Synthesis and Preliminary Characterization of a New Fully Aromatic Mesogenic Polyester Containing a 2-Phenylbenzoxazole Group

U. Caruso, R. Centore, A. Roviello, and A. Sirigu*

Dipartimento di Chimica, Università di Napoli "Federico II", Via Mezzocannone 4, 80134 Napoli, Italy

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ABSTRACT: The synthesis of a new fully aromatic thermotropic polyester obtained by reaction of terephthalic acid and 2-[4-(acetyloxy)phenyl]-6-(acetyloxy)benzoxazole is described. A preliminary characterization of the polymer is reported, based on DSC, TGA, X-ray diffraction analysis, optical observations, and dynamic mechanical thermal analysis. The polymer as prepared is a semicrystalline material, with a glass transition of 181 °C, that melts at 408 °C to give a liquid crystal phase of probable nematic nature. Relevant chemical decomposition takes place in the temperature range 510–620 °C. A remarkable crystallinity has been observed also in samples obtained by cooling the liquid crystal phase. Fibers were obtained by melt extrusion which show a high degree of macroscopic orientation.

Introduction

Mesogenic polymers with a rodlike, fully aromatic structure are receiving considerable attention because of their use in the manufacture of materials having exceptionally good mechanical properties at high temperatures.

A rigid polyaromatic structure, particularly if it is constitutionally homogeneous, implies high melting temperature, and it is most usual that extensive thermal degradation may take place at temperatures lower than melting.[1]

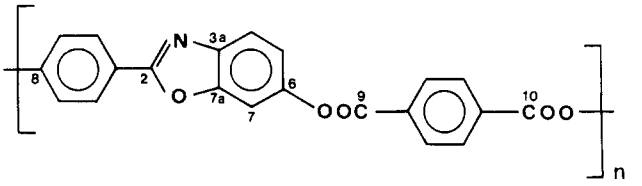
On the other hand, the same stereochemical features promoting high melting temperature are responsible for the very poor solubility of the polymers. This hampers their manipulation as lyotropic mesophases in nondegradative solvents. As a consequence, a considerable effort has been devoted to the design of polymer structures which favor acceptable melting temperatures and/or solubility without destroying the mesogenic character.

Inclusion of comonomers that increase the flexibility of the chain, interrupt its linearity, or enlarge its local cross section is an effective mean to depress melting temperature and allow thermotropic liquid crystalline behavior to show up within an adequate temperature range.[1] Insertion of flexible lateral substituents favoring solubility has also been considered as a modification of lyotropic polymers.[2]

Quite recently it has been shown that thermotropic mesomorphism may also be induced in fully aromatic homopolyesters based on complex rodlike diphenols or aromatic dicarboxylic acids which form ester bonds whose directions along the polymer chain are neither collinear nor parallel. This is the case, as an example, of the poly(ester imide)s reported by Kricheldorf et al.[3,4]

For such systems it may be expected that the head to tail constitutional disorder present along the polymer chain and the increased chain waviness, although still compatible with a mesophase to occur, allow lower melting temperatures and easier processability.

In the present paper we report the synthesis and the preliminary characterization of the benzoxazole-containing polyester



which is based on terephthalic acid and 2-[4-(acetyloxy)phenyl]-6-(acetyloxy)benzoxazole. As will be seen below, this polymer, notwithstanding its fully aromatic and homopolymeric structure, exhibits a well-defined thermotropic liquid crystalline behavior.

Aromatic polybenzoxazoles are well-known for their good thermal and oxidative stability;[5-8] in some cases lyotropic mesomorphism has been observed in such systems.[9,10] Low molar mass liquid crystals containing the benzoxazole moiety are also known.[11] However, as far as we know this is the first example of a thermotropic benzoxazole-containing liquid crystalline polyester.

The synthesis and the phase behavior of other classes of mesogenic polyesters containing benzoxazole, of either the fully aromatic type or semiflexible ones, will be reported in future publications.

Experimental Section

The homopolymer was synthesized by transesterification of terephthalic acid with 2-[4-(acetyloxy)phenyl]-6-(acetyloxy)benzoxazole. Terephthalic acid was purified through the dimethyl ester, which was prepared by reaction of terephthaloyl chloride (Fluka, >99%) with methanol; it was purified by several crystallizations from chloroform/ethanol and finally saponified.

