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The conformations of poly(butylene-terephthalate) and poly(butylene-2,6-naphthalate) chains in their α and β crystalline polymorphs

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Abstract

Both thermoplastic polyesters, poly(butylene-terephthalate) (PBT) and poly(butylene-2,6-naphthalate) (PBN), have been observed to undergo solid–solid phase transitions between α and β crystalline polymorphs. Fiber repeat distances determined by X-ray diffraction in the β polymorphs of PBT and PBN are larger than those observed in their α polymorphs. This has generally been attributed to an extension of the butylene glycol portion of both polyesters, where the $O{-}CH_2{-}\curvearrowright\varphi{-}CH_2{-}CH_2$ and $(C{=}O){-}O{-}\curvearrowright\psi{-}CH_2{-}CH_2$ bonds are transformed from $\varphi = G$ to S and $\psi = G$ to T or S to T conformations, respectively, when PBT or PBN transform from their α to their β polymorphs. However, this interpretation is not consistent with solid-state ^{13}C NMR observations made on the α and β crystalline forms of PBT and PBN. In both instances, only very small differences (0.4–0.8 ppm) in the resonance frequencies of the butylene carbon resonances are observed between the ^{13}C NMR spectra recorded for both polymorphs. Similar small differences in the aromatic carbon resonance frequencies are observed between their α and β polymorphs. Thus, we conclude that the extension of both PBT and PBN chains, as they are transformed from their α to their β crystalline polymorphs, is more likely a consequence of an increase in the coplanarity of their ester groups and their phenyl or naphthyl rings, rather than conformational extensions of their butylene glycol fragments. A search for PBT and PBN conformations, both of which match the fiber repeat distances observed for their α and β crystalline polymorphs and are consistent with the closely similar ^{13}C chemical shifts observed in both of their crystalline phases, lends further support to this suggestion. © 2002 Published by Elsevier Science Ltd.

Keywords: Polymorphs; X-ray diffraction; ^{13}C NMR spectra

1. Introduction and discussion

Recently a series of studies [1–4] have revisited the crystal structures and polymorphism in the related polyesters poly(butylene-terephthalate) (PBT) and poly(ethylene-2,6-naphthalate) (PBN). Both PBT and PBN exhibit α, β crystalline polymorphs, as a consequence of uniaxial sample extension or specific crystallization techniques (isothermal and non-isothermal), with fiber repeats of 11.59, 12.95 and 14.36, 15.31 Å for PBT and PBN, respectively. This polymorphism has generally been interpreted [1–6] to result from the extension of the butylene glycol fragments in both polyesters $[{-}O{-}\curvearrowright\psi{-}CH_2{-}\curvearrowright\varphi{-}CH_2{-}^{T}{-}CH_2{-}\curvearrowright\varphi{-}CH_2{-}\curvearrowright\psi{-}O{-}]$ from compact conformations, such as $\psi = gauche(G = \pm 120°)$ or $skew\ (S = \pm 60°)$ and $\varphi = G$ in the α polymorphs, to extended conformations, with $\psi = trans(T = 0°)$ and $\varphi = S$ in the β polymorphs.

