

Synthesis and thermal properties of new polyester based on indane-1,3-diol and terephthaloyl chloride

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SUMMARY

New aromatic polyester was synthesized by polycondensation of indane-1,3-diol and terephthaloyl chloride. The indane-1,3-diol was synthesized by metal hydride reduction and characterized by IR, ¹H and ¹³C NMR. Two polycondensation methods were used: solution and interfacial polycondensation in presence of various quaternary ammonium salts. The obtained polymers were characterized by differential scanning calorimetry (DSC) and viscosity measurements. All polymers had glass transition temperature (T_g) in the range of 72–77°C and melting temperature (T_m) in the range of 152–184°C.

INTRODUCTION

Many studies concerning terephthalate based polyesters are regularly reported in the literature. Properties of these polymers are closely dependent on the structure of the diol molecule used and the structure of the terephthalate unit used with or without substituents in the phenyl ring (1–3). In this polycondensation the terephthaloyl chloride is generally used rather than the terephthalic acid owing to its higher reactivity (4–6). The polymerization mode used is another important factor which may influence some physical properties of the polymer such as viscosity or molar mass etc. . . Among all the techniques of polycondensation, the interfacial polycondensation method using ammonium quaternary salts as phase transfer catalyst is the most widely preferred one in polyesters synthesis (7–11) and its mechanism was discussed by Starks (12–14).

In the present work we report the earliest results of synthesis, viscosity and thermal properties of a new polyester obtained by polycondensation based on the indane-1,3-diol and terephthaloyl chloride. On the other hand, we have not found any literature reference

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concerning the preparation of this diol, then we synthesized it by chemical reduction of its precursor the indane-1,3-dione.

EXPERIMENTAL

Solvents reagent grade (from Fluka, Prolabo and Aldrich) were used without purification. Indane-1,3-dione m.p 136 °C (Aldrich) was purified according to the procedure described in literature (15) m.p 130°C, NaBH₄ (Fluka). Terephthaloyl chloride (Fluka) was purified by recrystallization from n-hexane. The following catalysts (from Aldrich, Fluka and Janssen) were used as received : tetramethylammonium bromide (TMAB), hexamethylene bis (trimethylammonium) chloride (HMBTMAC), dibenzyltrimethylammonium chloride (DBDMAC) and benzyl tributylammonium bromide (BTBAB).

Viscosities of polymers were determined by using an Ubbelohde viscometer at 25 °C in DMF solution of 0.5 g.dl⁻¹ concentration. Differential scanning calorimetry (DSC) measurements were performed with Mettler DSC 12E apparatus, using 1.6 to 3.3 mg of polymer and a heating rate of 20°C/min. The IR spectra were recorded on Bruker IFS 45 spectrometer. The ¹H and ¹³C NMR spectra were recorded respectively at 200 MHz and 50 MHz on a Bruker AC 200 spectrometer in DMSO-d₆ as solvent and TMS as internal standard.

Monomer :

We introduced in a three necked round flask the reducing agent NaBH₄ (3.12g, 8.2 mmol) and 80ml of 1,2-dimethoxyethane. To this mixture was added dropwise a solution of indane-1,3-dione (6g, 4.1mmol) in 150ml of 1,2-dimethoxyethane. The reaction was carried out under gentle reflux. After two hours, the reaction was quenched with ice and extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous magnesium sulfate MgSO₄ and concentrated to give a crude product which was recrystallized in methanol -chloroform (1/1 v/v). Yield: 78. _m.p 194 °C-195°C. A.E. : C₉H₁₀O₂ (146,16) calc.: C=72.0%, H= 6.6% ; found: C=71.9%, H= 6.53%.

IR (KBr pastille, cm⁻¹) (OH 3312-3253), (C-O 1040).

¹H NMR (DMSO-d₆, δ in ppm) Cis isomer: 1,6 (m, 1H, >CH₂), 2,74 (m, 1H, >CH₂), 4,8 (q, 2H, >CHOH), 5,5 (d, 2H, 2OH), 7,3 (m, 4H arom). Trans isomer: 2,1 (m, 2H, CH₂), 5,1 (m, 4H, 2 >CHOH and 2H >CHOH), 7,3 (m, 4H arom).