The second monomer was synthesized through the multistep route reported in Scheme I.

Resorcinol 3-benzoate (step a), 6-nitroresorcinol 3-benzoate (step b), and 6-aminoresorcinol 3-benzoate (step c) were prepared according to procedures already described;[12,13] the remaining steps will be described in detail.

Step d. A total 5.0 g of 6-aminoresorcinol 3-benzoate was dissolved in 100 mL of boiling ethanol; to this was added a solution of 4.9 g of 4-(benzoyloxy)benzaldehyde (previously prepared by esterification of 4-hydroxybenzaldehyde with benzoyl chloride) dissolved in 100 mL of boiling ethanol. The resulting solution was stirred until a yellow, crystalline precipitate of Schiff base (IV) formed, which was recovered by filtration. Yield: 8.1 g (86%). Mp: 188 °C. IR (KBr): 3362 (s, OH), 1730 (vs, C=O), 1628 (s), 1597 (s), 1263 cm^{-1} (vs, CO).

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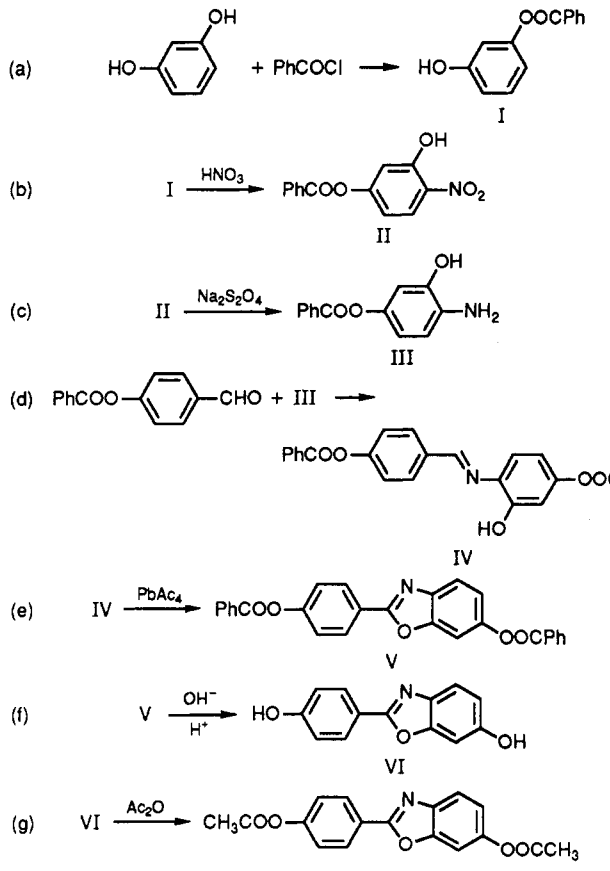
Scheme I



Step e. A total of 3.0 g of the Schiff base (IV) was dissolved in 150 mL of boiling chloroform, previously passed on activated alumina. To this solution, under stirring, was added 3.0 g of lead tetraacetate. The mixture was stirred until a solid residue of $Pb(Ac)_2$ formed, which was removed by filtration. The solution was concentrated, and a large volume of ethanol was added in order to precipitate V. Yield: 2.2 g (74%). Mp: 198 °C. IR (KBr): 1744 (vs, C=O), 1622 (m), 1601 (m), 1497 (s), 1475 (s), 1250 cm^{-1} (vs, CO).

Step f. A total of 4.1 g of V was dissolved in 120 mL of boiling ethanol; to this solution under stirring was added 6.0 g of potassium hydroxide, previously dissolved in 40 mL of water. To the boiling mixture was added gradually 500 mL of water, and the solution was refluxed for 30 min; then it was cooled to ambient temperature, acidified with dilute hydrochloric acid, and filtered to collect the final product (VI). Yield: 1.9 g (86%). Mp: 316 °C. IR (KBr): 3281 (s, OH), 1612 (s), 1594 (s), 1502 (s), 1482 cm^{-1} (s).

