# Infrared Spectra and Crystallinity. Part I. Polyesters.

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The infrared spectra of crystalline and amorphous aliphatic polyesters show marked differences. The spectra of the crystalline materials are consistent with an approximately planar *trans*-configuration of the acid portion of the chains; this configuration is not shown in the molten state.

The acid portions of the molten polyesters are considered to have a continuous random configuration, rather than to consist of discrete rotational isomers.

THE infrared spectra of many compounds show appreciable differences between the crystalline and in the amorphous state (Richards and Thompson, *Proc. Roy. Soc.*, 1948, A, **195**, 1); *e.g.*, *n*-alkyl bromides (Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 535) and *n*-paraffins (Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261; Sheppard and Simpson, *Quart. Reviews*, 1953, **7**, 19) show more bands in the liquid, due to additional rotational isomers. On the other hand, long-chain monocarboxylic acids (Sinclair, McKay, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2570) show fewer bands in the liquid, and this is also attributed to the presence of rotational isomers, whose absorptions are not resolved. Many polymers also show spectral changes on crystallising (Nichols, *J. Appl. Phys.*, 1954, **25**, 840; Sutherland and Jones, *Discuss. Faraday Soc.*, 1950, **9**, 281; Mochel and Hall, *J. Amer. Chem. Soc.*, 1949, **71**, 4082). Polymorphic modifications also may give rise to spectral differences (Kendall, *Analyt. Chem.*, 1953, **25**, 382; Sutherland and Jones, *loc. cit.*).

The extent to which the spectrum of a compound may depend upon the state of aggregation and even polymorphic form has not always been sufficiently realised. When such differences have been noted, they have usually been avoided by working in dilute non-polar solutions (*e.g.*, Cole, *Chem. and Ind.*, 1954, 661). However, the conscious use of these differences can assist in structural diagnosis and identification. Furthermore, an improved understanding of the complex relationship of vibrational spectra and state of aggregation would assist in the interpretation of the spectra of complex molecules; conversely, it should increase our knowledge of the structure of crystals and of liquids.

We now report and discuss the spectra of crystalline and amorphous aliphatic polyesters; since the completion of this work, Coffey and Meyrick (" Third Rubber Technology Conference," London, 1954) have reported and used the appearance of crystallinity bands in polyethylene sebacate and adipate, but without discussion of their origin. The dicarboxylic acids and their nonpolymeric esters will be the subject of future publications in this series.

### EXPERIMENTAL

The polyesters were made on a 10—15 g. scale by Carothers and Arvin's method (*J. Amer. Chem. Soc.*, 1929, **51**, 2560), and the condensation continued until a crystallisable polyester was obtained of molecular weight about 2000. Several other samples of polyethylene adipate from various sources and of different molecular weight had essentially the same spectra. Normally, the polyesters had hydroxyl end-groups, but propane-1:2- and butane-2:3-diols gave products of low molecular weight with acid end-groups.

*Infrared spectra of polyesters.*

(A) Polyethylene succinate.
(B) Polybutane-1 : 4-diol succinate.
(C) Polyethylene adipate.
(D) Polybutane-1 : 4-diol adipate.
(E) Polyethylene sebacate.
(F) Polybutane-1 : 4-diol sebacate.

Note : Full-line (———), crystalline.
Broken line (– – –), molten.
‖ = parallel dichroism.
⊥ = perpendicular dichroism.

In (A), (C), and (D), spectra of thinner
crystalline samples in KCl discs
are shown in part.
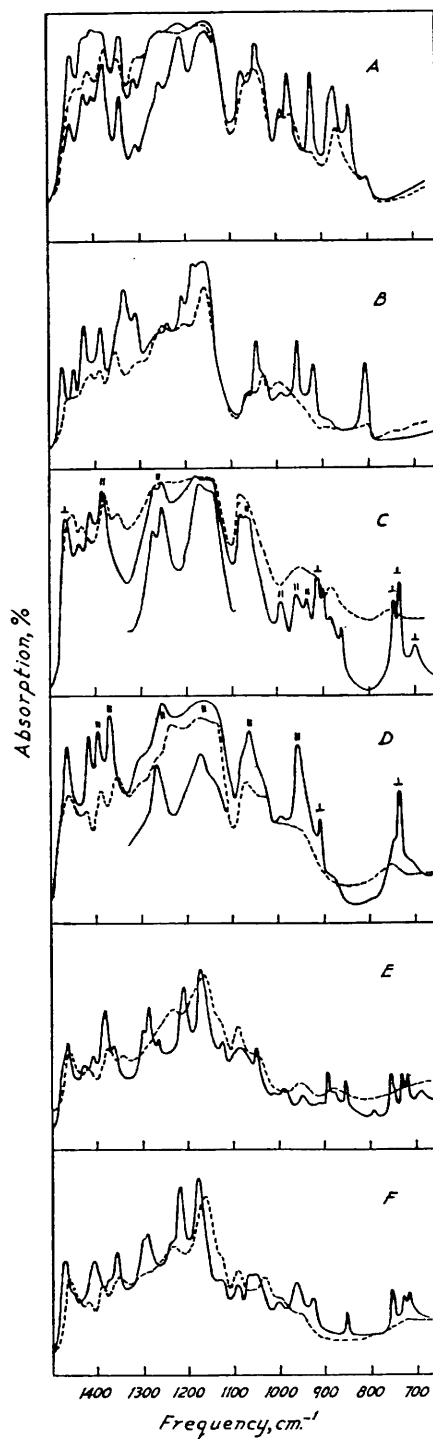
Some of the polyesters were purified by solution in chloroform and precipitation with light petroleum, but the physical and spectroscopic properties were not thereby appreciably altered.

