An infra-red study of model compounds of poly(tetramethylene terephthalate)

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(*Received* 14 *October* 1981; *revised* 3 *March* 1982)

An infra-red spectroscopic investigation of the poly(tetramethylene terephthalate) model compounds butyl-dibenzoate: $C_6H_5COO{-}(CH_2)_4{-}OCOC_6H_5$ (i), 1,4-bis-butyl terephthalate: $HO(CH_2)_4{-}OCO_6H_4COO{-}(CH_2)_4{-}OH$ (ii), α-butyl-ω-butoxyterephthalaoyl-di-(tetramethylene terephthalate): $H{-}(CH_2)_4{-}(OCOC_6H_4COO{-}(CH_2)_4{-})_3{-}OH$ (iii), and α-butyl-ω-butoxyterephthalaoyl-tetra-(tetramethylene terephthalate): $HO(CH_2)_4{-}(OCOC_6H_4COO{-}(CH_2)_4{-})_5{-}OH$ (iv) is presented. The synthesis of (i) is also described. Spectroscopic evidence indicates that the crystal conformations of the aliphatic segments in (i) and (ii) closely resemble the extended all *trans* beta form of PTMT. Oligomers (iii) and (iv), however, are found to be more similar to the crumpled alpha crystal phase of PTMT.

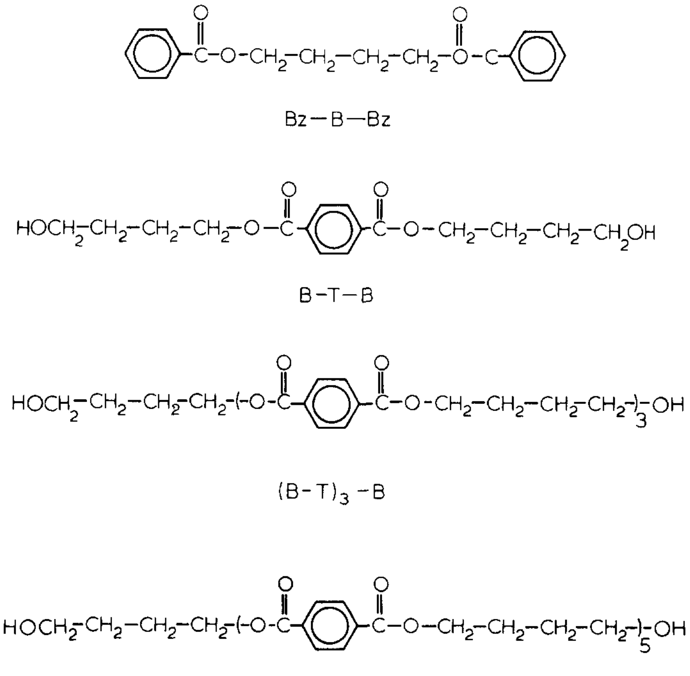
Keywords Infra-red; model compounds; poly(tetramethylene terephthalate); synthesis; spectroscopy; crystal conformations; alpha crystal phase

INTRODUCTION

In spite of widespread commercial production of poly(tetramethylene terephthalate) (PTMT or PBT), a most interesting feature of this polymer remains unresolved. The application of uniaxial stress induces a reversible crystal:crystal phase transition[1]. X-ray investigations of PTMT have produced conflicting results[2–10]. The major distinctions between the alpha and beta phases have been found to lie in the conformation of the flexible tetramethylene segment of the molecule. In the unstressed form, the aliphatic residue assumes a crumpled conformation which is converted to the extended moiety upon the application of stress[4–10]. Variations in the O–C–C–C torsional angle of the aliphatic segment range from essentially *gauche* (−57 degrees[9]) to clearly non-*trans*:non-*gauche* (−88 degrees[6]).

Infra-red spectroscopic investigations have detected a number of conformationally sensitive bands[10–17]. The most sensitive bands are found to occur in the methylene rocking region[6,7], although the C–H bending modes also exhibit good sensitivity. Recent fast scan time resolved Fourier transform infra-red work[14–17] has permitted the characterization of this transition on a much smaller time scale than has been possible with either conventional infra-red, Raman, or X-ray diffraction. This technique has detected the onset of the phase transition at strain levels of 2%. Siesler has reported[17], however, that the transition is not fully reversible since the intensities of conformationally sensitive modes do not revert to their original unstressed values upon relieving stress. One explanation of this phenomenon may lie in the possibility of intensity changes arising from orientation effects induced by the application of stress, although this possibility certainly requires further investigation. Unfortunately the several modes used to monitor the transition are extensively overlapped.

