribution of correlation times[8] would describe our data as well as model II. However, Heatley et al.[33,34] have recently demonstrated that the latter approach is more realistic and for this reason it has been adopted here.

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Stopped-Flow Study of the Cationic Polymerization of Styrene Derivatives. 1. Direct Observation of the Propagating Species in the Polymerization of *p*-Methoxystyrene in 1,2-Dichloroethane

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Received September 12, 1977

ABSTRACT: Stopped-flow spectroscopy allowed the direct observation of the propagating species in the cationic polymerization of *p*-methoxystyrene in 1,2-dichloroethane at 30 °C. The reactions with four initiators (iodine, CH_3SO_3H, $BF_3O(C_2H_5)_2$, and $SnCl_4$) gave almost identical absorption spectra centered at 380 nm, which were assigned to the propagating carbocation. The absorbance changes at 380 nm showed a quantitative correlation with monomer consumption rate (monitored at 295 nm) to give propagation rate constants (k_p). The k_p values for the four initiator systems ranged from 4×10^3 to 2×10^4 M^{-1} s^{-1} and were practically independent of the initiators, indicating that the nature of the observed propagating species does not depend on counterions. On the other hand, the maximal concentration ($[P^*]_{max}$) of the propagating species strongly depended on the initiators; i.e., with the metal halides $[P^*]_{max}$ was 5–25% of the initiator concentration ($[C]_0$), whereas iodine and CH_3SO_3H gave much smaller $[P^*]_{max}$ (ca. 0.1% of $[C]_0$).

The chemistry of the propagating species is one of the most important but still unsolved problems in the cationic polymerization of vinyl compounds. In most studies this has been discussed in an indirect manner based on overall polymerization kinetics and the structure of product polymers. Our recent work also deals with the rate and molecular weight distribution of polymers in styrene polymerization.[1] Direct and quantitative information on the propagating species may be given by its spectroscopic observation.

Stopped-flow spectroscopy allows the sensitive detection of transient reaction intermediates with a millisecond time resolution.[2] Pepper and his co-workers[3,4] recently applied this technique to the cationic polymerization of styrene by perchloric acid in dichloromethane at low temperatures. They detected a transient absorption at 340 nm, which was assigned to the polystyrylcarbenium ion. Kunitake and Takarabe[5] have also reported the observation of carbocationic intermediates in several systems. In spite of these results, however, there is a substantial lack of information on the propagating species.

This first paper of our series describes a stopped-flow study of the cationic polymerization of *p*-methoxystyrene by a variety of initiators in 1,2-dichloroethane. We have chosen the monomer because it is reactive in polymerization and should form a relatively stable carbocation that is suitable for spectroscopic observation. With four initiators (iodine, CH_3SO_3H, $BF_3O(C_2H_5)_2$, and $SnCl_4$), we found a common intermediate absorption to be due to the propagating species. This led to the determination of its concentration and propagation rate constant discussed below.

Experimental Section

Materials. *p*-Methoxystyrene was prepared from *p*-methoxyacetophenone by the reduction with $LiAlH_4$ followed by the dehydration of the corresponding alcohol with $KHSO_4$.[6] Distillation over calcium hydride under reduced pressure gave a monomer with a gas-chromatographic purity better than 99%. Iodine (Nakarai Chemicals, purity ≥99.8%) was used as received without further purification. Methanesulfonic acid (CH_3SO_3H), boron trifluoride etherate ($BF_3O(C_2H_5)_2$), and stannic chloride ($SnCl_4$) were purified by distillation of commercial products. 1,2-Dichloroethane as solvent

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