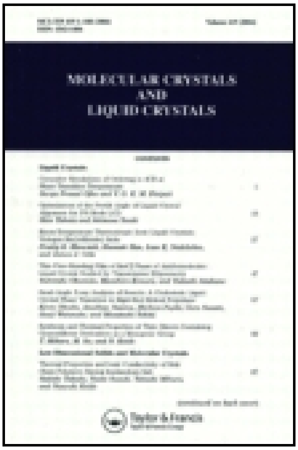

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CONFORMATIONAL AND CONFIGURATIONAL CHARACTERISTICS OF 3,4'-DIHYDROXYBENZOPHENONE TEREPHTHALATE

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Abstract This paper describes the structure, and properties of a thermotropic fully aromatic polyester that exists in a helical conformation in the solid state and an extended conformation in the nematic phase. The polymer is prepared from 3,4'dihydroxybenzophenone (34'PCOPG) and terephthalic acid (T). The polymer can be highly crystalline and has a K-N transition at 285 °C and a sharp N-I transition at 360 °C.

The unique properties of 34'PCOPG-T result from the asymmetry and flexibility of the 34'PCOPG moiety. Because it is asymmetric, the diol can be incorporated into the polymer chain randomly, head-to-tail or head-to-head. The flexiblity of the unit gives the diol the ability to adopt either a bent or extended conformation. In the solid state two crystal structures having extended conformations are found.

INTRODUCTION

In this paper we describe the structure and properties of a unique thermotropic polyester derived from 3,4'-dihydroxybenzophenone (34'PCOPG) and terephthalic acid (T). The structure of the intermediates are shown in Fig. 1. Because the substituted benzophenone is asymmetric, it can be inserted into the chain pointing either "up" or "down". Consequently, the benzophenone can be incorporated into the chain randomly or in a stereoregular manner. Two possible stereoregular conformations, shown in

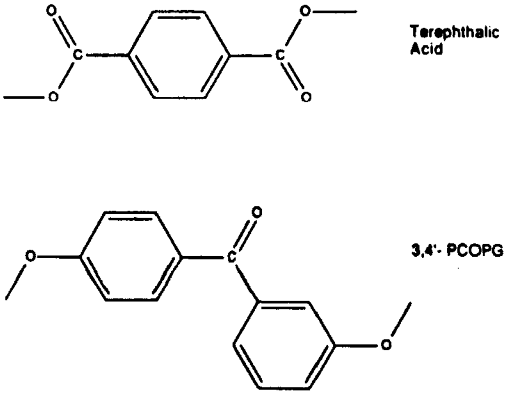
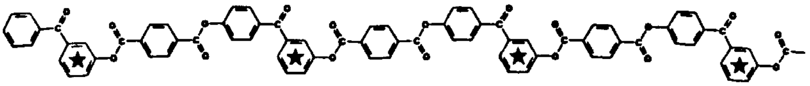


FIGURE 1 Structure of polymer intermediates.

Fig. 2, are head-to-tail (T-34'-T-34'-T-34'-T) and head-to-head (T-34'-T-4'3-T-34'-T). The 3,4' substitution on the benzophenone also results in the possibility that the benzophenone can adopt either an extended "trans" conformation or a bent "cis" conformation (Fig. 3).

- **Head-to-Tail**



- **Head-to-Head, Tail-to-Tail**

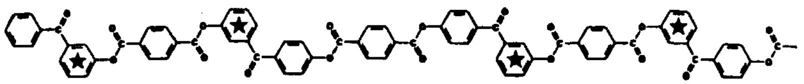


FIGURE 2 Stereoregular configurations that are possible due to asymmetry of 34'PCOPG unit.

