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Structure of Oligo (Butylene Terephthalate)s

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Summary

The structure of uniform oligomers of poly(butylene terephthalate) (PBT) was investigated by X-ray and IR methods. It was found that the oligomers crystallize in a lattice similar to the α-form of PBT.

Introduction

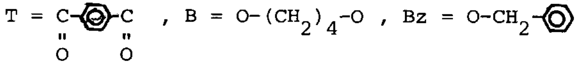
Poly(butylene terephthalate) (PBT) undergoes a stress induced reversible crystal-crystal transition which is mainly due to a change of the conformation of the tetramethylene groups. An extended discussion of the different structure investigations on PBT has been published by DESBOROUGH and HALL (1977). It has been established that the conformation of the tetramethylene group is all-trans in the β-form. For the conformation of the unstressed α-form, a non-trans non-gauche CH_2-CH_2 structure has been proposed (MENCIK 1975, HALL and PASS 1976).

Recently, we have reported on the synthesis and properties of uniform oligo(butylene terephthalate)s (HÄSSLIN et al. 1978,1980, HÄSSLIN and DRÖSCHER 1980). These oligomers have proved to be good models for the polymer. It was found that the melting behaviour was strongly influenced by the degree of polymerization and the nature of end groups. In this report we discuss the structure of the oligomers as determined from X-ray and IR investigations. In Table 1 the nomenclature and abbreviations are listed.

TABLE 1

Nomenclature and abbreviations used in this report

oligomer series	structure
1-n (esterdiols)	$H-(B-T-)_nB-H$
2-n (dibenzylesters)	$Bz-T-(B-T-)_nBz$
3-n (benzylesters)	$H-(B-T-)_nBz$



$T = \underset{\overset{\|}{O}}{C}-C_6H_4-\underset{\overset{\|}{O}}{C}$, $B = O-(CH_2)_4-O$, $Bz = O-CH_2-C_6H_5$

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Experimental

The X-ray investigations were carried out with Ni-filtered Cu Kα radiation. Powder diagrams were obtained with a Debye Camera. For the detection of the (001) reflections a flat film camera with 100 mm chamber length or a Kiessig Camera with 200 mm chamber length were used. The IR measurements were performed with an UNICAM SP-1000 IR spectrometer using KBr pellets which contained 2% of the oligomer. To insure complete crystallinity the oligomers were crystallized from solution.

Results and discussion

X-ray investigations

The wide angle diffraction patterns of the esterdiols 1-n are strongly related to the pattern obtained from the triclinic α-structure of PBT. In Figure 1 the d_{010} and the d_{100} values are plotted as a function of the degree of polymerization n. For the (100) reflection only a slight increase of the d value is observed; for (010) the increase is larger.

The assignment of the hkl indices to the X-ray reflections of the dimer, trimer and pentamer esterdiols could be carried out with a least square refinement program.x) For starting values of a,b,α,β,γ the lattice parameters of the α-structure of PBT (YOKOUSHI et al. 1976) were selected. For c, $d_{001}\cdot\cos 33{,}1^{\circ}$ was chosen. In the case of the α-form of PBT 33,1° is the angle between the c and the c^{*} direction. In Table 2 the resulting lattice parameters are listed together with the calculated densities ranging from 1,313 to 1,393 g cm^{-3}, as compared with the value for PBT of 1,404gcm^{-3} (YOKOUSHI et al. 1976)

TABLE 2

Unit cell dimensions for the esterdiols 1-n

sample	PBT a)	1-5	1-3	1-2
a /nm	0,483	0,477	0,464	0,482
b /nm	0,594	0,598	0,575	0,592
c /nm	1,159	6,53	4,24	3,03
α /deg	99,7	98,4	104,9	102,4
β /deg	115,2	115,0	114,9	114,0
γ /deg	110,8	111,8	105,7	110,5
V /nm^3 b)	0,261	1,462	0,895	0,672
ρ_c/gcm^{-3} c)	1,404	1,352	1,393	1,312

a)according to YOKOUSHI et al. (1976)
b)unit cell volume c) X-ray density

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x) On the average 20 reflections were used for the refinement procedure.

