Aliphatic–aromatic copolyesters: synthesis and crystallization studies

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A melt condensation technique has been employed for the synthesis of aliphatic–aromatic copolyesters using bisphenol-A, resorcinol, hydroquinone and 4,4'-dihydroxydiphenyl sulphone. The incorporation of bisphenols was ascertained by chemical composition using infra-red and nuclear magnetic resonance spectra. The effect of the catalyst and stirring during condensation has been studied. The dependence of thermal properties and crystallization behaviour on copolyester composition has been considered. The results are compared with those obtained by wide-angle X-ray diffraction and density studies.

INTRODUCTION

The introduction of appreciable amounts of alicyclic[1] or aromatic diol[2] as third components in polyesters is expected to improve dyeability and moisture sorption properties by its ability to increase disorder and cause interruption of crystallinity. Syntheses of such copolyesters containing bisphenols[3,4], hydroquinone[5-7], etc., have been recommended, employing a preformed polyester, an acid and a bisphenol diacetate. Fibres of high tenacity and high modulus have been prepared from poly(phenyl-1,4-phenylene terephthalate)[8]. Aliphatic–aromatic copolyesters have also been synthesized by melt condensation using diphenyl ester[9-11] which requires preparation of the ester and the handling of phenol. Hence, this process is not desirable for commercial applications.

Here, some results from studies on the influence of the bisphenols and their concentration on the transesterification process as well as on the crystallization temperature and crystallinity of the copolyesters are reported.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) was recrystallized from methanol and carefully dried in vacuum (m.p. 141–142°C). The bisphenols were purified by the method reported earlier[12].

Bisphenol diacetates were prepared according to Levine and Temin[13] by refluxing bisphenol/hydroquinone in acetic anhydride and sodium acetate, m.p. 82° and 122°C, respectively.

Preparation of polymers

Poly(ethylene terephthalate) (PET) was prepared by ester interchange using 19.4 g (0.1 mol) DMT and 13.6 g (0.22 mol) of ethylene glycol (EG) in the presence of 0.046 g (0.25 mol %) of $Mn(OAc)_2$ and 0.072 g (0.25 mol %) of antimony trioxide as catalyst at 185°C in a current of dry nitrogen. After 4 h when methanol ceased distilling over, 0.172 g (0.60 mol %) of triphenyl phosphate (TPP) was added and vacuum was applied gradually to 0.1 mmHg and temperature was raised to 285°C to distill off the excess ethylene glycol.

Copolyesters were prepared in the same manner using different amounts of bisphenols. The polycondensation temperature was kept 275°C due to the susceptibility of bisphenol degradation at higher temperatures[14], while polycondensation time was increased by 30 min.

Synthesis of copolyesters with bisphenol diacetates

Melt–solid process. A mixture of 19.2 g (0.1 mol) PET ($\eta = 0.81$), 1.66 g (0.01 mol) terephthalic acid, 3.12 g (0.01 mol) bisphenol diacetate and 0.005 g dibutyltin oxide was placed in a 100 ml flask fitted with a nitrogen inlet. The flask was inserted in a metal bath at 280°C, and during stirring nitrogen was passed over the mixture. After 3 h, the mixture was a clear, homogeneous melt and a vacuum of 0.1 mm was applied; after 1 h the vacuum was released. The intrinsic viscosity of the isolated polymer was 0.26.

The polymer was crushed to a fine powder on Dayton (Chicago) grinder to pass through 2 mm screen and placed in 250 ml of acetone overnight. The solid was filtered and dried in a vacuum oven at 80°C. The crystallized solid was heated at 220°C/0.1 mm for 12 h to give a polymer of intrinsic viscosity 0.36.

Polymer characterization

The melting points of the samples were determined by the capillary method at a heating rate of 5°C/min.

Intrinsic viscosity was determined with an Ubbelohde viscometer in *m*-cresol at 30°C and in phenol/tetrachloroethane (60/40 by wt) at 25°C.

Infra-red (i.r.) spectra of copolyesters were recorded on an infra-red spectrophotometer SP-1200 using thin films. The band ratio technique[15] was applied to find the amount of bisphenol incorporated in random copolyesters.

N.m.r. measurements were made on 100 MHz Varian Associates instruments, using tetramethylsilane as the internal standard and trifluoroacetic acid as a solvent.

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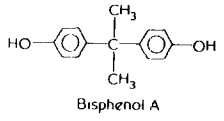
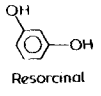
Table 1 Aliphatic–aromatic copolyesters by melt condensation without stirring, $Mn(OA_c)_2 + Sb_2O_3$ catalyst

Polymer code	Third component	(mol %)	$[\eta]$ (dl g^{-1})	Melting temperature (°C)
PET	NIL	–	0.46	260
B_1ET	 Bisphenol A	1.0	0.38	255
B_2ET	"	2.0	0.36	253
B_3ET	"	5.0	0.34	251
B_4ET	"	10.0	0.26	245
B_5ET	"	20.0	0.22	236
R_1ET	 Resorcinol	1.0	0.34	254
R_2ET	"	2.0	0.26	250
R_3ET	"	5.0	0.22	248
R_4ET	"	10.0	0.20	245

Differential scanning calorimeter (d.s.c.) was used for all calorimetric studies (Perkin–Elmer DSC-2 model). Polymers were studied as-prepared.