Referring to the drawings of the butylene glycol fragment and the Newman diagrams illustrating the conformations about the $O{-}CH_2{-}\curvearrowright\varphi{-}CH_2{-}CH_2$ and $(C{=}O){-}O{-}\curvearrowright\psi{-}CH_2{-}CH_2$ bonds shown in Fig. 1, we can readily conclude the following concerning effects these conformational changes proposed [1,3,5] to accompany the transitions between α and β polymorphs would be expected [7] to have on the ^{13}C NMR frequencies of the CH_2 carbons: (i) because the ester and $CH_2{-}CH_2{-}^{T}{-}CH_2{-}CH_2$ bonds remain T, we would expect very little change in the ^{13}C chemical shifts observed for the $O{-}\mathit{CH_2}{-}CH_2$ carbons in both PBT and PBN; (ii) both φ and ψ are proposed to be G in α-form PBT and S and T, respectively, in β-form PBT, so we expect the $CH_2{-}\mathit{CH_2}{-}\mathit{CH_2}{-}CH_2$ carbons in α-form PBT to resonate significantly upfield from those in the β polymorph, because they would be shielded by γ-*gauche* interactions [7] with –O– and –(C=O)– only in the butylene glycol conformation proposed for the PBT α polymorph; and (iii) the $CH_2{-}\mathit{CH_2}{-}\mathit{CH_2}{-}CH_2$ carbons in α-form PBN would also be expected to resonate significantly upfield from those in its β-form, because in the conformation proposed for the α polymorph they are shielded by a γ-*gauche* interaction with –O–.

These expectations concerning the effects of butylene

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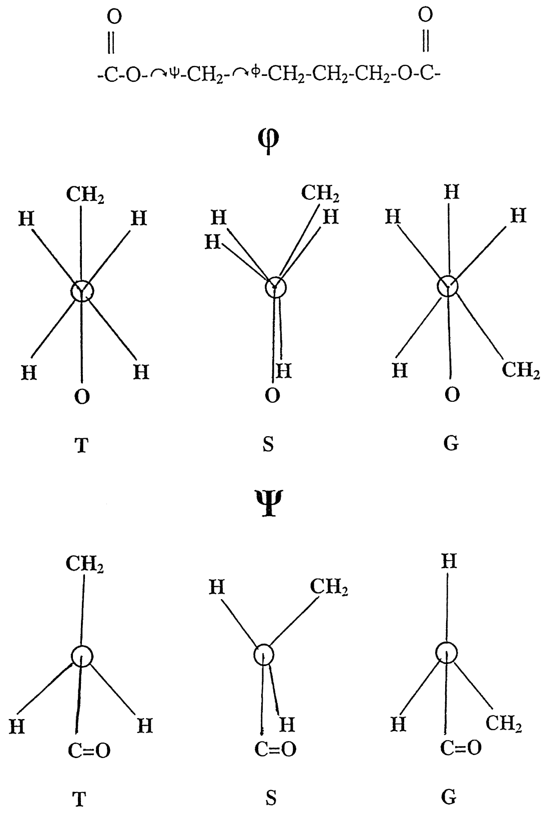


Fig. 1. Drawing of a butylene glycol fragment with Newman diagrams illustrating the conformations about the O–CH_2–⌒φ–CH_2–CH_2 and (C=O)–O–⌒ψ–CH_2–CH_2 bonds.

