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(34) **Note Added in Proof**: Solid-state ^{2}H NMR studies show that 180° phenylene ring flips occur in the amorphous regions of poly(butylene terephthalate).

NMR Relaxation in Poly(butylene terephthalate) and Poly(butylene terephthalate)-Containing Segmented Copolymers. 5

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ABSTRACT: Solid-state ^{13}C NMR has been used to estimate the rate of molecular motion for all of the alkyl carbons of the segmented copolymer poly(butylene terephthalate-*co*-tetramethyleneundecakis(oxytetramethylene) terephthalate). A combination of solid-state NMR techniques (see preceding paper) has been used in conjunction with solid-state ^{13}C NMR spin-lattice relaxation time (T_1) measurements, carbon spin-lattice relaxation times in the rotating frame $\langle T_{1\rho}(\mathrm{C})\rangle$, and nuclear Overhauser enhancements (NOE). These relaxation data (1) point to substantial molecular motions of the alkyl carbons of the hard-segment regions of the segmented copolymer, (2) indicate that either the rate or the amplitude of motions of the aliphatic carbons of poly(butylene terephthalate) is greater than those reported previously for poly(ethylene terephthalate), and (3) corroborate the occurrence of phenylene ring motions in the segmented copolymer containing 0.80 mole fraction hard segments. In addition, the field-dependent T_1 and NOE data for the soft-segment $-CH_2-$ carbons are analyzed in terms of a log χ^2 distribution of rotational correlation times and are found to fit this model very well when the width parameter, p, is 7. Further, solution-state ^{13}C and ^{2}H NMR relaxation measurements suggest that the enhanced motions of the central $-CH_2-$'s (compared to the $-OCH_2-$ carbons) in the butylene terephthalate units in the solid state persist in solution. The motions in solution suggest a nearly isotropic excursion for the central $-CH_2-$ carbons but not for the adjacent $-OCH_2-$ carbons. These results are discussed in terms of a three-bond type of motion for these carbons.

Introduction

Although a precise correlation of polymer molecular structure and observed macroscopic behavior has generally proved elusive, it is clear that molecular motion is the principal link between these two fields.[1] Of the techniques of studying molecular motion in bulk polymers, solid-state high-resolution ^{13}C NMR spectroscopy is useful for measuring internal conformational changes—as opposed to translational motions—which have frequencies ranging from ca. 10^3 to 10^9 hertz. In contrast to its broad-line proton NMR predecessor, solid-state ^{13}C NMR offers the advantage that separate resonances are generally observed for each chemically unique carbon. In addition, spin diffusion among carbons generally does not occur, and thus ^{13}C NMR relaxation times may be measured for each separate resonance.[2-5]

Here we employ high-resolution ^{13}C NMR relaxation in bulk polymers to identify and study the modes and rates of internal conformational changes in a series of thermo-

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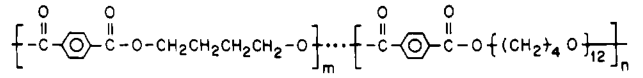
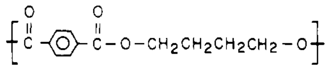
plastic elastomers.[6] In addition, we extend these studies to include a ^{13}C and ^{2}H characterization of NMR relaxation processes for these polymers in solution. These data, taken together with previous results,[7] enable us to estimate the nature and rate of molecular motion at each carbon of the segmented copolymer I. These results are compared to results for the homopolymer, poly(butylene terephthalate) (II).



m/n	SAMPLE
4:1	Ia
7:1	Ib
16:1	Ic
24:1	Id



II

Copolymer I and its solid-state ^{13}C NMR spectrum have been described previously.[7] In this paper we shall refer to the poly(butylene terephthalate) portion of copolymer I as the "hard" segment and to the poly(tetramethylene-undecakis(oxytetramethylene) terephthalate) section as the "soft" segment. This copolymer system offers several distinct advantages for a solid-state ^{13}C NMR study of molecular motion. First, the soft-segment carbons can be selectively observed,[8] if desired, or they can be observed in conjunction with the hard-segment carbons.[7] Second, the copolymer is available in a range of compositions, so it is possible to assess the effects that differing compositional ratios have on the relaxation parameters. In addition, the all-hard poly(butylene terephthalate) homopolymer provides a compositional control. Finally, other work[8,9] indicates that many of the motions of the carbons of this copolymer are rapid on the NMR time scale at ambient temperature—a convenient factor for the current technology of high-resolution solid-state NMR spectroscopy.

Materials and Methods

Samples. Copolymers I were provided by the du Pont Co. They were quenched from the melt and ground at cryogenic temperatures. The composition of these copolymers was established by ^{13}C NMR methods.[8] Poly(butylene terephthalate) was obtained from Eastman Chemical Co. It has $\bar{M}_w = 33\,500$ and a T_g of 80 °C. High-resolution solution-state ^{13}C NMR characterization showed no resonances due to end groups. The deuterated versions of polymers I and II were prepared by literature methods.[10]

Solid-State NMR Measurements. Solid-state ^{13}C NMR spectra were obtained at 47 kG (50.3 MHz for ^{13}C) both on a Varian XL-200 spectrometer and on a JEOL FX-200 spectrometer. The spectra measured at 14 kG (15.1 MHz for ^{13}C) were obtained on a home-built spectrometer, which has been described previously.[11] All spectrometers employ a two-level decoupling scheme with $\gamma B_2/2\pi$ greater than 45 kHz.

