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Synthesis, characterization and morphology of new aliphatic-aromatic copolyesters based on trans-1,3-indanediol

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ABSTRACT

In this article we report the study on the synthesis and thermal characterization of a new family of aliphatic/aromatic copolyesters that incorporate pure isomer trans-1,3-indanediol. The aromatic diacid terephthaloyl chloride and aliphatic diols HO-(CH₂)_n-OH with various methylene lengths have been used as co-monomers. The aliphatic diols employed in this study are 1,3-propanediol, 1,4-butanediol, 1,7-heptanediol and 1,10-decanediol. The relevant properties of the synthesized aliphatic-aromatic copolyesters involve viscosity measurements, IR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The obtained aliphatic-aromatic copolyesters present thermostable nature and semi-crystalline properties.

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Copolyesters; synthesis; trans-1,3-indanediol; properties; crystallinity

Introduction

Polyesters are materials with versatile physical and chemical properties. The diols and diacids monomers required for the synthesis of polyesters are diverse and varied. It is well known that the modulation of the molecular structure of polyesters allows the adaptation of their thermo-mechanical properties and their biodegradation behavior.^[1–6]

The influence of *cis*- and *trans*-isomers of the monomers on the physico-chemical properties of the resulting polyesters is a particularly interesting problem.^[7–11] Indeed, the stereochemical variation of the monomers gives rise to differences in the thermal properties of the resulting polyesters. For example, the use of pure *trans* 1,4-cyclohexanedicarboxylic acid (*trans*-CHDA) leads to polymers with a high melting temperature. It should be noted that, the structure of *trans*-CHDA is regular while that of its *cis*-counterpart is irregular.^[12–13] One can also cite the series of experiments carried out by authors^[14] to study the effects of *cis/trans* isomers of 1,4-cyclohexanedimethanol on the yield and properties of the obtained cyclic oligomers prepared by reaction of 1,4-cyclohexanedimethanol with terephthaloyl chloride^[14].

In our previous study, we have synthesized indanediol as 90/10 *cis/trans* isomeric mixture, which was used as building block in the synthesis of new polyester in combination with an aromatic acid terephthaloyl chloride.^[15] We also investigated the influence of using pure *cis* 1,3-indanediol as a building unit in the synthesis of a new aliphatic-aromatic copolyester obtained by polycondensation.^[16] The obtained polyesters showed good thermal stability as

evident from thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) measurements that revealed the existence of glass transition and melting temperatures. These polyesters exhibit semi-crystalline properties.^[16] Our growing interest in the structure of indanediol led us to explore the pure isomer trans-1,3-indanediol as a monomer for the synthesis of a variety of copolyesters. This is of interest because most recent literatures reveal that the polymers containing indan moieties are generally used in the preparation of dense membranes.^[17–19] It is important to note that the polymers based on trans-1,3-indanediol have not been described in the literature so far. The aim of this study is the synthesis of some novel copolyesters that incorporate pure isomer trans-1,3-indanediol as well as aliphatic diols HO-(CH₂)_n-OH. The following flexible diols: 1,3-propanediol, 1,4-butanediol, 1,7-heptanediol, and 1,10-decanediol have been used with aromatic diacid terephthaloyl chloride. The stoichiometric proportion of aromatic-aliphatic diols and diacid used is 0.5/0.5/1. All polyesters have been obtained with yields varying from 62 to 88%. The obtained polymers were characterized by various techniques such as FTIR, viscosities, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

Experimental section

Materials

Trans-1,3-indanediol is synthesized according to the procedure described in our previous work.^[16] Terephthaloyl chloride was purified by recrystallization from hexane. 1,3-Propanediol, 1,4-butanediol, 1,7-heptanediol, 1,10-decanediol, *N,N*-dimethylformamide (DMF) and pyridine were used without further purification. 1,1,2,2-tetrachloroethane (TCE) was dried by molecular sieves and distilled before being used.

Characterization techniques

Fourier transform infrared (FTIR) spectra of the polymers were recorded on a Bruker IFS 45 spectrometer (Bruker Corporation, Billerica, MA, USA) in 4000–500 cm⁻¹ wavenumber range by using KBr pellets. The inherent viscosities of the polymers were measured using an Ubbelohde viscometer at 0.5 dL/g concentration in DMF and at 25 °C. TGA was carried out with the help of a TGA 2950 apparatus from TA instruments. An empty alumina crucible was used as reference. Polymer samples were heated at ambient temperature to 500 °C at 10 °C/min under nitrogen flow. DSC measurements were carried out on DSC 2910 (TA Instruments) under nitrogen flow. The polymer samples were heated up to 250 °C, cooled down to -150 °C and heated up again to 250 °C at 20 °C/min. The glass transition temperatures *T*_g, the melting temperatures *T*_m, and the cold crystallization temperatures *T*_c were also measured. X-Ray diffraction (XRD) data were recorded on a Siemens D5000 (Siemens) diffractometer using CuK α radiation (1.5406 Å) at room temperature. Scanning electron microscopy of copolyesters was obtained with a JEOL JMS8 instrument (JEOL Solutions, USA).

