Synthesis and properties of some poly(bisphenol A iso/terephthalate) copolycarbonates

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Three hydroxy-terminated poly(bisphenol A iso/terephthalate) copolymer blocks have been prepared with molecular weights of 2400±5%, and isophthalate to terephthalate ratios of 25:75; 50:50; 75:25. Their properties have been determined. These blocks were then coupled with phosgene to give alternating polyester copolycarbonates of high molecular weight. A random copolycarbonate of 50:50 iso- and terephthalate blocks was also made. Physical properties were measured on the copolycarbonates. The glass transition temperature fell as the proportion of the isophthalate entity increased and at 50% isophthalate reached a value close to that of the pure isophthalate copolycarbonate. Tensile stress–strain curves indicated a changeover from near uniform extension (25% isophthalate) to the more normal type of necking behaviour with the isophthalate carbonates.

Keywords Copolymers; glass transition; bisphenol-A; terephthalate; heat capacity; tensile yield stress

INTRODUCTION

In previous work we reported some of the physical properties of a series of aromatic polyesters[1,2]. These polymers were hydroxy-terminated poly(bisphenol A terephthalate) (PBAT) or isophthalate (PBAI) blocks of various sizes, and the products of coupling them with phosgene to give the corresponding copolycarbonates, referred to as PBATC and PBAIC respectively. The following conclusions were reached:

(1) The glass transition temperatures (T_g) of the PBATC polymers were generally 20°–40°C greater than their isophthalate analogues and a maximum in the T_g was observed at certain phthalate/carbonate ratios. The higher T_g of the terephthalates creates certain moulding difficulties and provides an incentive to study copolymers.

(2) A relationship appears to exist between ΔC_p (the difference in specific heats for glass and liquid at T_g), the molar ratio of the ester to carbonate of the copolycarbonate and the reciprocal molecular weight of the polyester blocks[1].

(3) The PBATC polymers can give films which exhibit little fall in engineering stress after yielding in tension and so tend to deform in a uniform way. The PBAIC copolymers always neck. It has been argued elsewhere that this behaviour correlates with a more extended chain structure[3,4].

In the light of the above conclusions it would be desirable to retain as far as possible the tensile properties of the terephthalate carbonates (PBATC) and to improve the melt flow behaviour in the direction of the PBAIC polymers.

All the BPA phthalate blocks and their polycarbonates tend to be crystalline when precipitated from solution, but the unmodified BPA phthalate polymers have crystalline melting points ranging from 330° to 370°C which is above the temperature where oxidative degradation sets in. Thus with terephthalate carbonate copolymers the carbonate groups play an essential part in eliminating crystallinity in the bulk material. The use of mixed iso- and terephthalate copolymers and copolycarbonates was expected also to alleviate this problem further, as indicated in previous work on pure poly(bisphenol A phthalates) with different isomers[5–10]. The present paper describes some of the properties of such materials.

EXPERIMENTAL

Many of the experimental details of PBPAI/T and PBPAI/TC polymers are the same as previously reportes[1] and therefore only a summary of those details pertinent to the isophthalate/terephthalate polymers is given.

PBPAI/T block synthesis

Using a homogeneous reaction system, three hydroxy-terminated polyesters were made using similar bisphenol A to acid dichloride ratios. The purified acid dichlorides were premixed in 1,1,2,2-tetrachloroethane in the ratios (isophthalate to terephthalate) of 1:3, 1:1 and 3:1.

Copolycarbonate synthesis

The PBPAI/T blocks obtained above were further reacted with phosgene to give the corresponding copolycarbonate. In addition, a random block copolymer was made by coupling 50 wt% PBPAT, $\bar{M}_n$ 1810 and PBPAI, $\bar{M}_n$ 1960. All the PBPAI/TC polymer chains were terminated with *para*-cresol at the end of the phosgenation process and had a phthalate to carbonate ratio of 6.5–6.7.

