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PET versus PEN: what difference can a ring make?[☆]

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Abstract

Poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) are structurally related polyesters. In each polymer, the ethylene glycol diesters are separated by rigid rings and are attached to the 1,4-positions of the phenyl and the 2,6-positions of the naphthyl rings in PET and PEN, respectively. Because neighboring ethylene glycol units of each polyester are separated by phenyl or naphthyl rings, their conformations are independent of each other. As a consequence, their RIS conformational models should be identical, with the same populations of *trans*, *gauche* +, and *gauche*− conformations about the $\text{–O–CH}_2\text{–}$, $\text{–CH}_2\text{–CH}_2\text{–}$, and $\text{–CH}_2\text{–O–}$ bonds. This means that PET and PEN are equally flexible as judged by their conformational partition functions. However, because they differ geometrically, properties such as the mean-square end-to-end distance ($\langle r^2\rangle_0$) or characteristic ratio ($C_r = \langle r^2\rangle_0/n\langle l^2\rangle$), though averaged over identical conformations, are not expected to be coincident. The terephthaloyl portion of PET can be considered to consist of the $\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}C_1\text{-}$, the $\text{–}C_1\cdots C_4\text{–}$, and $\text{-}C_4\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}$ bonds, which are collinear and only the conformations about the carbonyl carbon to phenyl ring carbon bonds may be altered. This results in the terephthaloyl unit acting as a freely rotating link in both the statistical and dynamic senses. In the naphthaloyl residue, on the other hand, the carbonyl carbon to C_2 and C_6 to carbonyl carbon bonds are connected to a collinear, non-rotatable virtual bond between C_2 and C_5 and to the non-collinear, non-rotatable real bond between C_5 and C_6, respectively. These geometrical differences between PET and PEN result in distinctly different values for properties like $\langle r^2\rangle_0$ and C_r, even though they are averaged over the same conformational populations. Additionally, volumes occupied by their segments when confined to extended conformations and interconversions between these extended conformers were found to be particularly sensitive to the geometrical distinctions between PET and PEN and several differences in their physical properties are discussed in this context. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Poly(ethylene 2,6-naphthalate); Rings; Properties

1. Introduction

Recently poly(ethylene 2,6-naphthalate) (PEN), which is structurally similar to the most commercially important polyester PET [poly(ethylene terephthalate)], has begun to be produced and has become competitive with PET in certain performance-driven markets based on its superior strength, heat stability and barrier properties [1]. Both polyesters are semi-crystalline with closely similar melting temperatures. PEN has been crystallized into two polymorphs, α and β, by annealing amorphous films and crystallizing from the melt [2]. In both polymorphs, the ethylene glycol portion of the PEN chains adopt the extended, all-*trans* conformation, as do the PET chains in its crystals [3,4]. In crystalline PET and the α-polymorph of PEN, the attached ester groups adopt the *trans* arrangement across the phenyl and naphthyl rings, while in the β-polymorph of PEN, the ester groups on alternating naphthyl rings are attached in the *trans* and *cis* arrangements [5].

Differences in the physical properties of PET and PEN have generally been attributed to the assumed increased rigidity conferred upon PEN by its constituent naphthyl rings, which are clearly larger than the phenyl rings in PET. This supposition appears reasonable considering that the remaining portion of their repeat units, the ethylene glycol unit terminated by ester bonds, is common to both polyesters. In addition, the conformations available to the flexible portions of both PET and PEN $(C_{1,2}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-O-C-C-O-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}C_{4,6})$ and their populations are identical [6]. However, in PET the $\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}C_1\text{-}$, $\text{–}C_1\cdots C_4\text{–}$, and $\text{-}C_4\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}$

