

# Aromatic Polyesters via Transesterification of Dimethylterephthalate/Isophthalate with Bisphenol-A\*

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## SYNOPSIS

As a part of our work in the area of transesterification chemistry, we have studied the transesterification of dimethyl terephthalate/isophthalate with bisphenol-A for the synthesis of aromatic polyester. The process comprises two steps. The first step comprises preparation of aromatic polyester prepolymer by reacting the dimethyl esters of terephthalic/isophthalic acids and bisphenol-A in the melt phase via catalyzed interchange reaction. The second step involves the postpolycondensation of aromatic polyester prepolymer under reduced pressure, eliminating the by-product and driving the equilibrium of the reversible reaction to the formation of a high molecular weight aromatic polyester. In both steps, methanol is eliminated as a by-product. The method explored is the simplest one, permits the use of commercial materials as the feed stock, and leads to a low boiling by-product that can be recycled. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

There are three major processes described in the literature for the preparation of aromatic polyesters. These are (a) an interfacial polycondensation of terephthaloyl chloride/isophthaloyl chloride (TPC/IPC) with bisphenol-A (BPA) under phase transfer conditions,<sup>1-5</sup> (b) melt polycondensation of BPA-diacetate with terephthalic acid/isophthalic acid (TPA/IPA) in the presence of a catalyst,<sup>6-11</sup> (c) melt polycondensation of diphenyl terephthalate/diphenyl isophthalate (DPT/DPI) with BPA in the presence of a catalyst.<sup>12-14</sup> In all the above-mentioned processes, at least one monomer must be derivatized to enhance its reactivity, e.g., by acetylation of the hydroxyl group of BPA or by the transformation of the carboxylic groups in phenyl esters or chlorides. Surprisingly, the direct transesterification of the readily available dimethyl terephthalate or isophthalate with bisphenol-A has been studied far less. Extensive search of the literature revealed only a solitary reference, due to Oishi and Hall,<sup>15</sup> who studied the synthesis of aromatic polyester using

methyl esters of phthalic acid and BPA. However, very poor results were obtained in terms of polymer yield, molecular weight, and color.

In this paper, we describe an efficient two-stage melt polycondensation process for the synthesis of aromatic polyesters by transesterification of dimethyl terephthalate/dimethyl isophthalate with bisphenol-A.<sup>16</sup> The process is attractive as it permits the use of readily available starting materials. The by-product of the reaction is methanol, which is less hazardous compared to those produced by conventional methods. Furthermore, no special reactor construction materials are required for this process as compared to processes involving the use of bisphenol-A-diacetate.

## EXPERIMENTAL

### Materials

Bisphenol-A (BPA), a product of Cibatul (Bombay), was purified by distillation and subsequent crystallization in toluene. Dimethyl terephthalate (DMT) (E. Merck, Germany), dimethyl isophthalate (DMI), and diphenyl ether (DPE) (Aldrich Chemicals, USA) were used after drying without further purification. Dibutyltin oxide (DBTO) (FASCAT 4201 M & T

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**Table I** Preparation of Prepolymers

Prepolymer Code	Catalyst	Yield (%)	DP ( <sup>1</sup> H-NMR)	$\bar{M}_n$ (VPO)	$\bar{M}_n$ (GPC)	Polydispersity	$[\eta]^a$ (dL/g)
A	DBTO	90	4.75	1690	1763	1.92	0.13
B	DBTL	88	4.79	1695	1722	1.92	0.14
C	TNBT	83	17.32	6125	4491	2.94	0.24
D	TNPH	70	15.40	6510	2661	2.06	0.18

<sup>a</sup> Determined at 30°C in chloroform.

Chemicals, Rahway, NJ), dibutyltin dilaurate (DBTL), titanium butoxide (TNBT), and titanium phenoxide (TNPH) (Aldrich Chemicals) were used as received. All solvents were distilled prior to use.

