High-Resolution Solid-State ^{13}C NMR Study of the α and β Crystalline Forms of Poly(butylene terephthalate)

M. A. Gomez, M. H. Cozine,† and A. E. Tonelli*

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974.
Received July 15, 1987

ABSTRACT: Uniaxially strained poly(butylene terephthalate) (PBT) undergoes a reversible α to β crystalline phase transition, where the fiber repeat distance is increased in the β phase. The question of what the intrachain conformations of PBT are in both relaxed α and strained β crystalline phases has not yet received a completely satisfactory answer. We have performed variable-temperature ^{13}C CPMAS NMR measurements on both crystalline phases of PBT in the hope that their high-resolution solid-state spectra would permit us to compare the crystalline chain conformation in the α and β phases. In the spectra recorded between ambient temperature and ca. 90–100 °C, all resonances are broadened by contributions from the amorphous PBT chains. This broadening is presumably a consequence of the different local environments, both conformational and packing, experienced by the carbon nuclei of the sluggish, amorphous PBT chains which result in a dispersion of chemical shifts. However, above 100 °C a significant narrowing (better than a factor of 2) of the resonances is observed to occur presumably due to the increased mobility of the amorphous PBT chains which no longer cross-polarize efficiently. Comparison of the high-temperature spectra leads to the conclusion that the conformations of the tetramethylene segments are the same in the α and β phases. The only significant difference in the high-temperature spectra of α and β form PBT is between the resonances observed for the protonated aromatic carbons which differ by 0.9 ppm. This chemical shift difference is consistent with the conclusion, reached by Davidson et al. using broad line ^1H NMR, that changes in the conformation of the terephthaloyl residue $-C(=O)C_6H_4C(=O)-$ must accompany the solid-state transformation of PBT from the α to β form.

Introduction

It was first observed[1-3] over a decade ago that the uniaxial extension of poly(butylene terephthalate) (PBT) fibers is accompanied by a crystal–crystal transition. In the relaxed or α-form crystals the molecular chain or fiber repeat is ~10% shorter than observed in the stretched or β-form crystals. The transition between the α and β forms of PBT produced by mechanical deformation (uniaxial stretching) is reversible,[3-5] and only the α form is stable in the relaxed, unstretched state at ambient temperature.

X-ray structural studies have been reported[4,6-10] for both PBT crystal forms. Infrared and Raman spectroscopy[11] suggest a nearly trans–trans–trans sequence (ϕ_a, ϕ_b, ϕ_c) for the glycol residue in the extended structure (see Figure 1). However, the crystal structures proposed by Yokouchi et al.[4] and Hall et al.[7,8,10] depart significantly from the extended, all-trans glycol structure. All crystal structures proposed for the relaxed, contracted α form approximate a gauche–trans–gauche conformation for the glycol residue, although there are differences in detail among them.

As noted by Davidson et al.,[12] the low scattering power of hydrogen atoms makes X-ray diffraction a technique less than suitable for defining the conformation of the glycol residues in PBT. Instead, these same authors applied broad-line ^1H NMR measurements to oriented PBT in both the relaxed α and strained β forms and determined the second moments of the proton line shapes as a function of specimen orientation. They found the ^1H NMR results to be consistent with a nearly fully extended (trans–trans–trans) conformation for the stretched β form and to agree quantitatively with the X-ray structure proposed by Hall and Pass.[7] However, their NMR results for the relaxed α form were not consistent with any of the proposed crystal structures and suggest instead that the conformation and orientation of the central methylene pairs in the glycol residues are not substantially altered in the strain-induced transformation from the α to β form.

More recently, Greneir-Loustalot and Bocelli[13] studied the structures of four PBT model compounds by X-ray diffraction and high-resolution ^{13}C NMR in the solid state. Single-crystal X-ray diffraction revealed that two of the PBT model compounds crystallized with trans–trans–trans glycol residues, one with a trans–trans–gauche glycol conformation, and the remaining compound had its glycol residue in the gauche–trans–gauche conformation.