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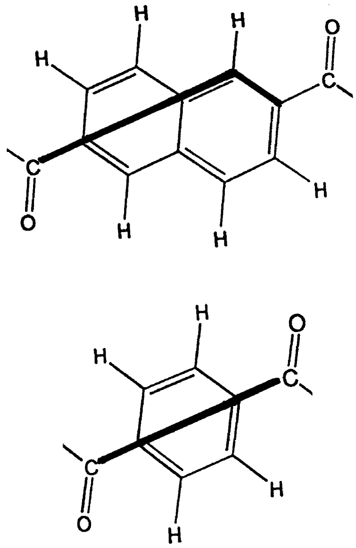


Fig. 1. Comparison of the terephthaloyl and naphthaloyl residues in PET and PEN.

bonds are collinear, so alteration of the conformations about the carbonyl to phenyl ring carbon bonds simply change the spatial arrangements of the ethylene glycol fragments that are attached across these collinear bonds. Because in the naphthyl ring the carbonyl carbon to C_2 and C_6 bonds are parallel, but not collinear, rotations about these bonds result in a greater relative displacement of the ethylene glycol fragments that are attached (see Fig. 1). Furthermore, unlike the phenyl rings in PET, the naphthyl rings may not be "flipped" by equal and opposite counterrotations about the carbonyl carbon to $C_{2,6}$ naphthyl carbon bonds, without altering the relative displacements of the attached ethylene glycol fragments [7,8].

Here we examine and compare properties of PET and PEN that are sensitive to their static conformations, such as $\langle r^2\rangle_0$ and C_r, and their ability to undergo interconversions between their highly extended conformations. Where they appear to exit, we draw connections between the microscopic conformational and dynamic characteristics of isolated PET and PEN chains and their bulk physical properties.

2. Conformational calculations

Fig. 2 presents drawings of three repeat unit fragments of PET and PEN chains in the fully extended all-*trans* conformation and in Fig. 1 the PET phenyl and the PEN naphthyl rings and their attached carbonyl carbons are shown. These drawings not only make apparent the disparity in sizes of the phenyl and naphthyl rings but clearly illustrate that the conformable, rotatable $\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—C_1}$ and $\mathrm{C_4—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}$ bonds in PET are collinear, while the $\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—C_2}$ and $\mathrm{C_6—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}$ bonds in PEN are not. This geometrical difference necessitates a minor modification of the RIS model developed for PET by Williams and Flory [6] in order that it may be applied to PEN. Because the carbonyl carbon to phenyl carbon bonds in PET are collinear, the distance between carbonyl carbons attached to the same phenyl ring is constant and may be treated as a virtual bond of ~5.74 Å in length (bold in Fig. 1). On the other hand, in PEN the distance between the carbonyl carbon attached at C_2 and the C_5 carbon is constant at ~5.65 Å (bold in Fig. 2) and of course, the distance between the C_5 and C_6 carbons is fixed at 1.39 Å. Thus, the PET fragment in Fig. 1 may be treated as a virtual bond of 5.74 Å in length with a net rotation angle given by the sum of the rotations about the real constituent carbonyl carbon to $C_{1,4}$ carbon bonds. At the same time, the PEN fragment in Fig. 1 may be treated as a virtual bond of 5.65 Å connecting the carbonyl carbon at C_2 to the C_5 carbon, with a net rotation the same as that of the real carbonyl carbon to C_2 bond and this is directly bonded at an angle of 120° to the rigid, real C_5–C_6 bond of length 1.39 Å, which in turn is bonded, also at an angle of 120°, to the real, conformable $\mathrm{-C_6—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-}$ bond. Thus, the statistical weight matrix row [1 γ] for the virtual bond spanning the ester carbonyl carbons attached across a phenyl ring in PET is replaced with row [1 γ] for the virtual bond from the carbonyl attached at C_2 to the napthyl C_5, column [1 1] for the C_5 to C_6 bond, and row[1 γ] for the C_6 to carbonyl carbon bond in PEN, where γ is the statistical weight for the *cis* conformation relative to the *trans* conformation, generally assumed as $\gamma = 1$. With this minor modification, the RIS model developed by Williams and Flory [6] for PET may now be used to calculate $\langle r^2\rangle_0$ for PEN as well.