For measuring the crystallization rates, polymer pellets were prepared and kept in d.s.c. sample pan. The instrument was calibrated using indium as standard. Annealing, quenching as well as scanning were conducted under a nitrogen atmosphere to prevent degradation of the polymer sample.

The heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) were determined by comparing the peak area of the sample to that of a known weight of the indium reference material using equation 1:

$$\Delta H_f = \frac{KRA}{WCS} \tag{1}$$

K is the instrument constant, determined using a known weight (W) of indium, which was found to be 1.46:

$$K = \frac{H_f WCS}{RA} \tag{2}$$

where W = weight of sample/standard in mg; CS = chart speed (in^2 s^{-1}); ΔH_f = heat of fusion (cal g^{-1}); R = range (m cal s^{-1}); A = area (mm^2).

After determining the apparent heat of fusion (ΔH_f), the polymer crystallinity was calculated from equation 3:

$$\% \text{ Crystallinity} = \frac{\Delta H_f}{31.77} \times 100 \tag{3}$$

where the value of 31.77 cal g^{-1} was assumed to be the heat of fusion of completely crystalline PET[16].

PET and copolyester samples melted in the d.s.c. were allowed to crystallize at different cooling rates. After complete crystallization from the melt at a particular cooling rate (40°, 20°, 10°, 5°C min^{-1}), the samples were remelted at a heating rate of 20°C min^{-1}. This process of melting, crystallization and remelting was conducted on the same sample so that endotherms could readily be compared.

X-ray diffraction studies

X-ray diffraction patterns (intensity vs. diffraction angle plots) were obtained on a Phillips X-ray diffractometer equipped with a scintillation counter and a chart recorder. CuKα radiation was used. The X-ray scan was divided into crystalline and amorphous regions according to the method suggested by Bell and Dumbleton[17]. The ratio of crystalline area to the total area (A_C/A_T) was taken as the crystallinity index.

Density measurement

Density measurements were carried out using a density gradient column (Davenport, London) comprising a mixture of xylene and CCl_4. Polymer pellets were prepared from finely divided powder under constant pressure and temperature and was then kept under vacuum at 60°C for 12 h prior to density measurement.

RESULTS AND DISCUSSION

The polymers obtained both without and with stirring are tabulated in *Tables 1* and *2*, respectively.

The stirring was found to enhance the viscosity of PET and other copolyesters significantly. $[\eta]$ of PET obtained in stirring system was 0.81 compared with 0.46 in the unstirred system. Similarly, the viscosities of bisphenol and resorcinol (10 mol %) copolyesters also increase from 0.26 to 0.46 and from 0.20 to 0.42, respectively. The results obtained after stirring in the same system indicate that fairly high molecular weight products are obtained due to uniform distribution of heat and also due to fast removal of excess ethylene glycol, which results in enhanced propagation of polycondensation.

Effect of catalyst combination on melt condensation

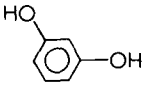
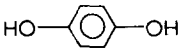
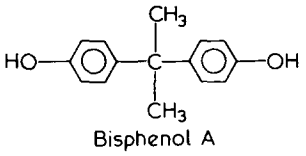
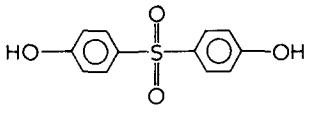
The catalyst combinations used in the present study include: $Zn(OAc)_2 + Sb_2O_3$; $Mn(OAc)_2 + Sb_2O_3$; and $Ti(OBu)_4 + Sb_2O_3$ (0.25 mol %).

As shown in *Table 3*, the various catalyst combinations have their own significant contribution to the viscosities of PET and other copolyesters. The relative effect of these catalysts was confirmed by the amount of methanol evolved during transesterification. Among the three catalysts studied, the $Mn(OAc)_2 + Sb_2O_3$ combination gave the theoretically calculated amount of methanol, i.e. 6.4 ml (with 0.1 mol DMT) accounting for its better efficiency, which can be further seen from the viscosity data.

Table 2 Effect of nature of catalyst on synthesis of PET and copolyesters by melt condensation in stirring

Sample code	Catalyst combination	$[\eta]$ (dl g^{-1})	Colour of polymer	Melting temperature (°C)
PET	$Zn(OAc)_2 + Sb_2O_3$	0.56	White	260
PET	$Ti(OBu)_4 + Sb_2O_3$	0.62	Yellowish	260
PET	$Mn(OAc)_2 + Sb_2O_3$	0.81	Greyish	260
(B_4ET) (10 mol % bisphenol-A)	$Zn(OAc)_2 + Sb_2O_3$	0.36	White	240
B_4ET	$Ti(OBu)_4 + Sb_2O_3$	0.38	Yellowish	240
B_4ET	$Mn(OAc)_2 + + Sb_2O_3$	0.46	Greyish	238