^{13}C NMR (DMSO- d_6 , δ in ppm): Cis isomer 46,8 ($>\text{CH}_2$), 70,4 (2 $>\text{CHOH}$), 123,5 and 127,25 (C arom.), 145,4 (C quat). Trans isomer 45,87 ($>\text{CH}_{2a}$), 72,39 (2 $>\text{CHOH}$), 124,45 and 127,72 (C arom), 145,81 (C quat).

Polymer :

Interfacial polycondensation :

In a flask fitted with stirrer, we introduced 0.5g (3.33mmol) of indane-1,3-diol, 8 ml of 1M (NaOH), and 1.67×10^{-4} mol of catalyst. After stirring a solution of 0.67 g (3.33mmol) of terephthaloyl chloride in 8 ml of nitrobenzene was added at once. The mixture was still stirred for two hours at ambient temperature and then quenched with 50ml of n-hexane to precipitate the polymer. The polymer was filtered and dried under vacuum at 50°C for 24 h.

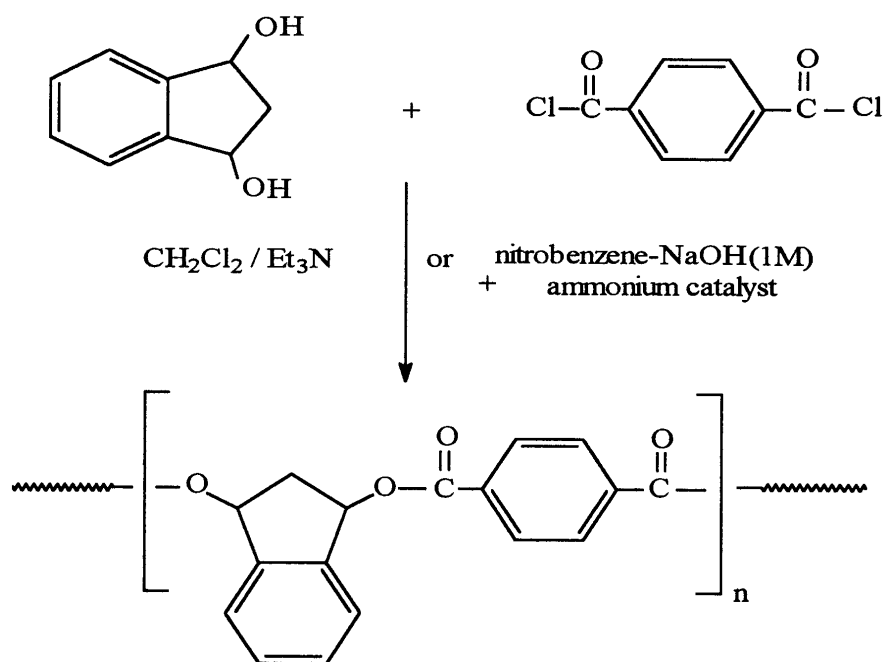
Solution polycondensation :

In three-neck round bottom flask, we introduced 0.5g (3.33mmol) of indane-1,3-diol, 15ml of dichloromethane, and 1.3 ml of triethylamine under nitrogen. After cooling this solution till 0°C, we added dropwise 0.67g (3.33mmol) of terephthaloyl chloride in 18 ml dichloromethane. The reaction mixture was stirred at 0°C for 1h and three hours at 25°C. Then, the solution was diluted with 5 ml of dichloromethane and precipitated with 50 ml of n-hexane. The polymer was filtered and dried at 50 °C for 24 h.

