

## POLYESTER-AMIDES WITH LIQUID-CRYSTALLINE PROPERTIES

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Some new polyester-amides were prepared by polycondensation reaction of 1,8-diaminooctane or 1,12-diaminododecane with diacid chlorides containing preformed ester groups. These polymers were characterized by DSC, polarized light optical microscopy, X-ray diffractions, FTIR and GPC. They show thermotropic liquid crystalline properties and are easily soluble in N-methylpyrrolidinone.

### INTRODUCTION

The polyester-amides are a particular class of compounds possessing a special structure due to the regular presence of ester and amide groups in the same macromolecular chain, which gives them the properties intermediate between the polyester and polyamide. Their rigidity caused by the double bond character of the amide group coupled with extensive hydrogen bonding influences ordering of polyester-amides.<sup>1, 2</sup> Polymeric liquid crystals are classified in two major groups: one is characterized by main chain mesomorphicity and the other exhibits liquid crystallinity due to the nature of its side groups. The onset of liquid-crystallinity behaviour of the main-chain mesomorphicity may occur in the bulk due to the temperature changes (termed thermotropic), or in solution as a result of changes in concentration (called lyotropic). According to the nature of the mesogenic groups and the interaction giving rise to mesomorphic behaviour, the main chain polymeric liquid crystals are divided into three major subgroups. The first subgroup consists of rigid or semirigid chain of macromolecules having rather large persistence length and the same average rigidity along the entire chain. This rigidity may arise from the aromatic backbone with rings connected in the *para* position by the groups such as amide, ester, trans-vinylene, azo, azoxy and azomethines, to