In the high-resolution solid-state ^{13}C NMR spectra of the PBT model compounds they observed the central methylene carbons that are gauche to their ester oxygens to resonate 3.0–3.7 ppm upfield from those central methylene carbons adopting the trans arrangement (see Figure 1). This is consistent with the often observed shielding of carbon nuclei whose γ-substituents are in a gauche arrangement, i.e., the γ-gauche effect.[14,15] The central methylene carbons in α form PBT were observed to resonate midway between the corresponding methylene resonances in the model compounds.

Grenier-Loustalot and Bocelli,[13] due to the broadness of the central methylene resonance in PBT (>3 ppm), which is likely a consequence of contributions from carbon nuclei in both the crystalline and amorphous regions of their sample (see below), were unable to draw conclusions regarding the conformation of the glycol residue in α-PBT. A similar study was attempted by Havens and Koenig,[16] but it too was plagued by broad resonances and, in addition, by an erroneous conformational assignment to one of their PBT model compounds, as pointed out by Grenier-Loustalot and Bocelli.[13]

Most recently, Perry et al.[17] employed high-resolution solid-state ^{13}C NMR techniques to study the crystalline conformations and dynamics of PBT chains in both the α and β crystalline forms. Their spectra also exhibited broad resonances, especially for the central methylene carbons (4–5 ppm). However, they concluded that as the amount of trans content in the glycol residue increases, the interior methylene resonance shifts to higher, field, so the β form resonance moves upfield from the α form resonance. This is in direct opposition to the model compound study of Grenier-Loustalot and Bocelli[13] and to the expected order of chemical shifts based on the conformationally sensitive γ-gauche effect.[14,15]

In an attempt to determine the conformations of PBT chains in their α and β form crystals, we have conducted variable-temperature, high-resolution solid-state ^{13}C NMR

† Department of Chemistry, Yale University, New Haven, CT.

0024-9297/88/2221-0388$01.50/0

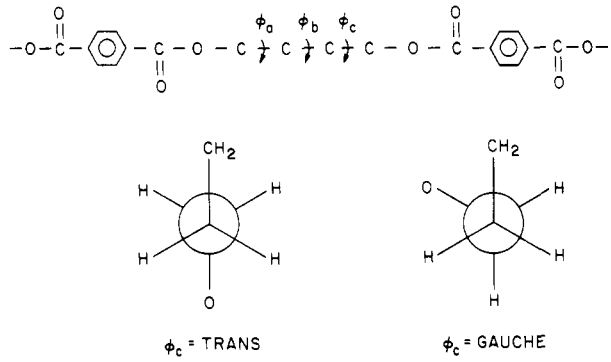

Figure 1. Schematic of PBT chain with torsions about C–C bonds indicated and Newman projections of the trans and gauche conformers about the terminal C–C bonds.

studies. We find that above ca. 100 °C the spectra are significantly better resolved, with resonance line widths not exceeding 1–2 ppm. This narrowing of resonances is apparently a consequence[18] of removing contributions made by the amorphous carbons, which no longer cross-polarize efficiently at temperatures well above the glass transition of PBT.[19] Comparison of the high-temperature, high-resolution solid-state ^{13}C NMR spectra recorded for α- and β-PBT with those of the PBT model compounds reported by Grenier-Loustalot and Bocelli[13] permits us to draw several conclusions concerning the conformations of PBT chains in the relaxed α and stretched β crystals.

Experimental Section

Sample Preparation and Characterization. PBT in the form of pellets was obtained from Aldrich (19,094-2). The pellets were cryogenically ground to a fine powder, which was annealed at 150 °C for 3 days to produce[4,20] the α form.

Melt pressing of the pellets at 250 °C produced thin films which were quenched into liquid nitrogen. Strips were cut from the film and placed in an Instron tensile testing machine. The strips were drawn to 300% elongation, held under tension, and annealed at 150 °C for several hours to produce[4] the β-form sample.

X-ray diffraction photographs were recorded for both samples in the film form and confirmed that we did indeed produce both α- and β-PBT samples. A flat-plate vacuum camera using Ni-filtered Cu Kα radiation was employed in the X-ray diffraction measurements.

