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# Multitechnique Solid-State NMR Approach To Assessing Molecular Motion: Poly(butylene terephthalate) and Poly(butylene terephthalate)-Containing Segmented Copolymers. 4

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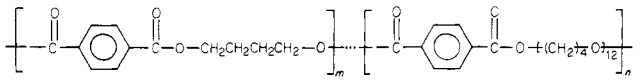
ABSTRACT: Solid-state $^{13}C$ NMR has been used to assess the nature of the molecular motions for every carbon of the segmented copolymer poly(butylene terephthalate-*co*-tetramethyleneundecakis(oxytetramethylene) terephthalate). Relaxation time experiments (see following paper) have been used in conjunction with low-temperature magic-angle spinning (MAS), spinning about an axis displaced from the magic angle, and static powder pattern difference spectroscopy. The results from these experiments (1) confirm that the chemical shift parameters obtained from earlier studies (Jelinski, L. W. *Macromolecules* **1981**, *14*, 1341) are correct, (2) suggest that the aromatic rings undergo 180° ring flips at 22 °C in the copolymer with 0.80 mole fraction hard segments, (3) indicate that the soft-segment ($CH_2$) carbons exhibit dipolar broadening at temperatures just below their glass transition temperature, and (4) establish that the chemical shift powder pattern line width for the $-CH_2CH_2CH_2CH_2-$ carbons of poly(butylene terephthalate) and the segmented copolymers is 17.6 ppm at 22 °C. The advantages and limitations of these solid-state NMR techniques, as they relate to polymers, are discussed in a parallel treatment with the NMR results.

## Introduction

We report here results of a solid-state $^{13}C$ NMR study of molecular motion in the segmented copolymer system poly(butylene terephthalate-*co*-tetramethylene-undecakis(oxytetramethylene) terephthalate) (I). The



"hard" segment "soft" segment

I

poly(butylene terephthalate) "hard" segments and the poly(tetramethyleneundecakis(oxytetramethylene) terephthalate "soft" segments of this copolymer are not miscible and thus lead to phase separation.[1] However, in contrast to the discrete domain structures found in polystyrene–polybutadiene[2] or polystyrene–polyisoprene,[2] for example, the hard and soft segments in copolyester I are more intimately dispersed. This copolymer thus presents a unique opportunity to study a system in which there is a large interfacial area. Further, the composition of the polymer can be varied by changing the $m/n$ ratio, which affords an additional experimental variable.

The results presented here, taken together with other data,[3-5] enable us to estimate the nature of the molecular motion in copolymer I. Our goals in this work are to elucidate the molecular motion at *each* carbon site, to clarify the influences that compositional differences have on these molecular motions, and thus to understand the relationships responsible for the molecular dynamics of this copolymer series.

As a technique for measuring motional frequencies and amplitudes in solids, high-resolution solid-state $^{13}C$ NMR is sensitive to motions spanning the kilohertz to megahertz frequency region. Spin–lattice relaxation and nuclear Overhauser enhancement measurements in the bulk are sensitive to spectral density at megahertz frequencies;[6] dipolar broadening phenomena give information about motions having correlation times of ca. $10^{-5}$–$10^{-6}$ s;[7,8] the chemical shift anisotropy[9] and spin–lattice relaxation in the rotating frame[8] give information about mid-kilohertz motions, and broadening caused by motions that occur during the revolution period of the magic-angle spinning rotor reflects low-kilohertz motions.[10] Of these techniques, we shall focus here on the chemical shift anisotropy, as measured by off-axis magic-angle spinning, by low-temperature MAS, and by static powder pattern difference spectroscopy. In addition, we present results obtained by observation of the onset of dipolar broadening in the soft-segment carbons. The advantage and limitations of these techniques, as they relate to polymers, are also discussed.

## Materials and Methods

**Samples.** Poly(butylene terephthalate) was obtained from Eastman Chemical Co., and the poly(butylene terephthalate-*co*-tetramethyleneundecakis(oxytetramethylene) terephthalate) samples were kind gifts from Mr. J. Hedberg of the du Pont Co. The deuterated segmented copolymers were prepared according to literature methods[11] using either butylene-*2,2,3,3-d*$_4$ glycol or butylene-*1,1,2,2,3,3,4,4-d*$_8$ glycol (Merck Isotopes) as the starting material. The purity and composition of all polymers were checked by solution-state $^{13}C$ NMR according to previously published procedures.[3] The integrity of the deuterated copolymers was established by solution-state $^{2}H$ NMR.