Step g. A total of 5.0 g of VI was dissolved in 60 mL of dry pyridine. To this solution, under stirring, was added 9.0 g of acetic anhydride. The mixture was heated and allowed to boil for 10 min, and then a large volume of ethanol (500 mL) was added. By cooling the resulting solution, 2-[4-(acetyloxy)phenyl]-6-(acetyloxy)benzoxazole precipitated as slightly tan needles. Purification was obtained by treatment of the chloroform solution with activated carbon and final precipitation with ethanol. Yield: 5.8 g (85%). Mp: 158 °C. ^1H and solid-state ^{13}C NMR data (Table I) are consistent with the formula and with values reported in the literature for 2-phenylbenzoxazole.[14] Anal. Calcd for $C_{17}H_{13}O_5N$: C, 65.59; H, 4.21; N, 4.50. Found: C, 65.41; H, 4.14; N, 4.47. IR (KBr): 1765 (vs, C=O), 1623 (m), 1607 (m), 1501 (s), 1484 (s), 1194 cm^{-1} (vs, CO).

Synthesis of the Polymer. Equimolar quantities of the two monomers (0.918 46 g of terephthalic acid and 1.721 72 g of 2-[4-(acetyloxy)phenyl]-6-(acetyloxy)benzoxazole) were mixed thoroughly by grinding in a mortar and transferred into a glass reaction vessel equipped with inlet and outlet tubes for argon. The reaction vessel was evacuated and purged with argon several times to remove all air, and then it was heated under reduced pressure (0.005 mmHg) for 30 min in an oil bath at 110 °C to dry the reactants. The flask was then removed from the oil bath and, under a flowing argon atmosphere, was placed into a metal bath (Sn) at 300 °C. Acetic acid evolving during the reaction was almost completely removed by the stream of inert gas passing through the vessel. After 30 min, the pressure was brought to 0.005 mmHg for 10 min. The vessel was then removed from the bath, and the temperature of the latter was raised to 360 °C. The reaction vessel was further evacuated and purged with argon several times, and, under a pressure of 0.005 mmHg, it was kept at 360 °C for 20 min. It was then removed, purged with argon and allowed to cool to ambient temperature to collect the final product which was slightly tan as already reported for other polybenzoxazoles.[5,6] Because of losses due to slight sublimation of the monomers at the beginning of the reaction and to nonquantitative recovery of the final material which strongly adhered to the walls of the reaction vessel, the reaction yield may be given only as a lower limit (>73%). The polymer (mp 408 °C) was insoluble in most organic solvents, including boiling pentafluorophenol and α-chloronaphthalene; it was only soluble in concentrated sulfuric acid, as already reported for other polybenzoxazoles,[5,6] but on recovering by precipitation a degradated material is obtained. Degradation probably involves acidolysis of the ester bond. Anal. Calcd for $(C_{21}H_{11}O_5N)_n$: C, 70.59; H, 3.10; N, 3.92. Found: C, 70.57; H, 3.26; N, 4.00. IR: 1744 (vs, C=O), 1624 (s), 1604 (s), 1496 (vs), 1477 (s), 1256 cm^{-1} (vs, CO).

Table I
Selected Solid-State ^{13}C NMR Chemical Shifts of the Polymer and of Monomer 2-[4-(Acetyloxy)phenyl]-6-(acetyloxy)benzoxazole[a]

atom	monomer	polymer
C8	148.5	149.1
C2	161.2	162.9
C3a	137.8	139.5
C6	146.9	147.0
C7	100.1	103.9
C7a	152.3	152.1
C9, C10	168.1, 170.4	162.9

[a] Chemical shifts are expressed in ppm and referred to TMS. Carbon numbering is as in the formula; for the monomer, C9 and C10 are the carbonyl carbons of the acetyloxy groups.

Solid-state ^{13}C NMR data are consistent with the structure of the polymer and are reported in Table I.

The differential scanning calorimetric analysis was performed using a Mettler DSC 20 apparatus, under nitrogen atmosphere. Indium, tin, and lead samples of high purity were used as standards to determine transition temperatures and enthalpies. Heating and cooling rates of 20 °C/min were used. Thermogravimetric analysis was performed using a Mettler TG 50 apparatus, under nitrogen atmosphere, at a heating rate of 20 °C/min. IR spectra were recorded using a Bruker IFS 66 FT spectrometer; for low molar mass compounds IR measurements were performed on KBr disks, while, for the polymer, compression-molded films were used. ^1H NMR measurements were performed using a Bruker AC 270-MHz spectrometer, while solid-state ^{13}C NMR measurements were performed on a Bruker AM 250 spectrometer. X-ray diffraction data collection was performed, using Cu Kα radiation, either photographically (flat film camera) or with the counter method (Philips powder diffractometer). Polarizing microscopy observations were made utilizing a Leitz microscope equipped with a Linkam microfurnace. Samples were examined under nitrogen atmosphere. The dyanmic mechanical thermal analysis was carried in a Polymer Laboratories DMTA apparatus, at a frequency of 10 Hz and a heating rate of 10 °C/min. Samples for dynamic mechanical analysis were prepared by compression molding of the as-prepared powders at 420 °C, followed by rapid cooling in air and subsequent annealing at 370 °C for 30 min. The samples obtained were about 0.3 mm thick and 4 mm wide.