Spin–lattice relaxation times were measured by using magic-angle spinning and high-power proton decoupling, either by the progressive saturation method or by inversion–recovery.[12] Plots of the data show slight deviation from single-exponential behavior at long values of the τ delay. Consequently, the T_1 values were taken from a least-squares analysis of the data points out to 2–3 T_1's to avoid cross-correlation contributions to the relaxation times.[13]

Carbon-13 $T_{1\rho}$ measurements were performed according to literature methods.[2] The curves at long delay times show considerable deviation from single-exponential behavior. Only the initial part of the relaxation curve, usually from 0.1 to 0.8 ms, was used in a least-squares fit for the $T_{1\rho}$ determinations. These are reported as average $T_{1\rho}$ values, or $\langle T_{1\rho}(C)\rangle$.

Table I
Solid-State ^{13}C T_1 (s) Values[a] for the Protonated Carbons of Polymers Ia and Id and Poly(butylene terephthalate) (II)

carbon	polymer Ia[b]	polymer Id[c]	polymer II[c]
protonated aromatic	0.25	3[d]	2[d]
soft $-OCH_2-$[8]	0.17	0.20	
hard $-OCH_2-$	0.19	0.2	0.47
hard and soft $-CH_2-$	0.16	0.2	
hard $-CH_2-$			0.3
soft $-CH_2-$[8]	0.20[e]	0.20[e]	

[a] Determined by inversion–recovery at 50.3 MHz and 18 °C unless noted otherwise. [b] Uncertainty ±15%. [c] Uncertainty ±20%. [d] Determined by progressive saturation, uncertainty ±25%. [e] Temperature = 34 °C.

The spectra for relaxation time measurements were generally obtained by repeatedly cycling through the different delay times, each time adding in a few free induction decays. This method of experiment interleaving eliminates possible errors from long-term changes such as spinner instability, amplifier droop, and gradual change in the magic-angle setting.

Solution-State NMR Measurements. Carbon-13 and deuterium NMR spectra were recorded on the Varian XL-200 at respective frequencies of 50.3 and 30.7 MHz. Relaxation time measurements were performed on 10–15 wt % solutions of the polymers in *m*-cresol (Aldrich, Gold Label). A capillary of ethylene-d_4 glycol provided the signal for the field-frequency lock for the ^{13}C experiments; the ^{2}H experiments were run in the unlocked mode. T_1 measurements were made by using the inversion–recovery pulse sequence.[12] Nuclear Overhauser enhancement (NOE) measurements were made by employing the gated decoupling method[14] and are reported as $1 + \eta$. The method of data interleaving was employed for all relaxation measurements.

Results

A. Spin–Lattice Relaxation in the Solid State. Except for the protonated aromatic carbons, the T_1 values for all of the other protonated carbons are sufficiently short that they can be measured by the inversion–recovery method. The results of T_1 determinations for the copolymer containing the smallest amount of hard segments (Ia), the copolymer containing largest amount of hard segments (Id), and the homopolymer II are listed in Table I. The T_1 values for the carbonyl and nonprotonated aromatic carbons are very long (>10 s) and are not reported here.

The short T_1 values for the protonated carbons of both the segmented copolymer and poly(butylene terephthalate) indicate that each of these polymers has substantial spectral density in the megahertz frequency range. Although T_1 values such as these almost certainly reflect a weighted average, it was found that at least 90% of the carbons contribute to the signal in each case. The T_1 values for the soft-segment carbons are on the fast correlation time side of the T_1 minimum,[8] whereas low-temperature MAS T_1 measurements on poly(butylene terephthalate) indicate that these hard-segment carbons are likely to have motions on the slow correlation time side of the T_1 curve. This latter finding is supported by chemical shift anisotropy[9] and ^{1}H–^{13}C second-moment[8] considerations.

Spin diffusion is generally negligible among dilute ^{13}C nuclei[15] and it is unlikely that spin diffusion is occurring here, as these spin–lattice relaxation times (Table I) are several orders of magnitude shorter than the time required for spin diffusion to occur.[15]

B. Relaxation in the Rotating Frame. Carbon-13 $T_{1\rho}$ determinations measure the loss of carbon magnetization in the rotating frame as a function of the time the proton

Table II
$\langle T_{1\rho}(C)\rangle$ Values[a] (ms) for the Soft-Segment Carbons of Polymers Ia and Id

carbon	polymer Ia	polymer Id
$-OCH_2-$	4.5[b]	1.7[c]
$-CH_2-$	5.9[b,d]	

[a] The $\langle T_{1\rho}(C)\rangle$ values were determined from the initial (0.05-0.1 to 0.8 ms) part of curve; observed to be independent of B_1; measured at 20 °C; estimated uncertainty ±10%. [b] Average of measurements at B_1 fields of 15, 20, 28, 37, and 41 kHz. [c] Average of measurements at B_1 fields of 15, 20, and 41 kHz. [d] This value represents contributions from 0.20 mole fraction hard-segment carbons.