Polymer synthesis

Synthesis of homopolyester

Trans-1,3-indanediol (6.66 mmol) was dissolved in 60 mL of 1,1,2,2-tetrachloroethane (TCE) as solvent and 1.6 mL of Pyridine. Then a solution of terephthaloyl chloride (6.66 mmol) in TCE was slowly added within 5 min through the funnel at room temperature under vigorous stirring. The mixture was stirred at room temperature for 25 min, and heated up to 80 °C for 5 h.

The precipitate was filtered off and washed several times with water, ether, and acetone. The obtained polymer dried under vacuum at 45 °C.

Synthesis of copolyesters

The procedure of polymerization used to prepare homopolyester described above was also used for the synthesis of copolyesters. The stoichiometric proportion of diols (aromatic aliphatic) and diacid used is 0.5/0.5/1. Trans 1,3-indanediol (3.33 mmol) with 1,7-heptanediol (3.33 mmol) in 60 mL of 1,1,2,2-tetrachloroethane (TCE) as solvent, 1.6 mL of pyridine was added into the flask. A solution of terephthaloyl dichloride (6.66 mmol) in the solvent was slowly added within 5 min through the funnel at room temperature with vigorous stirring. The reaction mixture was stirred for 25 min at 25 °C and then the whole mixture was kept at 80 °C for 5 h. The precipitate was filtered off and washed several times with water, ether and acetone. The obtained polymer dried under vacuum at 45 °C.

Results and discussion

Monomer and polymer synthesis

The isomers of 1,3-indanediol were separated by using the column chromatography method with a methanol:chloroform (1:9) mixture used as solvent.^[16] The obtained pure isomer *trans*-1,3-indanediol used in the present investigation is characterized by different methods such as NMR (¹H, ¹³C).

As far as the synthesis of polymers is concerned, we have adopted the following procedure. First, we synthesized homopolyester derived from pure *trans*-1,3-indanediol with terephthaloyl chloride by solution polycondensation. Then, we synthesized copolyesters by incorporating aliphatic units using the following aliphatic diols HO-(CH₂)_n-OH such as 1,3-propanediol; 1,4-butanediol; 1,7-heptanediol and 1,10-decanediol in stoichiometric conditions. The stoichiometric proportion of aromatic-aliphatic diols and diacid used is 0.5/0.5/1. The polycondensation was carried out in the presence of 1,1,2,2-tetrachloroethane as solvent and of pyridine as an acceptor of HCl. Scheme 1 illustrates the reaction of polycondensation, the nomenclature of each compound and the abbreviation adopted in this work. All polyesters have been obtained with yields varying from 62 to 88%.

Characterization

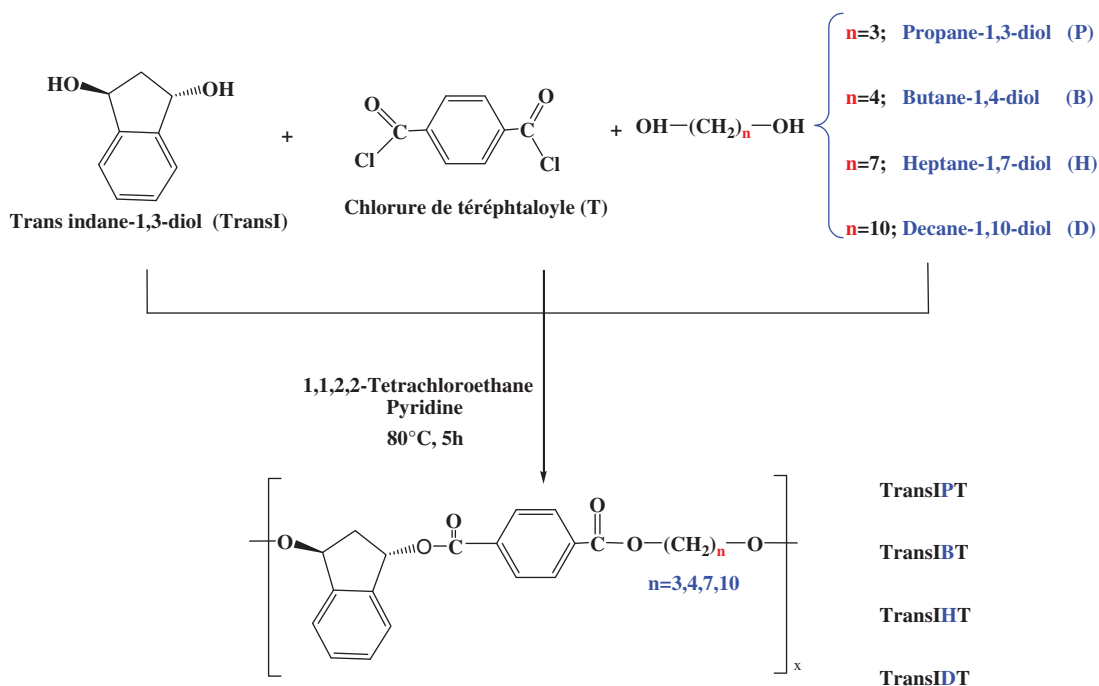
FT-IR study

The FT-IR spectra of homo- and copolyesters based on *trans*-1,3-indanediol are grouped and shown in Figure 1.