Results and Discussion

The thermal behavior of the polymer is summarized in Figure 1, which reports the results of the differential scanning calorimetric analysis.

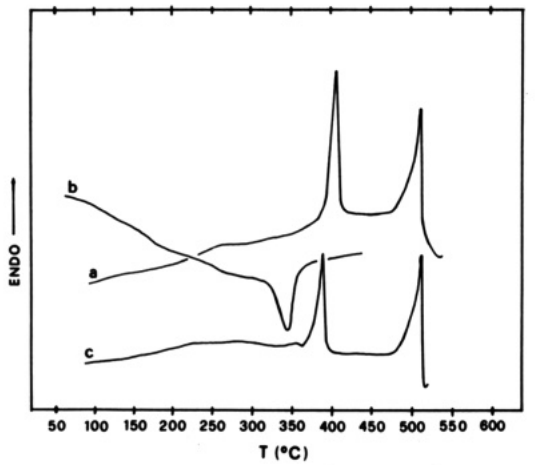


Figure 1. DSC thermograms of the polymer recorded at heating and cooling rates of 20 °C/min under nitrogen atmosphere: (a) heating cycle of the "as-prepared" polymer; (b) cooling cycle from the liquid crystal phase (the polymer sample has not undergone isotropization); (c) heating cycle of a melt-crystallized sample (same sample as for curve b).

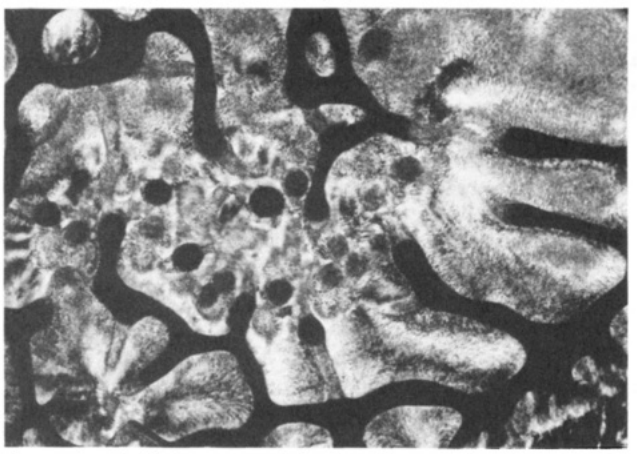


Figure 2. Optical texture of the liquid crystal phase at 420 °C. Cross polarizers. Dark regions correspond to thicker portions.

Two endothermic signals are observed in the DSC curve, on heating, of the "as-prepared" polymer (Figure 1a). The first, peaked at 408 °C, corresponds to the transition from the crystal phase to the liquid crystal phase, with an enthalpic change of 29 J/g. The second endothermic signal, peaked at 518 °C, might correspond to the isotropization of the liquid crystal phase. This pattern is consistent with the results of the optical observations; in fact, in the temperature range between the two endothermic signals, the observation at the polarizing microscope clearly indicates the optical anisotropy of the liquid phase (Figure 2), although no specific texture was recognized.

Near the temperature corresponding to the second endothermic signal, the polymer begins to decompose. Figure 3 reports the results of a thermogravimetric analysis, performed in the same experimental conditions of the DSC scans, whose curve is also shown superimposed. The observed weight loss is small (less than 2%) up to 450 °C, which is well beyond the melting temperature. Although the weight loss is still low at the onset of the second endothermic signal (2.3% at 470 °C), however, at the temperature corresponding to the peak (518 °C), it has risen to 11.7% and the rate of decomposition is close to its maximum value. Therefore, while the onset temperature of the transition to the isotropic liquid is safely defined, the peak temperature is not.