B_1 spin lock field is turned off. The $\langle T_{1\rho}(C)\rangle$ cannot be considered to be purely a measure of molecular motion, as in addition to the spin-lattice processes, spin-spin relaxation can also contribute to the loss of ^{13}C magnetization. Spin-spin relaxation is not a dominant contributor to $T_{1\rho}$ relaxation in glassy polymers, and Schaefer and co-workers have shown that $\langle T_{1\rho}(C)\rangle$ measurements generally can be used as a measure of molecular motion in glassy polymers at ambient temperatures.[2-5,16]

Several lines of evidence point to the dominance of spin-lattice relaxation for the $\langle T_{1\rho}(C)\rangle$ measurements of copolymers I and poly(butylene terephthalate) (II). First, our T_1 data (Table I) indicate that the protonated carbons have substantial spectral density in the megahertz frequency range. Second, chemical shift anisotropy considerations suggest that the aromatic carbons have motions that partially average the chemical shift anisotropy and thus have motions in the 10^3-Hz region.[7,9] Finally, the results of Sefcik et al.[3] point to $\langle T_{1\rho}(C)\rangle$ measurements as a measure of molecular motion in poly(ethylene terephthalate), and Schaefer et al.[4] find that average carbon $T_{1\rho}$'s (near 35 kHz) for a wide variety of glassy polymers at room temperature are predominantly spin-lattice in character. Poly(butylene terephthalate), with its two additional alkyl carbons, has additional modes of motion available to it, and it is therefore reasonable to expect that $\langle T_{1\rho}(C)\rangle$ measurements for polymers I and II will also reflect primarily spin-lattice relaxation.

Carbon-13 $T_{1\rho}$ measurements were performed on copolymers Ia and Id and homopolymer II at several carbon B_1 field strengths (including 15, 20, 28, 37, 41, and 44 kHz). The $\langle T_{1\rho}(C)\rangle$ values for the soft-segment carbons of copolymers Ia and Id are independent of the B_1 field. These data are listed in Table II. It is noteworthy that the soft-segment $-OCH_2-$ $T_{1\rho}$ values are very different for copolymers Ia and Id (4.5 and 1.7 ms, respectively) whereas the T_1 values for these carbons are identical (Table I).

In contrast to the soft-segment carbons, the hard-segment carbons exhibit $\langle T_{1\rho}(C)\rangle$ values that depend on the carbon B_1 field. Representative values are summarized in Table III. In all of these cases the magnetization decay data is clearly nonexponential (Figure 1 illustrates this point). A dispersion such as that shown in Figure 1 is generally observed for glassy polymers and has been attributed to a distribution of relaxation times.[3]

C. Solution-State Relaxation Measurements. The solution-state motional dynamics of the aliphatic carbons of segmented copolymer I and the poly(butylene terephthalate) homopolymer (II) were studied by ^{13}C and ^2H NMR relaxation measurements.

Table III
$\langle T_{1\rho}(C)\rangle$ Values[a] (ms) for the Protonated Hard-Segment Carbons of Polymers Ia and Id and Poly(butylene terephthalate) (II)

	polymer Ia		polymer Id		polymer II	
carbon	37 kHz	20 kHz	41 kHz	20 kHz	37 kHz	20 kHz
protonated aromatic	5.9[b]	0.7	6.7	2.5	8.3[d]	3.8
hard $-OCH_2-$	4.0[e]	1.4[c]	4.2	1.1	4.8	1.5
hard $-CH_2-$					5.0	1.8
hard and soft $-CH_2-$	6.5[f]	6.2[c,f]	3.0[g]	2.0[g]		

[a] Determined from linear (0.05-0.1 to 0.8 ms) part of curve; measured at 20 °C; estimated uncertainty ±10%; MAS at ca. 2 kHz unless noted otherwise. [b] B_1 = 41 kHz. [c] MAS at 3.9 kHz. [d] Values determined by curve analysis for overlapping peaks. [e] Contains contributions from soft-segment $-OCH_2-$carbons. [f] 0.80 mole fraction hard. [g] 0.96 mole fraction hard.

Table IV
Solution-State ^{13}C T_1 (s) Values[a] for the Aliphatic Carbons of Polymers I and II

carbon	polymer Ib	polymer II
soft $-OCH_2-$	0.19	
hard $-OCH_2-$	0.32	0.33
soft $-CH_2-$	1.07	
hard $-CH_2-$	0.50	0.50

[a] Measured by inversion-recovery at 50.3 MHz; 15 wt % polymer in m-cresol at 100 °C; uncertainty ±5%.