Table 3 Aliphatic-aromatic copolyesters by stirred melt condensation using $Mn(OAc)_2 + Sb_2O_3$ catalysts

Sample code	Third component	mol %	$[\eta]^a$ (dl g^{-1})	$[\eta]^b$ (dl g^{-1})	Melting temperature (°C)	$\bar{M}_v{}^c$ (Viscosity average mol. wt.)
PET	–		0.81	0.57	260	19510
R_4ET	 Resorcinal	10.0	0.42	0.38	252	11970
H_4ET	 Hydroquinone	10.0	0.45	0.39	239	10740
B_4ET	 Bisphenol A	10.0	0.46	0.41	238	10380
PS_1ET	 4,4'–dihydroxydiphenyl sulphone (PS)	5.0	0.50	0.42	255	12990
PS_2ET	"	10.0	0.36	0.32	232	8240
PS_3ET	"	15.0	0.34	0.30	225	7482

[a] Viscosity at 30° C/*m*-cresol
[b] Viscosity at 25° C/phenol/tetrachloroethane (60/40 by wt.)
[c] Viscosity average molecular weight by using equation 4

Metal acetates have advantage over other catalysts because of their good solubility and their strong catalytic effects on transesterification and polycondensation[8]. However, the titanium tertiary butoxide has been recommended by Inata *et al.*[10] for aliphatic–aromatic copolyesters $Mn(OAc)_2$ seems to be the best in the present study for transesterification. Further, antimony trioxide is widely used as a catalyst for polycondensation, because of its uniform dispersion in the polymer melt[19].

Effect of bisphenols on melt condensation

Previous[14] transesterification of bisphenols was discarded, as highly discoloured products were obtained by melt condensation. However, the results shown in *Tables 1* and *2* indicate that the process may be applicable for the synthesis of copolyesters with a limited molar ratio of bisphenols. It was observed during the transesterification reaction that bisphenols melt at 185°C in the presence of ethylene glycol and DMT and become mutually soluble. However, the evolution of methanol is slow in the presence of bisphenols, which may be due to the slow transesterification rate. Hence, the reaction time required for the synthesis of copolyesters was more than that for PET.

A gradual drop in viscosity has been observed with increasing bisphenol content in the copolyesters. The intrinsic viscosity of bisphenol copolyesters spanned the range $0.27 < [\eta] < 0.38$ and that of copolyesters with resorcinol covered the range $0.20 < [\eta] < 0.34$ (*Tables 1* and *2*). The drop in viscosity by incorporation of the bisphenols may be attributed to the difficulties in removing the bisphenol from the viscous polymer mass even at the reduced pressure (0.1 mmHg), which decreases the rate of propagation of growing polymer chain.

Molecular weight approximations

The molecular weight approximation for PET and copolyesters with identical molar ratios of various bisphenols was found by using equation (4):

$$[\eta] = 7.61 \times 10^{-4} M_n^{0.67} \quad (4)$$

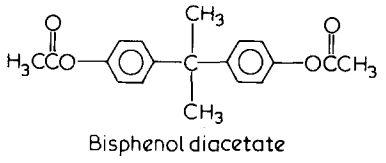
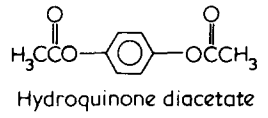
$[\eta]$ was determined at 25°C in phenol/tetrachloroethane (60/40 by wt).

Since PET is the major component in the copolyester, the above equation was used to obtain an idea of the range of molecular weights in the copolyesters. Zdrahala *et al.*[15], have carried out molecular weight approximations for aromatic–aliphatic polyamides in a similar way.

It is apparent from the results shown in *Table 2* that the viscosity as well as the molecular weight drop with increasing bisphenol content in the copolyesters. With 10 mol % of various bisphenols, the $[\eta]$ values for copolyesters are given in the following order: $B_4ET > H_4ET > R_4ET > PS_2ET$. The variation in the viscosity of the copolyesters may be attributed to the structural variations in the third component, which affect the hydrodynamic volume as well as the degree of polymerization of copolyesters.

Furthermore, higher $[\eta]$ values in *m*-cresol in comparison with phenol/tetrachloroethane solvent are observed in all the copolyesters (*Table 2*). These results suggest the expansion of polymer coils by polymer–solvent interaction in *m*-cresol. However, in the phenol/tetrachloroethane mixture, perhaps the agglomeration of polymer takes place which would explain the drop in $[\eta]$ values for all the copolyesters. As the solubility parameter of the solvent approaches that of the polymer, i.e. (PET $\delta_1 = 10.7$ [cal $cm^{-3}]^{1/2}$), *m*-cresol δ_2