NMR Measurements. ^{13}C NMR spectra were recorded between 20 and 110 °C on a Varian XL-200 spectrometer operating at a static field of 4.7 T. Magic angle sample spinning (MAS) at speeds of 1.5–3.5 KHz was achieved with a Doty Scientific probe, which utilizes a double air bearing design. The PBT samples were spun in aluminum oxide rotor with Kel-F [poly(chlorotrifluoroethylene)] end caps. PBT in the α form was placed in the rotor as a powder, while a strip of the β-form sample was wound under tension onto a spindle to form a spool, and the ends of the strip were glued to prevent relaxation to the α form. The spool wound with the β form strip was then inserted into the rotor and special end caps (Doty Scientific) were used to secure the ends of the spindle so that the β form PBT spool would rotate at the same speed as the rotor.

A 45 KHz rf field strength was used for dipolar decoupling (DD), with a decoupling period of 200 ms. The optimal cross-polarization (CP) contact times were found to be 1000 and 3000 μs for the α- and β-form samples, respectively.

A small portion of powdered poly(oxymethylene) (POM) was placed in the α-PBT as a chemical shift reference. Under CP conditions the POM resonance is expected[21] at 89.1 ppm downfield from tetramethylsilane (TMS).

Spin–lattice relaxation times, T_1, were measured for each carbon in both PBT samples under the CP condition by application of the pulse sequence developed by Torchia.[22] In addition, the usual inversion–recovery method[23] for obtaining T_1 was employed without CP, but with DD, to estimate the T_1's of the amorphous carbons.

Table I
^{13}C Chemical Shifts of α- and β-PBT

	^{13}C, ppm vs TMS[a]		
carbon	α	β	amorphous[b]
CH_2	27.2	27.6	26.6
OCH_2	66.2	66.7	65.9
PAR	130.8	131.7	130.2
NPAR	135.2	135.2	134.9
C=O	165.6	165.5	166.0

[a] Measured at 105 °C and referenced to the POM resonance at 89.1 ppm from TMS,[21] although we have observed a 0.3 ppm downfield shift with respect to ambient temperature. [b] Measured from spectrum obtained without CP, but with MAS/DD (see Figure 4b).

Table II
Spin–Lattice Relaxation Times, T_1, for α- and β-PBT

	T_1,[a] s		
carbon	α[b]	β[b]	amorphous[c]
CH_2	0.13	0.20	0.16
OCH_2	0.32	0.27	0.24
PAR	5.7	7.0	0.31
NPAR	18.9	12.7	
C=O	18.0	15.0	

[a] Measured at 105 °C. [b] Obtained under CP conditions with the Torchia[22] pulse sequence. [c] Obtained without CP by the inversion–recovery method.[23]

Results

X-ray Characterization of PBT Samples. Structural characterization of our samples was by X-ray diffraction. Flat film photographs of the α- and β-form samples are shown in Figure 2.

Drawn films annealed under tension and held under tension during the X-ray exposure give the diffraction pattern characteristic of the β form (see Figure 2b). When the tension is relaxed the α form is obtained as confirmed by X-ray (see Figure 2a). Drawn films annealed in the absence of tension also produce the α form.

The most significant difference observed in the X-ray patterns of both forms is the widely reported[4,7–9] lengthening of the c-axis fiber repeat. By measuring the spacings of the fourth layer meridional reflection, the values obtained for the c axis are 11.5 and 12.9 Å for the α and β forms, respectively. These values are in agreement with the fiber repeats reported previously for PBT and confirm the existence of the α and β forms in our samples.

^{13}C NMR. Figure 3 presents the CPMAS/DD spectra of α-PBT at ambient temperature and 105 °C. The spectrum of α-PBT obtained with and without CP at 105 °C is shown in Figure 4. A comparison of the CPMAS/DD spectra of α- and β-PBT recorded at 105 °C is made in Figure 5. Table I contains the observed solid-state ^{13}C NMR chemical shifts, and ^{13}C spin–lattice relaxation times, T_1, measured in the solid state at 105 °C, are given in Table II.