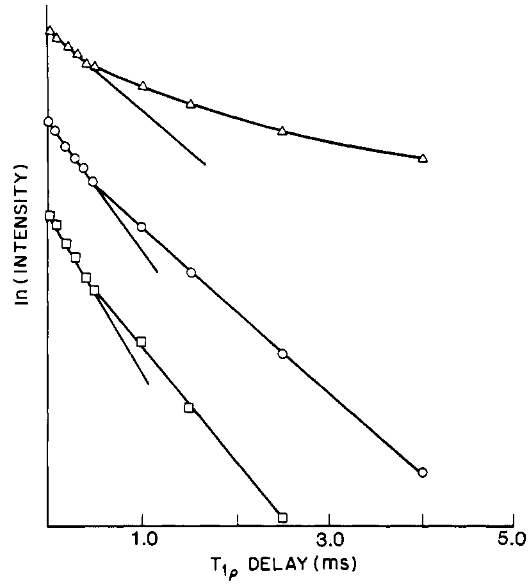


Figure 1. Typical ^{13}C $T_{1\rho}$ curve for poly(butylene terephthalate), illustrating the nonlinearity at long delay times. (The $T_{1\rho}$ delay is the time that the proton B_1 field is tuned off, before acquisition of the FID.) In this case the B_0 field is 15.1 MHz for ^{13}C; B_1 is 44 kHz, with MAS at 1.9 kHz. The average $T_{1\rho}$, $\langle T_{1\rho}(C)\rangle$, is taken from the initial part of the curves. (△) Composite curve for protonated and nonprotonated aromatics (these resonances are not resolved at this B_0); (○) $-OCH_2-$; (□) $-CH_2-$. The curves have been displaced vertically for visual clarity.

Table IV lists ^{13}C T_1 results for the hard- and soft-segment $-CH_2-$ carbons of copolymer Ib. The corresponding T_1 values for the homopolymer are also listed. Although the T_1 values for the hard-segment carbons in poly(butylene terephthalate) and in the segmented copolymer are identical (Table IV), the $-OCH_2-$ and $-CH_2-$ T_1 values within the hard segment are significantly different.

The nuclear Overhauser enhancements for the corresponding carbons are summarized in Table V. There are again no significant differences between the hard-segment carbons of both polymers. However, the hard-segment $-CH_2-$ carbon gives the maximum Overhauser enhance-

Table V
Solution-State ^{13}C Nuclear Overhauser Enhancements[a] for the Aliphatic Carbons of Polymers I and II

carbon	polymer Ib	polymer II
soft $-OCH_2-$	2.59	
hard $-OCH_2-$	2.61	2.73
soft $-CH_2-$	2.66	
hard $-CH_2-$	3.11	3.03

[a] Measured by the gated decoupling technique at 50.3 MHz; reported as $1 + \eta$; 15 wt % polymer in *m*-cresol at 100 °C; uncertainty ±5%.

Table VI
Solution-State ^2H T_1 Values[a] (s) for the Hard-Segment Carbons of Polymers I and II

	polymer Ib[b]	polymer II[c]
hard $-OCH_2-$	0.026	
hard $-CH_2-$	0.047	0.049

[a] Measured by inversion-recovery at 30.7 MHz; 15 wt % polymer in *m*-cresol at 100 °C; uncertainty ±5%. [b] The hard-segment carbons are selectively deuterated. [c] The aliphatic carbons are selectively deuterated.

ment, whereas its adjacent $-OCH_2-$ does not.

Based on work performed on other alkane chains,[17] it is assumed that relaxation of these aliphatic carbons is dominated by the dipole–dipole mechanism. Observation of maximum nuclear Overhauser enhancements (Table V) for some of these carbons supports this assumption. Nevertheless, it is advantageous to make measurements in such a way that the relaxation mechanism is known with certainty. Such is the case for deuterium NMR spectroscopy, in which the quadrupolar relaxation mechanism dominates relaxation.[18] Consequently, deuterium T_1 measurements were performed on the deuterated analogues of polymers Ib and II. The results of measurements performed at 30.7 MHz are listed in Table VI. The relaxation data display simple single-exponential behavior.

The data in Table VI suggest that there is no difference in the T_1 values for the hard-segment deuterons. They also support the ^{13}C T_1 findings, as there is a substantial difference in the relaxation rates for the $-OCD_2-$ and the $-CD_2-$ deuterons.

Discussion

The results from the solid-state ^{13}C NMR T_1 measurements, from the $\langle T_{1\rho}(C)\rangle$ experiments, and from the solution-state ^{13}C and ^2H NMR T_1 determinations are considered collectively. The Discussion section is thus divided into sections dealing with the interpretation of results for the soft-segment carbons, the hard-segment aliphatic carbons, and the protonated aromatic carbons.

The carbonyl and nonprotonated aromatic carbons have very long T_1 and $\langle T_{1\rho}(C)\rangle$ relaxation times. Since they bear no directly attached protons, their relaxation mechanisms are open to question, and thus discussion of these results would be somewhat speculative and premature. Throughout this Discussion it is stressed that the measured relaxation times reflect the averages of motional heterogeneities—that due to the composition of the polymers, the dynamics of a particular carbon must be considered in terms of a distribution of motional environments for that carbon.