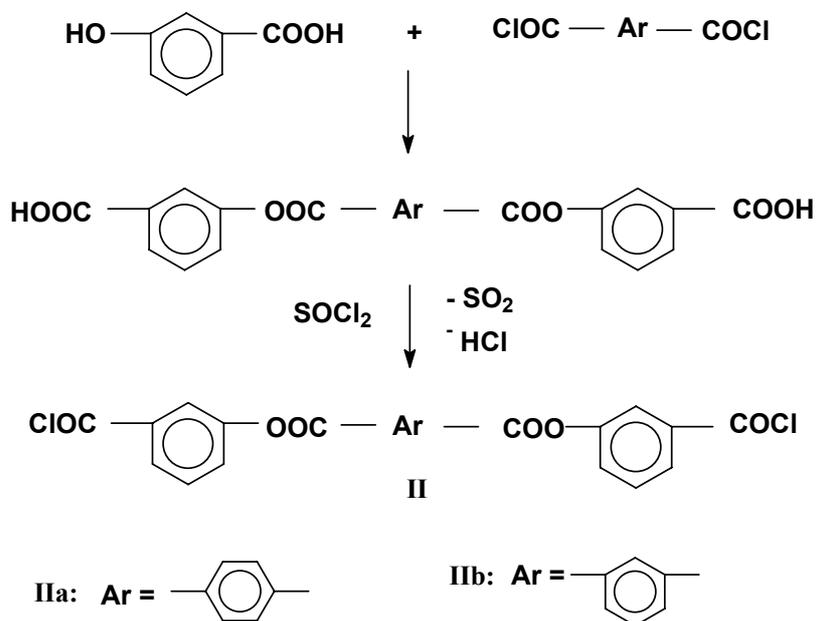
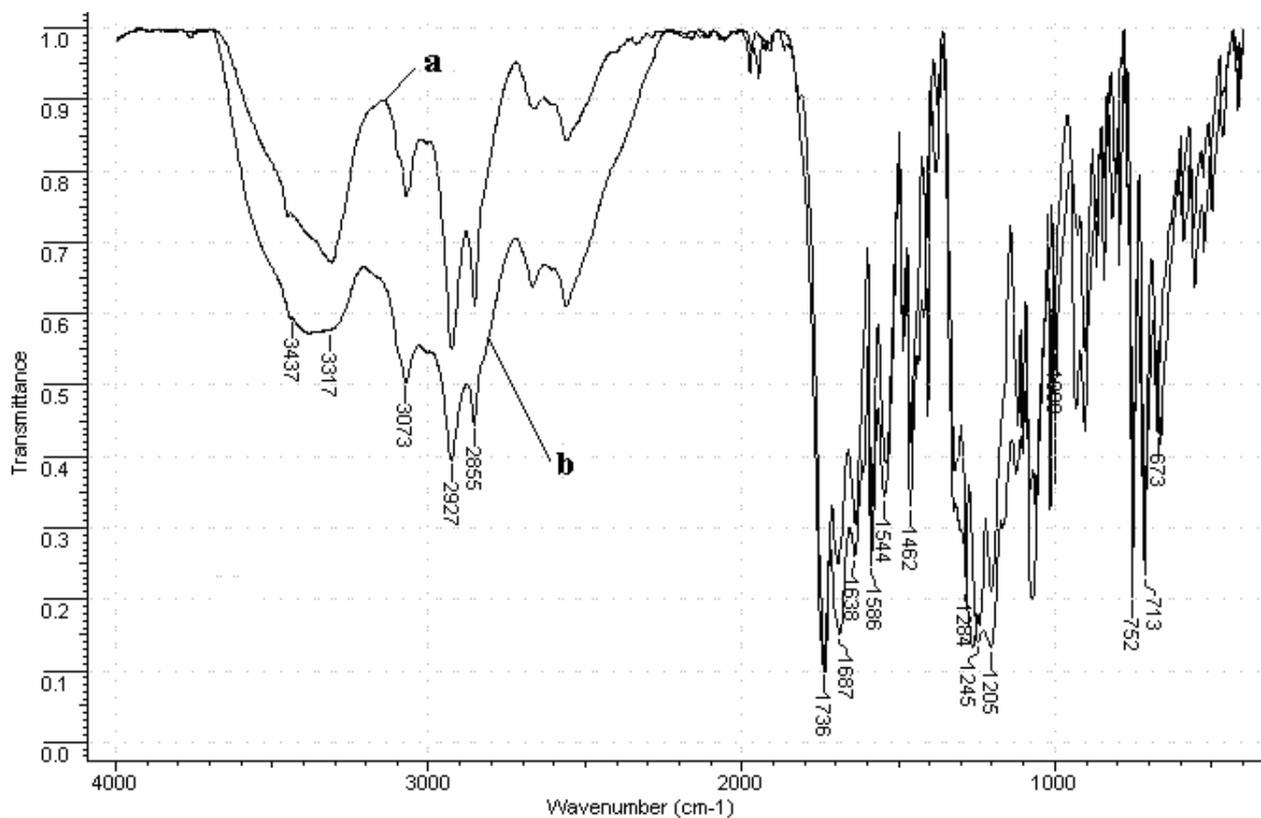
render them rectilinear or collinear.<sup>3-6</sup> When the bonds are replaced by polymer-polymer interchain hydrogen bonds, liquid-crystalline ceases to exist and the polymer precipitates out in a crystalline, semicrystalline or amorphous state. This phase change is utilized in spinning process from mesomorphic solution of highly oriented polymer fibers such as poly(*para*-phenyleneterephthalamide). A similar phase change occurs during the spinning of thermotropic polyesters into highly anisotropic fibers, except that no hydrogen bonds are involved and no solvent is removed.<sup>7-10</sup>

The second subgroup of main chain polymer liquid crystalline is characterized by chains consisting of rodlike mesogenic segments connected by flexible spacers. In order to attain liquid crystallinity, the axial ratio,  $x$ , of the rodlike segments must not be smaller than about 3.<sup>11</sup> The flexible spacer along the chain must be sufficiently long to allow for complete, or very large positioned and directional independence of each rodlike segment from its neighbours along the chain. Too short spacers hinder the onset of the mesomorphic behaviour.<sup>5,12</sup> The necessary axial ratio of the mesogenic segments is usually obtained by the segments comprising at least two *para*-substituted aromatic rings connected directly or through a substantially rigid group such as amide or ester. The important structural feature of the rodlike segments is their axial ratio which calls

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Scheme 2 – Synthesis of the diester-diacid chlorides, **II**.Fig. 1 – FTIR Spectra of the polymers **IIIa** and **IIIb**.

