Aromatic–aliphatic copolyesters: structure and properties

D. N. Khanna, P. Bajaj and A. K. Gupta
Department of Textile Technology, Indian Institute of Technology, Delhi, New Delhi 110 016, India
(Received 16 June 1982)

Aromatic–aliphatic copolyesters synthesized by interfacial polycondensation were characterized by differential scanning calorimetry. X-ray diffraction and density measurements. A decrease in the T_g and melting temperature was observed on increasing the glycol content of the copolyesters. The wholly aromatic polyesters showed changes both in the Bragg angle position and intensity of the reflections, whereas in the aromatic–aliphatic copolyesters no sharp change was observed.

Keywords Copolyesters; interfacial polycondensation; bisphenol A, 4,4'-dihydroxy diphenyl sulphone; polyethylene glycol; X-ray diffraction

INTRODUCTION

It has been established in preceding papers[1–3] that the properties of copolyesters are dependent on the structure of the diol and dicarboxylic acid and also on their method of synthesis. Coleman[4] has studied the structure and properties of poly(ethylene terephthalate)–poly(ethylene oxide) (PET–PEO) block copolyesters. The crystallizability of the polycarbonates by the incorporation of PEO has been reported by Merril and Petrie[5]. However, very little is known, so far, about the structure and properties of aromatic as well as aromatic–aliphatic copolyesters synthesized by interfactial polycondensation.

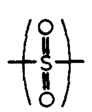
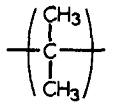
The present investigation is aimed at studying the structure and properties of the polyesters synthesized by interfacial polycondensation. The synthesis and characterization of these polyesters have been reported previously[6–8].

EXPERIMENTAL

The polymers were characterized by d.s.c., X-ray diffraction and density measurements. Experimental details have been given earlier[9].

RESULTS AND DISCUSSION

Differential scanning calorimetry

Among the aromatic polyesters, e.g. bisphenol terephthalate (BT), phenolphthalein terephthalate (PhT) and dihydroxydiphenylsulphone terephthalate (DHDPST), PhT showed the highest T_g (227°C) (*Table 1*). The exceptionally high T_g of PhT may be due to the rigidity in the structure. The lower T_g of DHDPST (195°C) than of BT (220°C) is perhaps due to the ease of rotation of  $\left(-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}}-\right)$ group in DHDPST as compared to *gem*-dimethyl  $\left(-\overset{\mathrm{CH_3}}{\overset{|}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}}}-\right)$ in BT.

It can be observed from the d.s.c. thermograms (*Figure 1*) that the aromatic polyesters are high melting (>400°C) and show a broad melting range instead of sharp melting.

Table 1 Differential scanning calorimetry (d.s.c.) data of polyesters

Polymer code	Diol (mol) feed ratio	$[\eta]$ (dl g^{-1})	T_g (°C)	Endothermic peak range (°C)
BT	Bisphenol-A (1.0)	1.30	220	305–457
BE_2T	Bisphenol-A/EG (0.7/0.3)	1.00	197	275–457
BE_3T	Bisphenol-A/EG (0.5/0.5)	0.70	190	236–446
BE_4T	Bisphenol-A/EG (0.2/0.8)	partially soluble	167	202–440
BI	Bisphenol-A	0.78	180	246–452
BE_2I	Bisphenol-A/EG (0.5/0.5)	0.58	157	236–433
BPE_3I	Bisphenol/ PEG^{1000} (0.8/0.2)	0.45	157	236–419
PhT	Phenolphthalein (1.0)	0.70	227	305–477
PhE_2T	Phenolphthalein/ EG (0.7/0.3)	0.24	216	305–462
DHDPST	DHDPS	0.70	195	–
$DHDPSE_2T$	DHDPS/EG (0.7/0.3)	0.37	184	–

T = terephthaloyl chloride
I = isophthaloyl chloride
EG = ethylene glycol
DHDPS = 4,4'-dihydroxydiphenyl sulphone