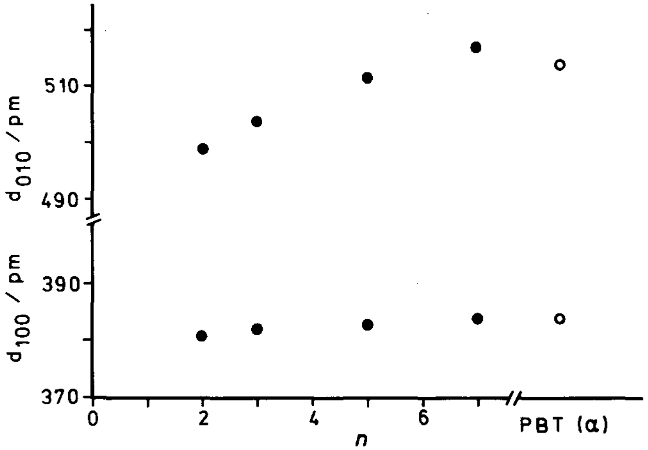

Fig. 1: d values for the (010) and (100) reflections of the esterdiols 1-n as a function of n, n>1.

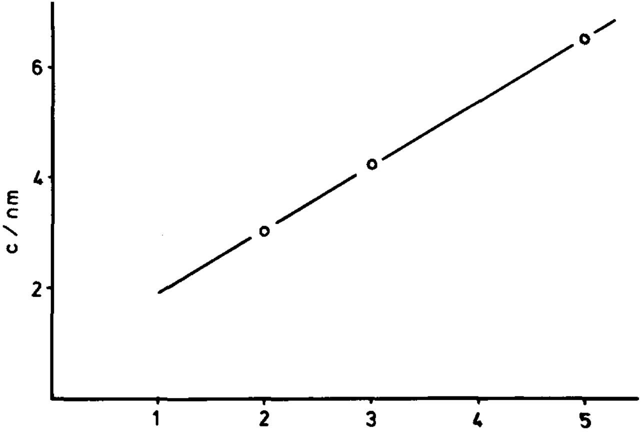

Fig. 2: Lattice parameter c as a function of n for the esterdiols 1-n, n>1.

In Figure 2 the lattice parameter c is plotted as a function of n for the esterdiols. The straight line can be represented by $c(n) = 0{,}73 + n \cdot c(PBT)$, where c (PBT) is the length of the repeat unit for α-PBT. Thus, the length of the oligomers increases by the same value of 1,16 nm per BT-unit as it is found for the polymer. As the angle between the c and the c^* direction is only ranging from 32 to 35°, we can state that the end groups (H-B-...H) contribute the same increment to the length of all of the oligomers. Hence, we can assume very similar packing in the esterdiols as in the α-structure of PBT, although some deviation of the lattice parameters is observed, as it is documented in Table 2.

The analysis of the more complecated powder diagrams of the other oligomers has not been completed, yet. We only present data for the (001) reflection.

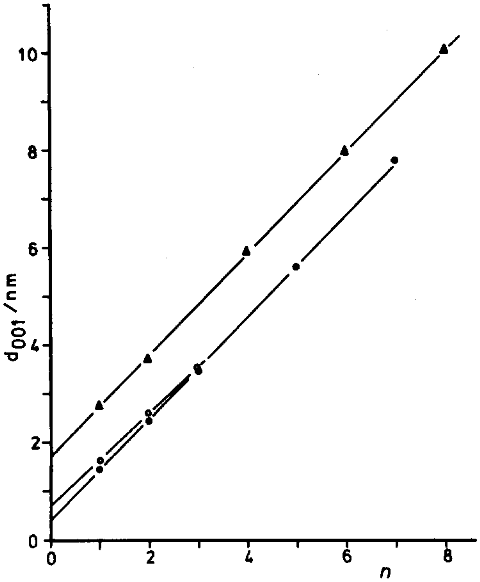

Fig. 3: d values for the (001) reflection of the esterdiols 1-n (●), dibenzylesters 2-n (▲), and benzylesters 3-n (o) as a function of n.

In Figure 3 the d_{001} values for all three sets of oligomers are compared. The data can be represented by the following relationships:

d_{001}(1-n) = 0,40 + 1,041 n for the esterdiols $(H-(B-T-)_nB-H)$

d_{001}(2-n) = 1,72 + 1,043 n for the dibenzylesters $(Bz-T-(B-T-)_nBz)$

d_{001}(3-n) = 0,68 + 0,953 n for the benzylesters $(H-(B-T-)_nBz)$.

In all cases at least three orders of the (001) reflections were observed.

From these results it can be concluded that the dibenzylesters behave similarly to the esterdiols. Both series contain only one type of end group; the different intercepts are due to the nature and size of the end groups. The asymmetrical benzylesters show a smaller increment per BT-unit as observed from the smaller slope of the linear fit.