Polymer characterization

The polymers were characterized by viscosity (1,1,2,2-

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Table 1 Properties of low molecular weight bisphenol A phthalates

Ester code PBPAI/T	L.v.n. ($cm^3 g^{-1}$)	Relative [iso] (%) in initial feed	Relative [iso] (%) found by n.m.r.	$\bar{M}_n$ ± 5% (v.p.o.)	T_g ± 2 (°C)	ΔC_p ± 10% ($J g^{-1} K^{-1}$)	T_m (°C)
25/75	17.10	25	24	2340	141	0.27	347
50/50	14.60	50	49	2420	132	0.25	338
75/25	13.25	75	73	2420	133	0.27	327
PBPAT	19.00	0	0	2230	147	0.20	371
PBPAI	14.20	100	100	2350	143	0.27	282

Note: T refers to terephthalate and I to isophthalate

tetrachloroethane, 25°C), vapour pressure osmometry, infra-red and n.m.r. spectral analyses as described before[1,3].

Thermal analysis

Differential scanning calorimetry. D.s.c. was performed using a Perkin-Elmer differential scanning calorimeter, Model DSC-2. Powdered or moulded samples of 5–10 mg were used. The general procedure and calibration of the instrument are described elsewhere[1,3,11]. The glass transition temperatures, T_g and ΔC_p values were measured at different heating rates and extrapolated to zero rate. Generally, heating rates of 10°, 20°, 40° and 80°C min^{-1} were used to avoid anomalous effects due to the thermal ageing seen at lower rates of heating[12].

Preparation of moulded films

The four PBPAI/T copolycarbonates (including the random block copolymer) were compression moulded at $T_g + 60$°C for one minute and then quickly quenched in iced water to produce amorphous, transparent, pale yellow plaques of thicknesses in the range 0.85 to 1.6 mm. The sheets were then reheated for a short period to a few degrees above the glass transition, to relieve stress, and cooled slowly under ambient conditions.

Tensile tests

These were performed on an Instron floor model TT-BM on specimens equilibrated at 23 ± 1°C and 40% humidity over 24 h. The test pieces, BS 2782 1970 301K type were cut from selected moulded films and tested at a nominal strain rate of 3.3×10^{-4} s^{-1}. Each test was performed five times, and the results averaged.

RESULTS AND DISCUSSION

Polyester copolymer blocks

Three polyphthalate ester copolymer blocks were prepared having approximately 25:75, 50:50 and 75:25 parts respectively of iso- to terephthalate. Details of their properties are given in *Table 1* where it will be seen that the control of block size by the imbalance of reactant ratios[13] was effective in producing polymers of closely similar molecular weight. The limiting viscosity numbers (l.v.n.) increased as the relative number of *para* linkages of the '*para–meta*' linked polymer was raised, a result which would accord with an increase in the persistence length in solution[13,14]. The ratio of iso- to terephthalate in the polyester blocks could be calculated from the i.r. spectral absorbances at 1400, 1290, 1250, 910 and 870 cm^{-1} relative to, e.g., the strong carbonyl absorption at 1740 cm^{-1}. However, it was found to be more convenient to determine composition by the average ratio of five integrations in the n.m.r. spectra of the isophthalate proton resonances centred at $\delta 8.3$. The percentage of isophthalate so determined is also given on *Table 1* and agrees well with the initial feed ratios.

Polyester copolycarbonates

All the high molecular weight copolycarbonates prepared for the above blocks were terminated by *p*-cresol with a view to increasing their thermal stability[2,3,15]. Apart from the carbonyl absorption their i.r. and n.m.r. spectra corresponded to the block composition. The same applied to the 50:50 block copolymer prepared from the separate iso- and terephthalate blocks.

Differential scanning calorimetry

Properties of low molecular weight blocks. Previously amorphous PBAT esters were found to crystallize more easily than the amorphous PBAI esters[1]. In the present copolymer series it was found that replacement of 25% of the terephthalate ester by the *meta* derivatives was sufficient to render it non-crystallizable in bulk when melted and then heated above T_g at rates of 5 to 20K min^{-1}. The crystalline melting points determined from the initial products precipitated from solution are given in *Table 1.*

The T_gs of the copolymer blocks are compared with homopolymers of similar molecular weight in *Table 1*, where it is shown that the lowest T_g is already reached when the proportion of isophthalate has reached 50%. Within the experimental error (±10%) the ΔC_ps of all the copolyesters were the same.