0032-3861/83/050596–03$03.00

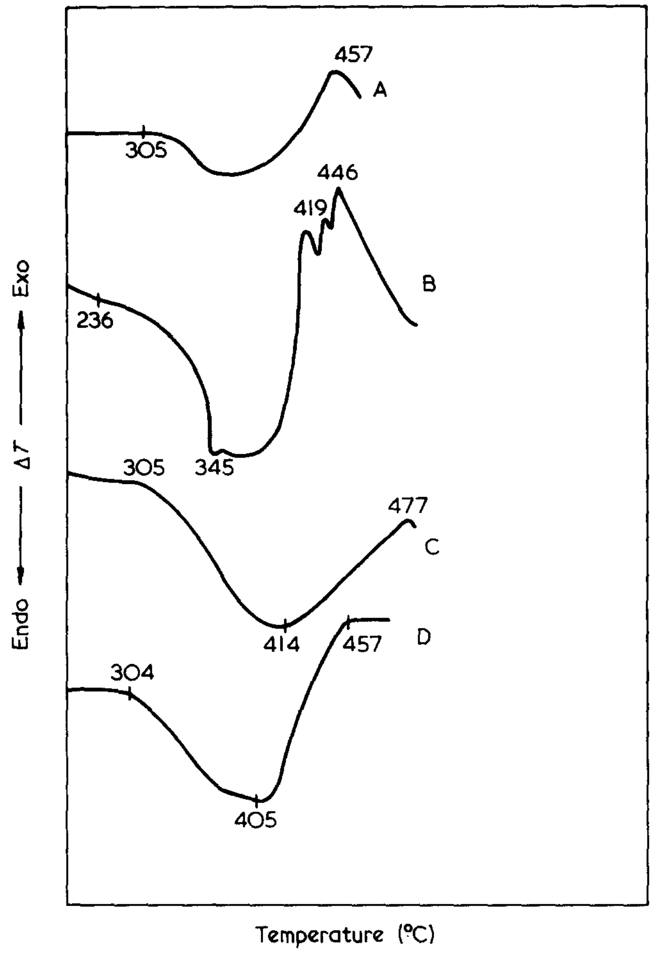


Figure 1 Variation in endothermic peak in d.s.c. thermograms: (A) BT, (B) BE_3T, (C) PhT and (D) PhE_3T

However, on incorporating aliphatic glycols (>20 mol%) into the aromatic polyesters, the melting range shifts towards lower temperature and follows a trend similar to that of decrease in T_g. Moreover, the broadening of the endothermic peak is also decreased. The change in the shape of the melting peak by the incorporation of flexible EG/PEG 200 units may be related to the (i) decrease in molecular weight and (ii) decrease in rigidity of the chain. A sharp melting peak and decrease in T_g in the polycarbonates by the incorporation of PEO has been reported in the literature[5].

X-ray diffraction studies

X-ray diffraction of various polyesters is shown in *Figures 2* and *3* in terms of intensity (I) vs. 2θ, where θ is the angle of diffraction (Bragg angle). The variation in the Bragg angle and the degree of crystallinity is presented in *Tables 2* and *3*.

In the case of wholly aromatic polyesters, e.g. resorcinol terephthalate (RT), dihydroxybiphenyl terephthalate (DHBPT), BT, DHDPST and PhT, the X-ray diffraction patterns show variation not only in the intensity of the reflections but also in the Bragg angle position (Figure 2). In BT and DHDPST polyesters, two sharp reflections appear at $2\theta = 16.8°$, $19.5°$ and $16°$, $25°$ respectively, whereas in DHBPT three sharp reflections occur at $2\theta = 19°$, $22.5°$ and $27.5°$. PhT does not show any sharp reflection, and this indicates a completely amorphous structure of the polyester. Owing to the wide variation in the chemical structure of these polyesters, the crystalline lattice for each of these is expected to be different, resulting in a marked difference in the X-ray diffraction pattern. The crystallinity index calculated from the diffractograms