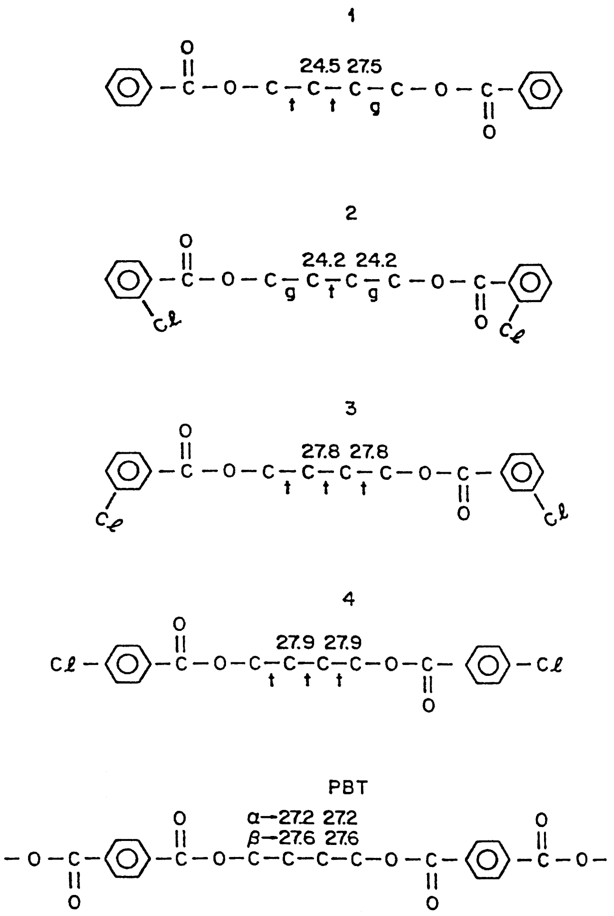


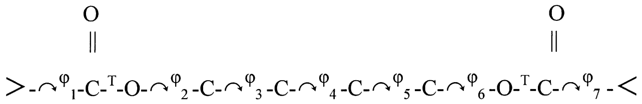
Fig. 2. Schematic drawings of the four PBT model compounds studied by Grenier-Loustalot and Bocelli [8] using single crystal X-ray diffraction and high resolution, solid-state ^{13}C NMR. The butylene conformation (t = *trans*, g = *gauche*), of each model compound is indicated, as are the ^{13}C chemical shifts observed for the central methylene carbons. At the bottom of the figure the structure of PBT is presented along with the ^{13}C chemical shifts observed [9] for the central methylene carbons in the α and β crystalline polymorphs.

glycol conformation on $-CH_2-$ carbon NMR frequencies are strongly supported by the data reported by Grenier-Loustalot and Bocelli [8] for the four PBT model compounds shown in Fig. 2. Single crystals of each of these PBT model compounds were grown and observed by X-ray diffraction to completely elucidate their crystalline conformations, which are partially indicated. (The O–CH_2 and ester bonds were observed to be *T* in all four PBT model compounds). In addition, high resolution solid-state ^{13}C NMR observations [8] yielded the CH_2–$\mathit{CH_2}$–$\mathit{CH_2}$–CH_2 chemical shifts also shown in Fig. 2, while the O–$\mathit{CH_2}$–CH_2 carbons in each PBT model compound resonated at ~66 ppm vs TMS. It is very clear from the observations reported by Grenier-Loustalot and Bocelli [8] that changing the conformation of the –O–CH_2–⌒φ–CH_2–CH_2– bond from *T* to *G* results in an ~ −3 to −4 ppm upfield chemical shift in the resonance frequencies of CH_2–$\mathit{CH_2}$–$\mathit{CH_2}$–CH_2 carbons in the butylene glycol fragment, as expected [7] based on the shielding produced by their γ-*gauche* arrangement with –O–.

Presented at the bottom of Fig. 2 is a PBT fragment with the ^{13}C chemical shifts observed [9] for the CH_2–$\mathit{CH_2}$–$\mathit{CH_2}$–CH_2 carbons in its α and β polymorphs, which are nearly identical to the chemical shifts of the internal methylene carbons observed [8] in the PBT model compounds 3 and 4, both with the TTT butylene glycol conformation. As a consequence, we can strongly suggest that the butylene glycol fragments in both α- and β-form PBT are also ~TTT, thereby discounting the conformational transition from $\varphi = G$ to S and $\psi = G$ to T suggested [1,3,5] to take place in the transition from the α to the β polymorph of PBT.

Yamanobe et al. [1] have reported chemical shifts of 25.8 and 26.6 ppm for the interior methylene carbons in α and β PBN polymorphs. The close similarity of these chemical shifts to each other and to the chemical shifts observed [8] for the PBT model compounds adopting the all *trans* butylene glycol conformation again suggests a nearly all *trans* conformation for the butylene glycol fragments in both PEN polymorphs rather than the $\varphi = G$ to S and $\psi = S$ to T conformational transitions proposed [1,3] to accompany the transformation between PBN polymorphs.