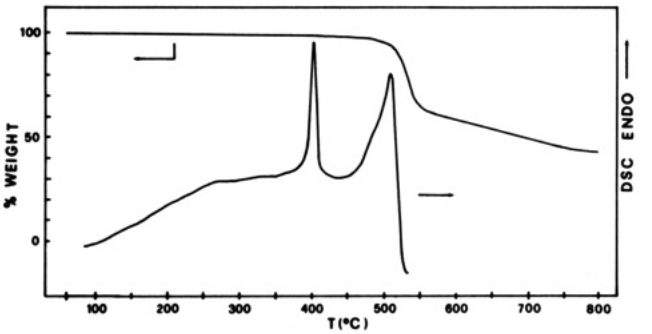


Figure 3. Thermogravimetric analysis of the as-prepared polymer at a heating rate of 20 °C/min, nitrogen atmosphere. The DSC thermogram of the polymer recorded in the same experimental conditions is also shown.

On cooling from the liquid crystal phase a polymer sample that has not undergone previous isotropization, crystallization occurs in the temperature range 374–290 °C (Figure 1b). The second heating curve (Figure 1c) is basically similar to the first one, with the exception of the melting temperature which is lowered to 392 °C. Also the enthalpic change at melting is somewhat smaller in the second heating run (21 J/g). These features that indicate a moderate decrease of crystallinity are at variance with the behavior reported in the literature for several fully aromatic thermotropic polyesters, which generally show the melting endotherm only in the first heating run.[15]

The X-ray powder diffraction pattern recorded for the as-prepared polymer is typical of a semicrystalline material, as it contains several diffraction peaks up to sin $(\vartheta/\lambda) = 0.252$ Å^{-1}, superimposed to a broad halo included between $2\vartheta = 15°$ and $2\vartheta = 30°$. This finding, which is consistent with the DSC analysis, may be connected with the solid-state nature of the polymerization process. A rough evaluation of the degree of crystallinity of the as-prepared polymer from the powder diffraction pattern, recorded by the counter method, yielded a value of 44%.

The degree of crystallinity of the material, however, may be greatly enhanced by annealing procedures, leading to higher melting temperatures and enthalpies. As an example, after annealing at 380 °C for 30 min a melt-crystallized sample, the melting temperature rises to 418 °C and the melting enthalpy is also significantly increased (40 J/g), while the small observed weight loss (1.2%) may be due to completion of the polymerization process.

Unambiguous evidence of the glass transition was not afforded by DSC measurements. However, the dynamic mechanical thermal analysis clearly showed this transition at 181 °C (Figure 4). This value is comparable with that reported by Kricheldorf et al. for a structurally similar poly(ester imide) (polymer **3a** in ref 3). However, as far as the thermal behavior of the latter polymer is concerned, a significant difference with respect to our polymer is the absence of a sharp melting point, notwithstanding its claimed semicrystalline nature.[3]

By extrusion of the polymer in the liquid crystal phase, followed by rapid cooling in air, fibers were obtained, which have been investigated by X-ray analysis. Fibers as obtained are poorly crystalline, but the degree of crystallinity may be enhanced by annealing close to the melting temperature, as previously discussed. Figure 5 reports the X-ray diffraction pattern recorded at room temperature for a fiber after annealing at 370 °C for 30 min. A high degree of macroscopic orientation of the polymer chains is clearly present. The identity period of the chain, as measured from the fiber spectrum, is $c = 36.1$ Å. This value, taking literature values for bond lengths and

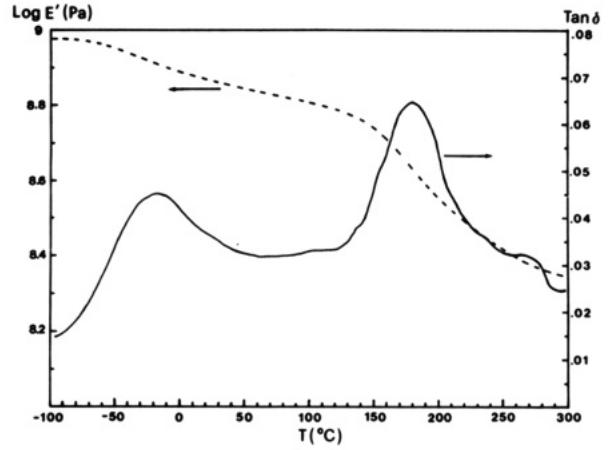


Figure 4. Dynamic modulus (E') and loss tangent (tan δ) of the polymer at 10 Hz. Heating rate of 10 °C/min.