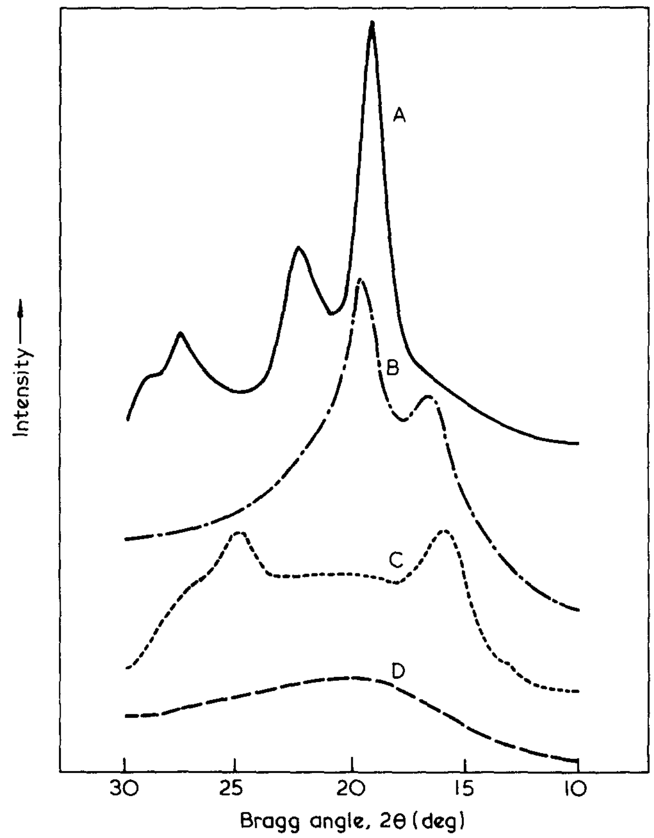


Figure 2 X-ray diffraction patterns of wholly aromatic polyesters synthesized by interfacial polycondensation: (A) DHBPT, (B) BT, (C) DHOPST and (D) PhT

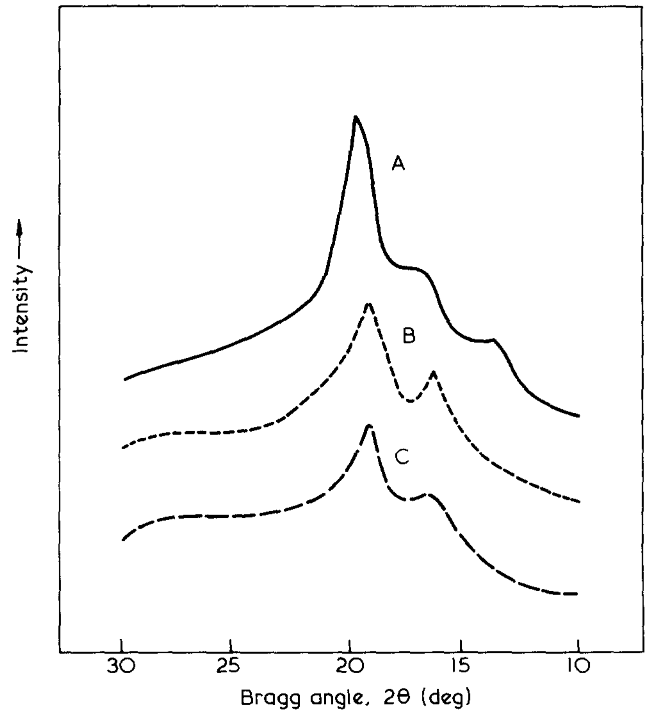


Figure 3 X-ray diffractogram of copolyesters prepared by interfacial polycondensation: (A) BPE_1I, (B) BPE_1T and (C) BE_3T

Table 2 **Bragg angle position of polyesters**

Polymer code	2θ value for the peaks (deg)	*d* spacing (Å)
BT	16.8, 19.5	5.28, 4.54
DHBPT	19, 22.5, 27.5	4.67, 3.96, 3.24
DHDPST	16, 25	5.54, 3.56
BE$_2$T, BE$_3$T and BE$_4$T	16.8, 19.5	5.28, 4.54