All the samples were characterized by strong absorption band at 1726–1699 cm⁻¹ characteristic of C=O stretching, which is also an indication of esterification. The second characteristic band is C–O–C stretching which is observed in the range of 1269–1292 cm⁻¹.

Detailed analysis of the FTIR spectra (Figure 2(c)) in the region 1726–1699 cm⁻¹ indicates that the corresponding band appears as a shoulder-type band in the various copolyesters, probably due to the presence of two types of carbonyl ester OC=O. From these initial observations, it is possible to confirm the progress of the copolymerization reaction.

Aliphatic C–H stretching is observed at 2974–2544 cm⁻¹ as sharp peaks. The number of sharp peaks increases from TransIPT to TransIDT as shown in Figure 2(a). The peaks corresponding to C–H bonds deformation movements appear in the range of 1435–1415 cm⁻¹ with an increase in the number of peaks from TransIPT to TransIDT, as shown in Figure 2(b). This phenomenon is due to the increase of the methylene groups in the aliphatic diols.



Scheme 1 Synthesis procedure of copolyesters, nomenclatures of each compounds and abbreviation adopted in this work.

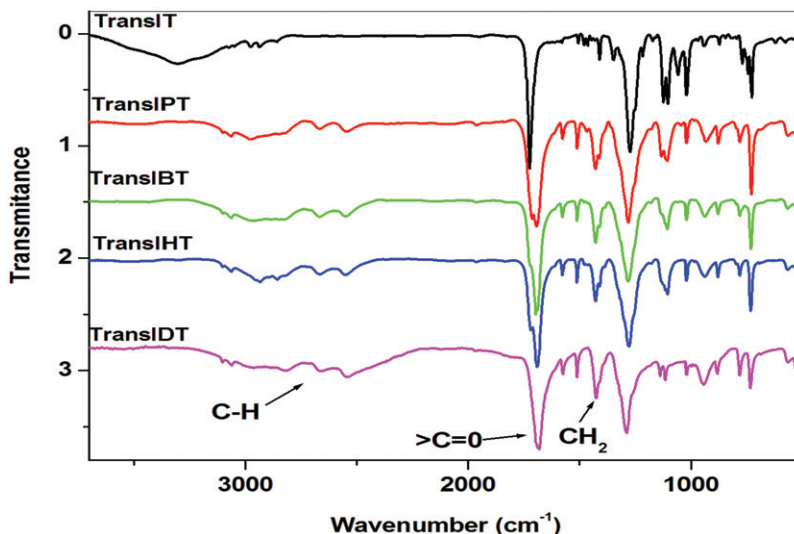


Figure 1. The FT-IR spectra of homo- and copolyesters.

Differential scanning calorimetry (DSC)

Thermal analysis of the synthesized copolyesters has been done using DSC. The DSC thermograms of transIPT, transIBT, transIHT and transIDT are reported in Figure 3. Note that, the transIHT copolyester obtained with heptanediol has a negative glass transition temperature -11°C . This result suggests that incorporating heptanediol increases the flexibility of the main chain in transIHT copolyester. It should be noted that negative value of glass transition