Table 4 Copolyesters with bisphenol/resorcinol discetates by melt condensation

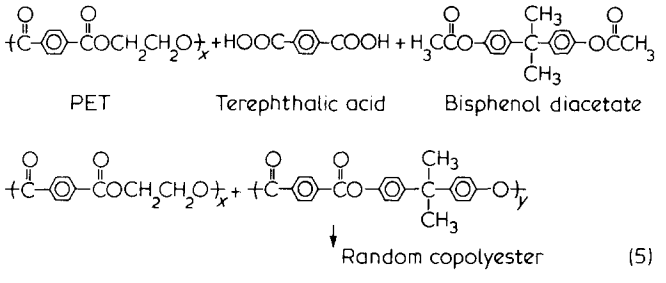
Polymer code	Third component	mol %	$[\eta]^a$ (dl g^{-1})	$[\eta]^b$ (dl g^{-1})	Melting temperature (°C)
PET	–	–	0.81	–	260
BAc_1ET	 Bisphenol diacetate	5.0	0.29	–	232
BAc_2ET	"	10.0	0.26	0.36	220
HAc_1ET	 Hydroquinone diacetate	5.0	0.24	–	245
HAc_2ET	"	10.0	0.22	0.30	235

[a] Viscosity at 30°C/*m*-cresol
[b] Viscosity after solid phase condensation for 12 h, at 30°C/*m*-cresol

$= 10.2$ [cal cm^{-3}]$^{1/2}$) the intrinsic viscosity is expected to increase[20]. This justifies the higher $[\eta]$ values in *m*-cresol as compared with phenol/tetrachloroethane (TCE) (TCE, $\delta_2 = 9.7$ [cal cm^{-3}]$^{1/2}$), (Phenol, $\delta = 14.5$ [cal cm^{-3}]$^{1/2}$).

Copolyesters with bisphenol diacetates

Another approach for synthesizing aliphatic–aromatic copolyesters involving acidolysis has also been utilized, as shown in equation 5:



(5)

From the above reaction, the following three observations were made (i) there was large initial decrease in viscosity, (ii) liberation of a small amount of acetic acid and (iii) an increase in viscosity with increase in reaction time.

The initial decrease in viscosity indicates that the first stage of the reaction may not be a polymerization but a chain scission which perhaps gives shorter chains of PET ending in bisphenol acetate and ethylene acetate. This could explain the small amount of acetic acid liberated during the reaction and the initial decrease in viscosity.

By this route, low viscosity copolyesters are obtained in comparison with those obtained by transesterification. The viscosity of PET decreases from 0.81 to 0.26 by the inclusion of 10 mol % of bisphenol diacetate (*Table 4*). However, the viscosity increased further to 0.36 by heating at 235°C/0.1 mm vacuum for 12 h, presumably by solid-phase condensation. F. L. Hamb[3] has also reported the viscosity increase in poly(ethylene-4,4'-isopropylidene-diphenylene terephthalate) (50:50) from 0.30 to 0.93 by heat treatment under vacuum for 72 h.

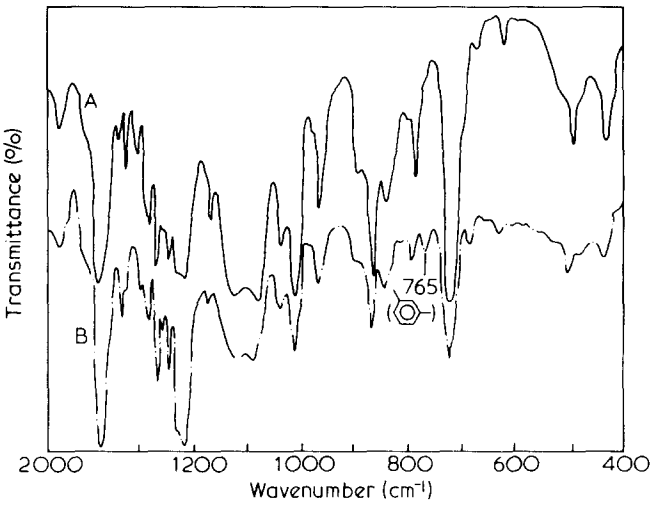
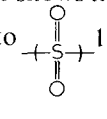


Figure 1 Infra-red spectrum of (A), PET; (B), R_4ET

Therefore, it is evident that there is a linear relationship with the duration of heat treatment and the viscosity increase. Buxbaum[21] has also noticed a similar relationship in poly(butylene terephthalate).

Infra-red spectra

A characteristic absorption peak at 1710 cm^{-1} for PET and copolyesters confirms the presence of ester linkage. The $-CH_2$ stretching at 2950 cm^{-1}, and a strong –CO stretching vibration at 1100 cm^{-1} is due to ethylene oxide (*Figure 1*). In resorcinol copolyesters, a distinct band at 765 cm^{-1} is due to *meta* substitution.

Bisphenol-A copolyesters show a characteristic peak at 1190 cm^{-1} due to gem dimethyl group (*Figure 2*). While 4,4'-dihydroxydiphenyl sulphone copolyester shows three characteristic bands at 1160 cm^{-1} ν due to  1070 cm^{-1} ν due to $-S=O-$ and at 585 cm^{-1} due to $-C-S-$ stretching.