A. Soft-Segment $-CH_2-$ and $-OCH_2-$ Carbons. Previous work[8] has shown that the T_1 values for the soft-segment carbons of copolymer I in the bulk (1) are independent of the mole fraction of hard segment in the copolymer, (2) increase with increasing temperature, and (3) increase with increasing magnetic field strength. In addition, the nuclear Overhauser enhancements $(1 + \eta)$ for these carbons do not have the maximum value of 3,[8] although by analogy to alkane models for polymers,[17] relaxation is assumed to be dipolar. We present here an analysis of these data based on a distribution of rotational correlation times.

The situation of nonmaximum nuclear Overhauser enhancements is often observed for highly viscous polymer solutions and for mobile polymers in the bulk, even when relaxation is known to be dominated by the dipolar mechanism.[19-21] This phenomenon has been attributed to the presence of some motions that have correlation times which are long compared to those determining T_1 but short compared to those determining T_2.[22] For cases such as these, Schaefer has set forth a model for interpretation of relaxation times in polymers based on a broad, asymmetric distribution of motional correlation times.[22] The distribution of correlation times model, in which the density function is characterized by a log χ^2 distribution,[22] has found much utility for interpretation of polymer NMR relaxation data,[23] and we shall employ it here.

The theory of isotropic reorientation in the presence of purely dipolar relaxation and a single correlation time has been extensively reviewed[22,24] and will be described here only to the extent necessary to show the form of the log χ^2 distribution function. For a single carbon with only one directly attached proton undergoing isotropic reorientation with a single correlation time, $1/T_1$, $1/T_2$, and the nuclear Overhauser enhancement (NOE) are given by

$$1/T_1 = \frac{\gamma_C{}^2\gamma_H{}^2\hbar^2}{10r_{CH}{}^6}[f(\omega_H - \omega_C) + 3f(\omega_C) + 6f(\omega_H + \omega_C)] \tag{1}$$

$$1/T_2 = \frac{\gamma_C{}^2\gamma_H{}^2\hbar^2}{20r_{CH}{}^6}[4g + f(\omega_C - \omega_H) + 3f(\omega_C) + 6f(\omega_C + \omega_H) + 6f(\omega_H)] \tag{2}$$

$$\mathrm{NOE} = 1 + \frac{\gamma_H}{\gamma_C}\left[\frac{-f(\omega_H - \omega_C) + 6f(\omega_H + \omega_C)}{f(\omega_H - \omega_C) + 3f(\omega_C) + 6f(\omega_H + \omega_C)}\right] \tag{3}$$

Here, γ_H and γ_C refer to the respective proton and carbon gyromagnetic ratios, r_{CH} is the carbon–proton internuclear distance, and the $f(\omega_i)$'s ($f(\omega_H - \omega_C)$, etc.) are given by

$$f(\omega_i) = \tau_C/(1 + \omega_i{}^2\tau_c{}^2) \tag{4}$$

where τ_c is the correlation time and $g = \tau_c$.

For a log χ^2 distribution of correlation times, we define a mean correlation time, $\bar{\tau}$, and the density functions $f(\omega_i)$ and g are given by[22]

$$f(\omega_i) = \int_0^\infty \frac{\bar{\tau}F^{(p)}(s)\{b^s - 1\}\,\mathrm{d}s}{\{b - 1\}\{1 + \omega_i{}^2\bar{\tau}^2[\{b^s - 1\}/(b - 1)]^2\}} \tag{5}$$

$$g = \int_0^\infty \frac{\bar{\tau}F^{(p)}(s)\{b^s - 1\}\,\mathrm{d}s}{b - 1} \tag{6}$$

where $F^{(p)}(s)$ ds and s are given by

$$F^{(p)}(s)\,\mathrm{d}s = \frac{1}{\Gamma(p)}(ps)^{p-1}e^{-ps}p\,\mathrm{d}s \tag{7}$$

$$s = \log_b [1 + (b - 1)\tau_1/\bar{\tau}] \tag{8}$$

$\Gamma(p)$ ensures normalization, so that $\int_0^\infty F^{(p)}(s)\,\mathrm{d}s = 1$; $\tau_1 = \bar{\tau}\tau_c$, and b is usually taken as 1000.

The result of this treatment is to produce an asymmetric distribution of correlation times, with a pronounced tail in the long correlation time region.[22] Such a model is

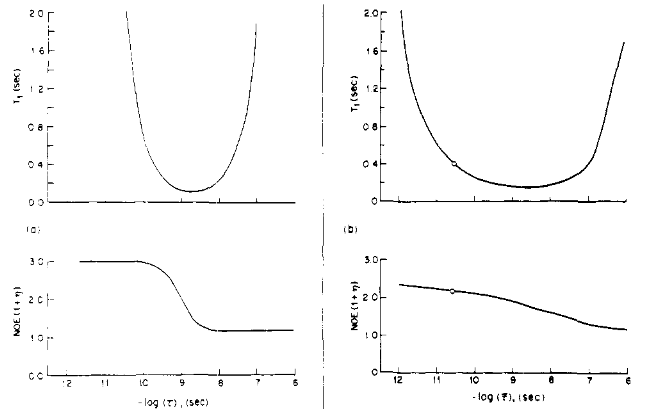


Figure 2. Calculated T_1 and NOE curves for carbon being dipolar relaxed by a single directly bonded proton at a B_0 of 50.3 MHz for ^{13}C. (a) Single τ_c model; (b) log χ^2 distribution of correlation times with a width parameter $p = 7$. The circles on the curves in (b) correspond to the relaxation data for copolymers Ia–d.

reasonable for the soft-segment carbons of copolymer I, as the ends of the soft segments must be anchored to the hard-segment regions. Toward the middle of the polyether chain the motions tend to increase and then decrease again as the next tie point is approached.

