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E.D.T. Atkins [a] , E. L. Thomas [a] & R. W. Lenz [a]

[a] Polymer Science and Engineering, University of Massachusetts at Amherst, Amherst, MA, 01003, USA

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X-RAY DIFFRACTION STUDIES ON ORIENTED SEMI-RIGID LIQUID CRYSTALLINE POLYESTERS

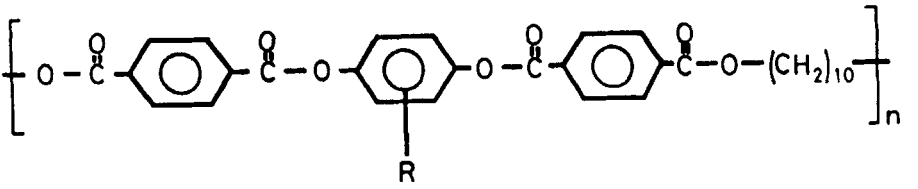
E.D.T. Atkins*, E.L. Thomas and R. W. Lenz
Polymer Science and Engineering, University of Massachusetts at Amherst,Amherst, MA 01003, USA.

* permanent address: H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL. U.K.

Abstract Four members of a family of thermotropic alkyl-substituted polyester based on two terephthalate units sandwiching a substituted hydroquinone as the mesogenic unit separated by a decamethylene flexible spacer have been examined using x-ray diffraction. Analyses of the x-ray diffraction patterns from oriented samples favour conformations close to the extended chain. A spacing of 0.42-0.44nm support face to face association of the mesogenic units but 00ℓ reflections occur off the meridian indicating relative shear, both parallel and perpendicular to the chain axes, and giving rise to triclinic unit cells.

INTRODUCTION

It is often desirable to lower the rather high melting temperatures of liquid crystalline rigid-rod polymers by chemically introducing more flexible substituent groups within the main chain itself. A family of thermotropic alkyl-substituted polyesters[1] based on the generalized formula:



have been examined using x-ray diffraction. In the polymers reported below the R groups are -H, $-CH_3$, $-(CH_2)_7CH_3$ and $-(CH_2)_9CH_3$. In order to attempt to relate properties to structure we have systematically prepared a series of oriented samples suitable for x-ray diffraction and considered the conformation and overall juxtapositioning of the molecules.

METHODS

Samples were obtained at elevated temperature to form films and fibres suitable of x-ray diffraction. The x-ray patterns were obtained using point collimated nickel filtered Cuka radiation.

RESULTS

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

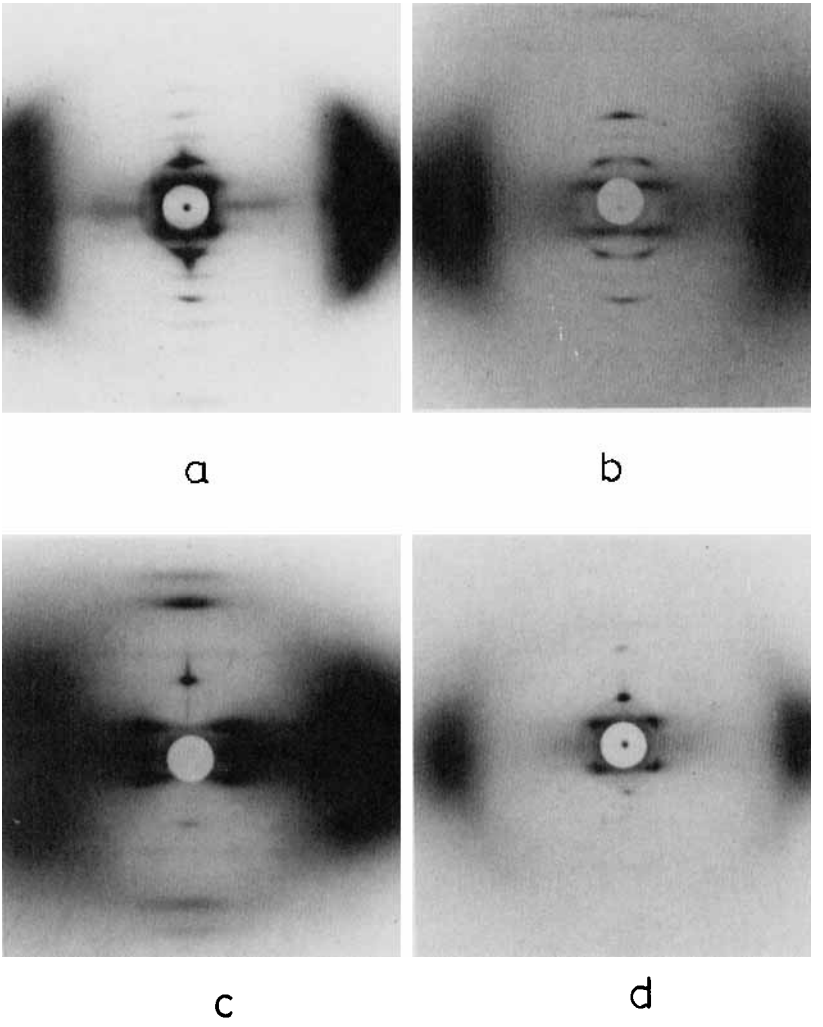


Fig. 1. X-ray diffraction patterns obtained from the oriented samples. Stretch and chain direction is vertical. (a) unsubstituted polymer, (b) $-CH_3$ substituted polymer, (c) $-(CH_2)_7CH_3$ substituted polymer and (d) $-(CH_2)_9CH_3$ substituted polymer.