Discussion

It is clear from the comparison of CPMAS spectra recorded at 105 °C and presented in Figure 5 and the corresponding chemical shifts listed in Table I that aside from the protonated aromatic carbons (PAR), the carbon nuclei in α- and β-PBT resonate at nearly identical frequencies. This observation is at variance with the results of Perry et al.,[17] who found the CPMAS/DD spectra of α- and β-PBT at 20 °C to be closely similar except for the resonances of the interior methylene carbons. The source of this disparity is revealed by comparing the spectra in Figure 5 with those presented by Perry et al.[17] (also see

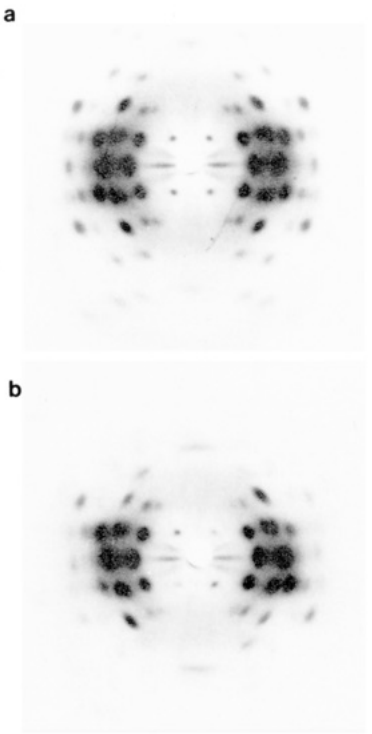

Figure 2. X-ray diffraction photographs of α- and β-PBT samples.

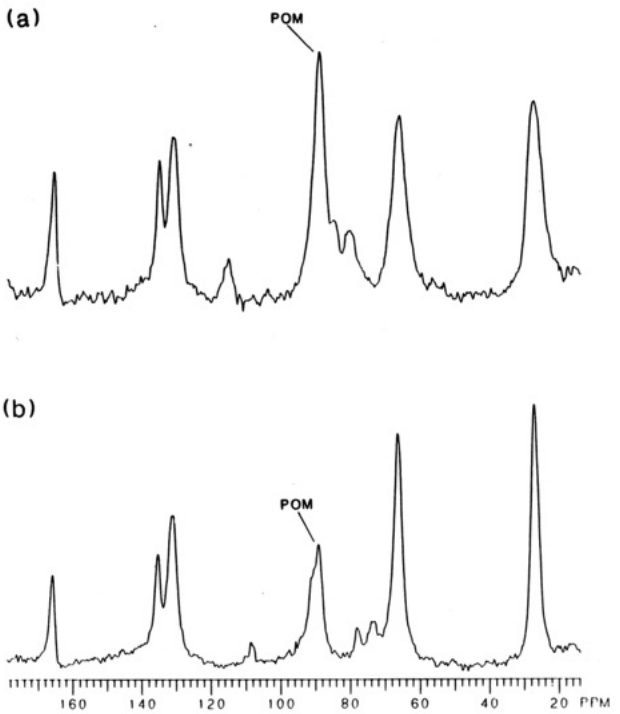

Figure 3. CPMAS/DD spectra of α-PBT at ambient temperature (a) and 105 °C (b).

Figure 3). The latter spectra are characterized by broad resonances, 2–3 times as broad as the resonances seen in Figure 5, presumably a consequence of the different local environments, both conformational and packing, experienced by the carbon nuclei of the sluggish, amorphous PBT chains which result in a dispersion of chemical shifts.

Recording the CPMAS/DD spectra of PBT at elevated temperatures (105 °C) results in enhanced resolution, because the amorphous carbons, which constitute 30–50%