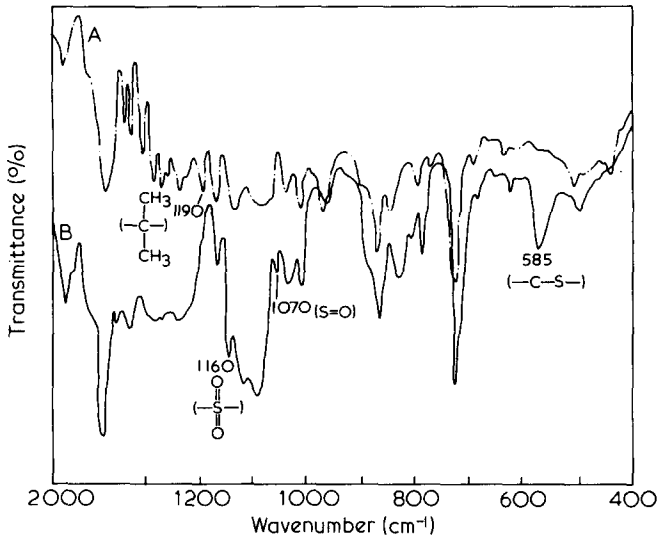


Figure 2 Infra-red spectrum of (A), B_4ET; (B), PS_2ET

OH stretching vibrations are assigned at 3440 cm^{-1} (*Figure 3*). The height of the –OH absorption band was normalized by dividing with ester peak at 1710 cm^{-1}.

As discussed earlier, the molecular weight of copolyesters decreases with incorporation of bisphenols, which can be confirmed from the number of end groups. The results shown in *Table 5* indicate that –OH peak height increases in the same order as the molecular weight decreases.

For determining the composition of copolyesters, the ratio of a common peak at 1100 cm^{-1} due to ν C–O in all the copolyesters and a characteristic peak for bisphenol copolyester at 1190 cm^{-1} due to gem dimethyl $-\overset{CH_3}{\underset{CH_3}{C}}-$ resorcinol copolyester at 765 cm^{-1} due to *meta* substitution and for 4,4'-dihydroxydiphenyl sulphone copolyester, a peak at 1160 cm^{-1} due to $-\overset{O}{\underset{O}{S}}-$ was considered. The composition determined by the band ratio technique was further confirmed by n.m.r. spectra (*Table 5*).

Nuclear magnetic resonance spectra

A singlet at 8.0 τ may be assigned to the methyl protons of the gem dimethyl unit in bisphenol-A copolyesters. The methylene protons of the ethylene unit $-CH_2-CH_2-$ are assigned to a singlet at 5.4 τ.

The mol fraction (X) incorporation of bisphenol unit in copolyesters was obtained from resonance spectra[15] using equation 6:

$$X = \frac{4A \text{ aromatic}}{6A \text{ aliphatic} + 4A \text{ aromatic}} \qquad (6)$$

where A aromatic is the area of the $-\overset{CH_3}{\underset{CH_3}{C}}-$ gem dimethyl unit and A aliphatic is the area of the $-CH_2-CH_2-$ methylene protons signal. The composition determined by n.m.r. was found to be in close agreement with quantitative i.r. studies.

Differential scanning calorimetry (d.s.c.)

Effect of bisphenols on glass transition temperature (T_g). A typical d.s.c. scan for the PET and (B_5ET) copolyester is shown in *Figure 4* and the results are presented in *Table 6*.

Upon heating the as-prepared samples at a particular heating rate, no endothermic peak was observed around the T_g. However, on quenching the same sample in liquid

Figure 3 Infra-red spectrum, showing variation in –OH peak heights (A), PET; (B), B_4ET; (C), PS_2ET; (D), R_4ET

Table 5 Composition of copolyesters by infra-red and nuclear magnetic resonance spectra

Sample code	Peak Ratio –OH/–C=O 3440/1710 (cm^{-1})	Bisphenol content		
		Theoretical	Found by i.r.	Found by n.m.r.
PET	0.1383	–	–	–
B_3ET	–	5.0	–	5
B_4ET	0.2820	10.0	10.0	10
B_5ET	–	20.0	21.0	22
R_4ET	0.2017	10.0	9.5	–
PS_2ET	0.3494	10.0	8.8	–

nitrogen a sharp endothermic baseline shift was observed and the middle point of the shift indicated the T_g.

As shown in *Table 6*, the T_g for PET is 82°C and a small variation in T_g values was observed on the insertion of the bisphenol unit into the polyester. Initially up to 10.0 mol % insertion of the bisphenol units gave a negligible decrease in the T_g values, and on a further increase in the bisphenol content up to 20 mol %, the T_g increased from 79°C to 83°C. The negligible variation in T_g may be attributed to the fact that the low content of bisphenol retains the large symmetrical sequences of PET. The drop in T_g values in resorcinol copolyesters is comparatively greater than that for bisphenol copolyesters (*Figure 5*), perhaps due to the significant interruption in the polymer symmetry owing to *meta* substitution in resorcinol.

There are, therefore, two competing factors, namely, (i) the introduction of rigid rings which will sterically hinder the chain rotation, thereby increase the T_g, and (ii) the introduction of large bulky groups presumably increasing the amount of free volume available and causing a lowering of the T_g. The small variation in the T_g values of copolyesters studied here may be related to the concurrent effect of both the above factors. A similar observation has also been made by Onder *et al.*[22] for polyester–urethanes.

