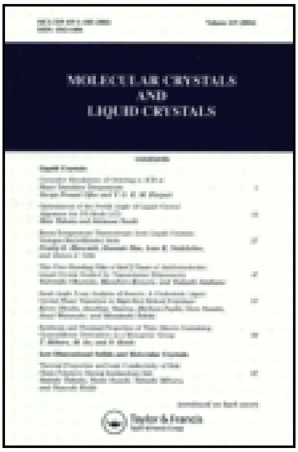

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thermal and X-Ray Investigation of a New Mesophasic Semiflexible Polyester

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Version of record first published: 24 Sep 2006.

To cite this article: Emo Chiellini, Giancarlo Galli, Bin Yang, Oriano Francescangeli, Savino Melone, Annino Sante Angeloni, Michele Laus & Daniele Caretti (1992): Thermal and X-Ray Investigation of a New Mesophasic Semiflexible Polyester, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 215:1, 279-286

To link to this article: http://dx.doi.org/10.1080/10587259208038535

THERMAL AND X-RAY INVESTIGATION OF A NEW MESOPHASIC SEMIFLEXIBLE POLYESTER

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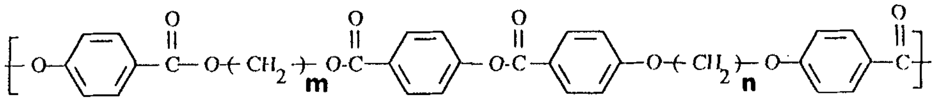
(Received March 12, 1991)

Abstract A thermal and X-ray investigation is reported of a main-chain polyester consisting of two p-oxybenzoate diads alternatively spaced by a pentamethylene and an heptamethylene segment. Evidences are provided for the existence of an enantiotropic smectic C phase and a monotropic nematic phase. Cooling from the mesophase allows for the lock-in of the smectic C structure in the glassy state.

Keywords: LC-polyester, rein-chain, smectic C, x-ray investigation

INTRODUCTION

Main-chain polyesters consisting of a rigorous alternating arrangement of mesogenic groups and flexible spacers are attracting ever growing interest for their thermotropic liquid crystalline behaviour in respect of dependence from specific structural parameters[1]. For this class of polymers it is well established that spacer groups play a fundamental role in determining nature and stability of the liquid crystalline phases[2-6]. To further substantiate the basic knowledge of the molecular engineering of main-chain liquid crystalline polymers a systematic investigation was undertaken[4-6] concerned with the thermotropic behaviour of different series of polymer samples whose general structure is schematically represented in the formula:



C_mC_n

The polymer repeating unit contains two mesogenic p-oxybenzoyl dyads interconnected by two linear aliphatic chains containing variable numbers m and n of methylene units. These polymers are designated as C_mC_n according to the number m and n of methylene groups in the alkylene spacers connected to the mesogenic groups by ether and ester linking groups respectively. By allowing independent variations in either flexible spacers, a large variety of mesomorphic polymers is obtained and comprehensive correlations between structural features and mesomorphic properties are developed. Within this general scope, in the present study we report on the liquid crystalline behaviour of polymer sample C_5C_7 clarified through differential scanning calorimetry, optical microscopy and X-ray examination of unoriented and oriented specimens.

EXPERIMENTAL PART

Polymer C_5C_7 is synthesized by polycondensation reaction between the sodium salt of 1,5-pentamethylene bis(4-hydroxybenzoate) and the diacid chloride of

4,4'-(heptamethylenedioxy)dibenzoic acid in the presence of benzyltributylammonium bromide as phase transfer catalyst[7]. The number average molecular weight ($\overline{Mn}$) and first polydispersity index ($\overline{Mw}/\overline{Mn}$) evaluated by size exclusion chromatography (SEC) result 23300 Da and 1.96 respectively. The mesomorphic properties are studied by thermal analysis (DSC) and polarizing microscopy. The mesophase structure is investigated by X-ray diffraction measurements. X-ray diffraction patterns are recorded using nickel filtered CuKα radiation (λ=1.54 Å) both on a powder specimen, from room temperature up to the isotropization point, and on oriented fiber prepared first by pulling up the high viscous isotropic melt at 440 K with tweezers and then submitting it to an elongation with a speed of 1 m/s. Accordingly the fiber axis coincides with the average chain axis of the polymer.