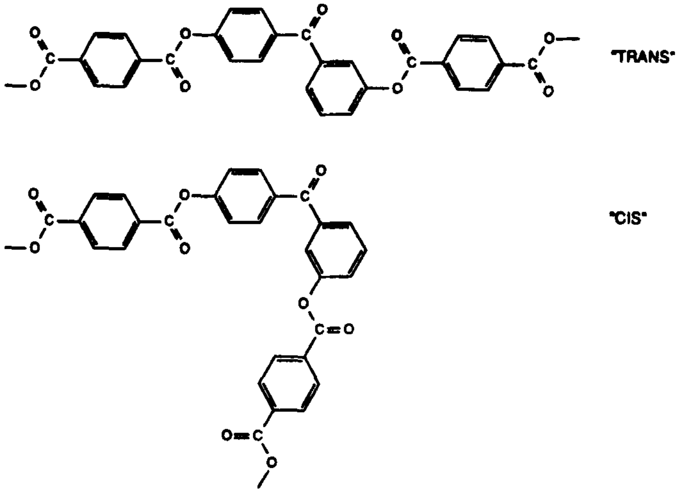


FIGURE 3 Bent "cis" and extended "trans" conformations accessible to the polymer.

These chemical features have a dramatic effect on the polymer structure and properties. Although the polymer forms a nematic melt, it appears to adopt a random coil in dilute solution, consistant with the presence of 34'PCOPG-T in both "cis" and "trans" conformations. X-ray studies of non-crystalline as-spun fibers indicate a predominance of the extended "trans" conformation. Stereo-regular configurations are observed in fibers depending on polymerization route and processing conditions. Polymer that incorporates the head-to-tail configuration forms an extended four-fold helix. To our knowledge this is the first observation of truly helical, fully aromatic thermotropic polyester.

Finally, this polymer is characterized by a sharp nematic to isotropic transition which occurs at approximately 360 °C. Although a number of nematic melts exhibit nematic to isotropic transitions, the transition generally occurs over a wide temperature range. For 34'PCOPG-T, the transition occurs over a narrow range and can be characterized experimentally.

RESULTS AND DISCUSSION

Polymer was prepared by melt acidolysis, melt phenylolysis and a low temperature solution polymerization.[1] A representative DSC trace for 34'PCOPG-T prepared by melt acidolysis is shown in Fig. 4. The transitions that were observed include a glass transition at 100 °C, crystallization at ca. 180 °C, crystal to nematic (K-N) transition at 285 °C and nematic to isotropic (N-I) transition at 360 °C. While the melting temperature and heat of fusion are dependent on the thermal history of a sample, the N-I transition temperature and enthalpy are independent of sample history (Table 1).

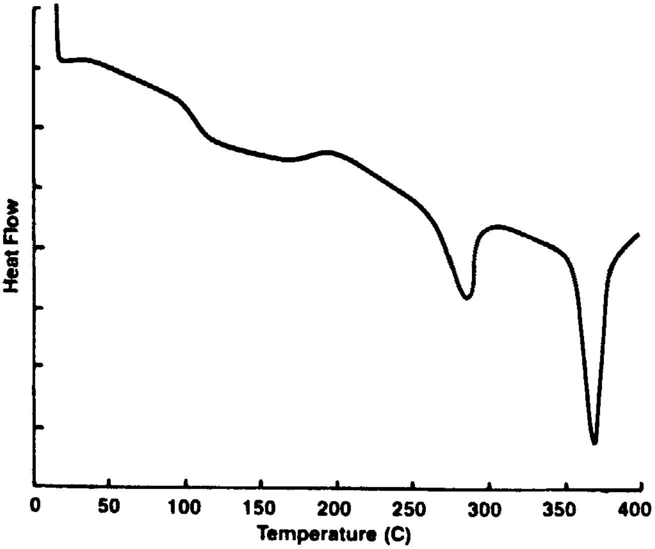


FIGURE 4 DSC trace of 34'PCOPG-T prepared by melt acidolysis.

TABLE I Summary of DSC data on 34′PCOPG-T.

Sample Description	T_{KN} (°C)	ΔH_{KN} (cal/g)	T_{NI} (°C)	ΔH_{NI} (cal/g)
Melt Polymerized	282	3.6	353	5.3
Solution Polymerized	276	2.6	360	5.5
As-Spun Fiber	282	2.4	348	5.0
Heat-Treated Fiber*	276	3.1	368	4.3
Solid Phase Polymerized**	320	10.3	378	4.8

*Annealed at 190°C for 60 hours. Similar results were found for shorter annealing times.
**Annealed at 190°C for 3 hours and 280°C for 48 hours.