The polymers for $^{13}C$ NMR measurements were quenched from the melt, ground at cryogenic temperatures, and packed into Kel-F sample rotors with a nonhydraulic pellet press. The sample weight

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Table I
Solid- and Solution-State $^{13}C$ NMR Chemical Shifts for Terephthalate-Containing Polymers

| carbon | poly(butylene terephthalate) solid | poly(butylene terephthalate) solution [b] | | copolymer I [a] solid | copolymer I [a] solution [b] | |
|---|---|---|---|---|---|---|
| carbonyl | 164.2 | 167.1 | (169.2) | 164.8 | 167.1 | (169.2) |
| nonprotonated aromatic | 133.5 | 139.9 | (134.4) | 134.3 | 139.9 | (134.4) |
| protonated aromatic | 129.2 | 134.2 | (130.1) | 130.4 | 134.2 | (130.1) |
| soft $-OCH_2-$ | | | | 71.1 | 70.8 | (71.2) |
| hard $-OCH_2-$ | 65.1 | 65.7 | (66.6) | 65.9 | 65.7 | (66.6) |
| soft $-CH_2-$ | | | | 27.5 | 26.4 | (25.6) |
| hard $-CH_2-$ | 25.8 | 25.4 | (25.3) | 27.5 | 25.5 | (25.3) |

[a] Contains 0.80 mole fraction hard segments. [b] 15 wt % polymer in *m*-cresol at 100 °C; referenced to the methyl group in *m*-cresol, taken as 20.90 ppm.[17] Values in parentheses are shifts of 15 wt % polymer in hexafluoro-2-propanol at 34 °C, referenced to $C_6D_6$ in an internal lock capillary, taken as 128.5 ppm from $Me_4Si$.

was generally 0.3 g. The solid polymers containing $^2H$ were quenched from the melt and used as solid plugs.

**NMR Measurements.** Most of the solid-state $^{13}C$ NMR spectra were obtained at 47 kG (50.3 MHz for $^{13}C$) on a Varian XL-200 spectrometer. The Varian spectrometer employs a two-level decoupling scheme, with a proton $B_1$ of 5.8 G and a $B_2$ field of ca. 12 G. MAS spinning rates were generally 2.2–3.0 kHz.

For routine proton-enhanced spectra, the Hartmann–Hahn condition[12] was optimized on adamantane and the magic-angle was adjusted on the carboxyl carbon of glycine. Static powder spectra were generally collected with a 40-kHz spectral window with 4K time-domain data points, and magic-angle spectra were collected with a 20-kHz window and 8K time-domain points. The proton-enhanced spectra were obtained using spin temperature alternation.[13]

The variable-temperature MAS experiments were performed with the standard Varian CP-MAS probe with its upper Teflon block removed. A high flow of cooled nitrogen was flushed over the sample. It was spun with a separate source of room-temperature nitrogen. Two interconnecting glass Dewars were fabricated to carry the cooled nitrogen from the heat-exchange coil down through the center bore of the magnet, so that the cooled gas exited ca. 3 cm above the sample. The temperature was monitored by means of a copper–constantan thermocouple positioned outside and to the side of the delivery Dewar, ~2 cm above the sample. The temperature remained stable to ±2 °C through the course of each experiment. The reported temperatures are considered accurate to ±10 °C. In this manner, excellent spinner stability and reliable operation were realized down to −89 °C (±10 °C). The MAS spinning rate at −89 °C was 1.8 kHz.

For the off-axis magic-angle spinning experiments, the displacement of the spinner from the magic angle was calibrated with the aromatic carbons of hexamethylbenzene. The chemical shift tensor for the aromatic carbons of hexamethylbenzene was taken as being axially symmetric, with $|\sigma_{11} - \sigma_{33}| = 168$ ppm at 20 °C.[14,15] Because of the design of the Varian spinners, the angular reproducibility from sample to sample is very good. (The Varian spinners contain a weighted "point" that extends 0.5 cm below the cone of the stator, thus providing stability and reproducibility in the magic-angle setting.) We consider uncertainties in the angle thus determined to be less than ±0.2°.

Chemical shifts in the solid state were referenced to $Me_4Si$ using the method of Earl and VanderHart.[16] They show that the relative chemical shifts of samples in coaxial cylinders rotating at the magic angle have no bulk susceptibility contributions and are equivalent to an internal reference in solution NMR. Thus, a glass capillary containing $Me_4Si$ was centered in the sample by means of a concentric hole drilled into the filled sample rotor from the top down 3 mm into the "point" of the Varian spinner. The spectra of the polymer plus $Me_4Si$ were accumulated simultaneously with high-power proton decoupling and Zeeman polarization, rather than the cross polarization sequence of Earl and VanderHart.[16] The chemical shifts obtained in this manner are considered accurate to ±0.5 ppm.

The spectra for the static powder difference spectroscopy were obtained by acquiring Hartmann–Hahn matched cross-polarization spectra of appropriately deuterium-labeled polymer samples and subtracting these spectra (in the absolute intensity mode) from the spectra of corresponding unlabeled polymers.