Table 3 X-ray and density data of copolyesters

Polymer[a] code	Density (g cm^{-3})	Degree of crystallinity (X-ray)
BT	1.2800	10.0
BE$_2$T	1.2854	12.7
BE$_3$T	1.2980	15.4
BE$_4$T	1.3125	22.25
BPE$_1$T	1.2840	12.4
BPE$_2$T	1.2790	13.0
BPE$_3$I	1.2800	13.40
BPE$_3$T	1.2833	13.35
RT	1.3250	16.0
RE$_3$T	1.3262	17.5
RE$_4$T	1.3294	28.4
PhT	1.1080	amorphous
DHDPST	1.2870	12.6
DHBPT	1.2920	36.0

[a] Refs 3 and 4

decreases in the following order: DHBPT > RT > DHDPST > BT > PhT (*Table 3*). The crystalline nature of bisphenol-A and resorcinol terephthalate polyesters synthesized by interfacial polycondensation using immiscible binary solvents (AN–CCl$_4$) has also been reported by Nakamura *et al.*[10]

Among the wholly aromatic polyesters, DHBPT has a linear structure, and hence may have a greater tendency to crystallize. In BT and DHDPST, the presence of

CHEM FORM B and CHEM FORM A

groups, respectively, may impose a greater restriction on the chain mobility and its arrangement on the crystalline lattice, thus resulting in lower crystallinity. The effect of the comonomers on crystallization, physicomechanical and dyeing behaviour of copolyester fibres has already been discussed in detail in preceding papers[9,11,12].

In bisphenol terephthalate polyester, two sharp reflections at $2\theta = 16.8°$ and $19.5°$ are observed. In bisphenol/EG copolyesters (EG 20–80 mol%), no change in the Bragg angle position is observed but the intensity of these reflections increases slightly on increasing the EG content. Introduction of EG makes the chain more flexible and interfacial polycondensation (in toluene–water) facilitates the anhydride formation[8]. As a result of the flexible nature of EG and the crystalline nature of the anhydride, the crystallinity increases on increasing the EG content.

In bisphenol isophthalate (BI) and its copolyesters, the sharp reflections in X-ray diffraction occur at $2\theta = 14°, 17°$ and $19.5°$ for all proportions of EG in the copolyesters (*Figure 3*). However, the intensities of these reflections vary with the variation of EG content in the copolyesters. The crystallinity index for BI and its copolyesters is slightly higher than that for BT and the corresponding copolyesters with ethylene glycol. The higher crystallinity index of BI and its copolyesters is due to the presence of one extra crystalline reflection in comparison to BT and its copolymers and also due to their lower intrinsic viscosities. An increase in the crystallinity with increase in the EG content is observed also for this class of copolyesters (*Table 3*).

ACKNOWLEDGEMENT

The Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged for providing a postdoctoral fellowship to one of us (D.N.K.).

REFERENCES

1 Charch, W. H. and Shivers, J. C. *Text. Res. J.* 1959, **29**, 536
2 Merril, S. H. *J. Polym. Sci.* 1961, **55**, 343
3 Goldberg, E. P. *J. Polym. Sci. C* 1964, **4**, 707
4 Coleman, D. *J. Polym. Sci.* 1954, **14**, 15
5 Merril, S. H. and Petrie, S. E. *J. Polym. Sci. A* 1965, **3**, 2189
6 Bajaj, P., Khanna, D. N. and Babu, G. N. *Eur. Polym. J.* 1979, **15**, 1083
7 Bajaj, P. and Khanna, D. N. *Eur. Polym. J.* 1981, **17**, 275
8 Khanna, D. N. *Ph.D. Thesis* (1981)
9 Bajaj, P. and Khanna, D. N. *Polymer* 1981, **22**, 1522
10 Nakamura, H., Imanishi, S., Sanui, K. and Ogata, N. *Polym. J.* 1979, **11**, 661
11 Bajaj, P. and Khanna, D. N. *Text. Res. J.* 1981, **51**, 696
12 Bajaj, P. and Khanna, D. N. *Text. Res. J.* 1982, **52**, 292