(2) (a) Reference 1a. (b) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125, and references therein.

(3) (a) In a previous publication, a different structure was reported for the product of the reaction between the trione and hydrazine; see: Stetter, H.; Landscheidt, A. *J. Heterocycl. Chem.* **1979**, *16*, 839. (b) Spectral data for product derived from hydrazine. ^{1}H NMR (CDCl$_3$) (ppm): 1.08 (t, J = 7.6 Hz, 6 H), 1.75–1.84 (m, 4 H), 2.17 (q, J = 7.6 Hz, 4 H), 2.18–2.25 (m, 4 H), 5.70 (s, br, 2 H). ^{13}C NMR (H coupled) (CDCl$_3$) (ppm): 11.0 (tq, J = 126.7, 4.7 Hz), 22.2 (t, J = 127.1 Hz), 28.4 (t, J = 129.6 Hz), 30.2 (qt, J = 126.2, 4.2 Hz), 60.1 (s), 150.5 (s). Ir (Nujol) (cm^{-1}): 1635 (C═N), 3350 (N–H). Mass spectrometry: 208 (M$^+$). (c) Spectral data for product derived from methylhydrazine. ^{1}H NMR (CDCl$_3$) (ppm): 1.01 (t, J = 7.6 Hz, 6 H), 1.62 (td, J = 12.9, 4.8 Hz, 2 H), 1.83 (td, J = 13.0, 8.8 Hz, 2 H), 2.11 (q, J = 7.6 Hz, 4 H), 2.13 (m, 4 H), 2.71 (s, 6 H). ^{13}C NMR (H coupled) (CDCl$_3$) (ppm): 11.5 (tq, J = 126.7, 4.7 Hz), 19.1 (mt, J = 130.5 Hz), 23.0 (mt, J = 127.8 Hz), 30.3 (qt, J = 126.5, 4.3 Hz), 36.8 (q, J = 135.7 Hz), 68.8 (s), 147.4 (s).

(4) Similar poly(ethylenepyrrole) polymers have been patented by Shell; see: Kiovsky, T. E.; Kromer, R. C. U.S. Patent 3979374, 1976. However, these have significantly fewer pyrrole units in the chain. The value of $2x/(2x + y)$ (see text) varied between 0.33 and 0.04 compared to ≥0.90 for the polymers that we report.

(5) This is true under conditions where the H$_2$O generated in the reaction is not removed, as is the case for the reactions described.

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Comments on the α to β Transition in Poly(butylene terephthalate)

A recent paper published by Tonelli et al.[1] using ^{13}C solid-state NMR to study the crystalline phase transition in poly(butylene terephthalate) (PBT) concluded that there are no chemical shift differences among the methylene carbons. From this experimental observation, it was concluded that the tetramethylene segment does not undergo any changes during the transition. This is contrary to the NMR data of Perry and Koenig[2] as well as to numerous other papers using infrared and X-ray.

PBT is known to undergo a reversible crystalline phase transition when uniaxially drawn. The phase change has been successfully followed by IR and X-ray measurements. A number of general conclusions have been obtained. The β phase has a larger unit cell that is evidenced by a lower density. This occurs as a result of the lengthening of the *c*-axis repeat distance.

The IR data conclusively show that the greatest changes occur in the methylene region of the spectra with the appearance of bands due to the β phase and the disappearance of those due to the α phase. The tetramethylene segment is in an extended configuration in the β phase and a crumpled configuration in the α phase. Intermolecular and intramolecular energy calculations on the β phase indicate that it is indeed a higher energy conformation.

Solid-state NMR is a useful technique for studying conformational changes as evidenced by the γ-gauche effect observed in polymers. However, a recent paper by Ando et al.[3] indicates that the trans and gauche conformations of the methylene carbons in poly(oxymethylene) have a nonlinear relationship with respect to the dihedral angle so that the chemical shift of two carbons in different conformational states may appear to be the same.