### Synthesis of the Aromatic Polyester Prepolymer

The prepolymer preparations were carried out in a two liter capacity stainless steel batch reactor equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum jacketed Vigreux column and distillation head. The reactor was charged with BPA (45.70 g, 0.2 mol), DMT (19.42 g, 0.1 mol), DMI (19.42 g, 0.1 mol), DBTO (0.25 g, 0.55 wt % based on BPA), and 120 mL of DPE. The system was purged with dry nitrogen (Iolar grade) for 15 min at room temperature. The reactants were heated to 260°C in a dry nitrogen atmosphere, when methyl alcohol, a by-product, started distilling out. The temperature was maintained at 260°C for 12 h. Finally, DPE was removed completely under vacuum (0.5 mm of Hg) at 160°C. Then the reactor was cooled to ambient temperature. Various catalysts were used for the preparation of aromatic polyester prepolymer. The results are given in Table I.

### Melt Polycondensation of the Prepolymer

To a cylindrical glass reactor (100 mL) fitted with a vacuum adapter, 2 g of prepolymer A was added,

along with 0.01 g (0.5 wt %, based on the prepolymer) of dibutyltin dilaurate. The pressure in the reactor was reduced to <0.5 mm of Hg. After five minutes at ambient temperature, the reactor was heated to 300–330°C, and the temperature was maintained at 300–330°C for about 60 min. After cooling the reactor to ambient temperature, the solid mass obtained was dissolved in chloroform and precipitated from methanol. The melt polycondensation of other prepolymers was also carried out in a similar manner. The results are shown in Table II.

### Measurements

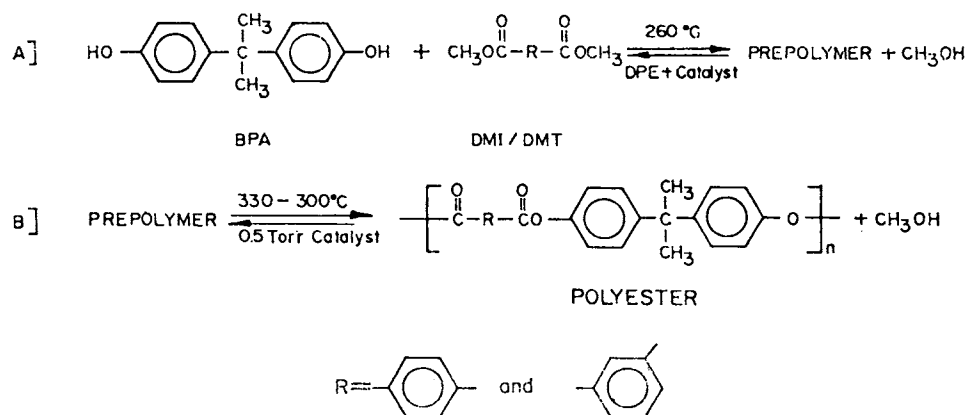
Viscosities were measured with Ubbelohde viscometer at 30°C in chloroform. <sup>1</sup>H-NMR spectra were recorded on a Bruker AC200 MHz FT-NMR spectrometer. Chemical shifts ( $\delta$ ) are expressed in parts per million (ppm) downfield from TMS. Infrared (IR) spectra were recorded on Perkin-Elmer 16 PC FT-IR spectrometer. Molecular weights of prepolymers were determined by vapor pressure osmometry (VPO) by using a Knauer (Germany) vapor pressure osmometer. The differential scanning calorimetry (DSC) was performed on Perkin-Elmer DSC-7 at the heating rate of 10°C/min under nitrogen atmosphere. The GPC measurements were carried out with a Waters 150 instrument with RI detectors using a column set 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, 500<sup>0</sup> and 100<sup>0</sup> Å  $\mu$  styragel and THF as mobile phase. The analysis was

**Table II** Melt Polycondensation of Prepolymers

Prepolymer Used	Polyester Yield (%)	$\bar{M}_w$ (GPC)	$\bar{M}_n$ (GPC)	Polydispersity	$[\eta]$ (dL/g) <sup>a</sup>
A	92	55,970	15,340	3.60	0.45
B	90	46,630	14,560	3.20	0.45
C	88	34,180	12,270	2.78	0.35
D	90	33,840	11,860	2.85	0.40

In all the cases, DBTL (0.5 wt % based on prepolymer) was used as a catalyst.

<sup>a</sup> Determined in chloroform at 30°C.



