Lack of orientation in the surface layer of wholly aromatic liquid-crystal polymer fibres

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A comparison of band dichroism in the transmission and attenuated total reflection infra-red spectra of poly(phenyl-*p*-phenylene terephthalate) fibres, prepared by jet drawing, showed low molecular orientation in a surface layer of about 1 μm thickness.

(Keywords: liquid-crystal polymer; orientation; surface)

Highly oriented as-prepared fibres of thermotropic main-chain liquid-crystal polyesters (LCPs) and copolyesters exhibit a tensile strength value of about 1 GPa, which can be enhanced two to three times by the appropriate heat treatment. The strength of LCPs may be associated with structural imperfection at molecular and supramolecular levels, including inhomogeneity in the fibre cross-section. The cross-section inhomogeneity is an inevitable consequence of the jet-drawing technology, since temperature–force conditions during fibre orientation vary throughout the specimen.

In the present communication, we report the primary results of a comparative study of the surface and bulk structure of fibres made of wholly aromatic LCP with a mesogenic group in the main chain. The experiments were carried out by combining the transmission and attenuated total reflection (a.t.r.) infra-red (i.r.) techniques, which characterize the bulk and the surface layer, respectively. Unfortunately, very few i.r. studies of LCP have been published to date. Usually consideration is focused on the structural role of the flexible spacers[1–3]. Any experimental i.r. data regarding wholly aromatic LCP are unknown to the authors.

The investigation was performed on poly(phenyl-*p*-phenylene terephthalate) (PPPT) fibres prepared by jet drawing. To obtain highly contrasted a.t.r. spectra, a semicylindrical thermoplastic a.t.r. element[4] was used. The thermoplastic optical material provides perfect contact between the element and a set of fibres arranged on a framework or substrate[5].

The spectra were measured on a grating Jasco DS403G spectrophotometer equipped with a variable-angle a.t.r. unit.

Figure 1 represents the region of greatest difference between the polarized transmission and a.t.r. spectra of the fibres. In this region (1500–900 cm^{-1}), the strongly polarized transmission bands at 1016, 1125 and 1405 cm^{-1}, ascribed to C–O stretchings, C–O–C and C=O deformations, respectively[6], transform to almost unpolarized features in the a.t.r. spectrum. In other words, the highly ordered bulk structure is in contrast with orientation disorder observed in the surface layer. The difference in molecular chain arrangement between the bulk and the surface is so great that one can conclude that there is a lack of orientation in a layer about 1 μm thick (a value determinated by the a.t.r. light depth penetration) at the chosen angle of incidence of 50°.

The surprisingly strong distortion of molecular ordering indicated in the surface layer of LCP fibres seems to be associated with the peculiarity of the sample preparation procedure.

A slightly reduced surface chain orientation was observed earlier in fibres and films made of flexible-chain polymers (FCP)[5]. The routine procedure for preparing highly oriented FCP fibre is multistep drawing under varying temperature–force conditions. The initial surface disorder, which could have been introduced at the stage of fibre forming, gradually disappears at subsequent stages of drawing.

Unlike the FCP fibres, the LCP fibres are usually produced by a single-stage forming–drawing process. The imperfection of the arrangement caused by contact with jet walls is conserved during the rapid cooling of the

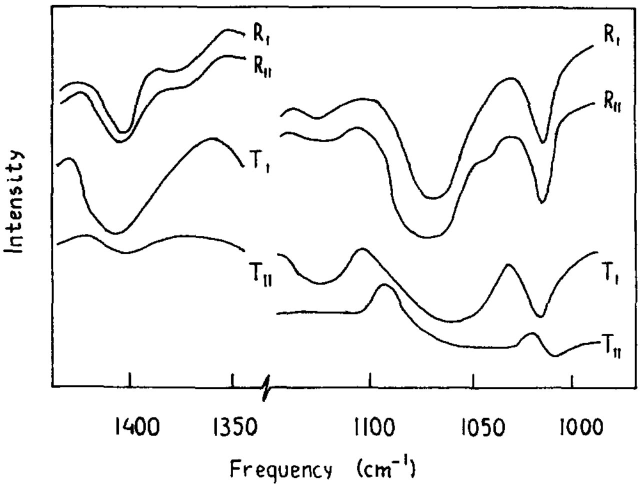

Figure 1 I.r. transmission (T) and a.t.r. (R) spectra of PPPT fibres recorded in two light polarizations relative to the drawing direction

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surface when drawing the fibre from the jet. The disordering might also have been produced by squeezing of the chain-ends and low-molecular-weight fraction from the bulk to the surface, as in the case of wet forming, when the liquid drops are pressed out owing to the stimulated syneresis phenomenon.

To establish other peculiar properties of the PPPT fibre surface structure (conformer geometries, chain-end distribution, etc.) further experiments are continuing. The principal difficulty arises from the poorly developed i.r. band assignment of wholly aromatic LCP.

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