In a previous study, we investigated the possibility that PET might be included in the narrow channels of inclusion compounds formed with small-molecule hosts such as urea, thiourea, perhydrotriphenylene, and cyclodextrins [9]. There it was found that PET chains may be accomodated in cylinders with diameters $D > 5.6$ Å. This observation resulted from a complete RIS conformational search of the three repeat unit PET fragment presented in Fig. 2, where the ester bonds were fixed in the *trans* conformation, the $-\mathrm{O{-}CH_2}-$, $-\mathrm{CH_2{-}CH_2}-$, and $-\mathrm{CH_2{-}O}-$ bonds were restricted to the *trans* (t) and *gauche* ±(g ±) conformations and because the two-fold barrier resisting out-of-plane rotation of the ester and phenyl groups is relatively low [8,9], ±30° deviations from their coplanar arrangements were permitted. Despite these conformational constraints, a total of 34,012,224 PET conformations were examined and searched for those with cross-sections narrow enough to fit in cylinders with diameters D.

Surprisingly, the slimmest PET conformation found

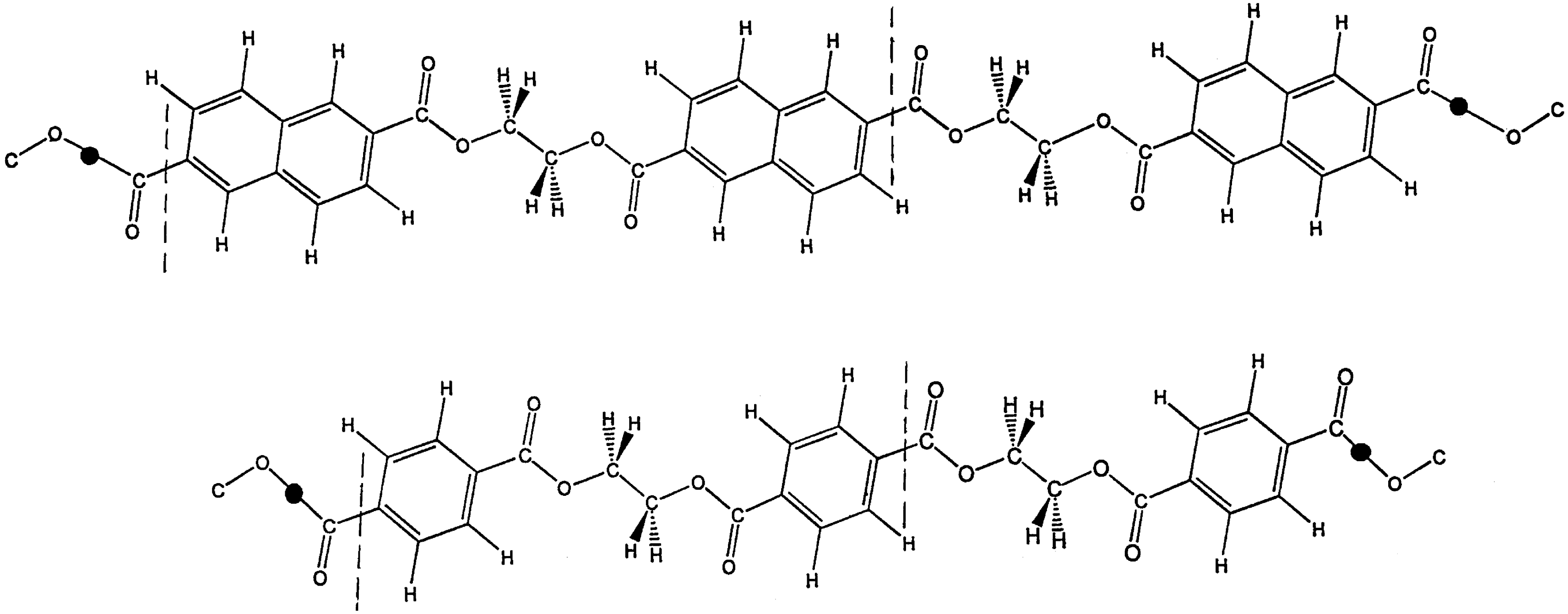


Fig. 2. Comparison of PET and PEN chain fragments employed in the search for narrow cylindrical conformations and for possible inter-conversions between them.