Scheme 1

carried out at 30°C and 1 mL/min flow rate. Narrow molecular weight polystyrene standards were used as the calibration standard. 200  $\mu$ L of 0.3% sample solution in THF was used for analysis.

## RESULTS AND DISCUSSION

The present process involves the reaction of bisphenol-A and dimethyl esters of terephthalic acid and isophthalic acids in presence of a catalyst. In this sequence, condensation occurs with the liberation of methanol. Since methanol is a low boiling compound, it can be removed conveniently and efficiently from the reaction to yield a high molecular weight polyester. This is an advantage over the conventional diacetate process for the production of aromatic polyester. The residual acetic anhydride in the final product from the diacetate process affects the color and thermal stability. On the contrary, the present process employs dimethyl esters of terephthalic acid and isophthalic acid having lower melting point and higher solubility in BPA and can usually be obtained at a higher purity grades than the corresponding acids, hence allowing the production of better quality products and easier process control.

The first stage of the two-stage process involves the synthesis of prepolymer having intrinsic viscosity in the range of 0.1 to 0.2 dL/g in chloroform by reacting the dimethyl esters of terephthalic and isophthalic acids and BPA at 260°C in the presence of a solvent and a catalyst under mechanical stirring (Scheme 1).

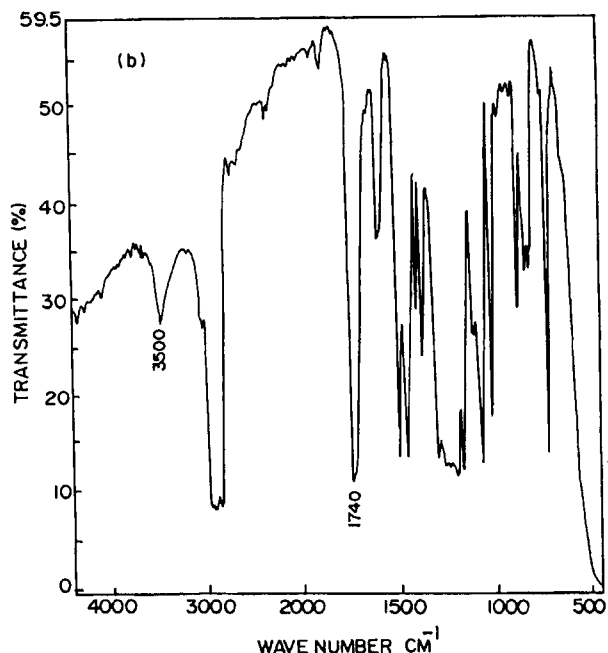
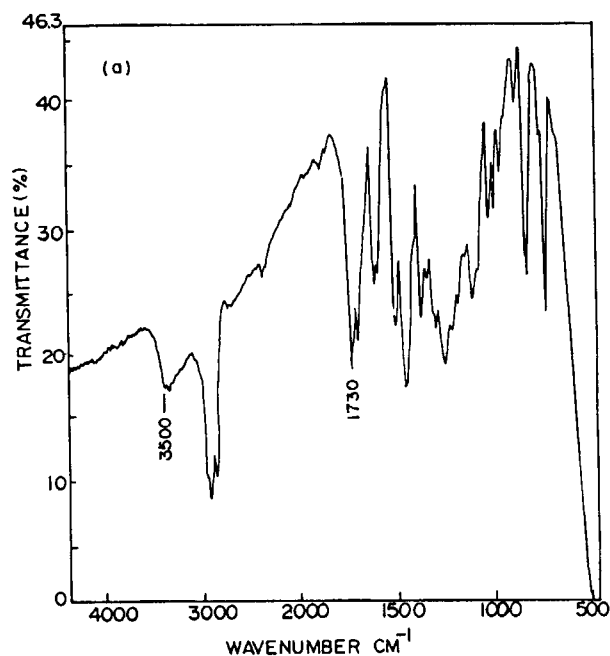
The catalysts selected for this study are known to be effective for aliphatic transesterification reactions. The presence of a catalyst during the transesterification reaction is necessary as no distillation

of methanol was observed when transesterification was carried out without a catalyst. The catalyst employed include alkoxides of group IVB metals, such as titanium butoxide, titanium phenoxide, and derivative of group IVA metals, such as dibutyltin oxide and dibutyltin dilaurate. The use of tin derivatives exhibited good conversions and color among all other catalysts studied. The amount of catalyst employed was 0.55 wt % with reference to BPA. The variation in  $\bar{M}_n$  (VPO) and  $\bar{M}_n$  (GPC) for prepolymers C and D (Table I) may be attributed to the difference in hydrodynamic volumes of these samples and the standard used for calibration during GPC measurements. The close agreement between  $\bar{M}_n$  (VPO) and  $\bar{M}_n$  (GPC) for prepolymers A and B was not expected and is coincidental.