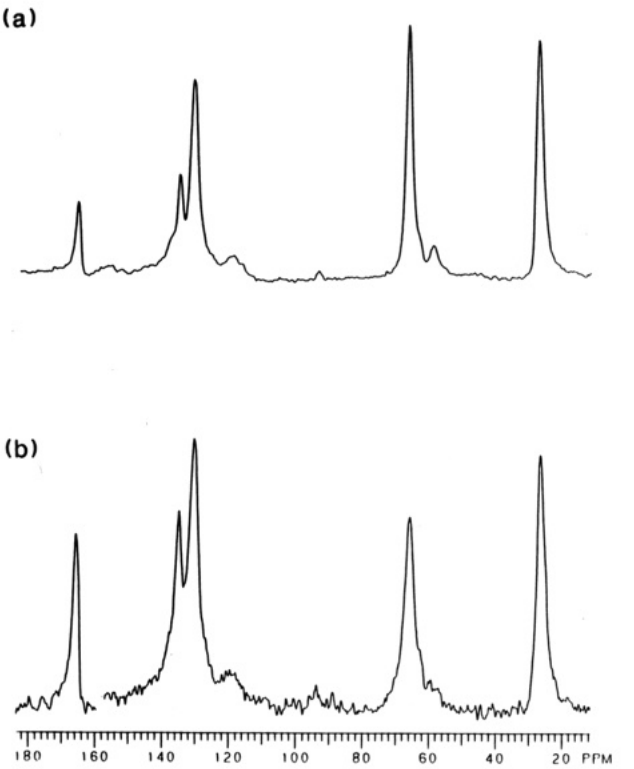

Figure 4. CPMAS/DD (a) and MAS/DD (b) spectra of α-PBT measured at 105 °C.

of the samples, are sufficiently above their glass transition (T_g = 50–55 °C)[19] to be mobile enough not to cross-polarize efficiently.[18] Comparison of the spectra recorded with and without CP (Figure 4) makes apparent that the crystalline and amorphous carbons resonate at similar frequencies, with the amorphous carbon resonances appearing upfield as expected (see Figure 3 and below). Thus at temperatures sufficiently close to T_g, where the amorphous PBT chains are relatively rigid and immobile, CPMAS/DD spectra would be expected[18] and in fact are observed to be significantly broadened by the overlap of crystalline and amorphous resonances (see Figure 3).

The near coincidence of methylene carbon chemical shifts observed for α- and β-PBT strongly suggests that in both the relaxed (α) and strained (β) crystals the glycol residues of the PBT chains are adopting very similar conformations. Just what conformation is adopted by the glycol residues in crystalline PBT?

In Figure 6 we present schematic structures of the four PBT model compounds studied by Grenier-Loustalot and Bocelli[13] and of PBT. The conformations of the glycol residues, as determined by X-ray diffraction,[13] are indicated on each model compound structure as t (trans) or g (gauche). Also the chemical shifts (ppm versus TMS) of the central methylene carbons observed by CPMAS/DD ^{13}C NMR are listed above the central methylene carbon in each of the four PBT model compounds and in PBT itself. A comparison of the central methylene carbon chemical shifts clearly indicates that the glycol residues in both α- and β-PBT crystals are in the nearly extended trans–trans–trans conformation found by Grenier-Loustalot and Bocelli[13] for the PBT model compounds **3** and **4**.

If the glycol residues of both α- and β-PBT are nearly fully extended, then what conformational differences can account for the 10% increase in the fiber repeat of the β-form crystals that are formed upon extension of α-PBT? The ester bonds [C(=O)O] in PBT are likely trans planar,