Fig. 1(a) was obtained for the -H or unsubstituted polyester. It is a reasonably crystalline pattern with layer lines indexing on a spacing of 3.13nm. The pattern can be indexed on a triclinic unit cell with the strong 001 reflections, at spacing 1.44nm, forming the four-point pattern close to the edge of the beam stop shadow. The broad area of enhanced intensity close to the equator, in the spacing range 0.5 - 0.3nm, emanates from a group of closely spaced individual and sharp diffraction signals, including one at spacing 0.43nm.

Fig. 1(b) was obtained from the $-CH_3$ substituted polymer. By the nature of the polymerisation the substituents are randomly arranged in the four sites on the hydroquinone unit. This layer line spacing is 3.16nm with again the prominent 001 signals forming a four point pattern. The equatorial diffraction is more diffuse compared with Fig. 1(a) but still masks one or two sharper diffraction signals.

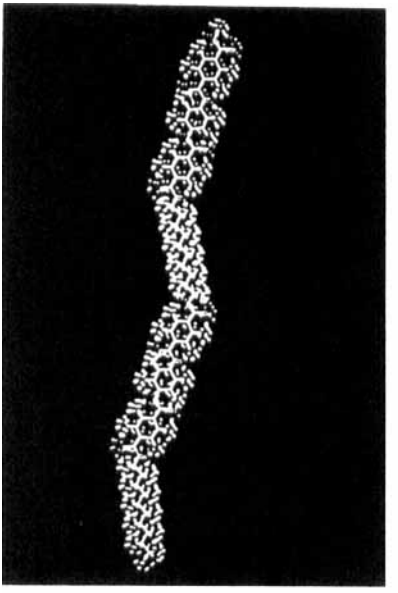
Fig 1(c), obtained from the $-(CH_2)_7CH_3$ substituted polymer shows a distinctive four point pattern on a layer line with spacing 3.09nm. The strong equatorial diffraction observed is centred on a spacing of 0.44nm and an additional broad and strong diffraction spot occurs at a spacing of 1.4nm. The spacing of the 001 signal is 1.44nm similar to the other polyesters. There is no

obvious sign of sharp reflections hidden under the 0.44nm equatorial peak, indicating poorer lateral association between the polymer chains.

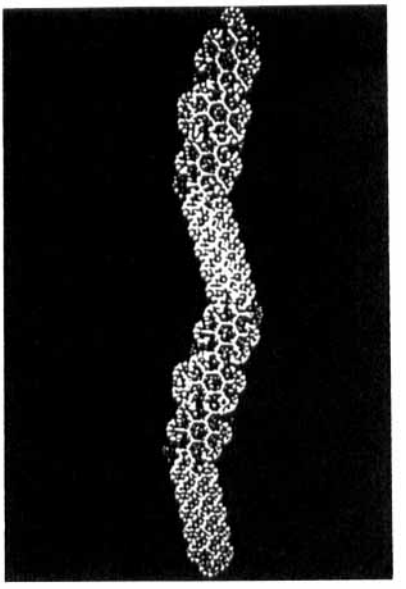
Fig. 1(d) was obtained from the $-(CH_2)_9CH_3$ substituted polymer and shows similar features to the other x-ray diffraction patterns. The layer line spacing was measured to be 3.05nm. Again a diffuse equatorial spot centred at 0.44nm is prominent in the diffraction pattern. One feature worth attention is that the four point 001 signals are a composite of a sharp arc and a diffuse streak indicating two levels of crystallinity in this sample.

DISCUSSION AND CONCLUSIONS

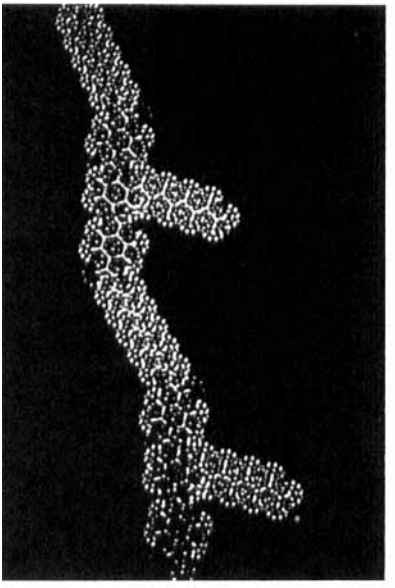
In all four polyesters the layer line spacing is close to 3.2nm. This value corresponds to the repeat of the extended chain which is illustrated in Fig. 2 for the four polyesters considered. It should be remembered that the substitution is random on the hydroquinone unit. The noticeable zig-zag conformation of the molecules offers a clue to their stacking and organization. The diffraction signals at about 0.43nm on the equator are expected from the close stacking together of the mesogenic units. Although the models