Consequently, high resolution, solid-state ^{13}C NMR observations of PBT model compounds and PBT and PBN polymorphs strongly suggest very similar, nearly all *trans*



$$>\text{-}\frown^{\varphi}{}_{1}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}^{T}\text{-O-}\frown^{\varphi}{}_{2}\text{-C-}\frown^{\varphi}{}_{3}\text{-C-}\frown^{\varphi}{}_{4}\text{-C-}\frown^{\varphi}{}_{5}\text{-C-}\frown^{\varphi}{}_{6}\text{-O-}^{T}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\frown^{\varphi}{}_{7}\text{-}<$$

Fig. 3. Drawing of the PBT fragment considered in the search for extended conformations with fiber repeat distances in agreement with those observed by X-ray diffraction for the α and β polymorphs.

conformations for the butylene glycol fragments in each of their polymorphs. This of course raises the question of what conformational changes do in fact accompany the α to β polymorphic transitions in PBT and PBN, and which are manifested in 12 and 7% increases, respectively, in the fiber repeat distances observed by X-ray diffraction? To address this question we have conducted a search for PBT and PBN conformations which both reproduce the fiber repeat distances and would be expected to evidence very similar ^{13}C NMR resonance frequencies, as observed [1,9] in their α and β polymorphs.

As an example, for the PBT fragment shown in Fig. 3, the distances between the centers of the phenyl rings were calculated as a function of its conformation, i.e. the values assigned to backbone rotation angles $\varphi_1 - \varphi_7$. Both ester bonds were fixed in the *T* conformation, φ_1 and φ_7 were permitted ± 20, ± 40, and ± 60° deviations away from the planar, $\varphi_{1,7} = 0°$, 0° terephthaloyl conformation [10], and $\varphi_2 - \varphi_6$ were restricted to ± 30° deviations away from the *T* conformation. PBT and PBN geometries (bond lengths and bond valence angles) were adopted from those given by Williams and Flory [11] for poly(ethylene-terephthalate). The search conducted for extended PBN conformers was very similar.

In this communication we were not overly concerned with the detailed energetic characteristics of the PBT and PBN polymorph conformers, except to require that they be of relatively low intramolecular energies [10,11]. Packing interactions between chains were completely disregarded, because we were simply looking for conformations which are consistent with the fiber repeat distances measured by X-ray diffraction [1–6] and the ^{13}C NMR frequencies observed [1,9] for the polymorphs, which we believe are independent of the other details of their crystal structures, such as how their chains are packed in their unit cells as reflected by their complete X-ray diffraction patterns and their crystalline densities, for example.

The results of the search for extended PBT and PBN conformations, which are both consistent with the X-ray diffraction fiber repeats [1–6] and the ^{13}C NMR resonance frequencies [1,9] observed for their α and β polymorphs can be summarized as follows: (i) the fiber repeats observed for the α polymorphs of PBT and PBN can be reproduced with nearly all *trans* butylene glycol fragments (all $\varphi_2 - \varphi_6 \sim 0°$) and non-planar terephthaloyl and naphthaloyl residues (φ_1, $\varphi_7 \sim \pm 40°, \mp 40°$); (ii) the increased fiber repeat distances observed in their β polymorphs can be reproduced with very similar nearly all *trans* butylene glycol conformations, but only when $\varphi_1 \sim 0°$ and the phenyl and naphthyl rings are coplanar with their attached ester groups; and (iii) the nearly all *trans* butylene glycol conformations with non-planar and planar attachments of ester groups in the terephthaloyl and naphthaloyl residues of their α and β polymorphs, respectively, would be expected [7] to result in very similar ^{13}C NMR frequencies for the carbon nuclei in both polymorphs.