Effect of bisphenols on crystallization temperature (T_c). As shown in *Figure 4*, after quenching the polymer in liquid nitrogen an exothermic peak due to crystallization was observed. The onset of crystallization occurs at a temperature between 155°–131°C for quenched copolyester samples (*Table 6*). The crystallization temperature shifts to a lower temperature with increase in the bisphenol content from 1 to 10 mol %. However, in 20 mol % bisphenol copolyester, an increase in the crystallization temperature was observed (*Figure 4*) due to the steric hinderance by the incorporation of the higher molar ratio of bisphenols. The half time of crystallization ($t_{1/2}$) also decreases with increase in the bisphenol content.

The T_c values for resorcinol copolyesters are lower than for bisphenol copolyesters. The decrease in T_c values in

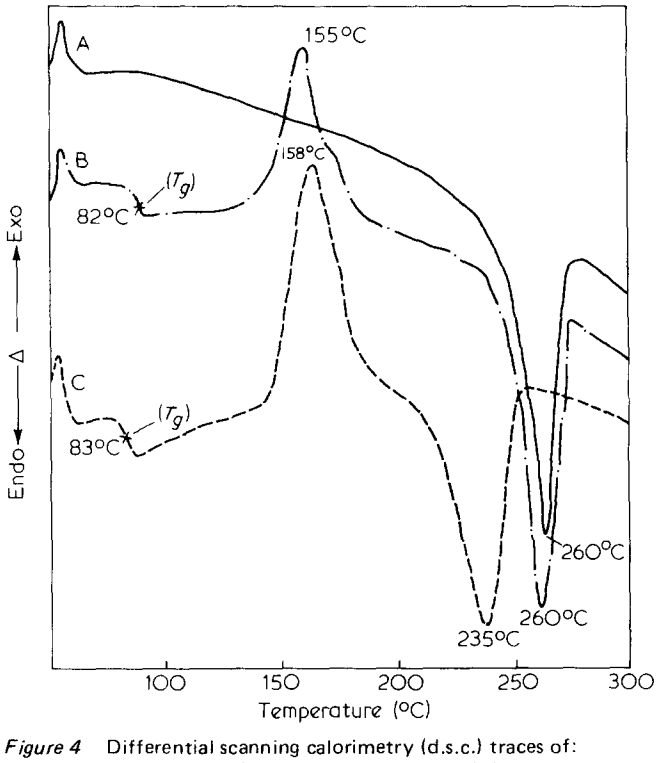


Figure 4 Differential scanning calorimetry (d.s.c.) traces of: (A), PET, as prepared; (B), PET, after quenching; (C), B_5ET, after quenching