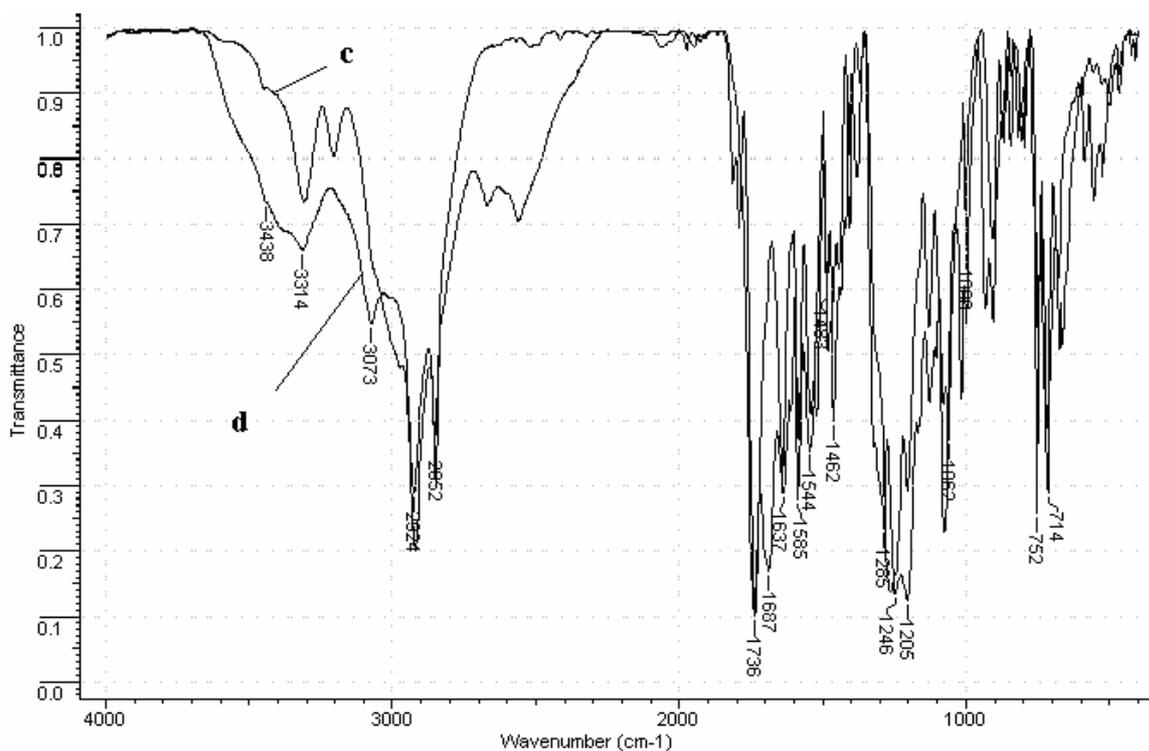
Fig. 2 – FTIR Spectra of the polymers **IIIc** and **IIIId**.