Spectroscopic measurements were made with a Grubb-Parsons S3 spectrometer (with sodium chloride prism) and a DB1 radiation unit. The polyesters were prepared for examination by melting and pressing them between rock-salt plates. Spectra were measured after the materials had crystallised; the same sample was then examined molten and again after recrystallisation. The last spectrum served to check decomposition or change of cell thickness.

Oriented films were made by rolling the molten polyesters between silver chloride sheets as they solidified. Polarised spectra were measured by using a 5-plate silver chloride transmission polariser immediately before the entrance slit of the monochromator. The polariser used for the initial measurements was kindly supplied by Mr. H. A. Willis. Polyethylene succinate and adipate, and polybutane-1 : 4-diol adipate were also measured crystalline in pressed potassium chloride discs (Schiedt, *Appl. Spect.*, 1953, **7**, 75.)

*Results.*—The spectra of the six polyesters from the condensation of ethylene glycol or butane-1 : 4-diol with succinic, adipic, or sebacic acid are shown in the Figure. The differences between the crystalline (full line) and amorphous (broken line) spectra are very marked, especially when it is realised that these materials do not completely crystallise.

Dichroisms are shown for the polyadipates; " perpendicular " or " parallel " refers to the plane of the electric vector with respect to the direction of rolling.

Spectra of the crystalline and amorphous polyesters from the condensation of propane-1 : 2-diol or butane-2 : 3-diol with succinic, adipic, or sebacic acid were also measured and showed similar spectral changes. These spectra are not reported in detail, since the polyesters were of low molecular weight with acid end-groups, and the crystallinity could be associated with the acid end-groups of the molecules. They showed the characteristic crystallinity bands at *ca.* 890 and 805 cm.$^{-1}$ for the succinates, 734 cm.$^{-1}$ for the adipates, and 855, 755, and 722 cm.$^{-1}$ for the sebacates, and a general blurring on melting.

## DISCUSSION

The spectra are dominated by the acid moiety; this is confirmed by the spectra of the acids (Part II, following paper) and their simple esters, and a detailed discussion of the bands associated with the acid moiety will therefore be the subject of a later publication.

The most conspicuous changes on crystallisation are in the 700—900 cm.$^{-1}$ region, in which a number of apparently new bands arise. In other regions, the changes are a general sharpening of absorptions and minor frequency shifts.

A general characteristic of the spectra of molten polyesters is the absence of sharp or well-defined bands in the skeletal area. This is in contrast to the increased number of bands in molten *n*-paraffins (Sheppard and Simpson, *loc. cit.*) but similar to the loss of bands on " melting " of many polymers (Nichols, *loc. cit.*) and monocarboxylic acids (Sinclair *et al.*, *loc. cit.*).

In attempting to interpret the spectral differences between crystalline and amorphous states, we can consider three major factors : (*a*) differences of association, *e.g.*, hydrogen-bonding; (*b*) differences of configuration; (*c*) intermolecular interactions. In the polyesters, association (*a*) cannot be important, but, since there are a number of C–C bonds about which rotation may occur, there are obvious possibilities of configurational differences (*b*).

Normally, the configuration in a crystal is one of the more energetically favoured rotational isomers present in the liquid, as in the case of the *n*-paraffins (Sheppard and Simpson, *loc. cit.*). In some cases, however, the crystal packing enforces a molecular configuration which does not occur in the liquid, *e.g.*, in diphenyl (Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408) for which remarkable differences between the spectra of liquid and solid have been reported (Richards and Thompson, *loc. cit.*).

The crystalline polyesters are known to have approximately planar *trans*-configurations of their acid moieties (Fuller and Erickson, *J. Amer. Chem. Soc.*, 1937, **59**, 344 ; Fuller, Frosch, and Pape, *ibid.*, 1942, **64**, 154) as have the dicarboxylic acids (Morrison and Robertson, *J.*, 1949, 980, 987, 993, 1001) and *n*-paraffins (Muller, *Proc. Roy. Soc.*, 1928, *A*, **120**, 437).

In the crystalline state the polyesters, dicarboxylic acids, and *n*-paraffins show a band in the 800—720 cm.$^{-1}$ region which is reliably assigned (Sheppard and Simpson, *loc. cit.*) to

the out-of-plane rocking deformation of a *trans*-$[CH_2]_n$ chain ($\delta[CH_2]_n$). However, this band virtually disappears in the amorphous polyesters and dicarboxylic acids (Part II), showing the absence of this configuration. Calculations (Person and Pimental, *J. Amer. Chem. Soc.*, 1953, **75**, 532) have shown that this band is very sensitive to deviations from planarity.

The absence of the $\delta[CH_2]_n$ band in molten polyesters is contrary to previously published correlations (Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397; Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, 1954, pp. 13, 26) and emphasises that this band is only associated with an essentially planar *trans*-configuration.

Comparison of the spectra of molten polyesters with those of liquid *n*-paraffins with corresponding methylene chains shows that, unlike the *n*-paraffins, the molten polyesters do not exist in a few discrete rotational isomers. Even the energetically favoured planar configuration is practically non-existent. This implies either a lowering of the potential barriers to rotation or, more probably, increased forces tending to deform the polymer chains from the energetically-favoured *trans*-configurations.

The number of possible rotational isomers in the polyesters is too great to distinguish between a large number of discrete isomers and a continuous range of non-discrete configurations. In the simpler dicarboxylic acids (Part II), the evidence supports the conception of a continuous range of non-discrete configurations.

The 735, 748 cm.$^{-1}$ doublet in crystalline polyethylene adipate probably arises from intermolecular interactions of the $\delta[CH_2]_n$ vibration, as in the case of polyethylene (Rugg, Smith, and Wartman, *J. Polymer Sci.*, 1953, **11**, 1).

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