The log χ^2 distribution is thus characterized by the mean correlation time $\bar{\tau}$, and the width parameter p. For a narrow distribution ($p = 100$), the distribution function reduces to the isotropic, single-τ case given by eq 1–4, where $\bar{\tau} = \tau_c$. Figure 2a shows the T_1 and NOE as a function of correlation time for this case, with $\omega_C = 3.16 \times 10^8$ rad s^{-1} and $\omega_H = 1.27 \times 10^9$ rad s^{-1}. In contrast, Figure 2b shows the T_1 and NOE curves for a broad ($p = 7$) distribution of correlation times. The nuclear Overhauser enhancement does not attain its maximum value of 3, as in the single correlation time model (Figure 2a), and the T_1 minimum becomes shallow and the curve exhibits asymmetry. (Line width data were not used for this analysis, as low-power decoupling experiments performed with MAS indicate that residual chemical shift anisotropy and dipole–dipole interactions contribute to the line widths.[8])

The T_1 (Table I) and NOE data[8] for the soft-segment carbons of copolymers Ia–d fit very well to a log χ^2 distribution of motional correlation times in which the width parameter, p, is 7. The data for the measurements at 50.3 MHz are entered as circles on Figure 2b. The data for the 22.6-MHz measurements also fit their respective curves very well. These data indicate that $\bar{\tau}$ for the soft-segment carbons of copolymers Ia–d at 34 °C is ca. 5×10^{-11} s. The T_1 and NOE data for the soft-segment carbons in the solid suggest that these carbons undergo some motions that are very fast, but the broad width parameter needed to fit these data ($p = 7$) suggests considerable heterogeneity or distribution of these motions. The dynamic behavior of the soft-segment carbons can be compared to that of polybutadiene[22,25] or polybutadiene in the graft copolymer polybutadiene–poly(styrene-*co*-acrylonitrile).[25] For polybutadiene in both cases the relaxation data fit a log χ^2 distribution of correlation times in which $p = 8$–9, and the $-CH_2-$ carbons at 34 °C have a mean correlation time, $\bar{\tau}$, of 5×10^{-11} s. Although the high-frequency mean correlation times and the width parameters for polybutadiene and the soft segments in copolymer I are similar, their cross-polarization behavior is markedly different. The soft-segment carbons of copolymers Ia–d give cross-polarization spectra with reasonable (ca. 750 μs) contact times, and these proton-enhanced spectra provide a fairly accurate representation of the amount of soft segment in the copolymer.[7] Polybutadiene, on the other hand, cross polarizes poorly and only at very long (>3000 μs) contact times.[25] Taken together, these results suggest that although the local, high-frequency motions must be similar for the $-CH_2-$ carbons in polybutadiene and in the soft-segment carbons of copolymers I, there must be angular ranges of space that are not covered by reorientation of the soft segments of copolyester I. Such a result suggests that the soft segments of copolyester I reside in channels in which completely isotropic reorientation is prohibited.

In contrast to the T_1 values for the soft-segment carbons of copolymer I—which are independent of the mole fraction of hard segment in the copolymer[8] (Table I)—the $\langle T_{1\rho}(C) \rangle$ values for these carbons show a clear dependence on the compositional ratios (Table II). These $\langle T_{1\rho}(C) \rangle$ values show no B_1 field dependence, a situation that arises when relaxation is due to motions which have frequency components much greater than B_{1C}.[3] The significant difference in the $-OCH_2-$ $\langle T_{1\rho}(C) \rangle$ values for the softest copolymer (Ia) and the hardest copolymer (Id) is probably related to differences in the amplitudes of the medium-frequency motions, a factor also suggested by the different line widths for these carbons.[8]

The solution-state T_1 (Table IV) and NOE (Table V) values for the soft-segment carbons of copolymer I at 100 °C do not fit a single-τ_c model (Figure 2a). The T_1 values for these carbons are larger than for their hard-segment counterparts, indicating that the polyether carbons appear to have greater segmental flexibility than the hard-segment aliphatic carbons. This result is not surprising, as other solution-state ^{13}C NMR relaxation data indicate that the terephthalate groups act as local centers of restricted motion.[26]

B. Hard-Segment $-CH_2-$ and $-OCH_2-$ Carbons. The T_1 values for the hard-segment aliphatic carbons for copolymers Ia and Id and for poly(butylene terephthalate) (II) are fairly short for glassy solids (Table I) and thus indicate that these polymers have a significant amount of spectral density in the megahertz frequency region. Table I also shows that the T_1 values for the hard-segment carbons in copolymers Ia and Id are not identical with those for the analogous homopolymer carbons, suggesting that the motions responsible for the short T_1 values in poly(butylene terephthalate) may be enhanced in the segmented copolymers. (Arguments were presented in the Results, showing that the poly(butylene terephthalate) T_1 values in the solid state reflect motions on the short correlation time side of the T_1 minimum.)