RESULTS AND DISCUSSION

We synthesized the indane-1,3-diol by the complete reduction of the two carbonyl groups of the indane-1,3-dione. The reduction was achieved with sodium borohydride (NaBH_4) as reducing agent in 1,2-dimethoxyethane (16). The diol was characterized by IR spectroscopy, elemental analysis and DSC analysis. The infrared spectrum exhibit a strong absorption band of hydroxyl groups at 3253-3312 cm^{-1} and the full disappearance of the carbonyl absorption band in the corresponding area of the spectrum. The NMR characterisation showed that the indane-1,3-diol is under its two stereoisomers forms. The ratio is 90 % for the cis and 10% for the trans, according to ^1H NMR. For this first work, polycondensation were performed with the mixture of the two forms, polycondensation with each isomer will be reported next. We attempted two methods to synthesis this new polyester based on indane-1,3-diol and terephthaloyl chloride. Solution polycondensation in dichloromethane was carried out in presence of triethylamine as an acceptor for the evolved

HCl. On the other hand, interfacial polycondensation in presence of quaternary ammonium salts as catalysts was realized in nitrobenzene and aqueous sodium hydroxide solution (1M) (schema I).



Schema 1

The polyesters obtained by the two polycondensation methods were characterized by viscosimetry and differential scanning calorimetry (DSC). The low solubility of the obtained polymers in common solvents used in NMR did not permit to obtain good spectra. All experiments results are summarized in table I

Reported results in table I show that inherent viscosity values of the polymers obtained from interfacial polycondensation depend on the nature of used catalyst. In fact, our experiments showed that the dibenzyl dimethylammonium chloride (DBDMAC) is the catalyst which has the lowest efficiency since the values of the inherent viscosity and ΔH_m are comparable with those of the polymer synthesized by the solution method. The hexamethylene bis (trimethylammonium) chloride (HMbTAC) enhance the viscosity up to $\eta_{inh} = 0.41 \text{ dl/g}$ would have the higher efficiency which does not correspond yet, to the low ΔH_m value, 4 J/g (see table 1), as compared to 49 J/g and 122 J/g values obtained in the cases of polymers n°2 and n°5 synthesised in presence of tetramethylammonium bromide and benzyltributylammonium bromide and which have lower viscosities.

Table 1 : Results of inherent viscosities and DSC thermal analysis.

N°	Catalyst	Polymerization Method ⁽¹⁾	yields (%)	η_{inh} ⁽²⁾ (dl/g)	Tg (°C)	Tm ⁽³⁾ (°C)	ΔH_m (J/g)
1	-	A	58	0.23	77	177	8
2	TMAB	B	61	0.32	75	184	49
3	HMbTMAC	B	56	0.41	76	152	4
4	DBDMAC	B	54	0.25	77	174	11
5	BTBAB	B	59	0.36	72	164	122

(1) A: Solution polycondensation; B: Interfacial polycondensation, the catalyst concentration was $1.67 \times 10^{-4} \text{ mol.l}^{-1}$ except n° 3 for which half value was used.

(2) Inherent viscosities in DMF at 25 °C.

(3) Tm (°C) : peak temperature of the first melting.

These DSC analysis show that our polyesters exhibit semicrystalline properties. The ΔH_m values of table 1 show notable difference between the crystallinity of the polymers. Only polymers n°2 and n°5 have a rather good crystallinity. If the polymers are melted, then cooled and reheated to melting, very few of them presents a second melting. In addition, when a second melting is present, polymer n° 2 for example, ΔH_m value for the second melting shift from 49 J/g to 29 J/g. For these reasons the values of table 1 concern only the first melting. The melting peak is well defined in the case of polymers n°2 and n°5 and this can be related to the crystallinity of these polymers. The relatively low crystallinity and the lack of a second melting for the others polymers would be due to the presence of low molar mass. The high rate of cooling could also explain the lack of the second melting.

In conclusion, the polycondensation of indane-1,3-diol and terephthaloyl chloride give us a new polyester by either solution method or interfacial polycondensation method. The thermal analysis showed that this polyester is semicrystalline. In the interfacial polycondensation catalysed by quaternary ammonium salts, all the used catalysts had not the same effect on the polycondensation reaction probably due to their structures, like the

DBDMAC catalyst which had negligible effect and gave similar results as in solution method polycondensation.

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