We have undertaken an oligomeric compound study of the conformations associated with the alpha and beta phases with the hope that oligomeric compounds could be discovered which would be representative of the alpha and beta phases of the polymer. Crystalline samples of model compounds afford one the unique opportunity of unequivocally isolating the infra-red spectra corresponding to a single conformation of that portion of the polymer in which the greatest differences between the alpha and beta forms manifest themselves: the flexible tetramethylene segment. Hence one is able to make accurate band assignments to those modes which are


Bz—B—Bz

B–T–B

(B–T)$_3$ –B

(B–T)$_5$ – B

Figure 1 Model compounds investigated

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conformationally sensitive. This situation is to be contrasted with samples of the polymer which always contain an amorphous component and one or both of the crystal phases thereby complicating the assignment of individual bands to specific conformations.

The spectra of the melt phase of the model compounds should be very similar to the amorphous phase of the polymer since in both instances a distribution of conformers is present. A comparison of the melt and crystal phase spectra of the model compounds to samples of PTMT which are highly amorphous, alpha, and beta crystalline in character achieves a twofold purpose: The demonstration of conformational equivalence *via* the correlation of gross spectral changes arising from differences in conformation in the polymer, and the possibility of the detection of conformationally sensitive modes in the polymer which are either too weak to be observed previously, or extensively overlapped.

A series of model compounds (*Figure 1*) were investigated. The compounds selected for research would also furnish some insight into the fundamental question of why the compound exists in the crumpled conformation found in the alpha phase. In particular, the crystal conformations associated with the model compounds Bz–B–Bz and B–T–B should provide important data to aid in answering this question since they permit one to assess the role of both the aliphatic and terephthalic segments in dictating the conformation found in the polymer.

EXPERIMENTAL

Samples of oligomeric model compounds of the general formula (B–T)n–B with $n=1$, 3, and 5 were generously supplied by Professor Gerhart Wegner of Universität Freiburg, Freiburg, West Germany. The synthesis of these compounds and the results of a variety of characterization techniques are described elsewhere[20–22].

The Bz–B–Bz model compound was prepared at CWRU. Previous synthesis work[23] concerning the esterification of hindered alcohols suggested that the utilization of a n-butyllithium intermediate would assure a high product yield. The steps involved in the condensation of the diol with the acid chloride to form the di-ester are outlined in *Figure 2*. All stages of the reaction were performed in an inert nitrogen atmosphere using commercially available nitrogen which was dried over anhydrous calcium chloride.

The following purification procedures were utilized: Trace quantities of residual water were removed from anhydrous ether by the addition of calcium hydride. After allowing the mixture to stand overnight, the majority of the ether was distilled off directly into the reaction vessel. Unreacted calcium hydride in the undistilled ether was destroyed by the careful addition of ethanol. Sodium sulphite was added to the 1,4-butanediol. The next day successive fractions of the anhydrous 1,4-butanediol were vacuum distilled. A 500 ml three neck boiling flask was fitted with condensor, nitrogen inlet, and 35 ml dropping funnel. To this flask 5.11 g (0.0568 moles) of 1,4-butanediol in 25 ml of ether and 25 ml (0.0625 moles) of a 2.5 M solution of n-butyllithium in hexane were added. After one hour of purging with nitrogen, 8.79 g (0.0625 moles) of benzoyl chloride were added dropwise. The following day an additional 25 ml (0.0625 moles) of 2.5 M n-butyllithium in hexane and 8.79 g (0.0625 moles) of benzoyl chloride were added and again allowed to react overnight. Water was then used to dissolve the lithium chloride salt. The crude product was subsequently crystallized upon distillation and evaporation of the ether. Repeated recrystallization of the crude product using hexane served to purify the final product. An approximately quantitative yield of the final product having a melting point of 81.0°–81.5°C was obtained.

All infra-red spectra were recorded using a Digilab FTS-14 Fourier transform infra-red spectrometer having a Data General Nova 1200 computer. To achieve a high signal to noise ratio while at the same time maximizing

Table 1 Model compound melting points

Compound	Melting point (°C)
B–T–B	72[19]
(BT)3–B	138[19]
(BT)5–B	195[19]
Bz–B–Bz	81

The sharp melting points and narrow infra-red bands atest to the high degree of purity and crystallinity of the model compounds