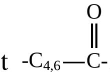
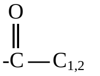
during this search was not the all *trans* crystalline conformation, but rather kink conformations with g ± tg∓ ethylene glycol fragments, which were estimated to have a 5.7 Å cross-section. The crystalline all-*trans* PET conformation could not be accomodated in a cylinder with $D < 6.7$ Å. Though considerably narrower in cross-section, the PET kink conformer is nearly as extended as the crystalline conformer, with a fiber repeat of 10.4 Å, which may be compared to 10.75 Å found for the fiber repeat in bulk crystalline PET [10,11]. When the volumes V of the smallest cylinders able to accommodate the kink and all-*trans* conformers of PET are calculated, we find $V_{\mathrm{ttt}}/V_{\mathrm{g\pm tg\mp}} = 1.5$. In the Williams–Flory RIS model for PET, neither the all-*trans* crystalline or the kink conformers are assigned the lowest energies or greatest populations, rather the tg ± t conformations with ester oxygens in a *gauche* arrangement are the most likely conformers with a probability of 27% at room temperature compared to 9% for the ttt crystalline and 5% for the g ± tg∓ kink conformers. However, the lowest energy PET conformer (tg ± t) is not highly extended, cannot be accomodated in narrow cylinders as found for the ttt and g ± tg∓ conformers and thus does not crystallize.

It is interesting that a mesomorphic form of PET has been recently discussed in the literature based on the X-ray scattering observed for samples drawn below T_g [12–16]. The mesomorphic form of PET is transformed into the usual triclinic, all-*trans* PET crystalline form upon heating above T_g. The X-ray diffraction patterns show sharp reflections only on the meridian, with spacings that lead to a periodicity of 10.3 Å [15,16]. By combination of X-ray diffraction measurements, conformational energy analysis and calculation of Fourier transforms for various extended chain conformers, Auriemma et al. [16] investigated the conformations of chains in the mesomorphic form of PET. They concluded that in the mesomorphic form of PET, extended chains in various low-energy conformations are likely packed in parallel arrangements, which lack rotational (around the chain axis) and translational (along the chain axis) order among the PET chains.

In a subsequent investigation, Auriemma et al. [17] performed a Monte Carlo analysis of extended PET oligomer conformations confined inside cylindrical tubes ($D = 12$ Å), which was very reminiscent of our search for narrow channel conformers of PET for possible inclusion in clathrate hosts [9]. They also found that the $-CH_2-CH_2-$ bonds must be *trans*, while t and g ± are possible for the $-O-CH_2-$ bonds. (For cylinders with diameters $D > 6.7$ Å, we also found that ttt, ttg ± , g ± tt, and g ± tg∓ PET conformers could be accomodated.) The average extension of the PET oligomers confined in a tube with $D = 12$ Å was found to be ~10–11 Å/repeat by Auriemma et al. [17], and so they concluded that these highly extended PET conformations may constitute the components of the rotationally and translationally disordered chains in mesomorphic samples of PET.

It appears that the geometry of PET chains enables them to adopt a large variety of highly extended conformations, which may be found in the mesomorphic regions of drawn PET. Consequently, in the present study, a similar analysis was performed on PEN. A Cartesian coordinate system was located at the midpoint (●) of the first ester bond in the PEN fragment shown in Fig. 2, and the x,y,z coordinates of each constituent fragment atom were calculated and expressed in this reference frame. These atomic coordinates depend, of course, on the fragment conformations, which were assumed to be identical in terms of bond lengths, valence angles, and rotation angles to those used to model PET [9], except for differences in the geometry of virtual bonds as discussed above for PET and PEN.