Past X-ray patterns indicate that there are significant differences between the two phases, most easily seen on the first and second layer lines (Figure 1). The X-ray patterns published by Tonelli et al. for the two phases both appear to be identical with the α-phase pattern of Figure 1 and not the β phase, also shown in Figure 1. It is also quite possible that some relaxation occurs at the elevated temperatures during the NMR measurements since the energy diffeences between the phases are quite small.

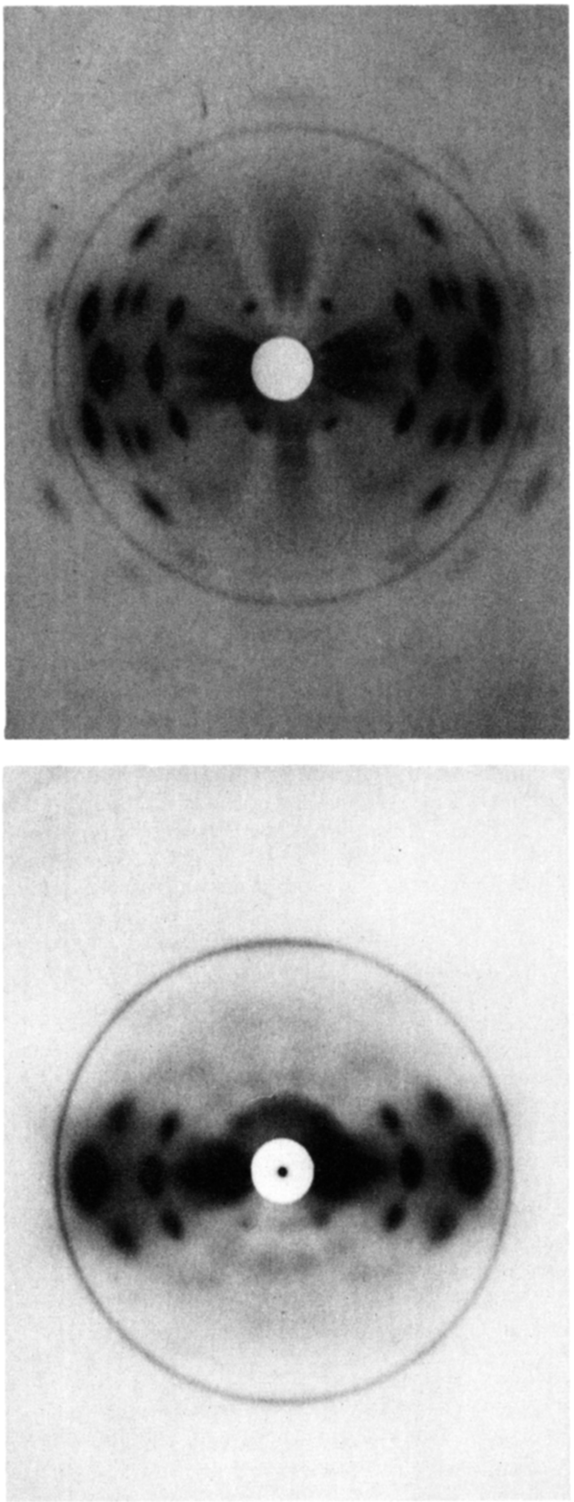

Figure 1. Wide-angle X-ray patterns of PBT in the (top) α phase and (bottom) β phase.

Considering the past IR and X-ray data and the similarities of the two X-ray patterns of Tonelli et al., we believe that one cannot conclude that there is no change in the tetramethylene segment of PBT when uniaxially drawn solely on the basis of the solid-state NMR measurements. An IR spectrum of the drawn sample before

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and after the NMR measurements would easily determine which crystalline phase is present.

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

References and Notes

(1) Gomez, M. A.; Cozine, M. H.; Tonelli, A. E. *Macromolecules* **1988**, *21*, 388.
(2) Perry, B. C.; Koenig, J. L.; Lando, J. B. *Macromolecules* **1987**, *20*, 422.
(3) Ando, I.; Komoto, T.; Yamanobe, T.; Kurosu, H. *Chem. Phys.* **1987**, *116*, 391.