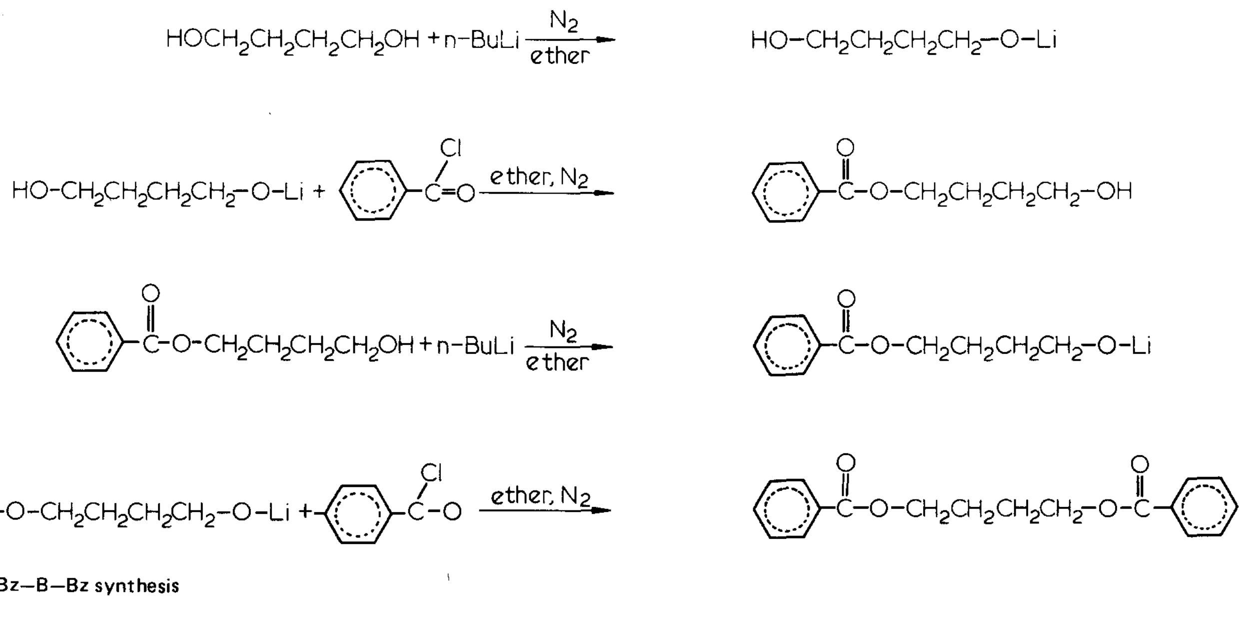

Figure 2 Bz–B–Bz synthesis

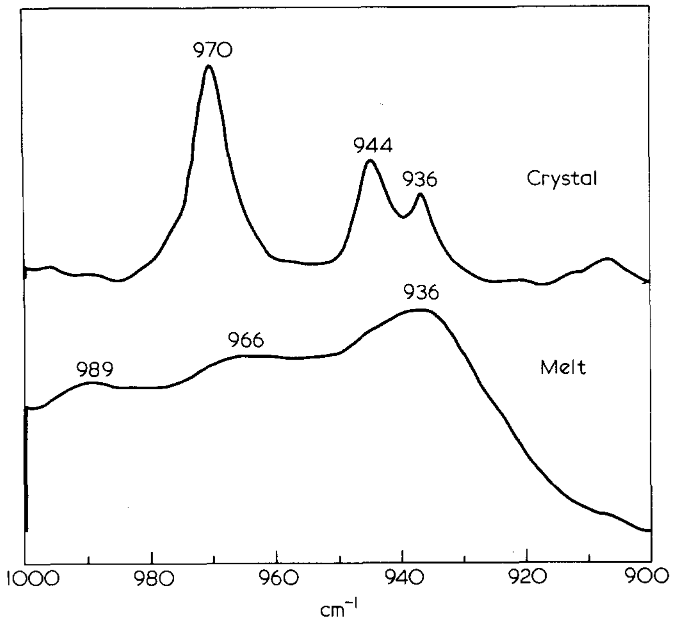

Figure 3 Bz—B—Bz infra-red methylene rocking region

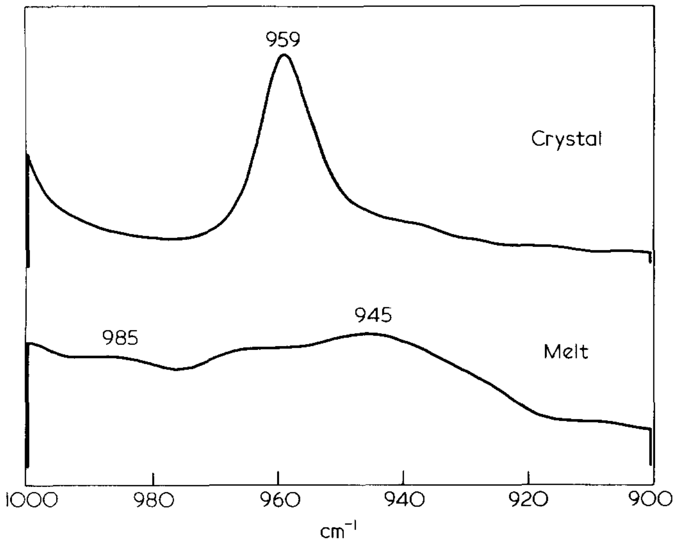

Figure 4 B—T—B infra-red methylene rocking region

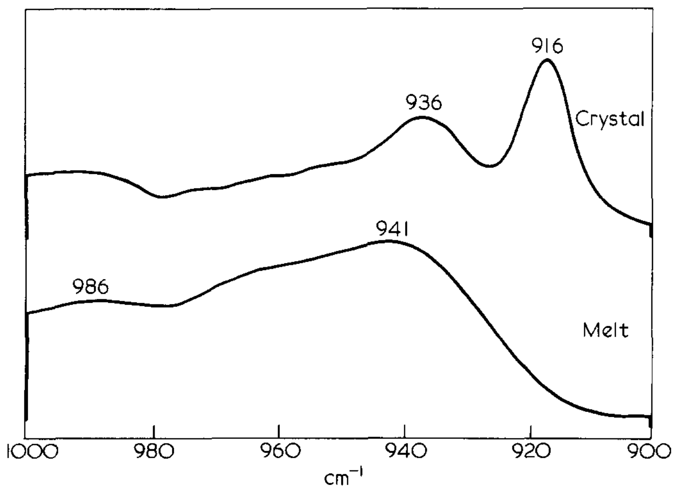

Figure 5 (B—T)3—B infra-red methylene rocking region

peak resolution, the following sampling parameters were used: All spectra were signal averaged with a minimum of 150 scans of the sample and reference (left blank). The He–Ne laser used to control interferogram sampling was sampled every second zero crossing (UDR = 2) to minimize the effects of spectral folding. Spectra of the crystal and melt phases were sampled at resolutions of 2 and 4 cm^{-1}, respectively. Fourier transforms of interferograms were calculated using triangular apodization and zero filled by a factor of 2 thereby minimizing artificial 'side lobes' arising from the discontinuous, finite sampling interval of the interferogram.

Samples of the crystalline solids of the model compounds were made in the form of KBr pellets. A specially designed thermo-cell fitted with 20 × 2.5 mm KBr windows was utilized to obtain the melt spectra of the model compounds at a temperature approximately 10°C above their respective melting points as indicated by the data in *Table 1*.

Predominately methylene rocking region (1000–900 cm^{-1})

The infra-red spectra corresponding to the crystal and melt phases of each of the four model compounds are depicted in *Figures 3–6*. In the spectrum of crystalline Bz–B–Bz the most prominent peak is observed at 970 cm^{-1}. A doublet is found at 944 and 936 cm^{-1}. The melt spectrum of this compound is marked by the appearance of a peak at 989 cm^{-1} which clearly arises from the presence of multiple conformers in this phase. Since the 970 cm^{-1} mode appearing in the crystal form is found to decrease in intensity in the crystal:melt transition it is, therefore, characteristic of the conformation found in the crystal phase. In the *trans* crystal form of PET this mode has also been observed[24], and a normal coordinate analysis[25] has indicated that it primarily arises from an O–CH2 stretching mode.

The spectra of the B–T–B model compound bear a strong resemblance to those of Bz–B–Bz just discussed. The strongest mode in the crystal phase is at 959 cm^{-1}. This peak is found to sharply decrease in intensity in the melt phase. New peaks in the melt spectrum of B–T–B are