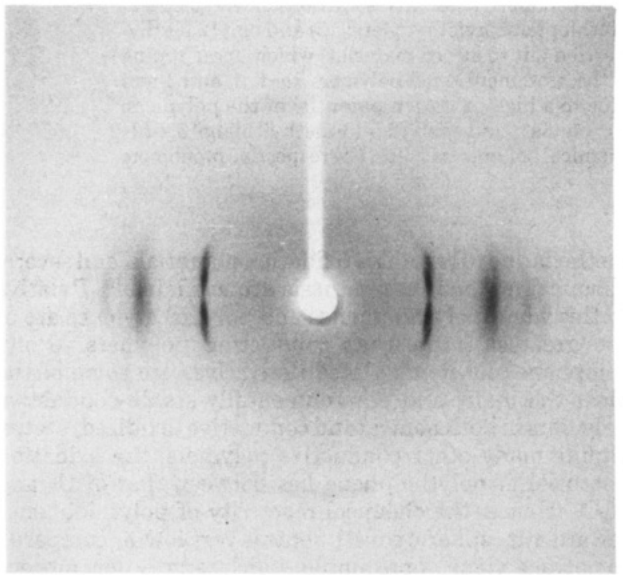


Figure 5. X-ray diffraction photograph of a fiber of the polymer previously annealed at 370 °C for 30 min. Room temperature.

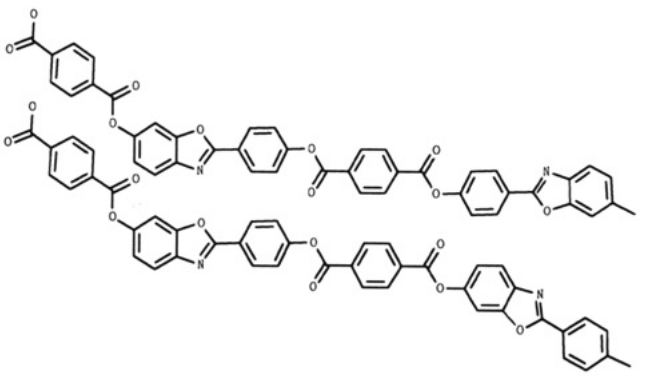


Figure 6. Sketch of possible sequences of monomeric units compatible with the observed identity period.

angles,[16,17] may well account for the length of a portion of the polymer chain which contains two monomeric units connected in extended conformation according to the two sequences reported in Figure 6. Several conformations involving different torsion angles around O–C_6H_4 bonds (which are likely to occur[17]) all correspond to identity periods coincident with the observed value of c, within the experimental error.

The liquid crystalline phase exhibited by the polymer is probably of the nematic type. The collection of direct X-ray diffraction evidence of this feature within the appropriate temperature range was discarded as unreliable because of some chemical degradation affecting the polymer. As an example, a weight loss of 6.2% was measured for a sample heated at 20 °C/min up to 420 °C and held at that temperature for 30 min. However, significant although indirect structural evidence in favor of the nematic structure is available. The X-ray diffraction pattern recorded at ambient temperature from a fibrous sample whose degree of crystallinity is about 13% (this value was estimated by comparison of its melting enthalpy with that measured for the as-prepared polymer) does not show any low-angle Bragg reflection, at least for lattice distances not larger than 56 Å. This means that the noncrystalline phase (~87% of the sample), formed on quenching the mesophase, has no structural periodicity of the smectic nature.

In conclusion, the possibility of obtaining highly oriented semicrystalline fibers by melt extrusion is rather uncommon in the field of fully aromatic mesogenic linear homopolyesters, which are usually infusible. This feature, together with the high melting temperature and the good thermal stability, suggests that this polymer is an interesting candidate for use in the field of liquid crystalline polymeric materials for structural applications.

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Registry No. III, 91271-40-8; IV, 139407-72-0; V, 139407-73-1; VI, 139407-74-2; $PhCO_2C_6H_4$-*p*-CHO, 5339-06-0; 2-[4-(acetyloxy)phenyl]-6-(acetyloxy)benzoxazole, 139407-75-3; (2-[4-(acetyloxy)phenyl]-6-(acetyloxy)benzoxazole)(terephthalic acid) (copolymer), 139407-76-4.