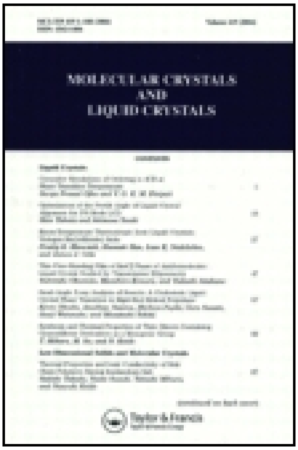

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X-Ray Diffraction Studies on Oriented Samples of Rigid-Rod Liquid Crystalline Polyesters

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X-RAY DIFFRACTION STUDIES ON ORIENTED SAMPLES OF RIGID-ROD LIQUID CRYSTALLINE POLYESTERS

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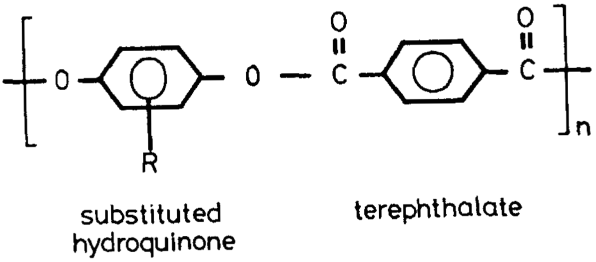
Abstract Three members of a family of rigid-rod thermotropic polyesters are examined using x-ray diffraction. The polymers are based on alternating substituted hydroquinone and terephthalate units. Analyses of the x-ray diffraction results show that the molecules lie with the mesogenic surfaces in contact with a chain-chain separation of 0.43nm. The separation of the chains in the other direction perpendicular to the chain axis varies from 1.38nm to 1.68nm as the side appendage changes from OEtOMe, through OEtOEt to OEtOEtOEt. The latter polymer exhibits textural features.

INTRODUCTION

Liquid crystalline aromatic polyester can form fibres or plastics of high strength and stiffness by melt spinning or injection moulding in the liquid-crystal state. However, the simplest aromatic polyesters of this type, those derived from terephthalatic acid and hydroquinone or from p-hydroxybenzoic acid, melt well above 500^oC, and processing of these polymers by conventional methods is not possible. One method that can be used to lower the melting point to a more amenable range is by introducing non-aromatic side appendages[1]. X-ray diffraction has been used to investigate the conformation and structure from oriented samples of three members of the family with generalised formula:



The substituted groups (R) for the samples examined were -OEtOMe, -OEtOEt and -OEtOEtOEt.

METHODS

The samples were oriented at elevated temperatures either in the form of films or fibres suitable for x-ray diffraction. The oriented samples were x-rayed using point collimated nickel filtered CuKα radiation.

RESULTS

X-ray diffraction patterns of the three polyesters are shown in Fig. 1.

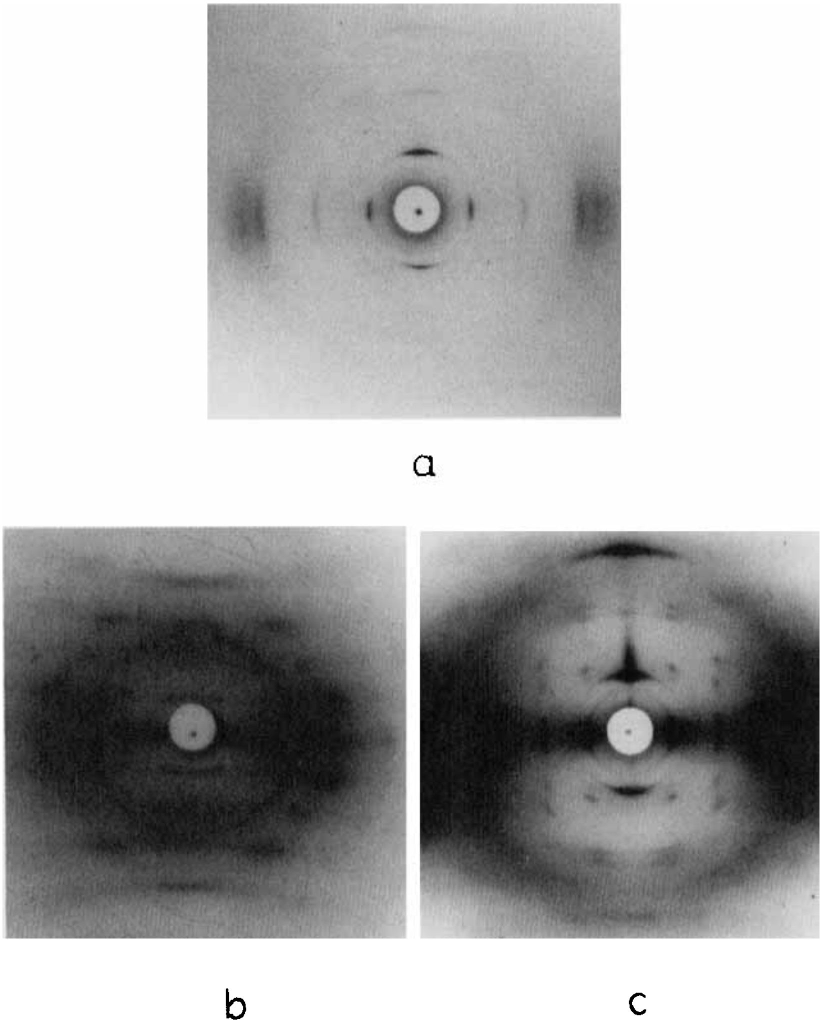


FIGURE 1. X-ray diffraction patterns of the three polyesters. Stretch and chain direction vertical. (a) -OEtOMe substituted polymer. (b) -OEtOEt substituted polymer. Note overlaying of 0.43nm less well oriented diffraction arc. (c) -OEtOEtOEt substituted polymer. Note splitting of diffraction signals either side of equator indicating textural features.