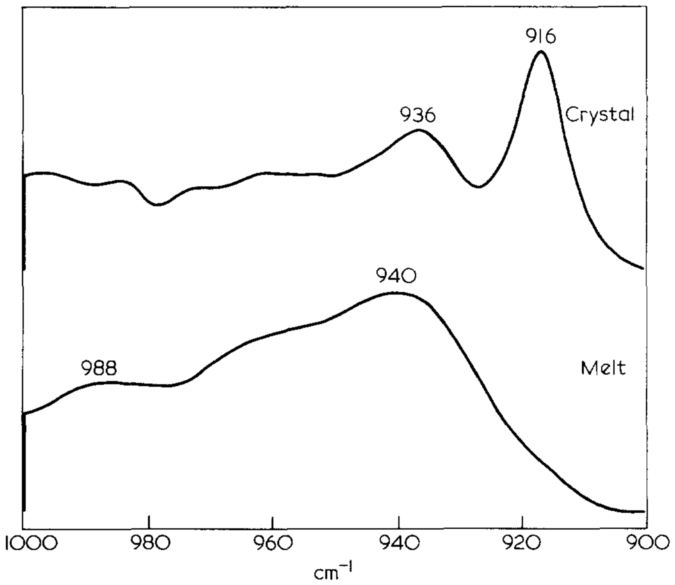

Figure 6 (B—T)5—B infra-red methylene rocking region

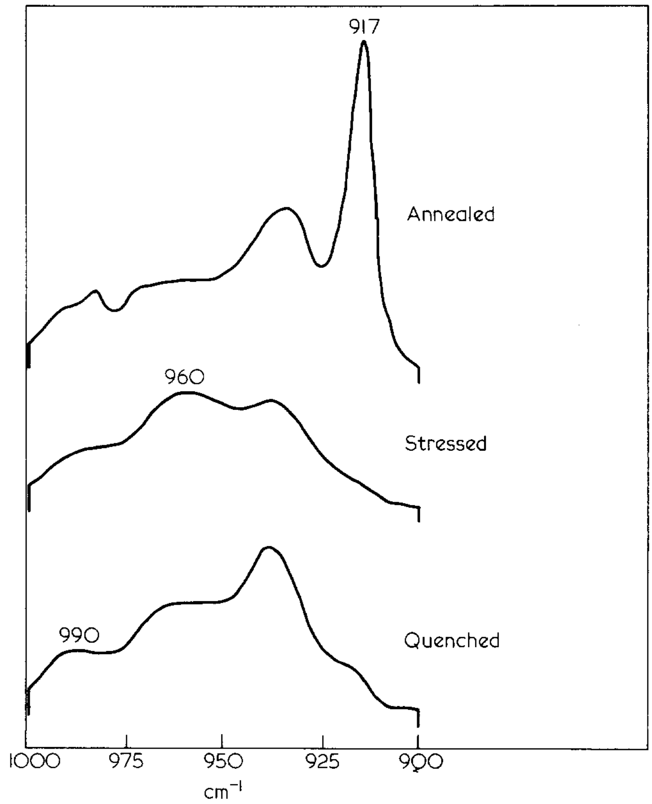

Figure 7 PTMT infra-red methylene rocking region[10]

observed at 985 and 945 cm^{-1}. The assignment of the 985 cm^{-1} band to a methylene rocking mode of *gauche* and non-*trans*:non-*gauche* conformers follows the same reasoning as with Bz–B–Bz.

Relative to the spectra of the crystal forms of Bz–B–Bz and B–T–B, the spectra of (BT)3–B and (BT)5–B in this region deviates significantly. No mode is observed at 970 cm^{-1} as was previously in the crystalline phase of Bz–B–Bz and B–T–B. Instead a strong peak at 916 cm^{-1} dominates the spectrum which totally disappears in the melt. This phenomenon indicates that the conformation associated with the crystal phase of (BT)3–B differs from the other two model compounds and is not present to any appreciable extent in the melt. The melt spectra of (BT)3–B and (BT)5–B are, however, virtually identical to the melt spectra of the other two model compounds in this region: All are characterized by a strong absorption at *ca.* 940 cm^{-1} and a weaker peak not present in any of the crystal forms at *ca.* 988 cm^{-1}

A comparison of the model compound spectra to PTMT spectra (*Figure 7*) in this region provides evidence of the conformational equivalence of (BT)3–B and (BT)5–B to the crumpled alpha form of the polymer, and Bz–B–Bz to the extended all *trans* beta form of PTMT. Previous work[10,12,13] has demonstrated that the mode at 917 cm^{-1} in PTMT is characteristic of alpha crystallinity. The strong absorption at 916 cm^{-1} occurring in (BT)3–B and (BT)5–B confirms that the tetramethylene segments associated with this oligomer and the alpha crystal phase of the polymer exist in the same conformation within the crystal lattice. Stambaugh *et al.*[10,12] have also noted the relative increase in intensity of the 960 cm^{-1} peak in PTMT upon the application of stress and, hence, the conversion to beta crystallinity. Both Bz–B–Bz and B–T–B crystalline samples exhibit a strong absorption in this region suggesting, therefore, that the tetramethylene segment of these compounds crystallizes in the extended all *trans* conformation as in the beta form of PTMT. The broad peak at *ca.* 990 cm^{-1} in samples of PTMT quenched from the melt (i.e. highly amorphous) is analogous to the peak observed in the melt spectra of all model compounds. It most certainly corresponds to a methylene rocking mode of *gauche* and non-*trans*:non-*gauche* conformers.

Methylene bending region (1550–1300 cm^{-1})

A number of conformationally sensitive modes for PTMT are also observed in the methylene bending region[10,13]. The corresponding infra-red spectra for the model compounds in this region are illustrated in *Figures 8–11*. Some caution must be exercised in the assignment of the bands in this portion of the spectrum since the differences in substitution with respect to the benzene ring being mono- or di-substituted are also manifested in this region.