Table 1

Properties of the polymers **III**

Polymer	Mn (g/mol)	Tcr-lc °C	Tlc-is °C
<b>IIIa</b>	3300	150	310
<b>IIIb</b>	2750	140	270
<b>IIIc</b>	2150	150	280
<b>IIIId</b>	2400	115	240

The thermal transitions of the present polymers have been studied by differential scanning calorimetry. Fig. 3 presents DSC heating traces for polyester-amides **IIIa-d**. It can be noted that each polymer exhibited a transition temperature from crystalline phase to liquid crystalline one (Tcr-lc) and a transition temperature from liquid crystalline phase to the isotropic one (Tlc-iz). Moreover, the existence of multiple endotherms in DSC heating scans concomitantly with a birefringent flowing mass in between or above these transitions indicated the presence of thermotropic liquid crystallinity. The isotropization temperature of polyester-amides which contain eight methylene units (polymers **IIIa** and **IIIb**) is higher than that of polyester-amides with twelve methylene units (polymers **IIIc** and **IIIId**). On the other hand, if we

compare the isotropization temperature of the polyester-amides with the same number of methylene units (eight and twelve, respectively) it is seen that polymers which have the aromatic rings connected in *meta*-position (polymers **IIIb** and **IIIId**) showed lower values.

Optical textures in polyester-amides were characterized by polarized light optical microscopy (POM). The textures of the polyester-amides are also dependent on the length of the alkylene groups in the diamine comonomer. At heating of polyester-amides with eight number of methylene units the birefringent mass appears with needlelike entities (Fig. 4, polymers **IIIa** and **IIIb**) while in the case of polyester-amides with twelve methylene units a grainy texture is clearly evidenced (Fig. 4, polymers **IIIc** and **IIIId**).

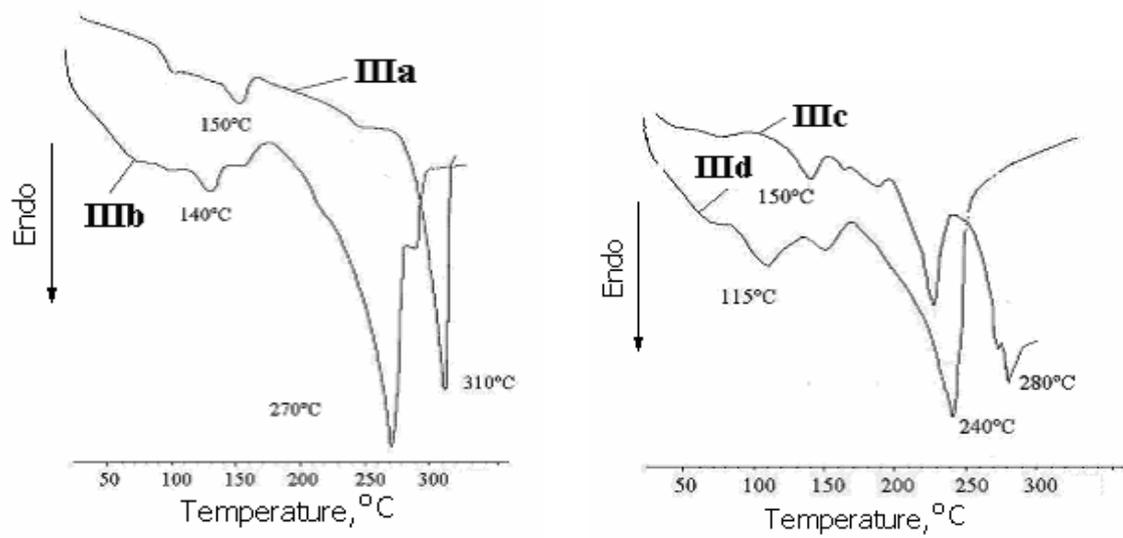


Fig. 3 – DSC curves of the polymers **IIIa – d**.