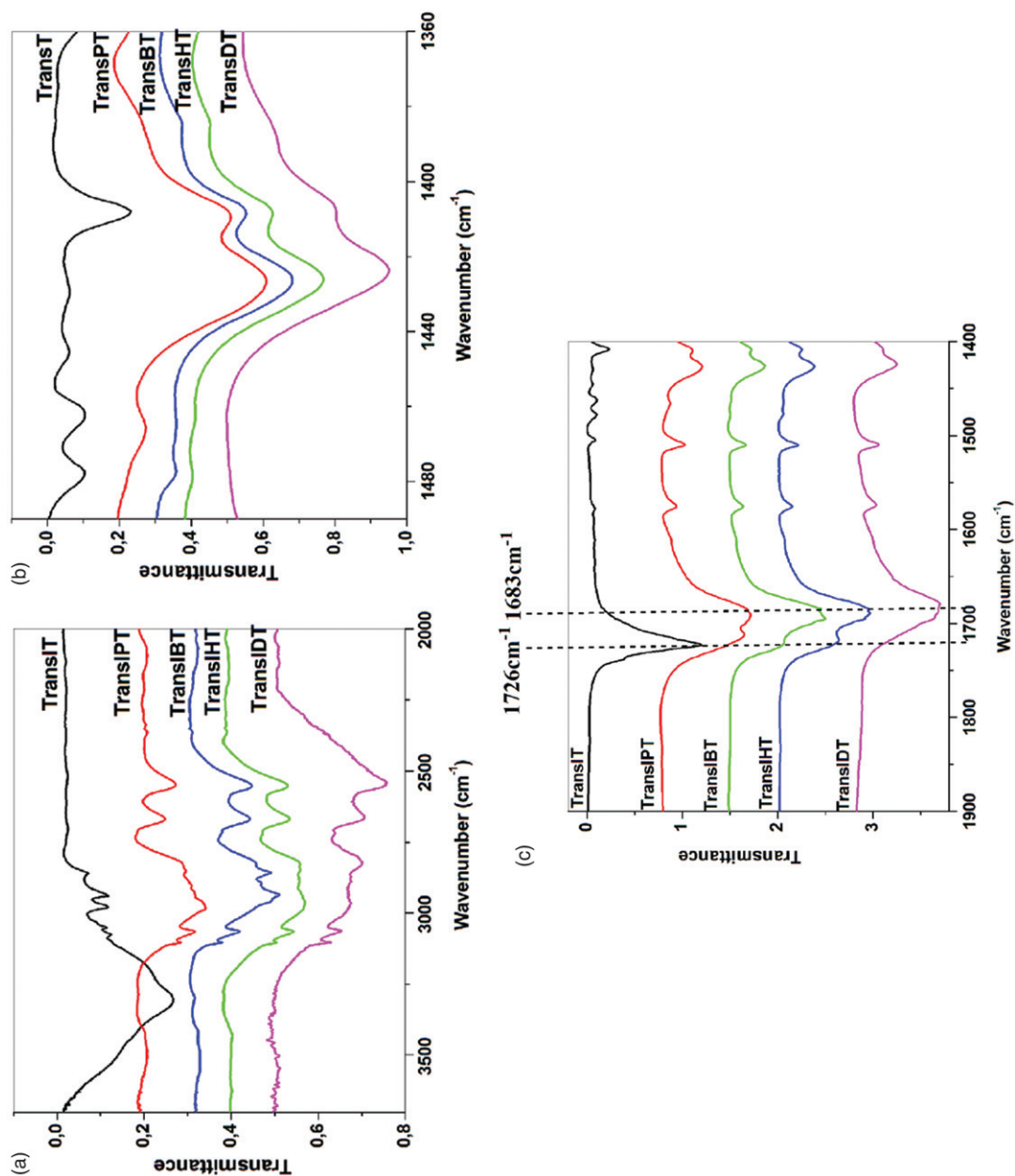


Figure 2. Zoom on the spectra of homo and copolymers derived from trans-1,3-indanediol (a) region 3600–2000 cm^{-1} (b) region 1490–1360 cm^{-1} (c) region 1700 cm^{-1} .

temperature has also been obtained for polymers containing heptanediol, such as poly (heptamethylene terephthalate) $T_g = -1.6^\circ\text{C}$.^[20] The observation of the spectrum transIHT (Figure 3(c)) reveals the presence of a small exothermic peak just after crystallization; it is the polymorphic temperature (T_p) at about 71°C for transIHT copolyester. According to scientific literature, the appearance of polymorphic temperature (T_p) is indicative of the presence of several crystalline structures (polymorphism).^[21–22] This polymorphic structure was already observed for poly (heptamethylene terephthalate).^[7,23]

In Table 1 we summarized the important DSC results obtained for homo and copolyesters upon a second heating of the samples at $20^\circ\text{C}/\text{min}$ under nitrogen. The ΔH_m values reported in Table 1 show considerable differences in the crystallinity of the polymers. The copolyesters involving large flexible spacers exhibit a rather good crystallinity.

DSC analysis reveals that the crystalline temperatures of the synthesized copolyesters follow the odd–even effect. In fact, copolyesters with odd number of methylene units (glycol co-monomer) show the absence of crystalline temperature, while the copolyesters having even number of methylene units exhibit crystalline temperature. According to the DSC thermograms, the various polymers prepared in this study indicated a predominantly semi-crystalline character.

The synthesized copolyesters obtained in this study show multiple melting behaviors. According to several studies^[24–26] this behavior is due to different factors, such as the presence of different crystal structure, crystal reorganization, whereas the incorporation of aliphatic chains used as flexible segments favored crystallization for several copolyesters, probably by folding chains. The presence of two endothermic melting peaks in the case of TransIDT was revealed by DSC analysis (Figure 3(d)). A double melting peak may reflect the presence of a double crystalline population that differs in size and perfection. Similar behavior was reported for PET^[27]. Thermal analysis by DSC shows that the polymers are semi-crystalline because they exhibit both a glass transition temperature (T_g) and melting temperature (T_m).