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Reply to the Letter of Perry, Grasso, Koenig, and Lando

Our recent observations[1] of poly(butylene terephthalate) (PBT) in the α and β phases by high-resolution, solid-state ^{13}C NMR prompted us to conclude that significant conformational changes in the tetramethylene portion of the PBT chains do not accompany the α to β transition. This conclusion was based on the nearly identical chemical shifts observed for the methylene carbons in both phases and on comparison to the chemical shifts observed by Grenier-Loustalot and Bocelli[2] for the single crystals of several PBT model compounds that crystallize with their tetramethylene segments $(\mathrm{O{-}C}\curvearrowright\mathrm{C}\curvearrowright\mathrm{C}\curvearrowright\mathrm{C{-}O})$ in the ttt, ttg, and gtg conformations, where t = trans and g = gauche. These authors found the resonances of the central methylene carbons in the model compounds with gauche bonds to appear 3 ppm upfield from those of the central methylene carbons in the ttt model compounds. Because the chemical shift observed for the central methylene carbons in both α and β PBT were nearly identical with each other and with those observed for the ttt model compound,[2] we concluded that both α and β PBT have nearly an all-t tetramethylene conformation.

It is not surprising that our ^{13}C NMR results disagree with those reported by Perry and Koenig,[3] because they recorded spectra at room temperature leading to broad resonances (4–5 ppm) probably resulting from contributions made by both the crystalline and amorphous carbons. By contrast, we observed much narrower resonances (1–2 ppm) for PBT when observing at $T > 100$ °C, which is well above the T_g of this polymer and prevents the efficient cross-polarization of the mobile amorphous carbon nuclei.

We do not agree that IR data demonstrate that the tetramethylene segments are in a crumpled conformation in the α phase and in an extended conformation in the β phase. All they show is that the methylene region of the IR spectrum is most sensitive to the presence of the α and β phases of PBT. In addition, we also mentioned that there are serious disagreements between the structures derived for α and β phase PBT from X-ray diffraction studies.

We agree that "solid-state NMR is a useful technique for studying conformational changes as evidenced by the γ-gauche effect observed in polymers", and we also believe it possible that "the chemical shift of two carbons in different conformational states may appear the same". However, the PBT model compound work[2] makes clear that the $\mathrm{CH_2}$ carbons in a gauche conformation resonate 3 ppm upfield from those in the trans conformation of the tetramethylene glycol fragment.

The X-ray patterns we observed for our α- and β-phase PBT samples are not identical. The pattern for our β PBT sample does show evidence for the presence of some α phase, but judging from the relative intensities of the α and β reflections, we believe our sample to be predominantly of the β phase. Yokouchi et al.[4] have demonstrated that annealing PBT under tension at elevated temperatures enhances the formation of the β phase. Rapid MAS should increase the tension on our β sample, which would also oppose a β to α conversion.

We agree that recording an IR spectrum of our β sample before and after the NMR measurements would be worthwhile, but we have not yet figured out how to accomplish this. On the other hand, we feel that IR measurements performed on the PBT model compounds of Grenier-Loustalot and Bocelli[2] would be most useful in determining whether or not IR is diagnostic for folded, or crumpled, and extended conformations of the tetramethylene glycol fragment in PBT crystals.

In summary, on the basis of the comments of Perry, Grasso, Koenig, and Lando, we see no need to alter the conclusions reached in our ^{13}C NMR studies[1] of α and β PBT.

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

References and Notes

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On the Phase Behavior and the Limits of Miscibility of Styrene-*co*-Vinylphenol Blends with Poly(alkyl methacrylates)

One of the more intriguing questions posed over the last decade by those working in the general field of polymer blends is "how many favorable intermolecular interactions are required in order to achieve miscibility"? To give an example relevent to this study, poly(methyl methacrylate) (PMMA) is immiscible with polystyrene (PS) but miscible with poly(vinylphenol) (PVPh). "How many vinyl phenol (VPh) units would we need to incorporate into PS to render it miscible with PMMA?" In other words, "what are the limits of miscibility for the PMMA–poly(styrene-*co*-vinylphenol) (STVPh) system"? Chen and Morawetz recently reported a seminal fluorescence study of blends of polymethacrylates with styrene copolymers containing