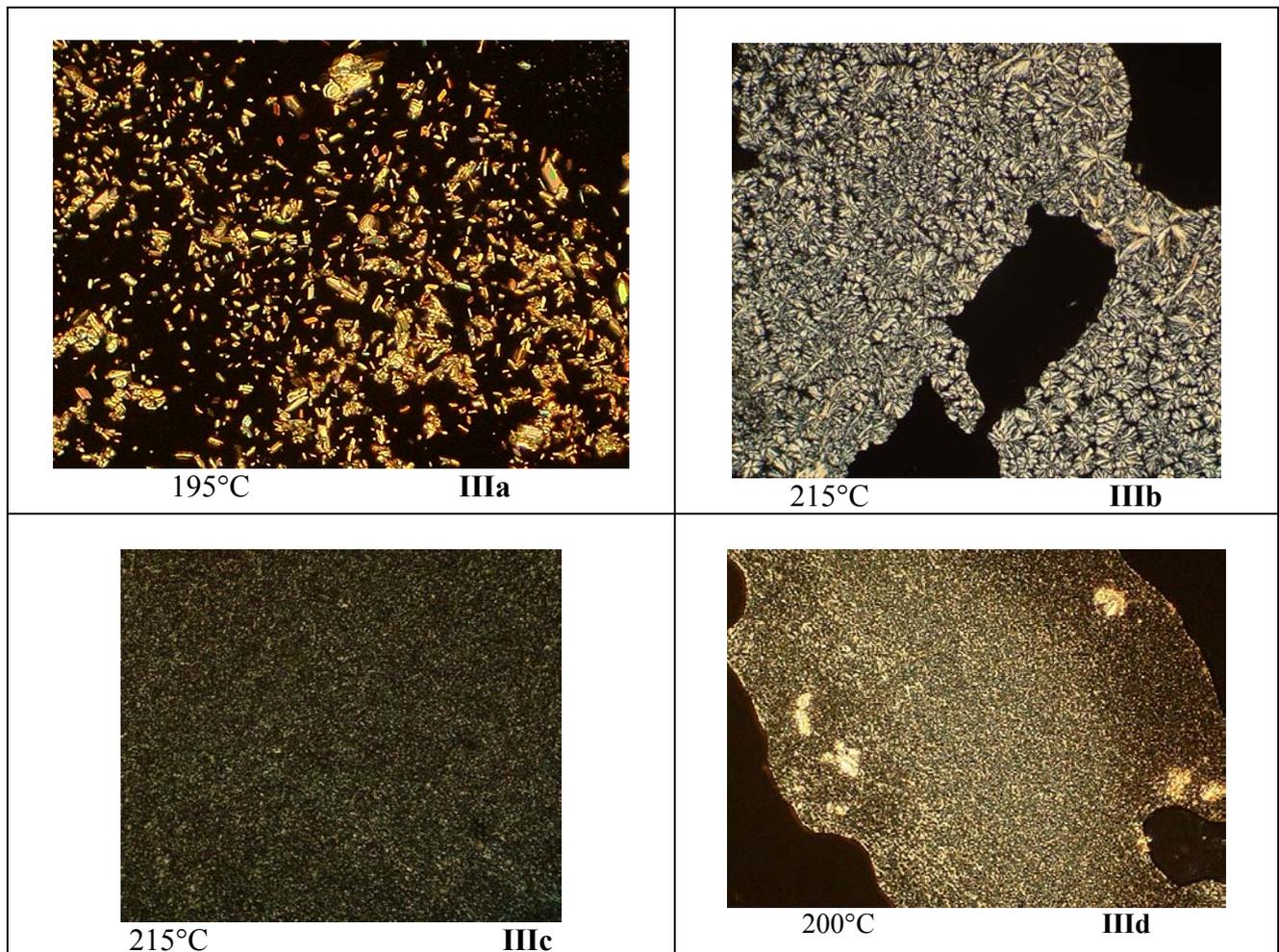


Fig. 4 – The optical textures of the polymers **IIIa-d** at different temperatures, original magnification 200x.

The X-ray diffraction studies showed essentially the same patterns (Fig. 5). The strong

and sharp diffraction peak at 15 Å indicates a strong tendency toward ordering. This X-ray

observation is in agreement with the DSC results shown in Fig. 3. Furthermore, from these figures is evident that the crystallinity of the polyester-

amides **IIIa** and **IIIb** is higher in comparison with the crystallinity of the polymers **IIIc** and **III d**.