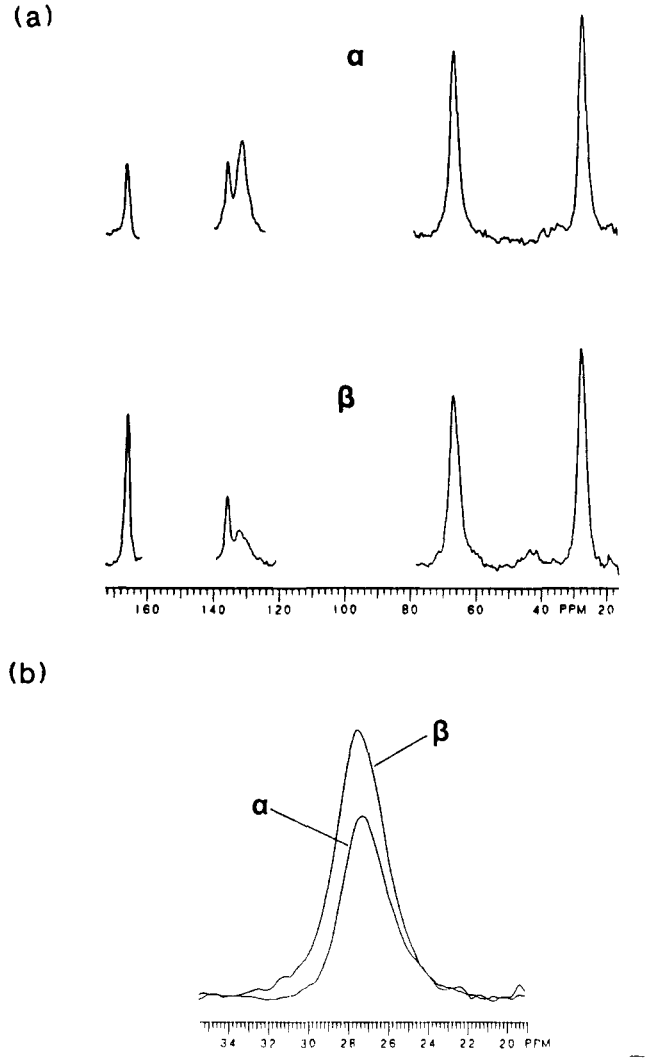

Figure 5. CPMAS/DD spectra measured at 105 °C for α- and β-PBT. Full spectra (a) and expansion of the central methylene carbon regions (b).

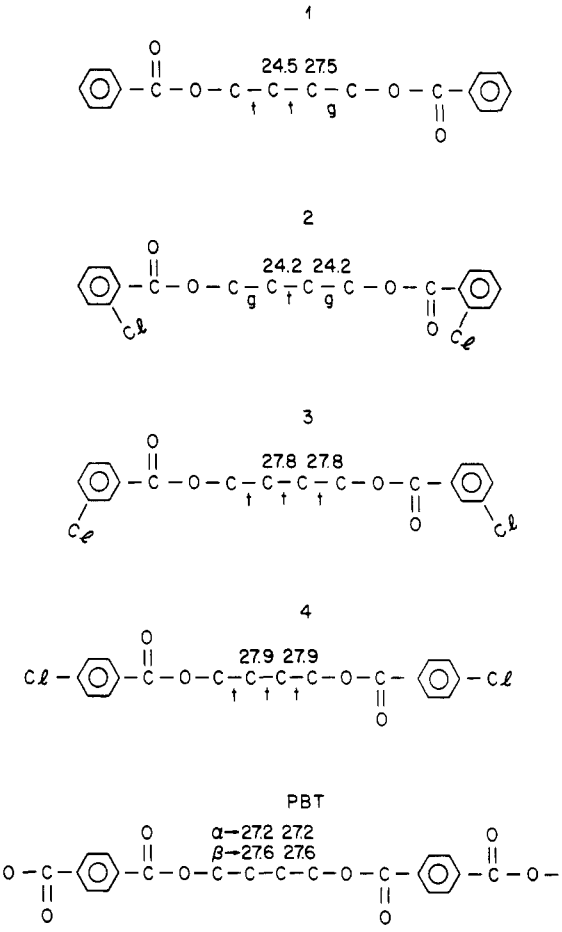

Figure 6. Schematic drawings of the four PBT model compounds studied by Grenier-Loustalot and Bocelli[13] using X-ray diffraction and high-resolution, solid-state ^{13}C NMR. The conformation of each glycol residues is indicated (t = trans, g = gauche) and the chemical shifts observed for the central methylene carbons are also listed. The structure of PBT is also presented and the chemical shifts observed in this work for the central methylene carbons in the α- and β-form crystals are indicated.

as they are in the four PBT model compounds. In each of the crystalline model compounds the CH_2—O bonds are also in the trans conformation. Because the chemical shifts of the central methylene carbons should be sensitive[14,15] to the conformations of these bonds (see Figures 1 and 6), as well as to the conformations of the terminal CH_2—CH_2 bonds, the CH_2—O bonds in α- and β-PBT are also most likely trans. If they were gauche in either or both polymorphs, then we would expect different chemical shifts for the central methylene carbons in α- and β-PBT, or chemical shifts reflecting the shielding[14] produced by γ-gauche carbonyl carbons. Instead, the chemical shifts of the central methylene carbons in both α- and β-PBT are very similar to the chemical shifts observed for the same carbons in model compounds **3** and **4**, where both the CH_2—O and terminal CH_2—CH_2 bonds are trans.