A variety of solvents have been suggested in the prior literature to assist in the use of the catalyst or to reduce sublimation of reactants.<sup>17</sup> The solvent used in the present case was diphenyl ether (DPE) to avoid any stoichiometric imbalance that might occur as a result of possible sublimation of reactants.

The second step consists of melt polycondensation of aromatic polyester prepolymer at 300–330°C in the presence of a catalyst under reduced pressure (0.5 mm of Hg). DBTL was employed as a catalyst. The amount of catalyst employed was 0.5 wt % based on prepolymer (Scheme).

Both stages of the process were followed by IR and <sup>1</sup>H-NMR spectroscopy. As an illustrative example, the IR and <sup>1</sup>H-NMR spectra for prepolymer A are presented in Figures 1 and 2, respectively. A variation of the carbonyl stretching of the aliphatic ester from 1730 to 1740  $\text{cm}^{-1}$  [Fig. 1(b)] is attributed to the progressive formation of aromatic polyester. This band is typical of an aromatic structure.<sup>18</sup> There is also an important relative reduction in the intensity of the —OH band at 3500  $\text{cm}^{-1}$  in Fig.



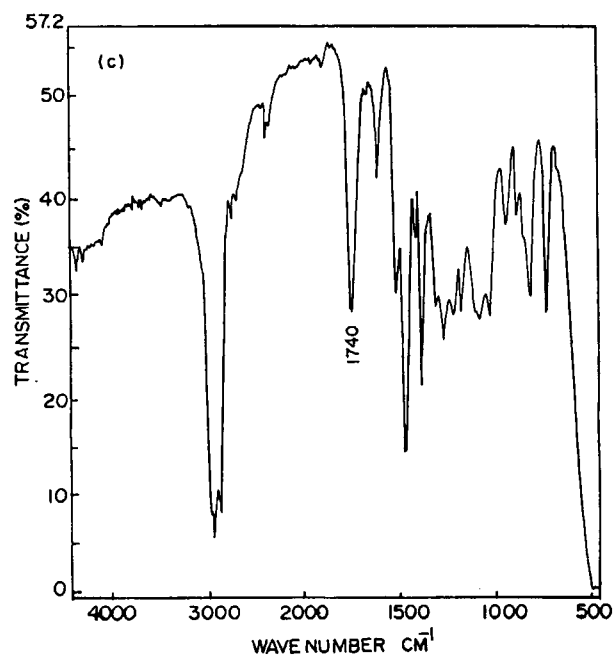
**Figure 1** (a) IR spectrum of initial mixture (BPA + DMT + DMI); (b) IR spectrum of the prepolymer; (c) IR spectrum of the crude final polyester.

1 (c) with respect to Fig. 1 (b). This is quite obvious because of the fact that the end group —OH concentration in the high molecular weight polyester will be very much less as compared to the prepolymer [Fig. 1 (b)]. The overall IR spectrum of the final polyester [Fig. 1 (c)] is identical with the IR spectrum of the authentic polyester sample obtained by interfacial polymerization.<sup>19</sup>

The proton NMR analysis of the samples after each stage is of great interest because important information concerning the structure of copolyester can be obtained from it. In the region between 8 and 8.4 ppm, typical of terephthalic unit, the NMR spectrum of the prepolymer [Fig. 2 (b)] shows four additional peaks between 8 and 8.35 ppm, in addition to the singlet at 8.4 ppm due to the symmetrical aromatic ester substituted terephthalate unit. The additional peaks between 8 and 8.35 ppm show a pattern of typical paradisubstituted benzene having dissimilar ester groups. The upfield doublet centered at 8.2 ppm is because of the aromatic protons, ortho-to-end methyl ester group, as expected, and the other doublet centered at 8.3 ppm is because of the aromatic protons, ortho to aromatic ester moiety. Similar observations have been reported by Gouinlock et al.<sup>20</sup> while studying bisphenol-*A*-neopentyl glycol-terephthalic acid copolyester.