Fig. 1(a) shows the X-ray diffraction pattern obtained from the polymer with substituent -OEtOMe. Discrete layer lines are evident with spacings which are orders of 1.24nm. This corresponds to the length of the chemical repeat in the chain direction as illustrated in Fig. 3. A strong equatorial diffraction signal occurs at a spacing of 0.43nm onto which is superimposed a much sharper but less well oriented diffraction arc. Broader equatorial signals occur at spacings centred on 1.38nm and 0.66nm, which is probably the second order.

Fig. 1(b) shows the X-ray diffraction pattern from the -OEtOEt substituted polymer. The intensity is concentrated on the meridian, with a series of orders of a 1.24nm spacing, and on the equator. The equatorial diffraction signals occur at 1.39nm together with the second and third orders plus a signal at 0.43nm.

Fig. 1(c) is a highly crystalline x-ray pattern obtained from the polymer decorated with the side appendage -OEtOEtOEt. Meridional reflections occur as orders of 1.23 spacing. A series of row lines, which are orders of 1.68nm can be seen and noticeable splitting of the diffraction signals either side of the equator indicating textural effects involving chain tilting occur. There is a strong signal on the equator centred at 0.44nm.

DISCUSSION AND CONCLUSION

The precise details of the structures will be published elsewhere but using the -OEtOEt substituted polyester as an example the salient points of the structures can be discussed. Fig. 2(a) shows a ball and stick computer drawn model of the chain and Fig. 2(b) has a van der Waal surface superimposed. The repeat distance along the chain direction of this structure matches the value measured from x-ray diffraction (1.24nm). Fig. 2(c) illustrates the stacking of such molecules with the mesogenic surfaces lying face to face. It turns out that this interchain spacing in the close packed pile is 0.43nm, which is commensurate with the measured X-ray diffraction value. Thus the molecules orient parallel to the draw direction and form flat ribbons. The broad faces of the mesogenic units stack in piles with intermolecular spacing of 0.43nm. The other dimension in the two-dimensional packing scheme increases from 1.38nm to 1.68nm as the side appendage increases. The patterns index on orthorhombic and monoclinic unit cells. The -OEtOEtOEt substituted polymer exhibits texture effects the details of which will be reported elsewhere, suffice to say that it involves molecular tilting.

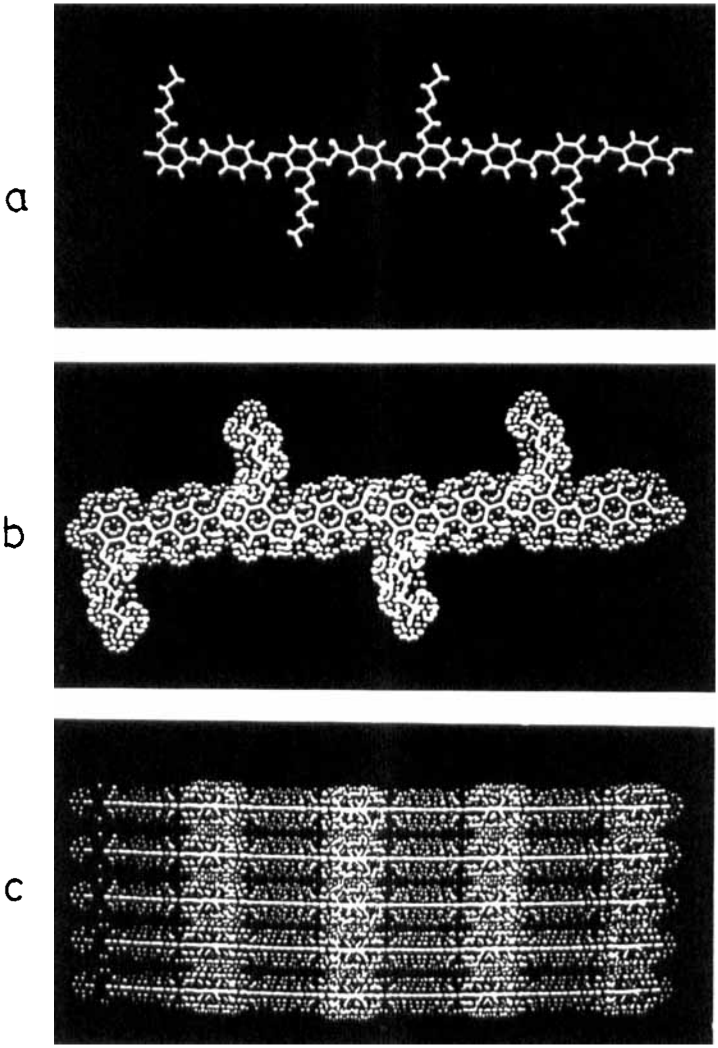


FIGURE 2. Computer (Evans and Sutherland) drawing of -OEtOEt substituted polymer. (a) ball and stick. (b) similar but with van der Waal surfaces superimposed. (c) close packed stack of chains in contact at 0.43nm (viewed edge on).

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