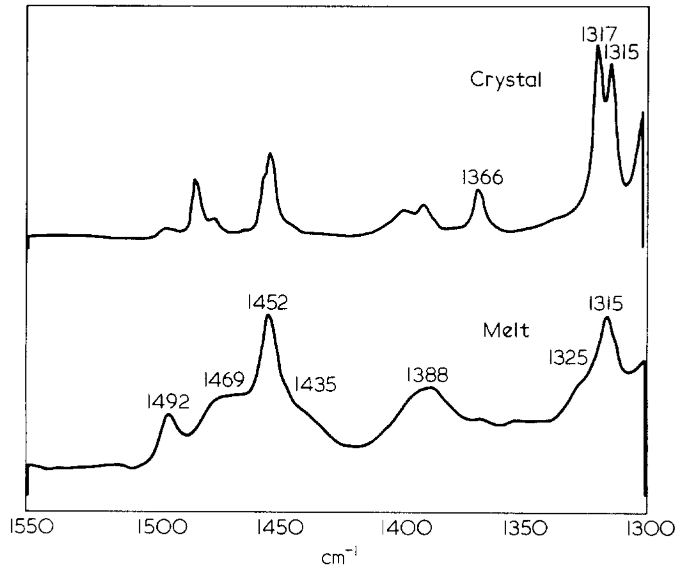

Figure 8 Bz–B–Bz infra-red methylene bending region

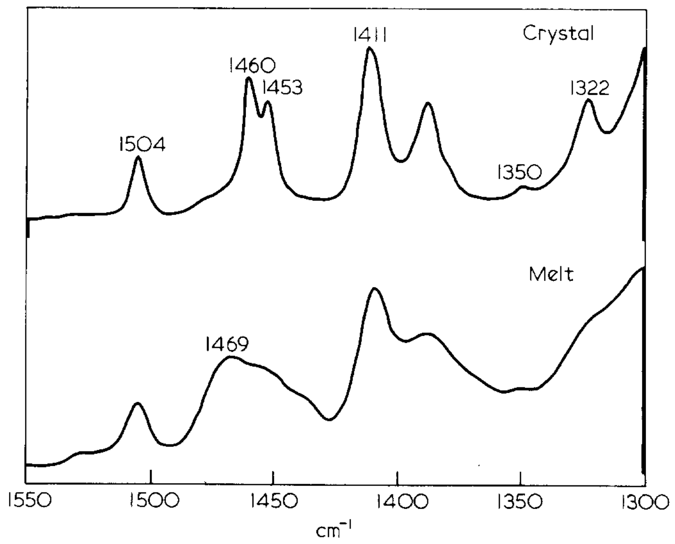

Figure 9 B–T–B infra-red methylene bending region

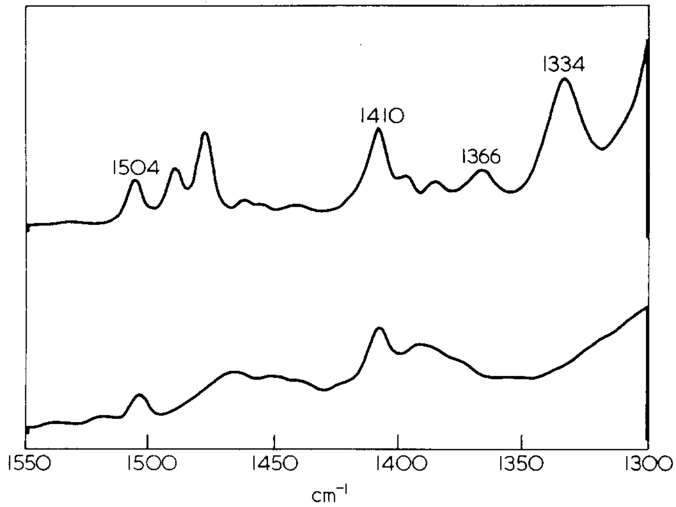

Figure 10 (B–T)3–B infra-red methylene bending region

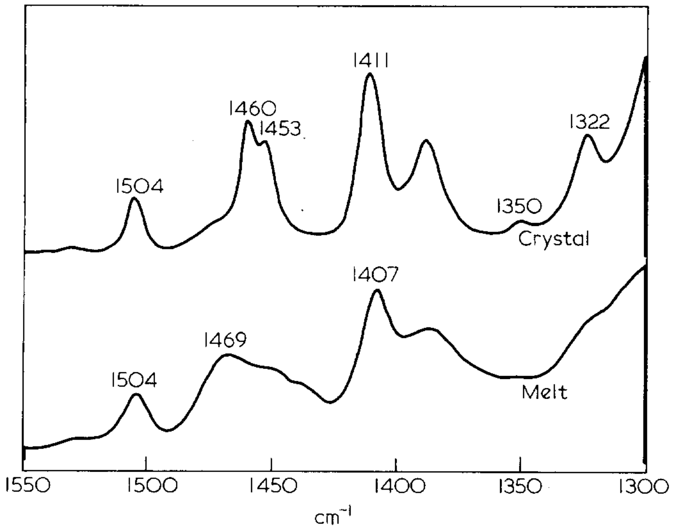

Figure 11 (B–T)5–B infra-red methylene bending region

In the crystal to melt transition of Bz–B–Bz a number of differences are evident (*Figure 8*). The peak observed in both spectra at 1492 cm^{-1} is well known to correspond to vibration v19a of mono-substituted benzene derivatives[26]. Common to both phases is a mode appearing at 1452 cm^{-1} which has been attributed to the v19b mono-substituted benzene C–C stretching mode[26]. In the spectrum of the melt, peaks are found on both sides of the 1452 cm^{-1}, being centred at approximately 1469 and 1435 cm^{-1}. These peaks most certainly may be assigned to the presence of *gauche*, non-*trans*:non-*gauche* conformers in this phase. The normal coordinate analysis of PET[25] suggests that they may be assigned to methylene bending modes. Observed at 1317 and 1313 cm^{-1} is a relatively strong doublet in the crystal spectrum which may be attributed to a combination of several modes which are extensively overlapped. Vibration 14 of benzene has been suggested to occur in this region, although a conclusive assignment has not been made[26]. Another possibility is that these peaks arise from methylene and OCH_2 wagging modes. The reasoning is supported by the appearance of a shoulder peak at 1325 cm^{-1} in the melt spectrum.