The symmetrical aromatic ester substituted isophthalic unit shows proton shifts at 9.05, 8.5, and 7.7 ppm. However, the proton region of the iso-

phthalic unit also shows additional peaks at 8.9, 8.4, and 7.6 ppm. These upfield shifts observed for all the three protons of the isophthalic unit can be attributed to the end methyl ester of the isophthalic unit. The analysis of this part of the spectrum clearly shows that the prepolymer contains terephthalic/



**Figure 1** (Continued)



**Figure 2**  $^1\text{H-NMR}$  spectra of (a) initial mixture (BPA + DMI + DMT) in dimethyl- $d_6$  sulfoxide, (b) prepolymer A in  $\text{CDCl}_3$ , and (c) crude final polyester in  $\text{CDCl}_3$ .

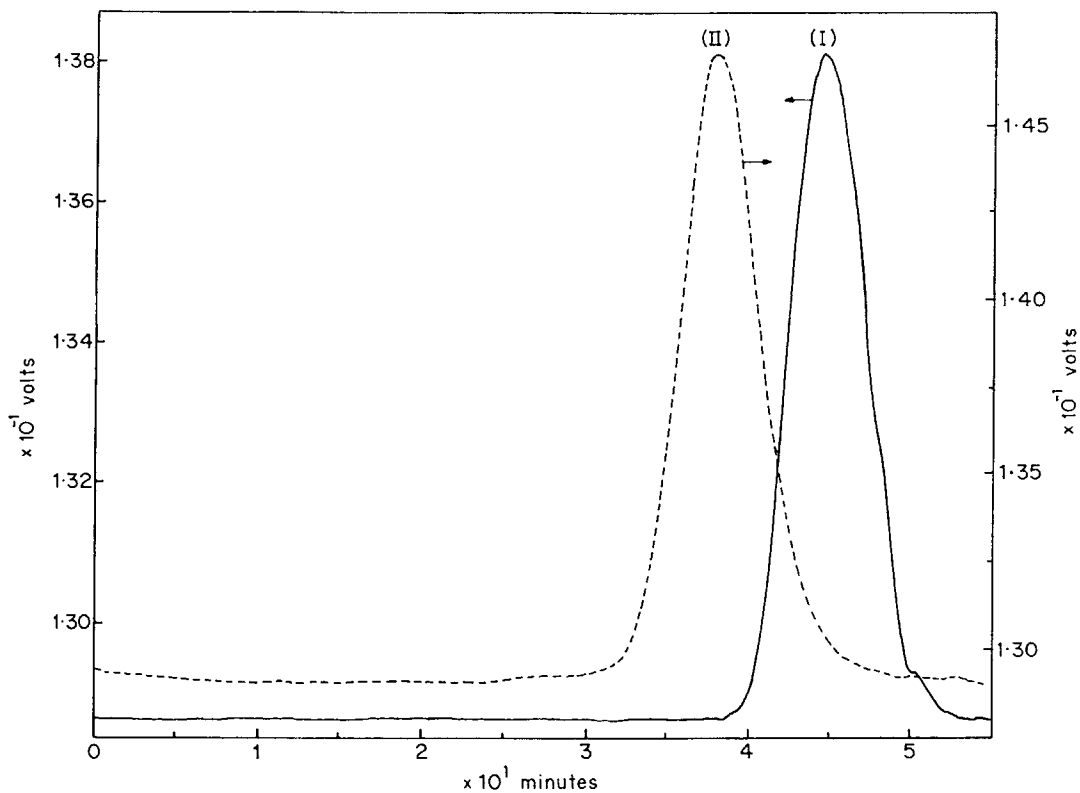
isophthalic units having methyl ester end groups in addition to terephthalic/isophthalic units substituted by aromatic ester groups.