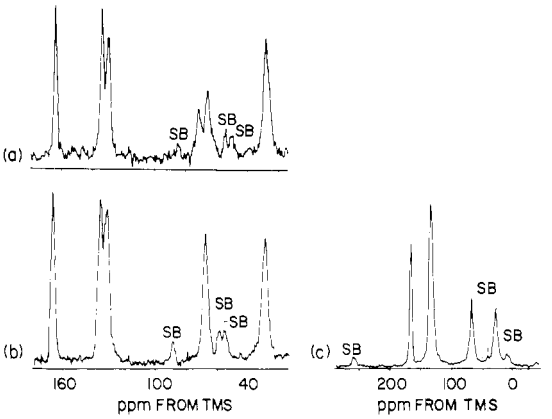


**Figure 1.** Solid-state $^{13}C$ NMR spectra of (a) segmented copolymer I, containing 0.96 mole fraction hard segments, at 50.3 MHz, (b) poly(butylene terephthalate) at 50.3 MHz, and (c) poly(butylene terephthalate) at 15.1 MHz. All spectra were recorded at ambient temperature. The sidebands are labeled SB. Spectral assignments are given in the text.

## Results and Discussion

**A. General Description of the Spectra.** Solid-state proton-enhanced $^{13}C$ NMR spectra of copolymer I and of the homopolymer poly(butylene terephthalate) are shown in Figure 1. In Figure 1a, the copolymer peaks are assigned in increasing upfield order to the carbonyl carbon, the nonprotonated aromatics, the protonated aromatics, the soft-segment $-OCH_2-$, the hard-segment $-OCH_2-$, and a combined resonance for the hard- and soft-segment $-CH_2CH_2CH_2CH_2-$ carbons.[4] The chemical shifts for these carbons are summarized in Table I, where they are compared to the solution-state chemical shifts for this copolymer. The corresponding $^{13}C$ NMR spectrum for poly(butylene terephthalate) is shown in Figure 1b; noticeably absent are the soft-segment resonances. Solid- and solution-state chemical shifts for poly(butylene terephthalate) are also listed in Table I. The data in Table I show that there are no marked differences between the solid-state and solution-state $^{13}C$ NMR chemical shifts, with the exceptions of the "central" $-CH_2-$ carbons of copolymer I and the carbonyl carbons of the terephthalate residues. (The aromatic carbons exhibit solvent-dependent shifts, presumably due to selective interactions with the aromatic solvent, *m*-cresol.) The large shift differences for the carbonyl carbons may reflect packing effects in the solid that are not present in solution. Table I also shows that the solid-state chemical shifts for poly(butylene terephthalate) and for poly(butylene terephthalate) in copolymer I are identical, again with the exception of the "central" $-CH_2-$ carbons.

The solid-state chemical shifts for the poly(butylene terephthalate) residues (carbonyl, nonprotonated aromatic,

Table II
Chemical Shift Parameters for Poly(butylene terephthalate) (PBT) and Related Compounds[a]

| sample | $\omega_{rot}$, kHz | carbonyl carbon $\lvert\sigma_{33} - \sigma_{11}\rvert$,[b] ppm | carbonyl carbon $\rho$[c] | nonprotonated aromatic $\lvert\sigma_{33} - \sigma_{11}\rvert$,[b] ppm | nonprotonated aromatic $\rho$[c] | protonated aromatic $\lvert\sigma_{33} - \sigma_{11}\rvert$,[b] ppm | protonated aromatic $\rho$[c] |
|---|---|---|---|---|---|---|---|
| dimethyl terephthalate | 2.21 | 137 ± 4 | +1.0 ± 0.1 | 201 ± 4 | −0.24 ± 0.02 | 215 ± 4 | −0.38 ± 0.03 |
| PBT | 1.14 | 127 ± 5 | +1.0 ± 0.1 | 202 ± 5 | −0.20 ± 0.03 | 198 ± 5 | −0.39 ± 0.02 |
| I (96 mol% hard) | 2.18 | 130 ± 4 | +1.0 ± 0.1 | 199 ± 5 | −0.15 ± 0.07 | 196 ± 3 | −0.40 ± 0.01 |
| I (80 mol% hard) | 2.05 | 132 ± 3 | +1.0 ± 0.1 | 203 ± 5 | −0.25 ± 0.05 | 187 ± 3 | −0.40 ± 0.02 |

[a] Chemical shift parameters were obtained from the ratios of spinning-sideband intensities by the method of Herzfeld and Berger;[20] each value represents the average of at least two independent measurements. [b] $\lvert\sigma_{33} - \sigma_{11}\rvert = \mu\omega_{rot}/\gamma B_0$. [c] $\rho = (\sigma_{11} + \sigma_{33} - 2\sigma_{22})/(\sigma_{33} - \sigma_{11})$; $\sigma_{33} > \sigma_{22} > \sigma_{11}$.

protonated aromatic, and $-OCH_2-$) in Table I can be compared to the respective chemical shifts for amorphous poly(ethylene terephthalate)[16] (PET shifts in parentheses): 164.2 (166.5), 133.5 (133.9), 129.2 (130.3), 65.1 (64.4). With the possible exception of the carbonyl carbon chemical shift, all of the values are identical, within experimental error.

The data presented in Figure 1 bear several comments. First, a comparison of the 15.1-MHz $^{13}C$ NMR spectrum of poly(butylene terephthalate) (Figure 1c) with the 50.3-MHz spectrum (Figure 1b) shows that in this case, the higher static magnetic field is desirable. The protonated and nonprotonated aromatic carbons are clearly resolved in the 50.3-MHz spectrum, whereas in the 15.1-MHz spectrum they are not.