The T_1 values for the $-OCH_2-$ and the central $-CH_2-$ of poly(butylene terephthalate) in the solid state are significantly different (Table I). This difference is observed also in the solution-state ^{13}C NMR T_1 values (Table IV), in the solution-state ^{13}C NOE measurements (Table V), and again in the solution-state ^2H NMR T_1 determinations (Table VI) for this polymer. This difference must reflect different frequencies and/or amplitudes of motion for the $-OCH_2-$ and $-CH_2-$ carbons of poly(butylene terephthalate). The results indicate that the central $-CH_2-$ carbons in the solid state must undergo motions of larger amplitude or greater frequency than the $-OCH_2-$ carbons and that these differences are preserved in solution.

An interpretation of these results is suggested by structural studies on poly(butylene terephthalate). X-ray fiber diffraction[27,28] and rotational isometric state calculations[29] show that poly(butylene terephthalate) has the shortest unperturbed dimensions per methylene unit in the homologous series of poly(methylene terephthalate) polymers. Other infrared, Raman, differential scanning

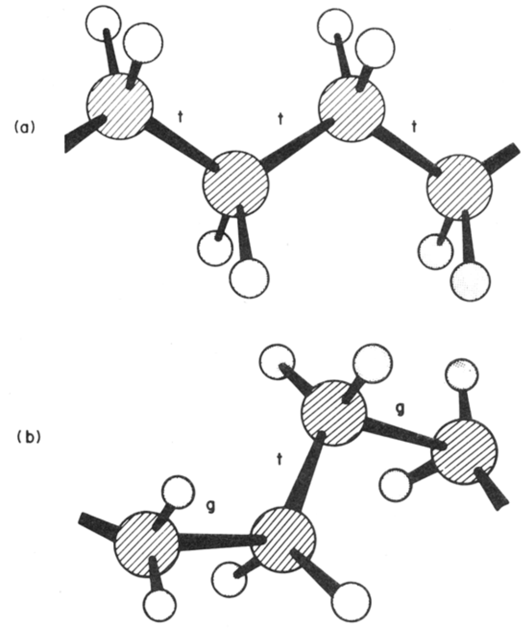


Figure 3. Conformations for the methylene units in poly(butylene terephthalate): (a) All trans; (b) gauche–trans–gauche.

calorimetry, and X-ray data[30-34] show that poly(butylene terephthalate) exists in two modifications, the α and β forms. The β form is produced by stretching poly(butylene terephthalate) to ca. 10% elongation and holding it under stress. The butylene unit has an all-trans conformation in the β form[34] (Figure 3a). In the absence of stress the β modification relaxes to the α form, which has an "approximately" gauche–trans–gauche conformation[30] (Figure 3b).

Infrared, Raman, and X-ray spectroscopies, by their time scales, lead to a static concept of conformation and structure. The NMR relaxation data presented here require a dynamic model for the conformation of the methylene carbons in unstressed poly(butylene terephthalate). One such model that fits the NMR relaxation data presented here, as well as the known gauche–trans–gauche conformation of poly(butylene terephthalate) in the unstressed solid state, is a type of three-bond motion.[35] For this type of motion, the terephthalate groups remain relatively fixed and the central $-CH_2-$ groups undergo large-amplitude excursions. The butylene unit is the shortest unit that can undergo a three-bond type of motion,[36] and the longer range motions (such as five-bond motion[37] and longer[38]) are prohibited by virtue of the terephthalate groups. Preliminary solid-state ^{2}H NMR results are in agreement with this interpretation.[39]

The $\langle T_{1\rho}(\mathrm{C})\rangle$ values for the hard-segment $-OCH_2-$ and central $-CH_2-$ carbons of poly(butylene terephthalate) are essentially identical with each other at all B_1 fields examined (Figure 4, lower line). The amount of soft segment in the copolymer does not appear to influence the $\langle T_{1\rho}(\mathrm{C})\rangle$ values for the hard-segment $-OCH_2-$ and $-CH_2-$ carbons (Table III). These values are the same, within experimental error, for polymer Ia and Id and the poly(butylene terephthalate) homopolymer (II). The hard-segment aliphatic $\langle T_{1\rho}(\mathrm{C})\rangle$ values in Table III exhibit an approximately square-law dependence on the B_1 field. Such behavior is predicted when relaxation is caused by motions that are less than $B_{1\mathrm{C}}$.[3]

C. Protonated Aromatic Carbons. The terephthalate groups form the chemical interface between the hard and soft segments of copolyesters I. Each hard segment terminates with a terephthalate residue, which may contain another butylene terephthalate hard segment as a neighbor or may lead into a poly(tetramethylene ether) soft segment. Thus the aromatic residues reside in markedly different environments in the copolymer—those embedded in long stretches of hard segments and those capping the soft sequences. The number of aromatic residues in each environment is related to the composition of the copolymer. Thus, any relaxation data for the aromatic residues will necessarily reflect a weighted average of their environments.