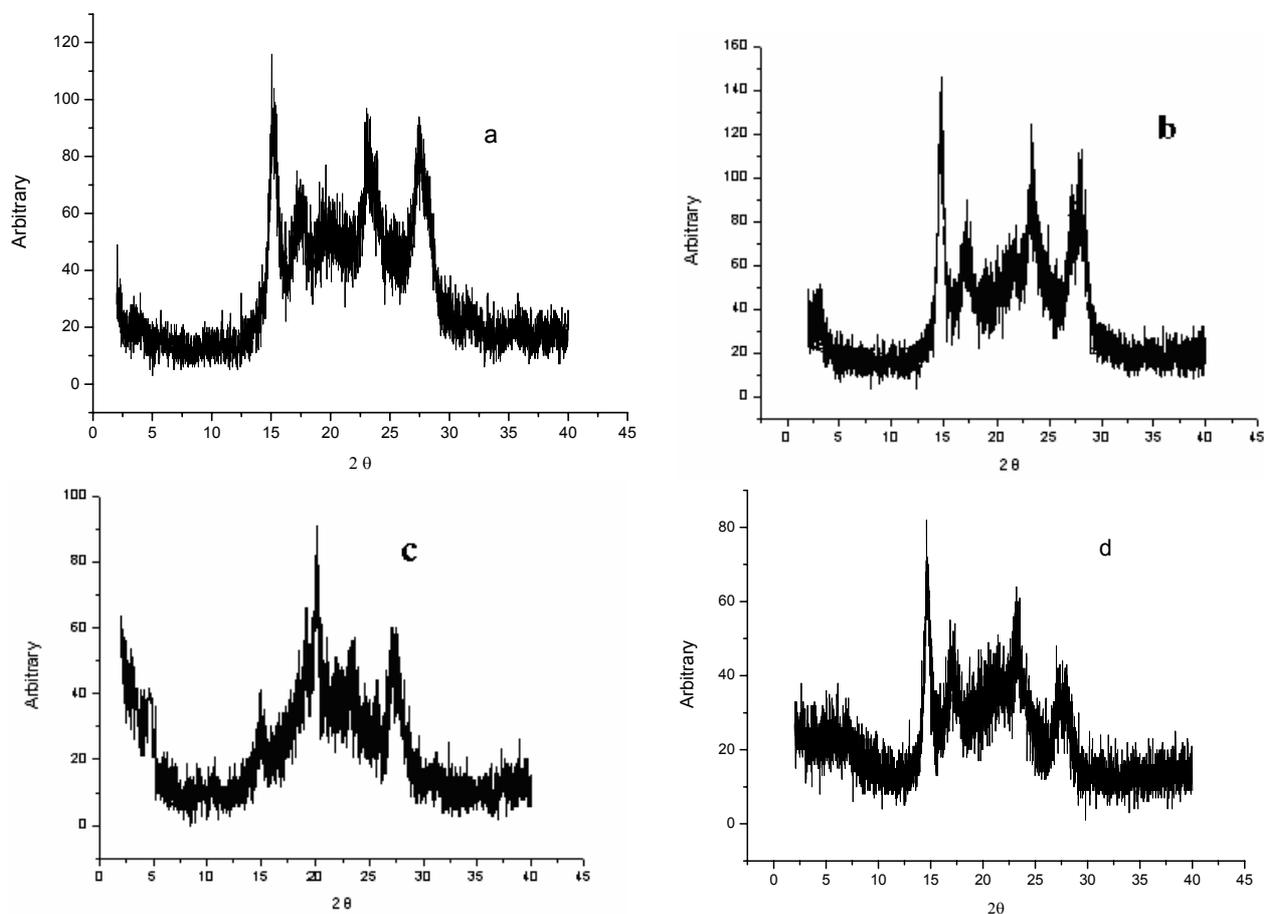


Fig. 5 – The X-ray diffraction of the polymers **a-d**.