The spectrum shown in Figure 1a also illustrates that the resonances from the hard- and soft-segment aliphatic carbons are clearly resolved, thus enabling selective observations of carbons unique to the hard or soft segments of the copolymer. It is also notable that the soft-segment carbons do cross polarize. The ratio of the integrated intensities for the hard and soft $-OCH_2-$ carbons in the proton-enhanced, solid-state NMR spectra generally agrees with that obtained from solution-state NMR, suggesting that the soft-segment carbon signal is properly represented in the solid-state NMR spectrum in Figure 1a. Reliable representation of the soft-segment carbons suggests that even in the "softest" copolymer, there are some angles of conformational space that are not sampled (on the time scale of the NMR experiment) by the rapidly reorienting soft-segment carbons.[18] The observation of a cross-polarization signal for the soft-segment carbons in copolymer I is in marked contrast to the cross-polarization dynamics of free radical polybutadiene, either as the pure polymer or in a graft copolymer system.[19] With respect to motional dynamics, the soft segments of copolymer I behave as though they are in channels—much as nematic liquid crystals—where local reorientation about the long axis is constrained.

Careful inspection of the aromatic carbon signal intensities in Figure 1 also reveals that the protonated aromatic carbons are somewhat underrepresented. Instead of the predicted 1:1:2 intensity ratio for the carbonyl:nonprotonated aromatic:protonated aromatic carbons, a ratio of ~1:1:1.2 is actually observed (taking into account the intensity found in the spinning sidebands). The exact mechanism for the underrepresentation is not clear, but low-temperature MAS experiments (see below) and $\langle T_{1\rho}(C)\rangle$ measurements (see following paper) show that it is clearly related to motion of these carbons.

**B. Off-Axis Magic-Angle Spinning.** We have reported previously[4] on the use of the Herzfeld–Berger technique[20] to reconstruct the chemical shift parameters ($\sigma_{11}$, $\sigma_{22}$, and $\sigma_{33}$) for the carbonyl, nonprotonated aromatic, and protonated aromatic carbons of a series of poly(butylene terephthalate)-containing polymers. The primary conclusions from that work are (1) that the carbonyl carbons of the terephthalate esters exhibit axially symmetric chemical shift tensors, (2) that the carbonyl carbon axial symmetry is not related to molecular motion, and (3) that the chemical shift anisotropy of the aromatic carbons shows a partial collapse, which was attributed to torsional oscillations about the 1,4-phenylene axis. (These chemical shift parameters are repeated here in Table II for the convenience of the reader). The good match between the observed and calculated chemical shift tensor powder patterns was used as the criterion to ensure that the chemical shift parameters obtained from the Herzfeld–Berger analysis did in fact represent the true chemical shift parameters.[4] The calculated chemical shift tensor powder pattern is comprised of three overlapping tensors and thus allows considerable room for error. Here we subject the chemical shift parameters to a far more stringent test: that of off-axis magic-angle spinning.

Off-axis MAS has been proposed as a method whereby the chemical shift parameters can be retrieved from spinning experiments[21] and has recently been employed in conjunction with least-squares fitting of the powder line shape to obtain the principal values of the $^{13}C$ chemical shift tensor for poly(ethylene terephthalate).[22] The chemical shift parameters in an off-axis MAS experiment are scaled by a factor $(1 - 3\cos^2\theta)/2$, where $\theta$ represents the angle between the spinner axis and the magnetic field, $B_0$.[21,22] If the angle $\theta$ is known and if the isotropic chemical shift is obtained from complementary experiments, the scaled spectrum can be used to estimate the values for $\sigma_{11}$, $\sigma_{22}$, and $\sigma_{33}$.

The results of off-axis MAS have in the past been used to *determine* the chemical shift parameters. Here we use off-axis MAS instead to *test* the chemical shift parameters obtained by independent methods. In Figure 2 are shown the isotropic MAS spectrum and several off-axis MAS spectra for poly(butylene terephthalate). On the right are the corresponding calculated spectra, based on the chemical shift parameters listed in Table III. The calculated and experimental spectra are in good agreement, particularly in the case of the carbonyl carbon. (Intensity problems related to overlap with spinning sidebands pertain to the aromatic carbons and are discussed below.) These results corroborate the chemical shift parameters[4] obtained by the Herzfeld–Berger method[20] and thus validate the conclusions reviewed above.