When the values of T_g and T_m of copolyesters are plotted against the number (n) of methylene units (Figure 4), a zigzag curve and an odd–even effect of these methylene groups were observed for both T_g and T_m (Figure 4). Similar behavior has been previously observed in the case of polyesters referred to in the literature.^[28–30] It is important to note that polyesters having an even number of methylene units have higher melting points characterized by an odd number of methylene units.^[28–30] Explanation is due, in part, to the flexibility of the system, the crystal structure, and the chain conformation.

Thermogravimetric analysis TGA/DTG

The thermal stability of the polyesters reported in this study was evaluated through the TGA in order to know the influence of aromatic–aliphatic diols structures on thermal stability of synthesized copolyesters. Figure 5 shows the (ATG/DTG) curves of homo and copolyesters based on pure isomer trans 1,3-indanediol. The copolyesters' temperatures used to assess the relative thermal stability of polyesters temperature T_{\max} at maximum rate of decomposition, and %Y (residue yield at 500°C) are reported in Table 1. From the thermogravimetric curves, we can see that the temperatures of maximum weight-loss rate are above 400°C . Among all copolyesters synthesized in this study those resulting from aliphatic decanediol (TransIDT) exhibit higher thermal stability, probably due to their crystalline nature. Note that the copolyesters' (TransIPT and TransIDT) present values of maximum degradation temperature are 413°C and 411°C (Table 1), as compared to the copolyester TransIBT, which has the lowest value of maximum degradation temperature of 355°C .

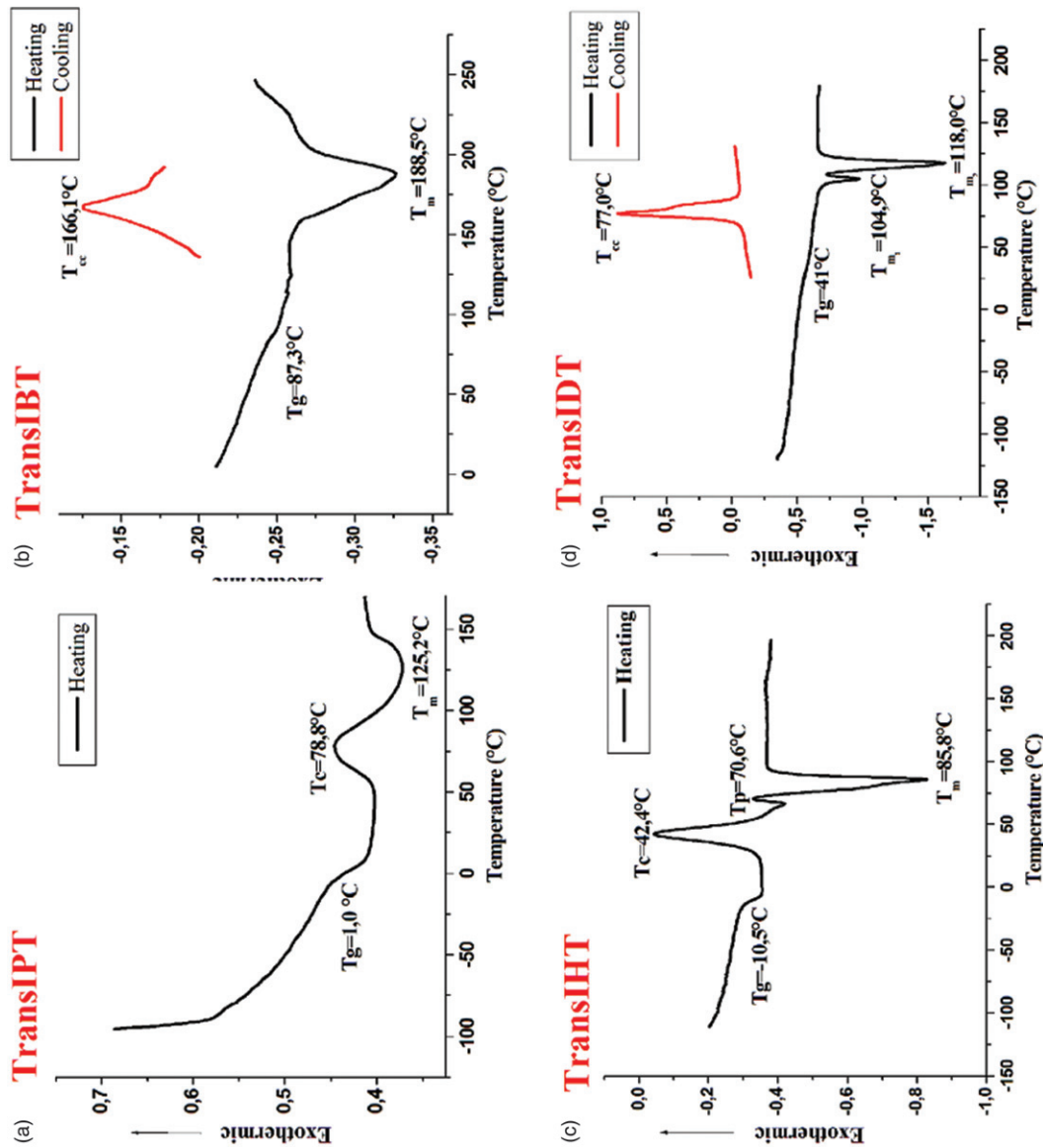


Figure 3. DSC curves (second heating/cooling rate 20 °C/min) of copolyesters (a) TransIPT, (b) TransIBT, (c) TransIHT, and (d) TransIDT.