IR investigations

In an extended IR study of PBT, STAMBAUGH et al. (1979) have assigned the bands in the 900-1000 cm^{-1} methylene rocking region. The band at 917 cm^{-1} was ascribed to the non-trans non-gauche methylene sequence in the α-form. The band around 938 cm^{-1} was observed for samples in the α-form as well as for samples under tension, where the β-form exists. There was, however, a slight shift detectable from 938 cm^{-1} in the amorphous PBT and the β-form to 935 cm^{-1} in the α-form. The authors assigned the components to the motion of structures with two methylenes in two distinct environments. Finally, a weak band was observed at 960 cm^{-1} which was more intense for PBT under tension than in the α-form. It was ascribed to a conformation found in both the extended β-form and the amorphous state.

We found that the methylene rocking region is verysuitable for the comparison of the oligomers and the polymer. The corresponding IR spectra from 900 to 1000 cm^{-1} are plotted in Figure 4.

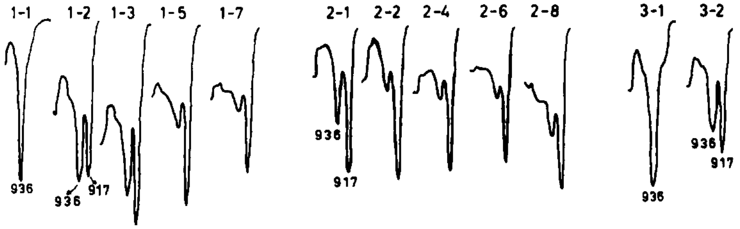

Fig. 4 : IR spectra from 900 to 1000 cm^{-1} for the esteridols 1-n, the dibenzylesters 2-n, and the benzylesters 3-n.

The monomers 1-1 and 3-1 which only contain B-units as end groups show one band at 936 cm^{-1}. With increasing n, the band at 917 cm^{-1} becomes more intense. Thus, this band is only due to the middle standing B-units. This finding is in agreement with the results of STAMBAUGH et al. (1979) for the α-form of PBT.

As shown in Figure 5, a linear relationship between the intensity ratio of the bands at 917 and 936 cm^{-1} and the mole fraction of the end standing B-units (x_{EG}) is observed. The straight line extrapolates to a value of 2,6, which is slightly higher than 2,2 which is calculated from Figure 1 in the report of STAMBAUGH et al. (1979) for α-PBT. However, the crystallite thickness in semicrystalline PBT is only of the order of 7 nm. Thus, the amount of the B-units in the crystal surface is about 15%. Assuming a similar behaviour of B-units in the crystal surface and of end standing B-units in the oligomers we now obtain a good agreement of the found value for α-PBT with the predicted value from Figure 5 for $x_{EG} = 0,15$. The dibenzylesters which do not contain end standing B-units show an intensity ratio of the order of 2.

At 960 cm^{-1} only a weak shoulder is observed for most of the oliogmers, obviously increasing in intensity with n.

Conclusion

From X-ray and IR data it can be concluded that the oligoesters have structures similar to the α-form of PBT. The intensity ratio of the absorption bands at 917 cm^{-1} and 936 cm^{-1} is determined by the concentration of the end standing B-units.

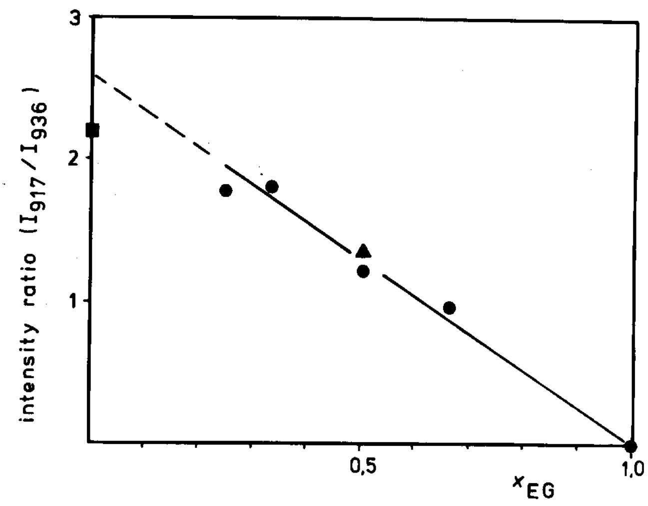

Fig. 5: Intensity ratio for the absorption bands at 917 and 936 cm^{-1} for the esterdiols (1-n) (●), the benzylester 3-2 (▲), and α-PBT (according to Figure 1 in STAMBAUGH et al. (1979)) (■)

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