This example illustrates that the most accurate and reliable method to extract chemical shift parameters from overlapping chemical shift tensor powder patterns involves a combination of techniques: sideband intensity analysis,[20] moment analysis,[9] least-squares fitting of the powder line shape,[22] and off-axis MAS.[21] Each of these methods has its advantage and limitations, and those of off-axis MAS are set forth here. The primary problem is caused by

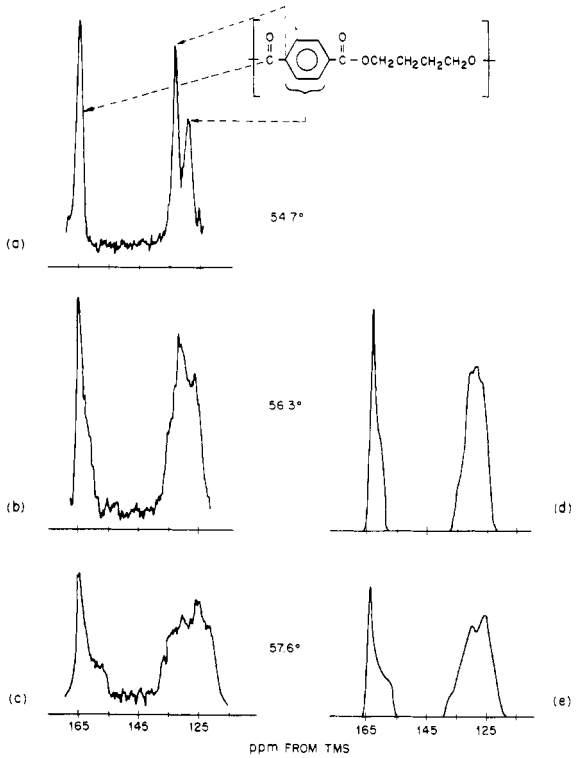


**Figure 2.** Carbonyl and aromatic region of off-axis MAS $^{13}C$ NMR spectra of poly(butylene terephthalate): (a) on-axis (54.7°) isotropic spectrum; (b) spectrum obtained at 56.3° with respect to the magnetic field; (c) spectrum at 57.6° with respect to the magnetic field; (d) and (e) calculated spectra for (b) and (c), respectively. The parameters used in the calculation are listed in Table III.

Table III
Values of the Chemical Shift Parameters[a] Used in the Calculation of the Off-Axis[b] MAS Spectrum of Poly(butylene terephthalate)

| carbon | $\sigma_{11}$ | $\sigma_{22}$ | $\sigma_{33}$ |
|---|---|---|---|
| carbonyl | | | |
| $\theta$ = 56.3° | 165.8 | 165.8 | 161.0 |
| $\theta$ = 57.6° | 167.1 | 167.1 | 158.4 |
| nonprotonated aromatic | | | |
| $\theta$ = 56.3° | 137.6 | 133.0 | 129.9 |
| $\theta$ = 57.6° | 140.9 | 132.6 | 127.0 |
| protonated aromatic | | | |
| $\theta$ = 56.3° | 133.5 | 128.2 | 125.9 |
| $\theta$ = 57.6° | 136.9 | 127.4 | 123.3 |

[a] In ppm from $Me_4Si$, calculated from principal values from ref 4 and from isotropic chemical shifts in Table I. [b] See Materials and Methods for manner in which the angle was determined.

interference from spinning sidebands, resulting in intensity overlap and line shape distortion. In addition, any hysteresis in the setting of the angle contributes an uncertainty to the results. Furthermore, the signal-to-noise ratio degrades as the spinner axis is removed from the magic angle. Nevertheless, several of the above techniques, taken together, appear to be sufficient to provide accurate values for the chemical shift parameters in powders.

**C. Low-Temperature MAS.** The results from the previous section validate earlier conclusions, suggesting that the phenyl rings in the "softest" copolymer undergo torsional oscillations about the 1,4-phenylene axis.[4] Our goal in this section is to establish the nature of these oscillations—i.e., whether they represent small-angle librations or 180° ring flips. (Large-amplitude aromatic ring rotations can be ruled out on the basis of the data in Table II. Large-scale rotations would require substantial narrowing of the aromatic chemical shift tensors. Large-amplitude ring rotations are also not consistent with the known partial double-bond character of the carbonyl-aromatic bond. In order to preserve resonance stabilization, the carbonyl and aromatic carbons must remain coplanar.)

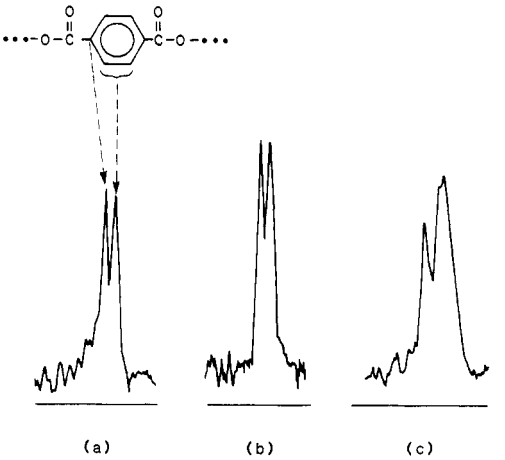


**Figure 3.** Variable-temperature MAS $^{13}C$ NMR spectra of the aromatic region of segmented copolymer I containing 0.80 mole fraction hard segments: (a) 22 °C; (b) −58 °C; (c) −89 °C.