A unique feature of 34′PCOPG-T is the presence of a sharp N-I transition. In most main chain thermotropic polymers the decomposition temperature is reached before the N-I transition. This is due in a large part to the rigid nature of the polymers studied. In systems which are modified to reduce chain stiffness by incorporation of a comonomer, e.g. p-hydroxybenzoic acid/polethylene terephthalate copolymers, regimes of composition exist where nematic and isotropic coexist over a wide temperature range.

The x-ray fiber diffraction pattern from an as-spun fiber of melt polymerized polymer is shown in Fig. 5a. There is good orientation with no evidence of lateral order or crystallinity. The scattering is characterized by two broad overlapping maxima on the equator ($2\Theta = 18.6°$, $22.4°$) and a series of sharp, periodic reflections along the meridian of the diffraction pattern (Fig. 6). The meridional reflections can be indexed as orders of a 1.661 nm repeat, a value consistent with the benzophenone in an extended "trans" conformation.

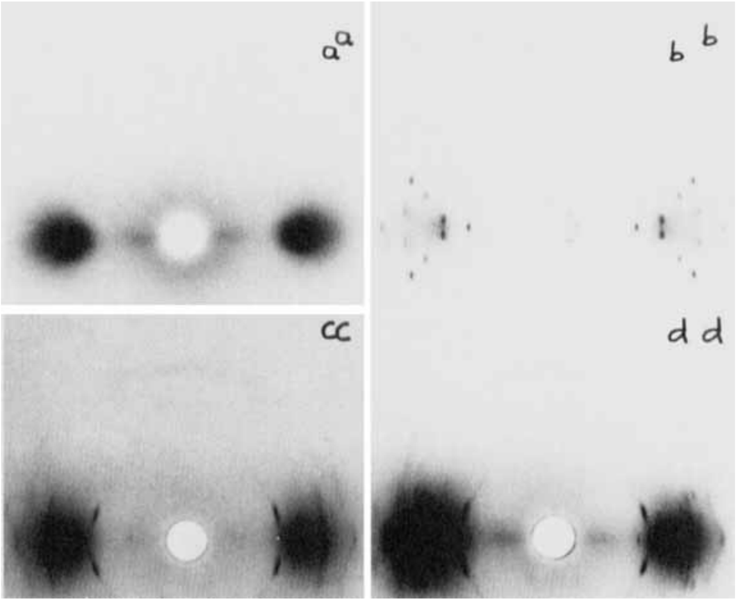


FIGURE 5 X-ray fiber diffraction patterns from single filaments of a) as-spun fiber of melt polymerized 34'PCOPG-T, b) as-spun fiber heat treated at 190 °C, c) as-spun fiber of low temperature solution polymerized 34'PCOPG-T, d) low temperature polymer heat-treated at 280 °C for 4 hrs.
See Color Plate XIII.

Fibers, heat-treated at 190 °C, where ester interchange does not occur, develop substantial crystallinity and have improved orientation (measured crystalline persistance lengths parallel and perpendicular to the chain axis are 20 nm and 15 nm respectively; filament orientation angle is 4.6°). The diffraction pattern (Fig. 5b) consists of a series of sharp reflections superimposed upon the non-crystalline scattering seen in the as-spun fiber.

It is clear that the intensity distribution in this pattern, and therefore, the structure of the crystalline component, is different in kind from other thermotropic polyesters such copolymer of p-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid.[2] In these thermotropic polyesters the diffraction patterns are dominated by strong equatorial and near-equatorial reflections; features that are a consequence of the rod-like nature of these polymers. Their absence in our diffraction patterns is a clear indication that 34'PCOPG-T is not a simple rod-like molecule but in fact helical. To have a helical structure a head-to-tail configuration is required.