Table 1. Properties of polymers tested.

Polymers code	Yield (%)	η_{red}^a (dL/g)	T_{max}^b (°C)	V^c (%/°C)	γ^d %	T_g °C	T_c (°C)	T_m (°C)	ΔH_m^f J/g	Crystallinity ^g (%)
<i>TransIT</i>	70	0.21	300	1.3	28.0	53.0	–	113	11	66
<i>TransIPT</i>	74	0.24	413	1.7	9.3	1.0	78.8	125.2	7	nd
<i>TransIBT</i>	62	0.20	354	0.8	20.5	87.3	–	188.5	11	62
<i>TransIHT</i>	88	0.45	415	2.0	5.1	–11	42.4	85.8	31	68
<i>TransIDT</i>	75	0.34	411	1.9	12.3	41	–	105.118 ^e	39	58

^aMeasured at a concentration 0.5 dL/g in N,N-dimethylformamide at 25 °C;

^bTemperature of maximum weight-loss rate (T_{max});

^cMaximum speed;

^dResidue yield at 500 °C;

^eDouble melting peak;

^fMeasured in DSC during the 2nd heating scan at 10 °C·min⁻¹; ^gCrystallinity (%) was determined from X-ray diffraction.

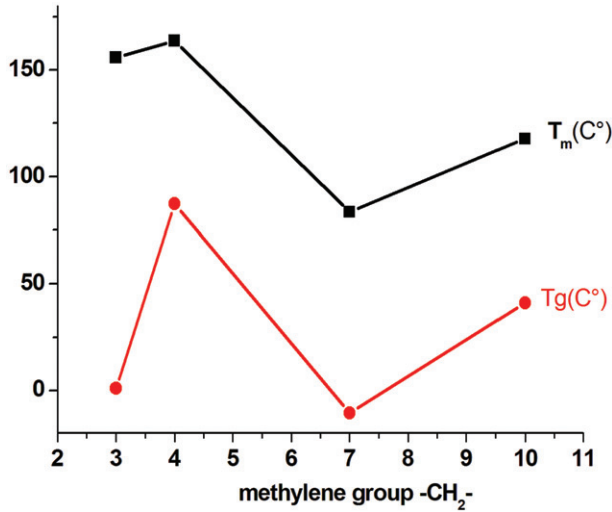


Figure 4. Variation in melting temperature and glass transition temperature as a function of spacer length of methylene groups CH₂.

X-ray diffraction

The X-ray diffraction pattern, indicative of the structural properties of the polyesters based on the isomer *trans*-1,3-indanediol, is shown in Figure 6.

All the X-ray diffraction patterns showed crystalline peaks, which are superimposed on an amorphous halo. The % of crystallinity of the polymers was determined by the mathematical processing performed on the spectra, the crystallinity, may be calculated from integration on the areas of the crystalline peaks with respect to signal area in the range 10° < 2θ < 30°. Using the method proposed by Hermans and Weidinger,^[31] crystallinity of the copolyesters could be calculated and summarized (Table.1).

$$x_c = \frac{A_c}{A_t} = \frac{A_c}{A_c + A_a} * 100$$

The % crystallinity varies from 58 to 62% depending upon their methylene group content in the polymer. Copolyesters (*TransIBT* and *TransIHT*) have the same crystalline peaks, indicating that the same crystalline form has been observed. These polyesters show two main diffraction peaks at 2θ = 17.2°, d = 5.1 Å and 2θ = 27.7°, d = 3.2 Å. Another low intensity peak appears at