If the phenyl rings are static or are undergoing very small angle librations, one would expect a priori to observe two peaks for the protonated aromatic carbons, as the ortho carbons (see structure in Figure 3) reside in markedly different electronic environments. Such doubling of aromatic resonances has been observed in a number of synthetic polymers, notably in epoxy resins,[23] poly(ethylene terephthalate),[24] poly(phenylene oxide),[25] and crystalline aromatic polyesters.[26] In Figure 3a is shown the aromatic region of the $^{13}C$ NMR spectrum of the softest copolymer sample (the one containing 0.80 mole fraction hard segments). This spectrum was obtained at 22 °C and shows one peak, albeit broadened, for the protonated aromatic carbons. The observation of a single peak for the protonated aromatic carbons at 22 °C does not prove that rapid ring flips are occurring, as the single peak, and particularly the broad line, could represent degeneracy or near equivalence of the chemical shifts of the ortho carbons. As the temperature is lowered, however, the line for the protonated carbon preferentially broadens (Figure 3b), and at ca. −89 °C, may show evidence of splitting (Figure 3c). This behavior is reminiscent of the coalesence phenomenon in solution-state NMR and is taken here to provide evidence that the phenyl rings in the segmented copolymer I (containing 0.80 mole fraction hard segments) undergo 180° ring flips about the 1,4-phenylene axis at ambient temperature.[34] These motions at ambient temperature are rapid on the time scale of the chemical shift anisotropy. Relaxation data for the protonated aromatic carbons are consistent with this interpretation.[5] The exact free volume considerations governing 180° flips of phenyl rings are not known for certain at this time. As a striking example, the phenyl rings in phenylalanine hydrochloride undergo 180° ring flips at ambient temperatures,[27] whereas in phenylalanine in the zwitterion form, they do not.[28] These differences have been related to differing crystalline environments.

In addition to the preferential broadening associated with low temperature, the protonated aromatic carbons also exhibit an increase in relative intensity as the temperature is lowered. These results are consistent with the slowing of motion about the 1,4-phenylene axis. The ratio

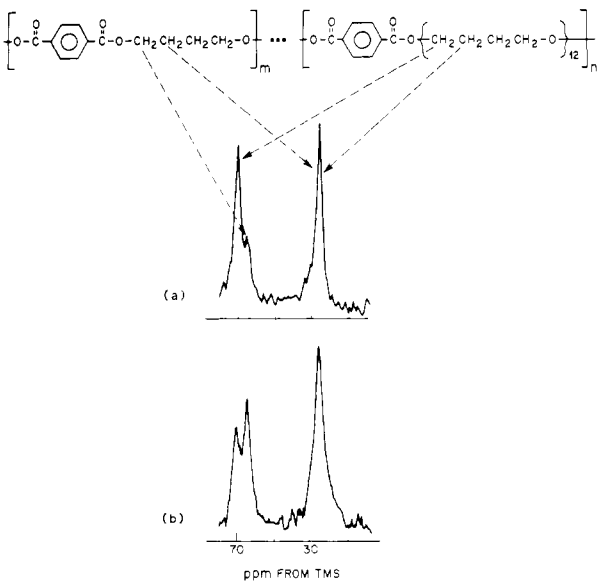


**Figure 4.** Low-temperature MAS 50.3-MHz $^{13}C$ NMR spectra of the alkyl carbons of copolymer I containing 0.80 mole fraction hard segments: (a) spectrum obtained at 22 °C; (b) spectrum obtained at −58 °C.

of the center band of the nonprotonated to protonated signal intensity is 1:1.2 at 22 °C (Figure 3a) and goes to 1:1.4 at ca. −89 °C (Figure 3c). This finding is consistent with motion being responsible for the underrepresentation of the protonated aromatic carbon intensity at ambient temperatures. The protonated aromatic carbon resonances also exhibit a small (ca. 0.2 ppm) shift to higher field at −89 °C. Such a shift may reflect "freezing-in" of certain conformations.

Sufficient data are not presently available to determine unambiguously whether all of the phenyl rings in copolymer I are involved in these motions or whether the motions are heterogeneous. However, in view of the structure of the polymer and given the fact that the broadening of the protonated aromatic resonance occurs gradually over an ~80–100 °C range in temperature, it is likely that the motion of the phenyl rings is best represented by a distribution of processes.

As the temperature of copolymer I is lowered, the $^{13}C$ NMR spectra also show changes in the peaks arising from the soft-segment carbons (Figure 4). At temperatures just below the $T_g$ of the soft-segment carbons (ca. −50 °C), the soft-segment carbon lines show the onset of dipolar broadening. Dipolar broadening arises when the motions of the group under consideration give rise to strong fluctuating dipolar fields.[7,8,29] The broadening caused by this phenomenon generally cannot be removed by high-power proton decoupling because of limitations on the amount of power that the sample probe can handle. Thus, the onset of diplar broadening can be associated with motions having correlation times in the $\sim 10^{-6}$-s region. Figure 4 shows what appears to be an intensity reversal for the hard and soft $-OCH_2-$ resonances. The soft-segment $-OCH_2-$ peak at −58 °C has become preferentially broadened, as has the central $-CH_2-$ peak.