For each of these conformers, the x,y,z coordinates were calculated and transformed to the Cartesian coordinate system x',y',z' whose z'-axis connects the midpoints of the terminal ester bonds of the PEN fragment (from ● to ● in Fig. 2). The radius r of the corresponding cylindrical coordinate system with coincident z'-axis is $r = (x'^2 + y'^2)^{1/2}$. In our selection of PEN fragment conformers accommodated in a cylinder with diameter D, we simply required that $r < (D + 1\ \text{Å})/2$ to reflect the assignment of van der Waals spheres of 0.5 Å radius to each hydrogen atom. If each PEN fragment atom passed this test, then that conformation was considered a channel conformer.

In an attempt to characterize the mobilities of PET and PEN chains when confined to occupy narrow cylindrical channels, we performed a test to determine the possibility of interconverting between channel conformers without any part of the PET or PEN fragments leaving the channel during any portion of the interconversion process. Only those portions of the PET and PEN fragments in Fig. 2 between vertical dashed lines were considered in the test for interconversion between channel conformers. The conformations of both of these sub-fragments depend solely on the conformations adopted by the first  $\text{-C}_{4,6}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}$, $-O-CH_2-$, $-CH_2-CH_2-$, $-CH_2-O-$, and  $\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—C}_{1,2}$ bonds. Because all channel conformers were found to have *trans* $-CH_2-CH_2-$ bonds, rotations about this bond were limited to 0 ± 30°. Each of the other four rotatable bonds was free to adopt conformations throughout their complete range in 20° increments.

One of the nine channel conformers was selected as the starting conformation, where ttt, ttg ± , g ± tt, g ± tg ± , and g ± tg∓ are the available starting ethylene glycol fragment conformations. As each rotation angle was incremented, the x',y',z' coordinates of each atom in the fragment between vertical dashed lines were calculated and checked to see if all atoms remained inside the cylinder of the starting channel conformer. This procedure was repeated until one or more atoms passed through the cylinder wall or another channel conformer was reached. If the former occurred, then another channel conformer was selected as the starting conformer and the interconversion process was repeated. When the passage of atoms through the cylinder wall was detected, the sense of all bond angle rotations were reversed to determine whether or not this could elevate cylinder penetration. When another channel conformer was reached, all rotation angles were reinitialized to the values of the new starting channel conformer and the interconversion process was restarted. The test for interconversion between channel conformers was complete after each cylinder conformer had been used as the starting conformation. As discussed below, only in channels with $D \sim 8$ Å or larger can all nine possible PEN channel conformers with *trans* $-CH_2-CH_2-$ bonds and both all-*trans* and alternating *trans*,*cis* attachment of ester groups to the naphthyl rings be accommodated.

3. Results and discussion

Characteristic ratios of the mean-square end-to-end distances calculated for 64 repeat unit PET and PEN chains by averaging over all their RIS conformations are $C_r = \langle r^2\rangle_0/(n\langle l^2\rangle) = 4.11$ and 5.39, respectively. Williams and Flory [6] have shown that C_r is independent of n for PET chains of this length. To demonstrate that the difference in C_r is predominantly attributable to the collinear versus noncollinear attachments of ethylene glycol diester fragments in PET and PEN, respectively, we repeated the calculation for PET but assumed the phenyl ring to be twice its actual size (5.56 rather than 2.78 Å), which approximates the size of the naphthyl rings in PEN. This produced a $C_r = \langle r^2\rangle_0/(n\langle l^2\rangle) = 3.30$ for PET, which is further reduced from the characteristic ratio of dimensions obtained for PEN. It would appear that the static flexibility of PET as evidenced by its smaller C_r is greater than that of PEN as might have been anticipated from the freely rotating character of the terephthaloyl residue [7,8].