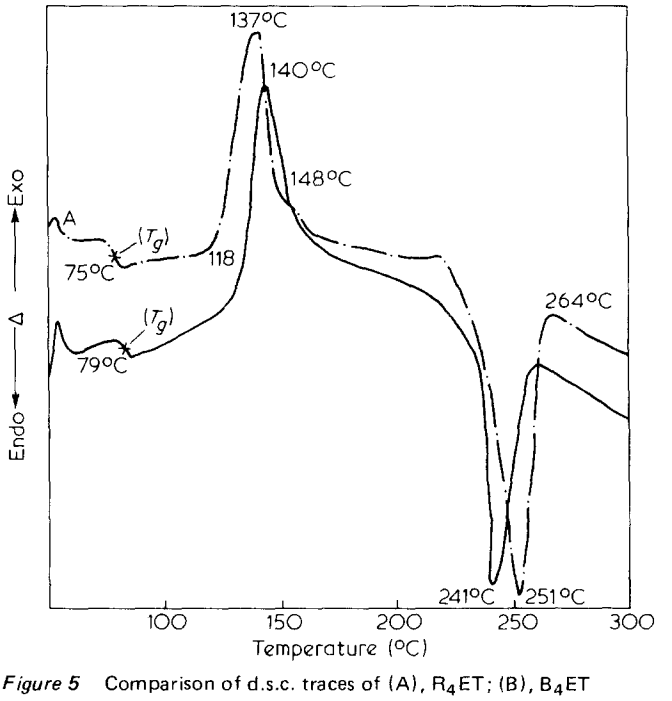


Figure 5 Comparison of d.s.c. traces of (A), R_4ET; (B), B_4ET

Table 6 Crystallization of PET and copolyesters of bisphenol and resorcinol

Sample code	Co-component Bisphenol-A/ resorcinol (mol %)	$[\eta]^a$ (dl g^{-1})	Glass transition peak (T_g) (°C)	Crystallization peak (T_c) (°C)	Melting peak (T_m) (°C)	T_g/T_m	Half time crystallization $t_{1/2}$ (min)	Heat of crystallization ΔH_c (Cal g^{-1})	Heat of fusion ΔH_f (Cal g^{-1})	Crystallinity by ΔH_f (%)
PET	–	0.42	82	155	260	0.65	1.1	9.28	8.68	27.3
B_1ET	1.0	0.38	80	152	255	0.675	1.0	10.2	9.05	28.5
B_2ET	2.0	0.36	80	152	253	0.675	0.95	11.9	10.2	32.1
B_3ET	5.0	0.34	78	149	251	0.67	0.95	12.32	10.96	34.5
B_4ET	10.0	0.26	79	140	241	0.675	0.90	13.64	11.0	34.9
B_5ET	20.0	0.22	83	158	236	0.71	0.975	16.04	11.54	36.3
R_1ET	1.0	0.34	76	139	258	0.657	0.90	11.45	13.45	42.3
R_2ET	2.0	0.26	78	131	255	0.665	0.875	16.75	13.90	43.75
R_3ET	5.0	0.22	79	131	253	0.67	0.85	20.8	14.30	45.0
R_4ET	10.0	0.20	78	137	251	0.674	0.83	24.8	14.18	44.6

[a] Viscosity at 30°C/*m*-cresol

Table 7 Effect of cooling conditions on crystallization

Sample code	Cooling conditions (°C/min)	Heat of crystallization, ΔH_c (cal g^{-1})	Crystallization peak, T_c (°C)	Degree of crystallinity
	40	5.74	177	18.06
PET	20	8.366	191	26.30
	5	9.367	202	29.50
	40	7.2	167	22.66
B_3ET	20	9.8	189	30.84
	5	11.08	195	34.87
	40	8.8	167	27.7
B_4ET	20	13.5	187	42.5
	5	17.09	194	53.8
	40	9.2	161	28.96
B_5ET	20	11.4	163	35.90
	5	12.2	197	38.80
	40	7.11	165	22.38
R_2ET	20	14.20	172	44.70
	5	20.12	189	63.3
	40	12.37	194	38.9
R_3ET	20	15.67	214	47.3
	5	16.04	222	50.5

resorcinol copolyesters indicated the ease of crystallization in comparison to bisphenol copolyesters. The ease of crystallization in copolyesters compared with PET may be due to the nucleating effect of bisphenols and also due to the decrease in molecular weight. Jackson and Longman[23] have also emphasized the decrease in T_c values in PET-sebacate/azealate copolyesters.

Thd quantitative values for the heat of crystallization (ΔH_c) were also calculated from the area under the crystallization peak[24]. The higher ΔH_c values for resorcinol copolyesters further confirms the fast rate of crystallization because the extent of crystallization (number of bonds formed) is directly proportional to the ΔH_c values.

Effect of bisphenols on melting temperature (T_m). The endothermic peak observed after crystallization peak is due to the melting of copolyesters. The observed melting points of copolyesters are lower than those for PET. The melting point determined by d.s.c. are comparable with those observed by the capillary method (*Tables 1, 2* and *6*).

The melting point of bisphenol copolyesters spanned the range 236°–260°C and resorcinol copolyesters 245°–260°C range by incorporation of bisphenol up to 20 mol % and 10 mol % of resorcinol respectively. It is evident from the results that there is a gradual decrease in the melting point of copolyesters with increase in bisphenol/resorcinol content. The decrease in melting point by the inclusion of bisphenol may be attributed to an interruption in the polymer symmetry and decrease in molecular weight. The effect of these two factors on T_m has also been reported by various workers[1–3,25].

It was observed during the d.s.c. scan that the peak position and peak area for melting peak remains unchanged even after quenching in liquid nitrogen. The heat of fusion (ΔH_f) was determined from the area under the endothermic peak (*Table 6*). The PET with symmetrical structure has a low heat of fusion and melts at higher temperature than copolyesters. The ΔH_f values increase with increase in the aromatic content, moreover, the ΔH_f values for resorcinol copolyesters are comparatively higher than for bisphenol copolyesters.

As shown in equation 3, there is a linear relationship with degree of crystallinity and ΔH_f values[26]. Evidently, the copolyesters having higher ΔH_f values show an increase in the degree of crystallinity. The increase in the degree of crystallinity is perhaps due to the nucleating effect of bisphenols during cold crystallization and secondly during d.s.c. scan, as stated before.

The interruption in symmetry of copolyesters by bisphenols has also been confirmed from the T_g/T_m ratio (*Table 6*). The simple numerical relationship observed by Lee and Knight[27] indicated that for symmetrical polymers $T_g/T_m \sim 0.5$, and for unsymmetrical polymers $T_g/T_m \sim 0.67$.

The increase in bisphenol content increases the aromatic content in the polymer backbone, which increases the ΔH_f values over PET, which contains $-CH_2-$ groups instead[28]. Further increase in ΔH_f values for resorcinol copolyesters rather than bisphenol copolyesters can be assumed to be due to the fact that a considerable contribution to the heat of fusion results from an average increase in the higher energy rotational isomer[29] by *meta* substitution in resorcinol copolyesters. Similar results for higher degree of crystallinity in resorcinol copolyesters has also been given by Korshak and Vinogradova[14].

Effect of cooling conditions on crystallization. With increasing cooling rates between 5°–40°C min^{-1} a decrease in both the heat of crystallization (ΔH_c) and crystallization temperature (T_c) has been observed.