That the onset of dipolar broadening occurs coincident with passing through the glass transition temperature of the soft-segment carbons is probably fortuitous, as the motional frequencies responsible for the two processes may be very different.

**D. Static Powder Pattern Difference Spectroscopy.** Static powder pattern difference spectroscopy, using suitably deuterium-labeled polymers, can provide information concerning the width of the chemical shift anisotropy ($|\sigma_{11} - \sigma_{33}|$). Of particular interest in the poly(butylene terephthalate)-containing series of polymers is the powder pattern width for the $-CH_2\mathbf{CH_2CH_2}CH_2-$ carbons. This width can be estimated fairly accurately for the poly(butylene terephthalate) homopolymer. However, for copolymer I, the complications due to the overlapping resonances from the soft-segment carbons prohibit any realistic estimate of the width.

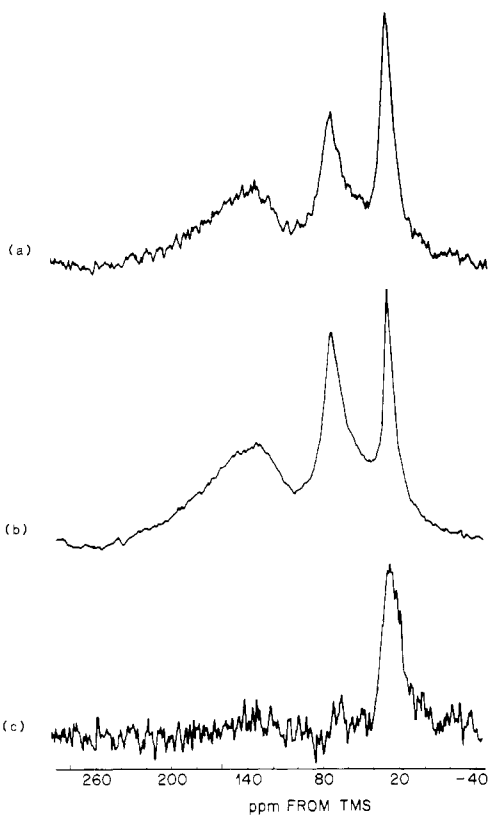


**Figure 5.** Static powder pattern difference spectroscopy for copolymer I: (a) $^{13}C$ NMR (50.3 MHz) static powder pattern of unlabeled segmented copolymer containing 0.88 mole fraction hard segments; (b) $^{13}C$ NMR spectrum of copolymer I in which the central alkyl carbons of the hard segments are labeled with deuterium; (c) difference spectrum, revealing the true line shape for the central $-CH_2-$ carbons of the hard segments.

The results of a difference spectroscopy experiment are shown in Figure 5. In Figure 5a is shown the static $^{13}C$ NMR powder pattern for unlabeled copolymer I. Figure 5b shows the corresponding spectrum for copolymer I, in which the hard-segment butylene unit bears deuterium atoms on the central carbons (i.e., $-CH_2CD_2CD_2CH_2-$). Because the signal in these spectra arises from polarization transfer from protons to carbons, those carbons bearing deuterium do not cross polarize well and effectively drop out of the spectrum. Figure 5c shows the result of the subtraction of the spectrum in Figure 5b from that in Figure 5a. From this spectrum, the width of the $-CH_2\mathbf{CH_2CH_2}CH_2-$ line can be measured; it is found to be 17.6 ppm.

The results of similar experiments on poly(butylene terephthalate) are shown in Figure 6. The difference spectrum in Figure 6c shows a considerable amount of additional intensity in the $-OCH_2-$ region of the spectrum, whereas the corresponding spectrum for copolymer I (Figure 5c) does not. (Characterization of the deuterated polymer samples by solution-state $^2H$ NMR spectroscopy reveals only one peak, in the correct position for the $-CH_2CD_2CD_2CH_2-$ deuterons.) The results presented in Figure 6c suggest that the $-OCH_2-$ carbons in poly(butylene terephthalate) receive a significant amount of their

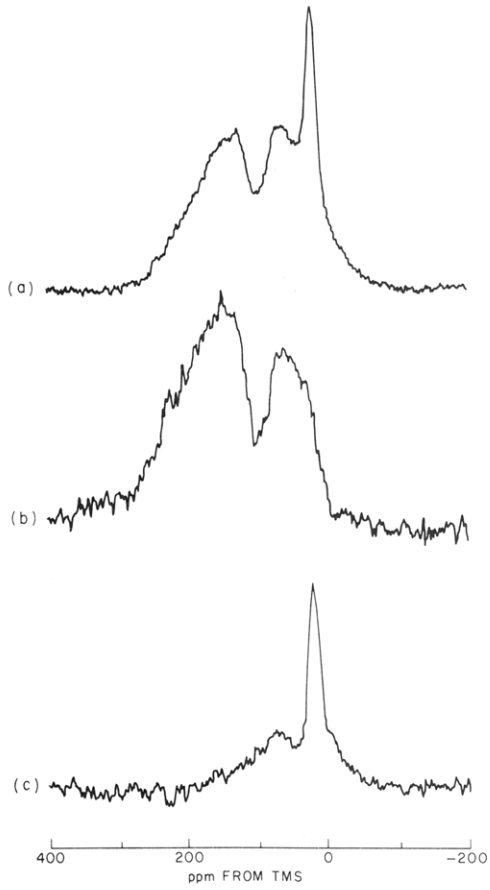


**Figure 6.** Static powder pattern difference spectroscopy for poly(butylene terephthalate): (a) $^{13}C$ NMR (50.3 MHz) static powder pattern of unlabeled poly(butylene terephthalate); (b) $^{13}C$ NMR spectrum in which the central alkyl carbons are labeled with deuterium; (c) difference spectrum.