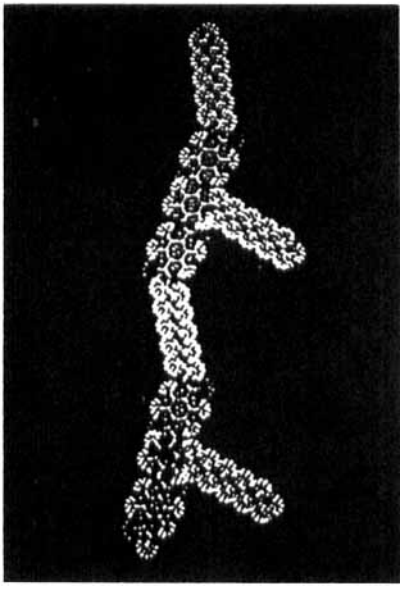
2a



2b



2c



2d

Fig. 2. Computer (Evans and Sutherland) models of the four polyesters. The models are ball and stick projections perpendicular to the faces of the mesogenic units overlaid with van der Waal surfaces. (a) unsubstituted, (b) $-CH_3$ substitution, (c) $-(CH_2)_7CH_3$ substitution and (d) $-(CH_2)_9CH_3$ substitution. In reality the substitution sites are at random on the hydroquinone unit.

shown in Fig. 2 are essentially planar the detailed scrutiny of the unit cells indicate a degree of rotation of the mesogenic units from this planar conformation without lowering the value of the chain repeat. In stacking together with intermesogenic spacing of 0.43nm it is necessary to slide adjacent mesogenic units parallel to the chain axis and unit cell parameters of the individual polyesters (to be published elsewhere) and density considerations argue for an additional slide perpendicular to the chain axis. The chain packing therefore falls within the triclinic system and the relative axial stagger in particular aligns the [001] direction at an angle to the chain direction. This accounts for the 001 reflections forming a four-point pattern (see Fig. 1). A generalised model for these polyesters is illustrated in Fig. 3. The repeat in the chain direction is 3.2nm and

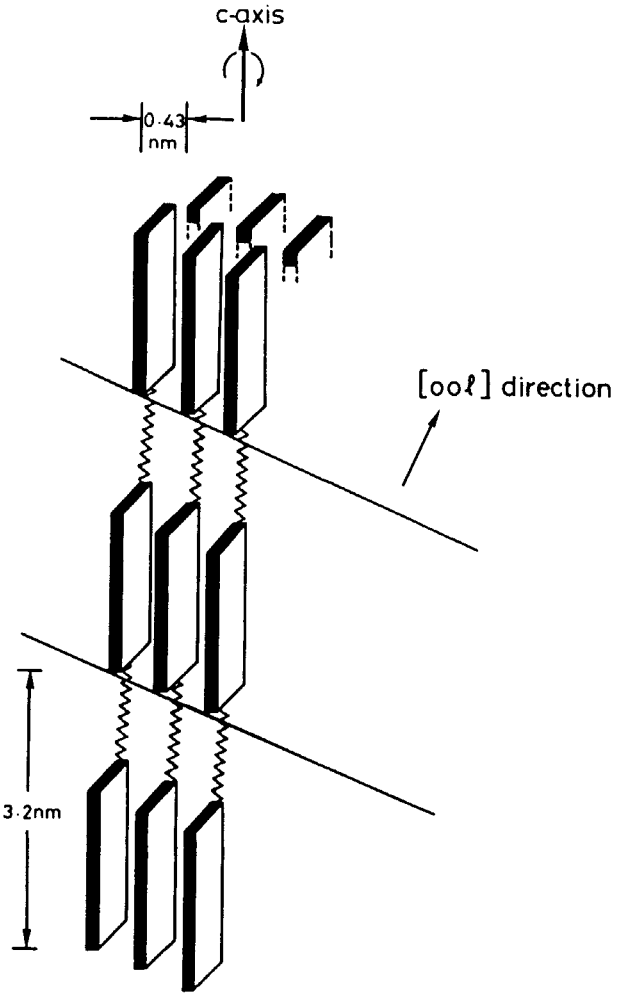


Fig. 3. Diagrammatic view of the generalised packing scheme for the four polyesters.

gives rise to the observed series of layer lines which are orders of this spacing. However the 001 reflection at spacing ~ 1.44nm is found off the meridian. The separation between the mesogenic slabs is shown as 0.43nm and the crystallites are cylindrically averaged about the chain direction (c-axis). The degree of order decreases as the length of the alkyl side chain increases. The diffraction signal which occur on the meridian are hkℓ reflections.

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