In examining the model compound spectra of the disubstituted materials, one finds a large number of differences relative to Bz–B–Bz. The peak observed at 1504 cm^{-1} in all spectra of B–T–B, (BT)3–T, and (BT)5–B is readily assigned to the v19a ring mode. Calculations done by Scherer[27] have indicated that the frequency of the v19a mode must be much higher than the v19b in *para* substituted rings. Katritzky[28] has reported that the v19b mode has a frequency of 1409 ± 8 cm^{-1} for *para* substituents. Common to all spectra of the model compounds possessing terephthalic residues is a band at 1410 cm^{-1}. The intensity of this mode is seen to vary only slightly in the crystal:melt phase transition for each of the compounds. For these reasons it must be assigned to the v19b ring mode.

A doublet is observed at 1460 and 1453 cm^{-1} in the spectra of both crystalline samples of (BT)3–B and (BT)5–B which shows a marked decrease in intensity in the melt phase. As was the case with Bz–B–Bz, a new mode is observed in the melt spectra of the terephthalic compounds at 1469 cm^{-1} which must be assigned to the presence of *gauche* and non-*trans*:non-*gauche* conformers.

Instead of a strong doublet observed in the crystal spectrum of Bz–B–Bz at 1317 and 1313 cm^{-1}, a single weaker peak is found at approximately 1322 cm^{-1} in the crystal phases of (BT)3–B and (BT)5–B. A somewhat more intense mode relative to that observed in (BT)3–B and (BT)5–B is evident in B–T–B. In the crystal to melt transition for these compounds a dramatic decrease in intensity is seen for this mode. This would seem to suggest that the peak is indicative of the non-*trans*:non-*gauche* conformation associated with (BT)3–B and (BT)5–B.

Common to both (BT)3–B and (BT)5–B crystal spectra is a band at 1350 cm^{-1} which is not found in the melt spectra of these compounds. The crystal spectra of Bz–B–Bz and B–T–B both have a band appearing at 1366 cm^{-1} which is seen to greatly broaden in the melt phase. These phenomena suggest the 1366 and 1350 cm^{-1} peaks arise from *trans* and non-*trans*:non-*gauche* crystal conformations involving the methylene wagging or twisting modes.