The symmetrical aromatic ester substituted bisphenol-A moiety shows aromatic proton shifts in the region of 7–7.5 ppm, with the aliphatic proton singlet at 1.68 ppm. In addition to these shifts, additional peaks are observed at higher field in both the regions. It is well-known that phenolic —OH group is a strong electron donor and exhibits shielding effect on ortho, meta, and para protons of the aromatic nucleus, causing upfield shifts.

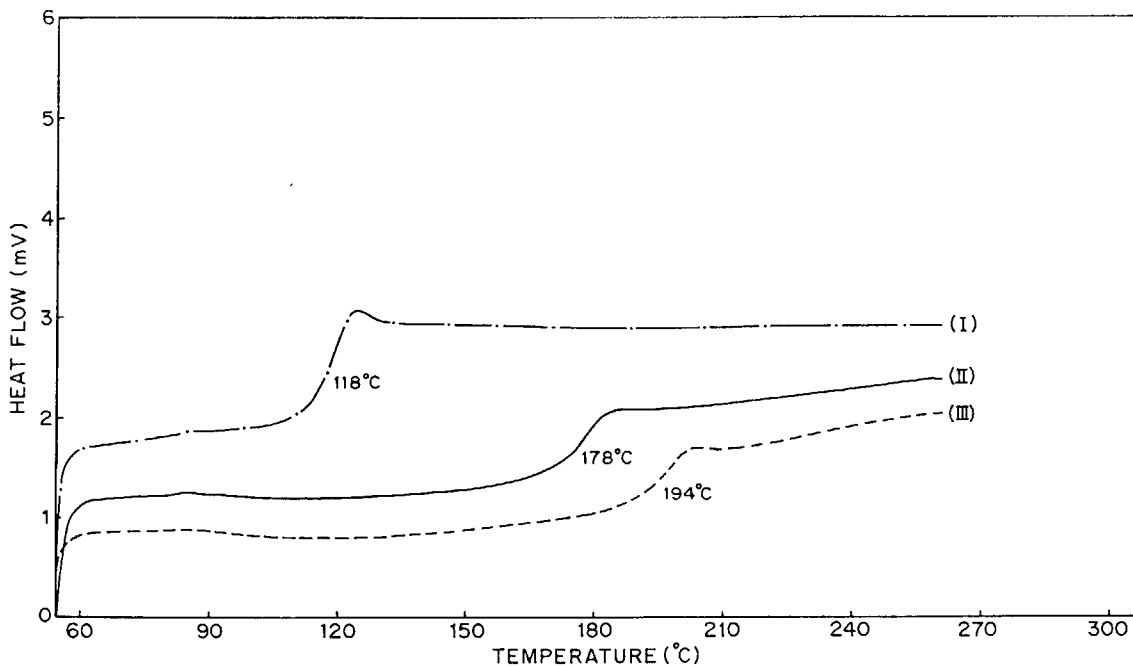
The upfield doublet centered at 6.75 ppm [Fig. 2(b)] is due to aromatic protons, ortho to the end —OH group of BPA moiety. The upfield shift in

the aliphatic region is due to the modification in the surroundings of methyl groups in the bisphenol moiety having the —OH end group.