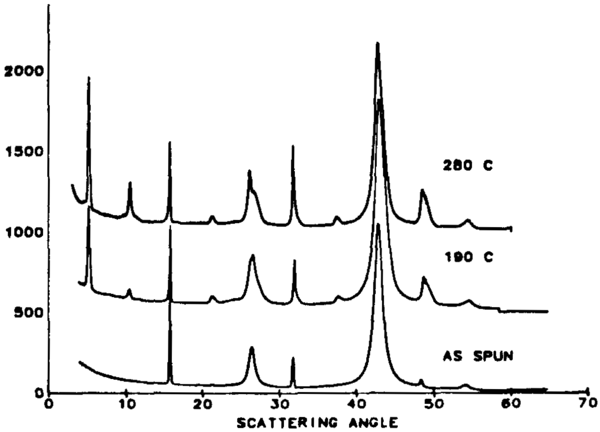


FIGURE 6 Meridional diffraction scans of melt polymerized 34'PCOPG-T fibers.

On heat-treatment under conditions where ester exchange can take place (280 °C) there is an increase in crystallinity due to the crystallization of newly formed head-to-tail runs.

The positions of 32 reflections in the crystalline pattern were indexed by a orthorhombic unit cell with dimensions a = 1.251(2)nm, b = 0.756(1)nm and c(fiber axis) = 6.765(6)nm. The molecule is a four-fold helix with a rise per chemical repeat of 1.681nm and there are four chain fragments in the unit cell. The observed and calculated densities are 1.430 g/cm^3 and 1.3812 g/cm^3 respectively. The presence of systematic absences in the diffraction pattern suggest that structure is A centered. The most likely space group is Ac2a (#41). The space group requires the presence of both left and right handed helices in the unit cell and that chains of opposite handedness be closer together than chains of like handedness. Figure 7a shows the positioning of the chains in the unit cell as required by the Ac2a space group. The asymmetric portion of a chain is a single chemical repeat, the remaining contents of the unit cell can be generated by helical and space group symmetry operations.

Using structural information from appropriate model compounds and the measured fiber repeat, models for an isolated four-fold helical chain were generated. The relative energies of the various models were evaluated after energy minimization. The isolated left-handed chain with the lowest energy is shown in Fig. 7b. The terephthalate group is incorporated in a manner that allows the carboxyl groups to be "trans" to each other. In general chain models incorporating "trans" conformations had less steric compression than those that incorporated "cis" conformations. The torsional angles that define the conformation of the ester groups are within the range of values observed in small molecules. The phenyl rings in the benzophenone are at approximately right angles to each other as expected. The helix can be thought of as a kinked rod. There are straight segments consisting of three phenyl groups separated by 90° kinks that are generated by the keto groups and compensated by the 1,3 phenyl group. There is a mirror generated right handed helix with equal energy. The complete structure is under study and will be reported when complete.

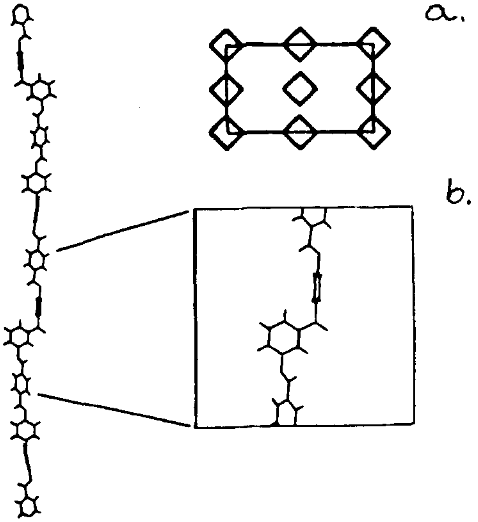


FIGURE 7 a) Schematic diagram showing chain packing looking down the fiber axis, b) conformation of an isolated 34'PCOPG-T chain (head-to-tail).

The polymer discribed so far was prepared by melt polymerization and is expected to have the 3,4'PCOPG units incorporated randomly (up & down) into the polymer chains. The presence of sharp meridional reflections in the as-spun fiber is not inconsistent with this expectation since both up and down segments in the extended trans conformation have the same projection onto the fiber axis.