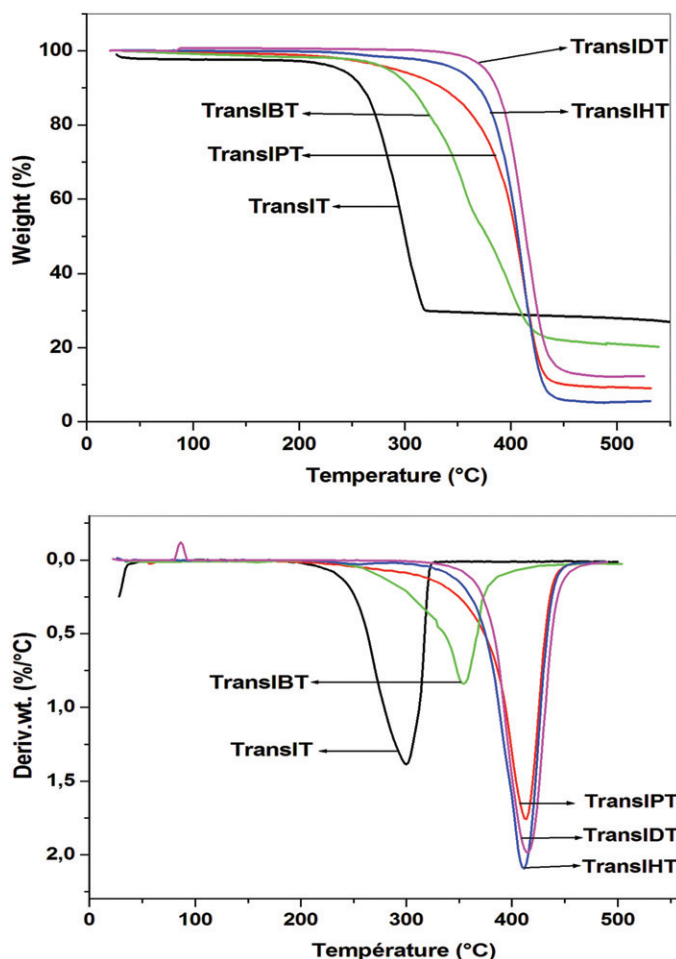


Figure 5. TGA/DTG thermograms of homo- and copolyesters.

$2\theta = 25^\circ$, $d = 3.2 \text{ \AA}$. In the case of the copolyester TransIPT we notice very broad peaks and a large amorphous part in region $2\theta = 15\text{--}30^\circ$ (Figure 6). The diffractogrammes of TransIBT and TransIHT have the same pace, with three identical peaks. Two high intensity peaks that appear at $2\theta = 17.2^\circ$, $d = 5.1 \text{ \AA}$ and $2\theta = 17.7^\circ$, $d = 3.2 \text{ \AA}$ and a low peak which manifests itself $2\theta = 25^\circ$, $d = 3.5 \text{ \AA}$. For the polyester TransIDT we notice the presence of peaks of the following values $2\theta = 17.7^\circ$, 20.1° , 22.2° , and 24.6° .

The X-ray diffraction pattern shows that the synthesized polyesters have crystallinity between 58 and 66%. X-ray diffraction spectra indicate that the copolyesters are semicrystalline materials. These results are in agreement with the results obtained by DSC.

Scanning electron microscopy (SEM)

The morphology of the prepared copolyesters was observed by SEM. Figure 7 reports the picture for TransIHT copolyester. SEM confirms the semi crystalline structure of the copolyesters. Indeed, the obtained photograph with enlargement ($10,000\times$) shows the presence of phase crystalline form crystals characteristic of semi-crystalline structure.

The image (Figure 7(i)) of TransIHT shows very thin slices ordered horizontally. Indeed, it can be seen that the TransIHT copolyester presents a lamellar structure characteristic of semi-