Table IV
Chemical Shift Tensor Powder Pattern Widths for $-CH_2CH_2CH_2-$ Carbons

| sample | temp, °C | $\lvert\sigma_{11} - \sigma_{33}\rvert$, ppm | ref |
|---|---|---|---|
| *n*-eicosane | −95 | 33 | 30 |
| polyethylene | ambient | 38 | 16, 31 |
| poly(butylene terephthalate) | 22 | 19.9 | |
| copolymer I [a] | 22 | 17.6 | |

[a] Containing 0.88 mole fraction hard segments.

polarization from the central $-CH_2-$ carbons, whereas in copolymer I, they do not. The reason for this anomalous behavior is not certain at this time. This result may indicate that the fluctuating local fields produced by motion of the central $-CH_2-$ carbons induce a dipolar broadening of some of the $-OCH_2-$ resonances. This broadening would not appear in the static powder spectrum of the deuterium-labeled polymer, thus accounting for the observed difference spectrum (Fig. 6c). The use of a delayed-decoupling scheme[32] would avoid these differences.

The results of this difference spectroscopy for copolymer I and for poly(butylene terephthalate) are summarized in Table IV, where the line widths are compared to static $-CH_2CH_2CH_2-$ anisotropies for other polymers. The reduced value for the poly(butylene terephthalate) "central" $-CH_2-$ carbons has been interpreted previously in terms of enhanced molecular motions of these carbons.[4] Here we deduce a more accurate value for this line width (Table IV) and illustrate that these motions occur and may be enhanced in copolymer I. Solution-state relaxation data

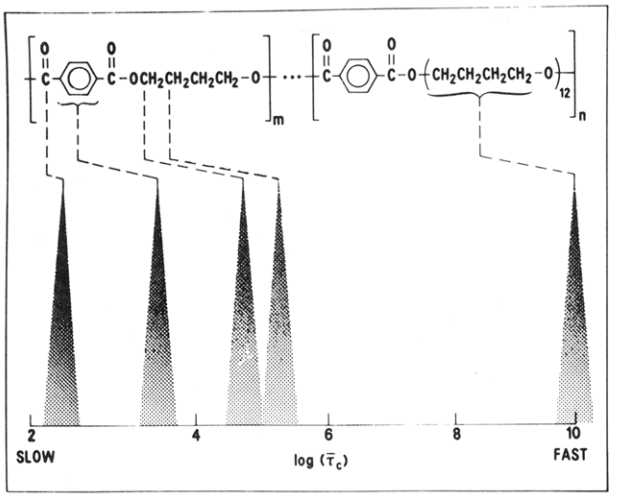


**Figure 7.** Schematic representation of the motional dynamics of various carbons of the segmented copolymer at ca. 25 °C.

suggest that these sorts of motions persist in solution,[5] and solid-state $^2H$ NMR data[33] suggest a mechanism for these motions.

## Summary

The off-axis MAS, low-temperature MAS, and static powder pattern results presented here, in conjunction with other data,[3-5] enable us to estimate the motional dynamics at every carbon in copolymer I. These results are summarized schematically in Figure 7.

The carbonyl carbon appears static on the NMR time scale, although the NMR results indicate that it has an axially symmetric chemical shift tensor. The aromatic rings show evidence of 180° flips about the 1,4-phenylene axis, and the low-temperature MAS results show that these motions can be frozen out at −89 °C in the copolymer containing 0.80 mole fraction hard segments at 22 °C. The alkyl carbons of the hard segments are involved in motions that partially average their shift tensors, with the central $-CH_2-$ carbons undergoing either larger amplitude or faster motions than the $-OCH_2-$ carbons. Finally, the soft-segment carbons have sufficient spectral density in the megahertz frequency regime to afford short relaxation times[3,5] and to partially average out dipolar interactions.[3] Upon cooling, the soft-segment carbons exhibit dipolar broadening at temperatures just below their $T_g$.

Although the motional dynamics are clearly addressed by the NMR results, the extent of the homogeneity or heterogeneity of these motions cannot be unambiguously assessed. Solid-state $^2H$ NMR experiments are in progress to determine the extent of motional heterogeneity and to propose specific motional models for the alkyl carbon reorientations.

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(34) **Note Added in Proof:** Solid-state $^2H$ 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 ($T_{1\rho}(C)$), 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 $\chi^2$ 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 $^2H$ 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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