The only conformational degree of freedom that remains to distinguish the α and β forms of PBT is the relative orientation of the carbonyl groups in the terephthaloyl residues, which are determined by the torsional angles about the sp^2–sp^2, carbonyl to aromatic C–C bonds (see Figures 1 and 6). In terms of γ-gauche shielding effects,[14,15] we would expect the chemical shifts of the protonated aromatic carbons (PAR) to reflect the conformations of these bonds.

In fact the 0.9 ppm chemical shift difference observed between the PAR's of α- and β-PBT is by far the largest difference between their high-resolution, solid-state ^{13}C NMR spectra (see Figure 5). Thus we agree with the conclusion reached by Davidson et al.[12] via analysis of broad-line ^{1}H NMR data; changes in the conformation of the terephthaloyl residue, but not in the glycol residue, must accompany the solid-state transformation of PBT from the α to β form.

As we have deduced by the comparison of solid-state ^{13}C NMR chemical shifts observed for α- and β-PBT and several of their model compounds, all of the bonds in crystalline PBT are nearly trans except the bonds connecting the ester groups to the aromatic rings. The bonds in amorphous PBT chains would be expected to be a mixture of trans and gauche conformations, the latter producing upfield chemical shifts via the γ-gauche effect. It follows that the amorphous carbon nuclei should resonate upfield from the corresponding carbons in α- and β-PBT. The solid-state ^{13}C NMR chemical shifts presented in Table I for the amorphous and crystalline carbons in PBT confirm this expectation.

Spin–lattice relaxation times, T_1, for both crystalline forms and amorphous PBT, as presented in Table II, serve to indicate the motional characteristics of solid PBT chains. The most striking observation is the near coincidence of the T_1's measured for the methylene carbons of the glycol residues in the α and β crystallites of PBT with those observed for the amorphous methylene carbons. By contrast, the T_1's measured for the crystalline PAR carbons are more than an order of magnitude longer than

observed for the amorphous PAR carbons. It would appear that the methylene carbons of the glycol residue are undergoing significant motion independent of whether they are included in the α and β crystallites or not.

In agreement with Perry et al.,[17] whose measurements were performed more than 80 °C below ours (105 °C), we do not find any significant differences between the spin–lattice relaxation times of the crystalline methylene carbons in α- and β-PBT. Similarly, the T_1's of the crystalline carbon nuclei belonging to the terephthaloyl residues in α- and β-PBT are also not markedly different. It does not appear that the α and β phases constrain the motions of their constituent PBT chains in any significantly different manner (also see Jelinski et al.[24] and Garbow and Schaefer[25] for further discussion of solid-state PBT motion).

High-resolution, solid-state ^{13}C NMR studies of α- and β-PBT have revealed several important features concerning the conformations and motions of PBT chains in both crystalline phases. We have found the glycol residues to be in the nearly extended (trans–trans–trans) conformations in both crystalline forms, while different orientations of the ester groups and phenyl rings probably account for the 10% difference in the fiber repeats of α- and β-PBT. In both crystals the methylene carbons are sampling rapid motions, which are significantly faster than the motions experienced by the carbons of the terephthaloyl residues.

These conclusions serve to recommend high-resolution, solid-state ^{13}C NMR spectroscopy as a powerful technique for studying the structure and dynamics of solid polymers.

Acknowledgment. We appreciate the help we received from T. H. Klein and J. T. Ryan during the preparation of our β-PBT sample in the Instron tensile tester.

Registry No. PBT (copolymer), 26062-94-2; PBT (SRU), 24968-12-5.