It is believed that as the cooling rate increases, the crystal size and perfection of the material is hindered as indicated by the ΔH_f values. As shown in *Table 7* the overall melting temperature of PET and the copolyesters decreases with increase in the cooling rates, because the driving force for recrystallization is higher, which leads to the formation of small imperfect crystals. Sweet and Bell[30] have also noticed the similar behaviour in PET by variation in the cooling rate.

X-ray studies

The X-ray pattern of PET and B_4ET copolyester with bisphenol is shown in *Figure 6*. Since the amount of bisphenol incorporated is small, the major peaks at $2\theta = 27.5°$, 25° and 17.5° remain unchanged, irrespective of the nature of third component. However, some extra peaks at $2\theta = 22.1°$, 21° and 16° revealed that in copolyesters, mixed crystallites containing both the units (aromatic and aliphatic) are formed and the intensity of the extra peaks due to the mixed crystallites change with the proportion of the third component. Furthermore, it is clear that copolyesters possess a higher degree of crystallinity than PET, the resorcinol copolyesters possess a still higher degree of crystallinity than that of bisphenol copolyesters (*Table 8*).

It is interesting to note that the crystallinity values obtained by d.s.c. are higher than the crystallinity values obtained by X-ray diffraction. The higher degree of crystallinity calculated by d.s.c. may be attributed to the fact that d.s.c.-2 is extremely sensitive and detects even small size crystals, which cannot be scanned by X-ray studies. Moreover, thermally induced crystallization during d.s.c. studies will also lead to a higher degree of crystallinity as compared with X-ray diffraction.

Table 8 Density and crystallinity of copolyesters

Sample no.	Sample code	Density (g cm^{-3})	Bragg's angle 2θ	d. spacing (Å)	Degree of crystallinity	
					X-ray	D.s.c.
1	PET	1.3420	27.5°, 25°, 17.5°	3.24, 3.56, 5.05	24.0	27.3
2	B_1ET	1.3416			25.0	28.5
3	B_2ET	1.3408	27.5°, 25.8°, 22.2°, 21°,	3.24, 3.45, 4.0, 4.24,	25.0	32.1
4	B_3ET	1.3400	17.5°, 16°	5.05, 5.54	26.5	34.5
5	B_4ET	1.3380			27.0	34.9
6	B_5ET	1.3362			27.5	36.3
7	R_1ET	1.4200			23.2	42.3
8	R_2ET	1.4138	26.5°, 23°, 17.8°, 16.5°	3.35, 3.94, 4.98, 5.36	25.3	43.7
9	R_3ET	1.4092			26.0	45.0
10	R_4ET	1.4010			28.0	44.6

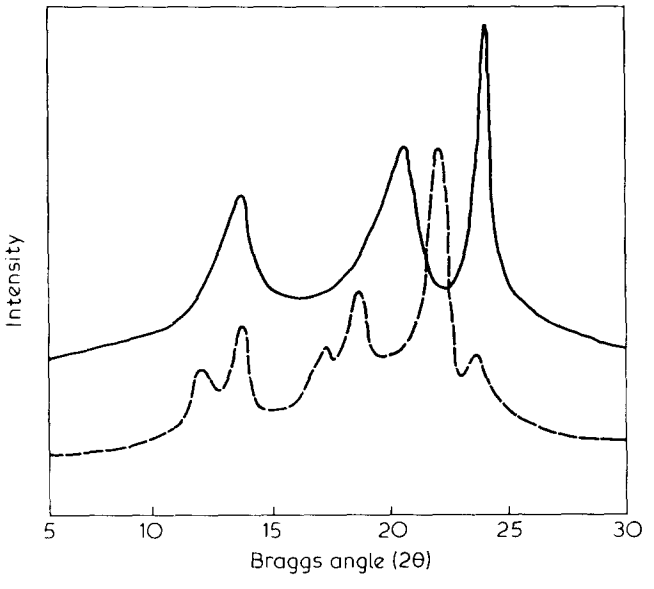


Figure 6 X-ray diffractograms of (A), PET; (B), B_5ET

Density

As shown in *Table 8*, the density of the copolyesters is less than that of PET. The drop in density as a result of the increase in the amount of the rigid aromatic moiety, may be attributed to the fact that intermolecular forces of attraction decrease rapidly and the chain bulkiness and irregular architecture renders the orientation and close packing more difficult.

Moreover, the density of the copolyesters rules out the concept that density should reflect crystallinity. The incorporation of unsymmetrical bisphenols decreases the molecular packing and thereby decreases the density. Kolbe and Izard[31] also observed that an increase in the density does not necessarily mean an increase in the crystallinity or *vice-versa*.

In conclusion, (i) transesterification appears to be feasible for the synthesis of aliphatic–aromatic copolyesters with limited molar ratio of bisphenols; (ii) $Mn(OAc)_2$ appears to be a suitable catalyst for catalyzing transesterification; (iii) introduction of bisphenol or resorcinol as a third component increases the rate of crystallization and also shifts the T_c and T_m to the lower temperature.

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