RESULTS AND DISCUSSION

Figure 1 reports the DSC thermograms of polymer C_5C_7. The DSC trace recorded on the virgin polymer sample (Fig. 1a) reveals two broad endothermic transitions centered at 355 K and 427 K. The lower temperature endothermic transition, which is preceded by a shoulder, is attributed to crystal melting while the higher temperature endothermic transition corresponds to mesophase isotropization. Upon cooling from the isotropic state, two transitions occur at 412 K and 404 K (Fig. 1b) with associated enthalpies of 0.30 kJ/mol and 4.4 kJ/mol respectively. Glass transition is also detected at 300 K while no crystallization exotherms are observed. On subsequent heating, the DSC thermogram (Fig. 1c) shows only the glass transition at 306 K and mesophase isotropization at 424 K with an associated enthalpy of 4.8

kJ/mol. Upon annealing on the hot stage of a polarizing microscope, focal-conic textures[8] with fans can be observed in the temperature range lying between the melting or glass transition temperature and the isotropization point suggesting a smectic structure for the enantiotropic mesophase. The existence of a nematic phase is inferred from the appearance of schlieren textures[8] upon cooling from the isotropic melt to 408 K. The smectic phase is somewhat undercooled and this allows for the occurrence of a new nematic phase, which is therefore monotropic, in agreement with DSC results.

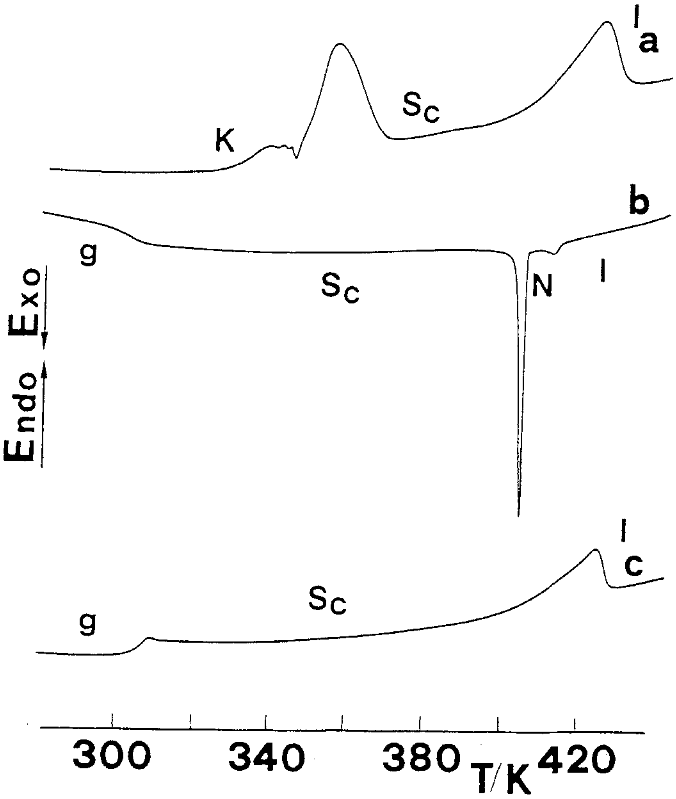


Figure 1 DSC curves of polyester C_5C_7: (a) first heating curve at 20 K/min; (b) first cooling curve at 10 K/min; (c) second heating curve at 10 K/min.

The X-ray diagrams recorded on unoriented polymer C_5C_7 samples at different temperatures are reported in Figure 2. The pattern of the as-received sample (Fig. 2a) shows five reflections corresponding to Bragg spacings of 14.8, 5.9, 5.0, 3.8 and 3.2 Å and indicates a fairly low degree of crystallinity (Xc ≈ 25 %) at room temperature.