FTIR studies of PBT and PBN polymorphs [4,12–14] show qualitatively distinct results. IR bands thought to be attributable to butylene glycol vibrations differ in their absorption frequencies between α and β PBT polymorphs [12–14], while they remain very similar in both PBN polymorphs. [4]. In the case of PBT, these differences have been interpreted as arising from distinct butylene glycol conformations in the α and β polymorphs, while similar butylene glycol conformations are presumed for the α and β polymorphs of PBN based on FTIR observations. On the other hand, interpretation of X-ray diffraction observations suggests substantial differences between the butylene glycol conformations in the α and β polymorphs of both PBT and PBN, while the ^{13}C NMR analysis presented here suggests very similar extended conformations for the butylene glycol fragments in all polymorphs, but with non-planar and planar terephthaloyl and naphthaloyl residues in the α and β polymorphs of PBT and PBN, respectively. Thus, if the assignments of conformationally sensitive vibrational bands to the butylene glycol fragments in PBT and PBN are correct, then neither the explanations for the transformation between their polymorphs derived from X-ray diffraction [1,3,5,6] nor from ^{13}C NMR observations is consistent with the current interpretation of FTIR results [4,12–14].

Very recently we have observed [15] that the FTIR assignments attributable to the vibrations of the ethylene glycol fragments in poly(ethylene terephthalate) (PET) may have to be reinterpreted in terms of their dependence on ethylene glycol conformations. It may also be possible that our current understanding of the conformational sensitivity of the vibrations of the butylene glycol portions of PBT and PBN is not complete.

2. Conclusions

The similar natures of the high resolution, solid-state ^{13}C NMR spectra of the α and β polymorphs of PBT and PBN [1,9] strongly suggest that the butylene glycol fragments adopt very similar conformations in all polymorphs. By comparison to the ^{13}C NMR spectra of PBT model compounds, whose butylene glycol conformations were determined from X-ray analyses of single crystal samples [8], it appears that the butylene glycol fragments in the α and β polymorphs of both PBT and PBN adopt a nearly all *trans* conformation. A search for extended, nearly all *trans* butylene glycol PBT and PBN conformations, which are consistent with the fiber repeat distances observed by X-ray diffraction in their α and β polymorphs and are expected [7] to evidence similar ^{13}C NMR spectra, indicates that in their α polymorphs the ester groups are rotated ~40° out of the phenyl and naphthyl ring planes to which they are attached, while nearly planar terephthaloyl and naphthaloyl residues are indicated for PBT and PBN chains in their more extended crystalline β polymorphs.

References

[1] Yamanobe T, Matsuda H, Imai K, Hirata A, Mori S, Komoto T. Polym J 1996;28:177.
[2] Koyano H, Yamamoto Y, Saito Y, Yamanobe T, Komoto T. Polymer 1998;39:4385.
[3] Takahashi Y, Murakami K, Nishikawa S. J Polym Sci, Part B: Polym Phys Ed 2002;40:765.
[4] Ju M-Y, Huang J-M, Chang F-C. Polymer 2002;43:2065.
[5] Liu J, Geil PH. J Macromol Sci, Phys 1997;B36:263. and references to PBT polymorphism cited therein.
[6] Watanabe H. Kobunshi Ronbunshu 1976;33:299.
[7] Tonelli AE. NMR spectroscopy and polymer microstructure: the conformational connection. New York: Wiley; 1989.
[8] Grenier-Loustalot M-F, Bocelli G. Eur Polym J 1984;20:957.
[9] Gomez MA, Cozine MH, Tonelli AE. Macromolecules 1988;21:388.
[10] Tonelli AE. J Polym Sci, Polym Lett Ed 1973;11:441.
[11] Williams AD, Flory PJ. J Polym Sci A-2 1967;5:417.
[12] Ward IM, Wilding MA. Polymer 1977;18:327.
[13] Hall IH, Pass MG. Polymer 1976;17:807.
[14] Stambough B, Lando JB, Koenig JL. J Polym Sci, Part B: Polym Phys Ed 1979;17:1063.
[15] Bullions TA, Wei M, Porbeni FE, Gerber MJ, Peet J, Balik M, White JL, Tonelli AE. J Polym Sci, Part B: Polym Phys Ed 2002;40:992.