## EXPERIMENTAL

### Starting materials

N-methylpyrrolidinone (NMP), (Merck) was dried over phosphorous pentoxide and distilled under reduced pressure. Thionyl chloride (Riedel de Haen) was freshly distilled before use. 3-hydroxybenzoic acid (Merck), p-aminophenol, terephthalic and isophthalic acid, sodium hydroxide, hydrochloric acid, pyridine were provided by different commercial sources and used as received.

### Diacid chloride with ester groups

1,8-Diaminooctane (**Ia**) and 1,12-diaminododecane (**Ib**) from Fluka were used as received.

Terephthaloyl-bis(3-oxybenzoyl-chloride) and isophthaloyl-bis-(3--oxybenzoyl-chloride) **II**, were prepared by treating the corresponding diester-dicarboxylic acids with thionyl chloride; the dicarboxylic acids have been obtained from the reaction of 3-hydroxybenzoic acid with terephthaloyl chloride or isophthaloyl chloride, respectively, by following a procedure previously reported (Scheme 2).<sup>14,15</sup> After recrystallization from chloroform, the melting points

correspond to those found in the literature: m.p. **IIa**: 239-241°C; **IIb**: 131-133°C.

### Synthesis of the polymers

Low temperature solution polycondensation reaction of equimolar amounts of aliphatic diamines (**I**) with diacid chlorides (**II**) which contain preformed ester groups was carried out in NMP using pyridine as acid acceptor and gave the polyester-amides, **III**, as shown in Scheme 1.

A general procedure is described below: in a three-necked flask equipped with mechanical stirrer and N<sub>2</sub>-inlet and outlet 0.396 g (0.002 mol) of diamine **Ia**, 16 ml NMP and 0.5 ml pyridine were placed, and the mixture was stirred under N<sub>2</sub> atmosphere. The solution was cooled to -5°C and 0.886 g (0.002 mol) of diacid chloride **IIa** was added as a fine powder under rapid stirring. The concentration of the solutions, after the addition of the diacid chloride, was 8.0% solids. The flask content was kept below 0°C for 30 min, then the cooling bath was removed and the reaction mixture was allowed to reach the room temperature and stirred further for 4 h and then at reflux temperature for 2 h. Approximately half of the polymer solution was used to prepare thin films. The other half was poured into water to precipitate the polymer. The resulting

solid was filtered, washed twice with water and once with ethanol, and dried under vacuum at 105°C for 2-3 h.

### Measurements

The FTIR spectra were recorded on a Perkin-Elmer spectrometer using KBr pellets.

The transition temperatures were measured on a Mettler DSC 12E apparatus in nitrogen with a heating rate of 20°C/min. Approximately 7 to 10 mg of the polymers were crimped in Al pans and run in nitrogen purge of 50 ml/min with a heat-cool-heat profile from 30°C to 320°C at 20°C/min, with 3 min isothermal stabilization times at the temperature extremes.

The average molecular weights of the polymers were determined by means of gel permeation chromatography (GPC) using a Waters GPC apparatus, provided with Refraction and Photodiode array Detectors and Phenomenex-Phenogel MXN column. Measurements were carried out with polymer solutions having 0.2% concentration, using dimethylformamide as eluent. Polystyrene standards of known molecular weight were used for calibration.

Polarized light optical microscopy was performed in an Olympus B20 microscope with a Linkam TP92 hot stage. Wide-angle X-ray diffraction (WAXD) patterns were collected at ambient temperature from powdered samples by using a Bruker AD8 ADVANCE X-Ray Diffractometer, operating in parafocus mode and using monochromatized copper K $\alpha$  radiation.

### CONCLUSIONS

New polyester-amides have been synthesized and characterized. These polymers showed thermotropic behaviour with transition from crystal

to liquid crystal in the temperature range of 115-150°C and with the isotropization temperature in the range of 240-310°C. The increasing of the number of methylene spacers and the presence of the *m*-incatenation in the polymers led to the decreasing of the isotropization temperature.

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