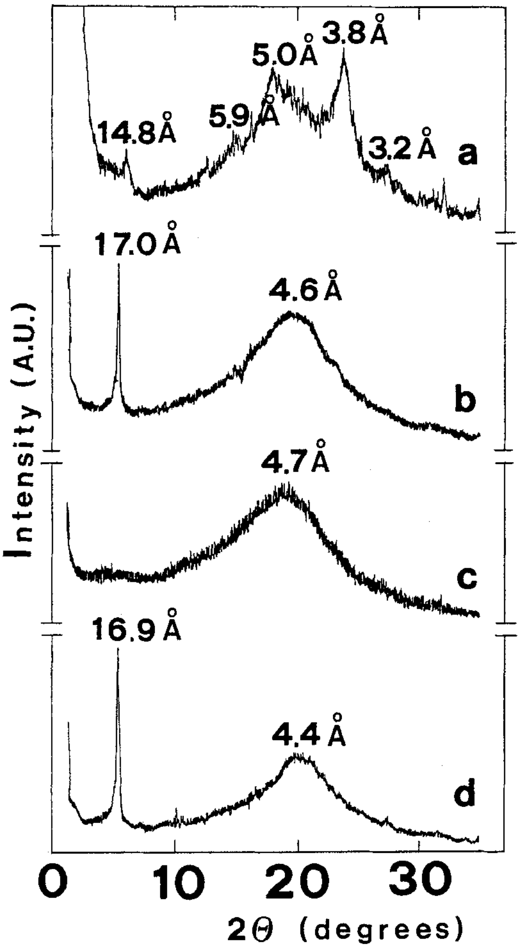


Figure 2 X-ray diffraction diagrams with Bragg periodicities of polyester C_5C_7 at different temperatures (a) 298 K, (b) 406 K, (c) 440 K, (d) 303 K.

Above the melting temperature the X-ray trace (Fig. 2b) displays a sharp peak in the small angle region and a diffuse halo in the wide angle region consistent with the existence of a disordered smectic mesophase. A smectic interlayer spacing d = 17.0 Å and an average intermolecular distance D ≈ 4.6 Å are evaluated. On further heating, d remains constant and above 420 K the small angle signal vanishes corresponding to the transition to the isotropic melt. On cooling to 400 K, a diffraction pattern constituted by a sharp inner reflection at d = 17.0 Å and a diffuse halo at D ≈ 4.6 Å is obtained which remains unaffected at room temperature (Fig. 2d).

Accordingly, a lock-in of the smectic structure in the glassy state can be realized. In all the smectic range the spacing of the innermost reflection is somewhat shorter than a half of the repeating unit length in the fully extended form (L/2 ≈ 20 Å), thus indicating that the structural element comprising each layer is constituted by one mesogenic group and one spacer segment. This behaviour appears to be consistent with the presence of an equal number of key atoms in both spacers placed in alternating fashion between the p-oxybenzoate diads.

Figure 3 reports the fibre X-ray pattern of the smectic mesophase of polymer C_5C_7. The inner layer reflections at d = 17.0 Å are exactly observed on a meridional line thus indicating that the polymer chain axis lies perpendicular to the smectic planes. The broad outer reflections are structured into two portions symmetrically placed above and below the equatorial line. Because the broad outer reflections result mainly from the lateral packing of the rigid mesogenic groups, they appear to be arranged with an appreciable tilt angle β of around $23 \pm 4°$ within a smectic layer. This type of smectic mesophase can be therefore classified as smectic C[9-10].

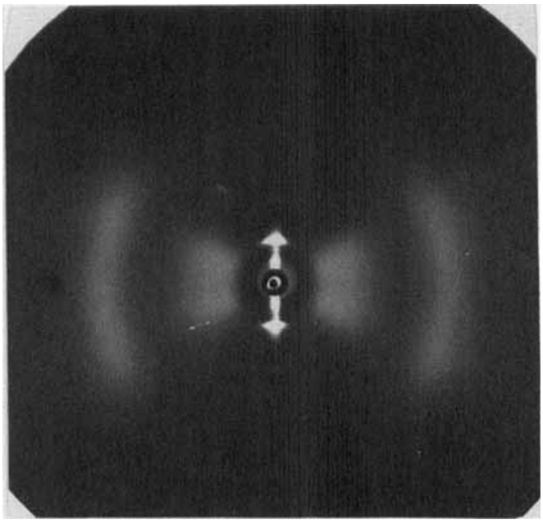


Figure 3 X-ray fiber pattern of the smectic mesophase of polyester C_5C_7. The fiber axis is in the vertical direction.

CONCLUSIONS

Evidences are provided for the existence in polyester C_5C_7 of an enantiotropic disordered smectic mesophase and a monotropic nematic mesophase. X-ray analysis indicates that only a half of the overall polymer repeating unit is comprised within a smectic layer. While polymer chain lies parallel to the layer normal, the mesogenic groups are tilted by about $\beta = 23°$ to it. Accordingly the smectic mesophase is recognized as unconventional smectic C. Polymer C_5C_7 does not crystallize from the anisotropic melt and a glassy unconventional smectic C phase is obtained at room temperature. This overall phase transition behaviour is very unusual in main chain liquid crystalline polymers and makes polyesters of general structure C_mC_n amenable to further investigation for a better understanding of their structure - properties relationships.

Acknowledgement

This work is performed with the support of Progetto Finalizzato CNR - Chimica Fine.

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