References and Notes

(1) Boye, C. A., Jr.; Overton, J. R. *Bull. Am. Phys. Soc.* **1974**, *19*, 352.
(2) Jakeways, R.; Ward, I. M.; Wilding, M. A.; Hall, I. H.; Desborough, I. J.; Pass, M. G. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 799.
(3) Jakeways, R.; Smith, T.; Ward, I. M.; Wilding, M. A. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 41.
(4) Yokouchi, M.; Sakakibara, Y.; Chatani, Y.; Tadokoro, H.; Tanaka, T.; Yoda, K. *Macromolecules* **1976**, *9*, 266.
(5) Brereton, M. G.; Davies, G. R.; Jakeways, R.; Smith, T.; Ward, I. M. *Polymer* **1978**, *19*, 17.
(6) Mencik, Z. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2173.
(7) Hall, I. H.; Pass, M. G. *Polymer* **1977**, *17*, 807.
(8) Desborough, I. J.; Hall, I. H. *Polymer* **1977**, *18*, 825.
(9) Stambaugh, B. D.; Koenig, J. L.; Lando, J. B. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *15*, 299; *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1053.
(10) Hall, I. H. *ACS Symp. Ser.* **1980**, *141*, 335.
(11) Ward, I. M.; Wilding, M. A. *Polymer* **1977**, *18*, 327.
(12) Davidson, I. S.; Manuel, A. I.; Ward, I. M. *Polymer (British)* **1983**, *24*, 30.
(13) Grenier-Loustalot, M.-F.; Bocelli, G. *Eur. Polym. J.* **1984**, *20*, 957.
(14) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.
(15) Axelson, D. E. *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH: Deerfield Beach, FL, **1986**, Chapter 6.
(16) Havens, J. R.; Koenig, J. L. *Polym. Commun.* **1983**, *24*, 194.
(17) Perry, B. C.; Koenig, J. L.; Lando, J. B. *Macromolecules* **1987**, *20*, 422.
(18) Lyerla, J. R.; Komoroski, R. A.; Axelson, D. E. In Chapters 2–5 of ref 15.
(19) The T_g of PBT has been reported in the literature as varying from 22 to 80 °C (see, for example: Lewis, O. G. *Physical Constants of Linear Homopolymers*; Springer-Verlag: New York, 1968; pp 150–151. Lee, W. A.; Knight, G. J. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Interscience: New York, 1966; p III-79). DSC measurements performed on our α-PBT sample and a quenched amorphous PBT sample yielded T_g = 50–55 °C.
(20) Lovinger, A. J.; Belfiore, L. A.; Bowmer, T. N. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1449.
(21) Earl, W. L.; Vander Hart, D. L. *J. Magn. Reson.* **1982**, *48*, 35.
(22) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.
(23) Farrar, T. C.; Becker, E. D. *Pulse Fourier Transform NMR*; Academic: New York, 1971.
(24) Jelinski, L. W.; Dumais, J. J.; Watnick, P. I.; Engel, A. K.; Sefcik, M. D. *Macromolecules* **1983**, *16*, 409.
(25) Garbow, J. R.; Schaefer, J. *Macromolecules* **1987**, *20*, 819.

Novel Polymer Electrolytes Based on ABA Block Copolymers

F. M. Gray,* J. R. MacCallum, and C. A. Vincent

Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, U.K.

J. R. M. Giles

Materials and Structures Department, Royal Aircraft Establishment, Farnborough, Hants GU14 6TD, U.K. *Received May 25, 1987; Revised Manuscript Received August 13, 1987*

ABSTRACT: Some properties of novel polymer electrolytes, based on a styrene–butadiene–styrene ABA block copolymer with pendant short-chain poly(ethylene oxide) (PEO), are described. The polymers were combined with lithium trifluoromethanesulfonate in different concentrations to form an ion conducting matrix. The concentration dependence of the conductivity was analyzed by fitting the data to a VTF type equation. Conductivities, typically 10^{-5} S cm^{-1} at ambient temperatures, were obtained by casting films from a selective solvent which favors microphase separation with PEO forming the continuous phase. The dimensional stability of the materials could be improved by adding quantities of polystyrene homopolymer. Providing the polystyrene molecular weight was low, the conductivity was not greatly affected. Ionic conductivity was enhanced by blending the polymeric material with low molecular weight PEO. These blends did not phase separate on a macroscale.

Introduction

The majority of polymer electrolyte systems reported in the literature to data have been largely based on high molecular weight poly(ethylene oxide), $-(CH_2CH_2O)_n-$ (PEO), incorporating an alkali-metal salt.[1-4] These systems exhibit poor (<10^{-6} S cm^{-1}) ambient temperature conductivities as a consequence of their high degree of crystallinity. Much interest recently has been focused on

0024-9297/88/2221-0392$01.50/0