The preceding conclusions are supported by a number of spectral changes observed in PTMT (*Figure 12*). Ring modes v19a and v19b already assigned to the 1505 and 1411 cm^{-1} peaks in the terephthalic residue compounds are not found to change in intensity as a function of treatment in PTMT. Stambaugh *et al.*[10] have postulated that the doublet observed at 1460 and 1453 cm^{-1} in PTMT is characteristic of the alpha phase. The presence of these modes in crystal samples of (BT)3–B and (BT)5–B confirms both the original assignment, and the fact that the aliphatic segment, or these model compounds has the same crystal conformation as in the alpha phase of PTMT. Since the crystal spectrum of B–T–B does not possess this band, the conformation of the aliphatic portion of this compound must not exist in the same non-*trans*:non-*gauche* conformation found in the alpha phase. Previous work[10] has indicated that the 1470 cm^{-1} peak observed in PTMT is primarily due to a beta conformation, although the difference between samples which are highly beta and highly amorphous is minimal. The absence of this band in the crystal spectrum of Bz–B–Bz suggests that it is more properly assigned to the distribution of conformers present in the amorphous phase. An assignment of the 1350 cm^{-1} mode to the alpha

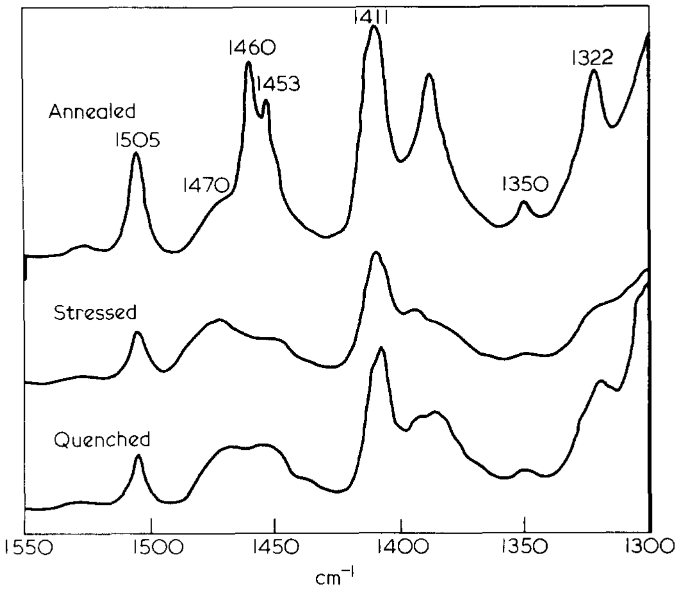

Figure 12 PTMT infra-red methylene bending region[10]

crystal phase has been reported[10,13]. Confirmation of this interpretation lies in the observation of this peak in crystal samples of (BT)3–B and (BT)5–B, and its absence in the crystal phases of B–T–B and Bz–B–Bz.

The 1322 cm^{-1} band observed in PTMT is found to decrease in intensity with the application of stress[10,13]. An analogous situation was observed in the crystal to melt transition for samples of (BT)3–B and (BT)5–B. Because of the overlap of the v19b ring mode in Bz–B–Bz, it is not possible to conclusively assign this mode entirely to the alpha phase conformation in a multiphase sample of PTMT. At the same time, however, the similarities between alpha and crystal (BT)3–B and (BT)5–B spectra do suggest that the aliphatic crystal conformation associated with these model compounds is the same as in alpha PTMT.

CONCLUSIONS

Infra-red analysis of the oligomers has demonstrated that the crystal conformations of (BT)3–B and (BT)5–B closely resemble that found in the alpha phase of PTMT. The crystal conformation of the aliphatic segments found in B–T–B and Bz–B–Bz, however, have been shown to be similar to the beta phase of PTMT. Spectra of the oligomer melts possess modes which are typical of highly amorphous samples of PTMT. The vast majority of changes noted would be extremely difficult to monitor accurately if one were to attempt to make dynamic measurements due to the extensive overlap of modes from the alpha, beta, and amorphous phases. The mode at 917 cm^{-1} is, however, fairly well isolated from neighbouring peaks and could be used as an indicator of alpha crystallinity since this mode is not active in the amorphous or beta phases to any appreciable extent as revealed by the model compounds.

The conformational equivalence of (BT)3–B and (BT)5–B to alpha PTMT is not surprising since one would anticipate that the inter- and intramolecular interactions found in these molecules are essentially the same. One cannot attribute the alpha conformation solely to a more efficient packing of the terephthalic groups since the B–T–B compound does not exist in the crumpled form. While the packing of the rings unquestionably plays a vital role, as Stambaugh *et al.* has previously indicated[12], the import of the intermolecular interactions of the aliphatic segments should also be considered. The effect of more than one terephthalic group within the molecule is also a factor in dictating the ultimate conformation as evidenced by the B–T–B compound which deviates from the other terephthalenyl compounds in that it possesses an all *trans* conformation.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Professor Gerhart Wegner of the Universität Freiburg for generously supplying a number of the model compounds studied, and to the Materials Research Laboratory of the National Science Foundation (grant number DMR 80-20245) for providing financial support of this research.

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