Heat treatment at 190 °C produces a diffraction pattern consistent with runs of head-to-tail segments crystallizing and random sequences not. The crystalline correlation length of 20 nm for 004 reflection indicates that crystallizable runs of at least 12 chemical repeats exist in as-spun polymer.

Low temperature solution polymerization results in a polymer with a second crystal form. The as-spun fiber, in contrast to fibers prepared from melt polymerized materials, is semicrystalline. The fiber diffraction pattern from a single filament is shown in Fig. 5c. The crystalline component of the diffraction pattern, and therefore the structure, is a very different from that found in the melt polymerized material. The reflections appear to lay on layer lines that can be indexed as orders of a ca. 3.5 nm spacing which, by analogy to the other structure, corresponds to two chemical moieties adopting the "trans" conformation in the fiber repeat. We have been unable to index this diffraction.

While there are two chemical repeats in the fiber repeat, there is no crystallographic evidence (002 reflection) for a regular helix. Thus the two chemical moieties in the fiber repeat are crystallographically nonequivalent. One likely source for the difference between melt and solution polymerized material is the manner in which the diols are incorporated into the polymer chain. In polymer produced by high temperature melt polymerization a random distribution of "up" and "down" segments within a given chain is expected. In contrast, at low temperature, where ester interchange does not occur, the difference in reactivity between the 3 and 4′ hydroxyls is enhanced and could lead to a more regular incorporation of monomers. Evidence that the difference in crystallization characteristics of material prepared by different polymerization routes is related to sequence distribution has been obtained from high temperature annealing studies.

Fig. 6d shows a diffraction pattern from a fiber of low temperature polymerized polymer that has been heat treated at 280 °C for 4 hours. Superimposed on the diffraction pattern of the low temperature phase (Fig. 6c) there are features from the diffraction pattern of the four-fold helical structure and an increased amorphous contribution. Eventually, with prolonged annealing times, the diffraction features we associate with the low temperature polymerization polymer completely disappear leaving a pattern very similar to Fig. 6b. A similar behavior is observed when polymer flake is examined.

CONCLUSIONS

The conformations accessible to the 3,4′ PCOPG-T chain results in a number of unique properties. The phase behavior of the polymer is one obvious example. A sharp nematic to isotropic transition has rarely been found for main chain nematic polymers. In contast to other monomers which are used to obtain rodlike chains, there are conformations for the 34′PCOPG-T chain which can result in considerable flexibility. Thus the chain can easily adopt a flexible conformation in an isotropic phase. Conformational selection or induced rigidity in the nematic phase results in the exclusion of the flexible "cis" conformation which produces the desired extended conformation in the nematic phase. It is difficult to achieve a similar result in 1,4 linked aromatic polymers. The para subtituted monomers have a conformation which under all circumstances deviates only slightly from a rodlike conformation. The flexiblity of the chain can be modified by the addition of nonconforming monomers, e.g., 1,3 linked aromatics, but these monomers increase the flexibility of the chain even in the nematic phase since there is no way in which the conformation can become rodlike. The importance of induced rigidity in 34'PCOPG-T phase transitions is consistent with theoretical predictions[3] and is supported by experimental evidence including DSC results for transition entropy and x-ray studies of as-spun fibers.

Because of the anisotropic nature of 34'PCOPG residue, the diol can be thought of as having a "head" and a "tail". Thus the diol can be incorporated into the chain in three distinct fashions: head-to-tail; head-to-head, tail-to-tail and in a random nature. All three configurations are observed in this study. The thermodynamically stable polymer configuration is that in which the diol is incorporated in a head-to-tail fashion. This configuration is characterized by a four-fold helical structure. This structure is seen in all samples held at temperatures where ester interchange takes place regardless of the configuration in the as-polymerized material.

The melt polymerized 34'PCOPG-T has an effectively random incorporation of the diol. In as-spun fiber there are significant runs containing the stable head-to-tail configuation. This conclusion is based on the observation of the diffraction pattern characteristic of the head-to-tail structure in fibers heat treated at 190 °C and the presence of a crystallization endotherm at 200° in melt spun material. In contrast, the diol in low temperature (slurry) polymerized polymer is incorporated in a head-to-head, tail-to-tail fashion.

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