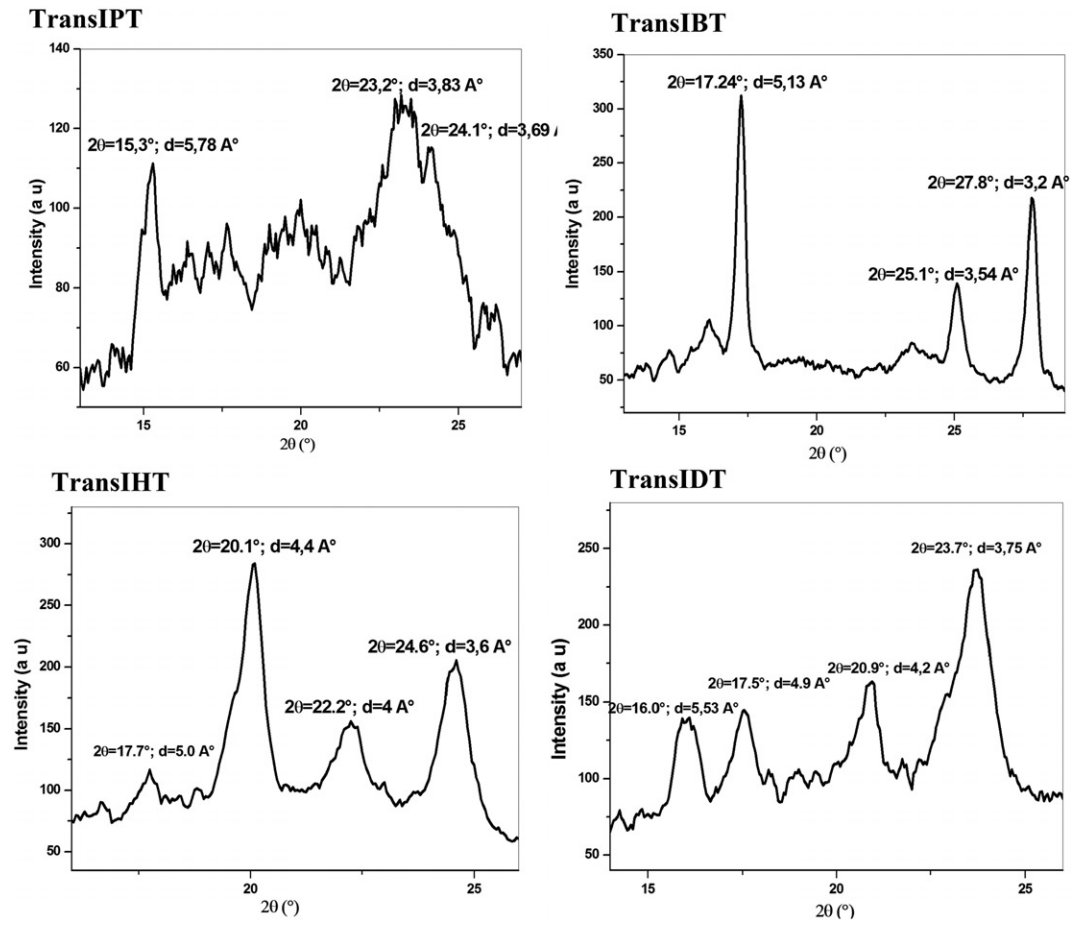


Figure 6. X-ray diffractograms of different copolyesters.

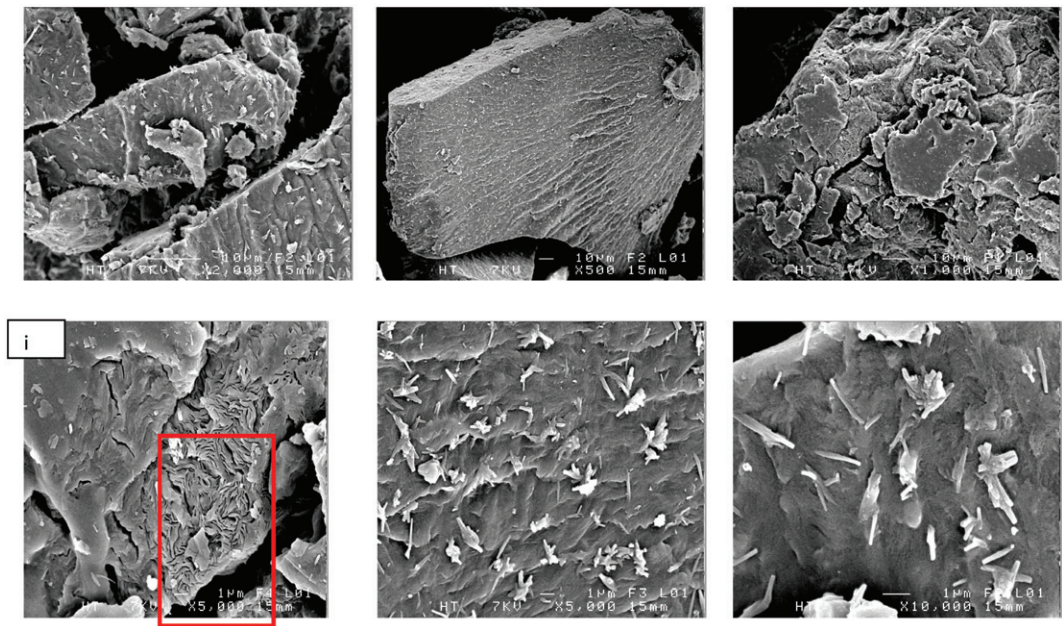


Figure 7. Scanning electron micrograph of copolyesters TransIHT.

crystalline structures. This result is in perfect agreement with the DSC and XRD characterizations.

Conclusions

The synthesis of copolyesters was based on terephthaloyl chloride (aromatic diacid) on a combination of aromatic (rigid) and aliphatic (flexible) diols. The effects of the structure of the trans 1,3-indanediol on physico-chemical properties of the resulting copolymers were examined. The structures of the synthesized polymers were confirmed by means of FTIR spectroscopy. TGA showed that the temperatures of maximum weight-loss rate are above 400 °C. They are directly proportional to the molecular size of the aliphatic diol component. For all polyesters, the DSC measurements revealed the existence of glass transition and melting temperatures. The glass transition temperatures obtained by DSC are not too high, probably due to the presence of methylene CH₂ groups that confer flexibility to the chain copolyesters. Therefore, the introduction of aliphatic diols results in a change in the levels of thermal properties of copolyesters synthesized. These copolyesters have in general a thermostable nature and semi-crystalline properties. The semi-crystalline structure was confirmed by different methods of characterization. The degree of crystallinity of the copolyesters was determined by X-ray diffraction, the degree of crystallinity of all synthesized polyesters is greater than 50%.

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