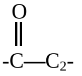
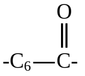
For PET and PEN, none of their conformers could be accommodated in channels with $D < 5.6$ and 6.4 Å, respectively. As mentioned previously [9], expansion of the channel beyond 5.6 Å allows incorporation of the $g \pm tg\mp$ kink conformers of PET and here we also find that the kink conformers of PEN have the narrowest cross-section with $D \sim 6.5$ Å. Beyond $D = 6.6$ Å, the $ttg\pm$, $g\pm tt$, and $g \pm tg \pm$ PEN conformers are also accommodated, and for $D > 6.7$ Å the ttt conformer found in the α-crystalline polymorph of PEN fits in the channel. The PEN conformer with the all-*trans* bond conformation for the ethylene glycol residues and alternating *cis*,*trans* attachment of ester groups to the naphthyl rings, as observed in its β-crystalline polymorph, is accomodated in channels only when $D \sim 8$ Å or greater. The volumes/repeat of the kink ($g \pm tg\mp$), α (ttt, with all-*trans* ester group attachment), and β (ttt, with alternating *cis*,*trans* ester group attachment) conformers were calculated to be 395, 472, and 586 Å, respectively. For PET, $V_{ttt}/V_{g\pm tg\mp} = 1.5$ was obtained, while for PEN this ratio is 1.2 and 1.5 when the volumes of the α- and β-PEN polymorph conformers are compared to its kink conformer and $V_\alpha/V_\beta = 1.2/1.5 = 0.80$ when compared to each other.

However, when the volume/repeat is calculated from the unit cells of the crystal structures reported for α- and β-PEN [2,5], $V_\alpha/V_\beta = 1.1$. It would appear that even though the maximum cross-section of the β-conformer found in our study of channel conformers of PEN is somewhat larger than that found for the α-conformer ($V_\beta/V_\alpha = 1.25$), assuming both have perfect cylindrical symmetry, apparently either or both conformers are sufficiently asymmetric to give $V_\beta/V_\alpha = 0.91$ when they are packed in their polymorphic unit cells.

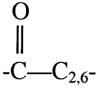
Both polyesters may adopt highly extended conformations ($g \pm tg\mp$ kinks), with narrow cross-sections that occupy less volume than the conformations adopted by the chains in their crystals (ttt). In isolation, these slimmer, extended conformations have energies and populations that are comparable to the all-*trans*, crystalline conformation, but kink conformers, such as $\ldots g \pm tg \mp | g \pm tg \mp \ldots$ and $\ldots g \pm tg \mp | g \mp tg \pm \ldots$ have a higher entropy content than the single $\ldots ttt|ttt\ldots$ conformer. Consequently, it might be reasonable to suggest that during the orientation of PET and PEN samples upon drawing, randomly coiling chains in their amorphous regions are likely to extend and adopt the kink conformers in preference to the all-*trans* conformer, without necessarily leading to crystallization, and also because PET and PEN kink conformations have *L*/*D*s higher than the crystalline all-*trans* conformation. However, these extended kink conformers apparently cannot be packed together as efficiently and so do not permit crystallization [16].

We noted that in cylinders with $D \sim 8$ Å all nine PET and PEN conformers with *trans* $-CH_2-CH_2-$ bonds can be accommodated. However, transitions between the PET conformers occur much more readily than those between PEN conformers. If we number the ttt, $ttg+$, $ttg-$, $g+tt$, $g-tt$, $g+tg+$, $g-tg-$, $g+tg-$, and $g-tg+$ consecutively 1–9, then we can summarize the direct inter-conversions observed between the $D \sim 8$ Å PET and PEN conformers as follows: for PET $2 \leftrightarrow 6 \leftrightarrow 9 \leftrightarrow 2$, $3 \leftrightarrow 8 \leftrightarrow 7$, and $4 \leftrightarrow 5$, while for PEN only $2 \leftrightarrow 6 \leftrightarrow 9 \leftrightarrow 2$ interconversions were observed. Note the glaring absence of interconversions between the all-*trans* crystalline conformation (1) and the other eight channel conformers for both polyesters. This may suggest a molecular interpretation for the slow rate of crystallization observed for both polyesters. Nucleation and/or growth of PET and PEN crystals may be retarded by the difficulty of converting similarly extended, but not all-*trans* conformations that cannot be packed efficiently, into the all-*trans* conformer, which can be packed very efficiently and therefore crystallize. In addition, the all-*trans* crystalline conformation is higher in energy than the non-crystallizable $tg \pm t$ conformer, and so this also may lead to the sluggish crystallization observed for both PET and PEN.