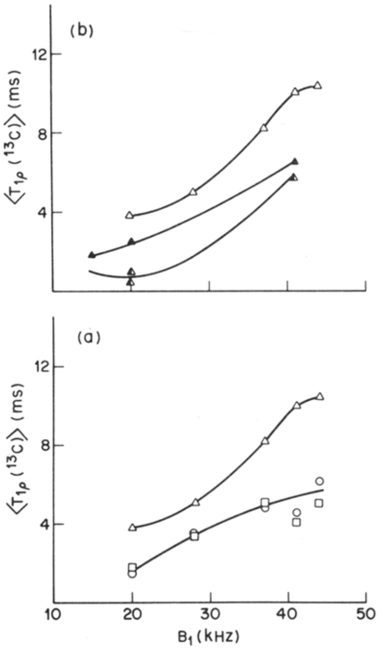


Figure 4. Graphical representation of $\langle T_{1\rho}(\mathrm{C})\rangle$ values as a function of B_1 field. (a) Poly(butylene terephthalate): (△) protonated aromatic carbons; (○) $-OCH_2-$; (□) $-CH_2-$. (b) Protonated aromatic carbons of poly(butylene terephthalate) (△); polymer Id (▲); polymer Ia (△).

The ^{13}C NMR T_1 values for the protonated aromatic carbons in the solid state clearly depend upon the mole fraction of soft segment units in the copolymer (Table I), with the T_1 for the aromatic carbons of the "softest" copolymer (Ia) providing evidence that the environment for these carbons is, on average, a mobile one. Previous data[7,9] has implicated the aromatic rings in copolymer Ia in 180° ring flips. These T_1 data corroborate those findings.

The $\langle T_{1\rho}(\mathrm{C})\rangle$ values for the protonated aromatic carbons also show a strong sensitivity to the copolymer composition (Table III). These $\langle T_{1\rho}(\mathrm{C})\rangle$ data are consistent with an approach to the $\langle T_{1\rho}(\mathrm{C})\rangle$ minimum as the mole fraction of soft segments in the copolymer is increased.

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Dynamics of Macromolecular Chains in Solution. Nuclear Magnetic Relaxation of Aryl–Aliphatic Polyesters

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ABSTRACT: Proton and carbon-13 NMR relaxation data at several field strengths have been determined as a function of temperature for two aryl–aliphatic polyesters differing by the length of the aliphatic segment separating neighboring terphenyl groups. The solution-state motional dynamics of these two polymers can be interpreted in terms of four correlation times: τ_0, τ_{ir}, θ, and ρ. The correlation time for overall isotropic reorientation of the terphenyl moiety is τ_0, τ_{ir} is the internal correlation time for phenylene ring rotation, θ describes the mean correlation time for isotropic reorientation of the aliphatic groups and is found to be equal to τ_0 for the methylene carbon next to the carboxyl unit, and ρ is the mean correlation time for the diffusive processes that relax the aliphatic subchain. According to the terminology of Helfand, results thus obtained show that these ρ processes are fast type 1 or type 2 short-range motions, whereas θ modes are much slower type 3 long-range motions. Moreover, type 2 motions are more likely in the longer aliphatic subchain whereas mainly crankshaft motions or three-bond jumps occur in the shorter one.

Over the past few years, a considerable amount of work has aimed at interpreting relaxation measurements on polymers in solution in terms of local chain motions. Several conformational jump models[1–3] have been proposed and lead to autocorrelation functions that have proved most powerful for accounting for fluorescence depolarization,[4] dielectric relaxation,[5] and nuclear spin relaxation[2,3,6–10] data. Extensive tests of these descriptions of the segmental motion of polymers have been performed by making use of, for example, carbon-13 NMR at two field strengths,[6] by investigating coupled relaxation between nonequivalent protons in vinyl polymers by three different experiments[8] probing both high- and low-frequency portions of the spectral density, and by carrying out proton spin–lattice relaxation time determinations over the observation frequency range 5–100 MHz,[10] thus extending the dynamic range over 5–200 MHz.

However, in spite of the success of these conformational jump models in representing these important sets of data obtained on a number of polymers in solution,[11] very little information is available on the detailed elementary molecular processes responsible for the segmental main-chain motion. Electron spin resonance experiments on spin-labeled polymers have pointed out the very local nature of the fastest modes: Measurements carried out on poly(ethylene oxide) have shown that about one monomer unit may be considered as involved in the ESR relaxation process.[12] The same study in the case of polystyrene leads to one to five monomer units, depending on the experimental conditions.[13] Even these short-range motions have not been yet identified. Certain modes of motion such as the Schatzki crankshaft[14] or the three-bond motion[15] have been proposed. The important point is that they involve two barrier crossings. Using Brownian dynamics simulations, Helfand has described other types of localized processes requiring only slightly more than one barrier height separating the trans and gauche state.[16] From an exper-

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