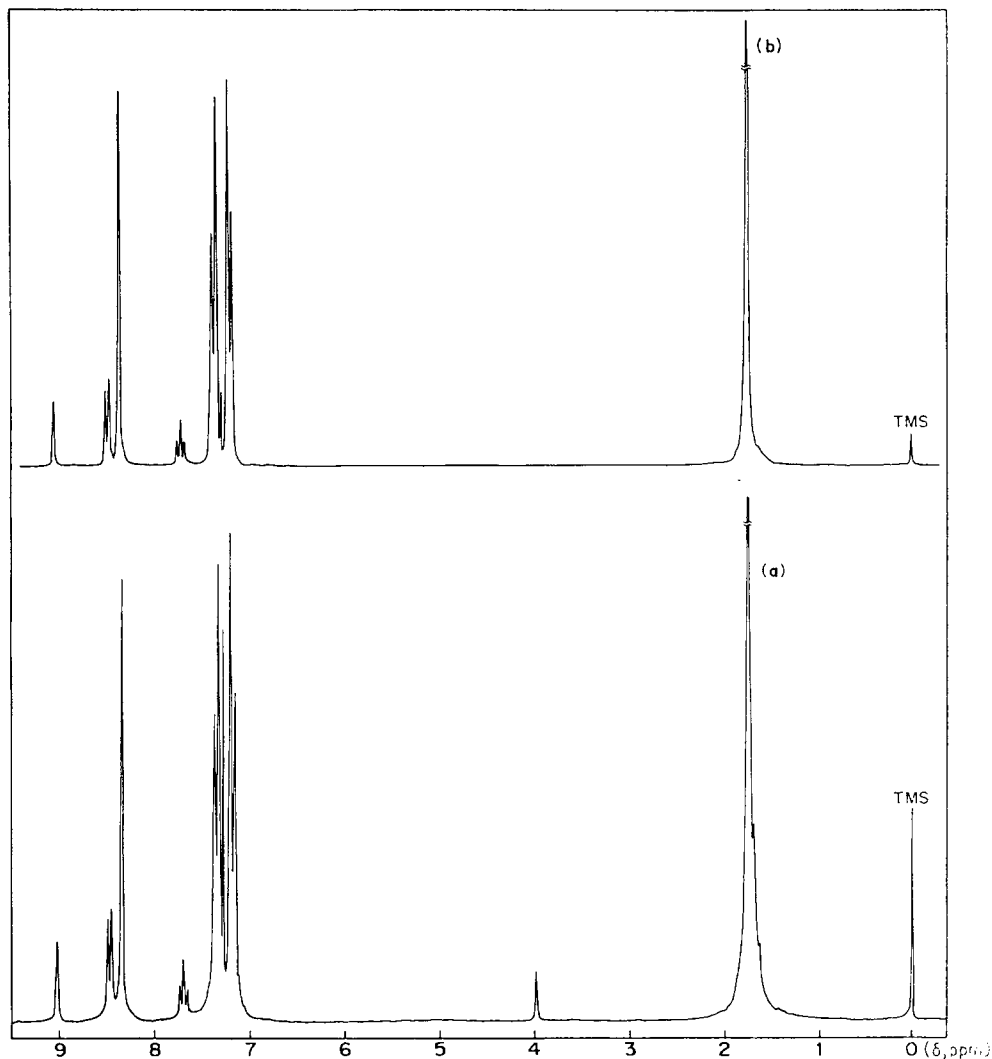
The  $^1\text{H-NMR}$  spectrum of final polyester [Fig. 2(c)] is identical with the  $^1\text{H-NMR}$  spectrum of an authentic sample of aromatic polyester obtained from bisphenol-A, terephthaloyl/isophthaloyl chloride by interfacial polymerization (Fig. 5). The intensity measurement of aromatic protons and terephthalic and isophthalic units confirm the presence of an equal number of terephthalic and isophthalic units in the final polyester. The GPC traces of prepolymer A and the final polyester obtained from it have been shown in Figure 3. The DSC thermograms of prepolymer A, the final polyester ob-



**Figure 3** GPC traces of prepolymer A (I) and final polyester (II).



**Figure 4** DSC thermograms of prepolymer A (I), final polyester (II) prepared by melt polycondensation, and polyester (III) prepared by interfacial polycondensation.



**Figure 5**  $^1\text{H-NMR}$  spectra of (a) polyester prepared by melt polycondensation and (b) polyester prepared by interfacial polycondensation in  $\text{CDCl}_3$ .

tained from prepolymer A, and the polyester obtained from bisphenol-A, terephthaloyl/isophthaloyl chloride, by interfacial polycondensation have been shown in Figure 4.

## CONCLUSIONS

In conclusion, a convenient synthetic route to aromatic polyesters has been demonstrated starting from readily available methyl esters of terephthalic/isophthalic acids and bisphenol-A. The synthesis involving two stages of condensation finally leads to aromatic polyesters with good color and intrinsic viscosity  $[\eta]$  in the region 0.35–0.45 dL/g. The key to the success lies in the use of a high boiling solvent, such as diphenyl ether, to suppress the loss of DMT/

DMI by volatilization and thus prevent stoichiometric imbalance in the reaction. The use of a tin catalyst gives a product with superior color.

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