The clear difference in the dynamic flexibilities of PET and PEN, as characterized here by the abilities of their extended conformations to interconvert without sweeping out significant excess volume beyond that necessary to accomodate them, also suggests molecular explanations for their different T_gs [18–20] and for the permeabilities [21,22] of their films to gases. At least internally from the point of view of the conformational behavior of individual, isolated polymer chains, PET would seem better able to change conformations than PEN, and so the T_g of PET (~70°C) might be expected to be lower than that of PEN (~115°C) because conformational interconversions necessarily accompany the glass transition. Furthermore, interactions between polymer chains and their effects on molecular motions would also be expected to be less for PET than PEN simply by virtue of the comparison between the bulkiness and steric requirements of their constituent phenyl and naphthyl rings.

Permeability of gases through films at $T < T_g$ might be expected to be fanourable in PET because in addition to its greater dynamic conformational flexibility, PET also has the freedom to "flip" its phenyl rings [7,8] without altering its overall conformation. PEN, however, cannot rotate or "flip" its naphthyl rings via appropriate counter-rotation of its  $-\overset{O}{\overset{\|}{C}}{-}C_2-$ and  $-C_6{-}\overset{O}{\overset{\|}{C}}-$ bonds. Flipping of phenyl rings might provide a diffusive pathway for gases to permeate through PET films, which is not available to PEN films, and so may account for the greater permeability of PET films to gases [21,22].

4. Conclusions

Primarily due to the collinear attachment of ethylene glycol diester residues to the phenyl rings in PET, compared with their parallel, but non-collinear attachment to the naphthyl rings in PEN, the PET chain appears to be more flexible. As a partial answer to the question raised in the title of this paper, the attachment of ester groups at positions 2 and 6 of the naphthyl rings results in a 1.2 Å displacement of their parallel axes of attachment and so rotations about the  $-\overset{O}{\overset{\|}{C}}{-}C_{2,6}-$ bonds in PEN cause the attached ethylene glycol diester fragments to exhibit relative displacements that are larger and differ from those attached collinearly in PET. In terms of static flexibility, PET has a smaller characteristic ratio $C_r = \langle r^2\rangle_0/n\langle l^2\rangle$ than PEN, and this was shown to be a consequence of the freely rotating nature of the terephthaloyl residue, which results directly from the collinear attachment of ethylene glycol diester residues. Dynamically it was observed that the interconversions between extended conformations that do not sweep out volume in excess of that occupied by them is more facile in PET than in PEN. These observations made on single isolated PET and PEN chain fragments seem to be consistent with, and may therefore contribute to, the differences observed in several of their bulk properties. It would appear that the different geometries of attachment of ester groups to the phenyl and naphthyl rings in PET and PEN play a role that is more important to their physical properties than simply the difference in the sizes of their aromatic rings.

Acknowledgements

In light of studies concerning the flexibilities of poly(alkene 2,6-naphthalates) via their RIS models and excimer fluorescence spectroscopy [Polymer, 33, 2031 and 4908, 1992] conducted by Prof. Wayne L. Mattice and his collaborators, it seems particularly appropriate and gives me great pleasure to dedicate this paper in honor of his brithday.

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