Properties of the high molecular weight copolycarbonates. The properties of the copolycarbonates having an l.v.n. of at least 80 are given in *Table 2.* At these molecular weights the values of ΔC_p relate smoothly to the composition and increase with the isophthalate content.

A plot of the value of T_g against the ratio of iso- to terephthalate in the PBAI/TC copolymers is shown in *Figure 1* where the results are also compared with those obtained by Bier[7] for the high molecular weight BPA pure phthalate esters (l.v.n. > 74 cm^3 g^{-1}). His values appear to be some 5–10K lower than ours which may be due to molecular weight differences or to the method of measurement. The trends are, however, the same. Clearly the introduction of isophthalate rapidly reduces the T_g but there is little change after the 50% level is reached.

Interestingly the random block copolymers formed by reaction with phosgene of separate isophthalate and terephthalate blocks showed only one T_g indicating a high degree of miscibility of the two constituents.

Mechanical properties

The results of tensile tests are shown in *Figure 2* and *Table 3*. For comparison the properties of PBATC (phthalate:carbonate ratio 4) and PBAIC 6 are also included. Ideally a moulded PBATC 6 should have been used for this work, in line with the ester/CO_3 ratios of the PBAI/TC polymers, but as mentioned previously moulded samples of PBATC ~ 6.0 are difficult to obtain owing to crystallinity.

The results show that as the concentration of isophthalate in the polyester increases from 0 to 100% the values of the engineering yield stress increase from 52 MPa to 57 MPa and the mode of deformation after yield changes from one of very diffuse necking to marked necking, as shown by the fall in engineering stress after yield. This result is in line with our earlier work and with the concept[1,4] that strain hardening is related to persistence length.

When the post-yield tensile deformation takes place the random conformation of the polymer coil is straightened out as in the extension of rubber, and the geometrical parameters of the coil determine how large a strain can be imposed before further extension becomes difficult, i.e. strain hardening sets in. In accordance with this hypothesis the present series of copolymers shows that the introduction of isophthalate units reduces strain hardening and facilitates the necking process. The changes in ΔC_p also favour the proposal that the bonds whose rotations occur during deformation below T_g are

Table 2 Properties of high molecular weight bisphenol A phthalate copolycarbonates

PBPAI/TC	L.v.n. ($cm^3 g^{-1}$)	$T_g \pm 2$ (K)	$\Delta C_p \pm 10\%$ ($J g^{-1} K^{-1}$)
25/75	102	485	0.145
50/50	83	464	0.205
75/25	119	466	0.18
Block 50/50	110	470	0.20
PBPATC 4.5*	100	485	0.1–0.15
PBPATC 5.6*	106	500	0.125
PBPAIC 6.0*	80	463	0.23

* Ester:carbonate ratio

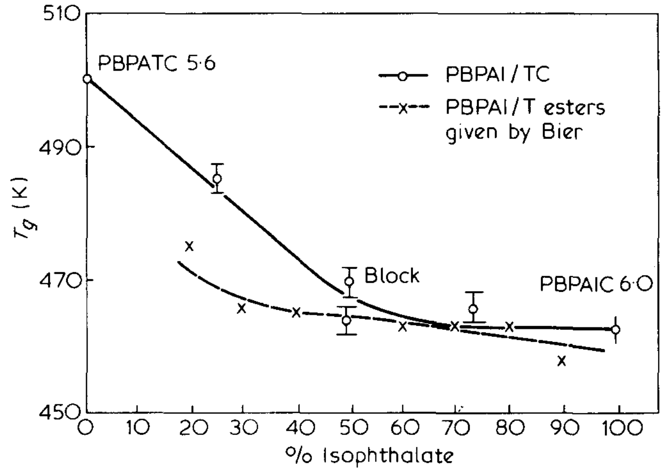

Figure 1 T_g *versus* percentage isophthalate in poly(bisphenol A phthalate carbonates)

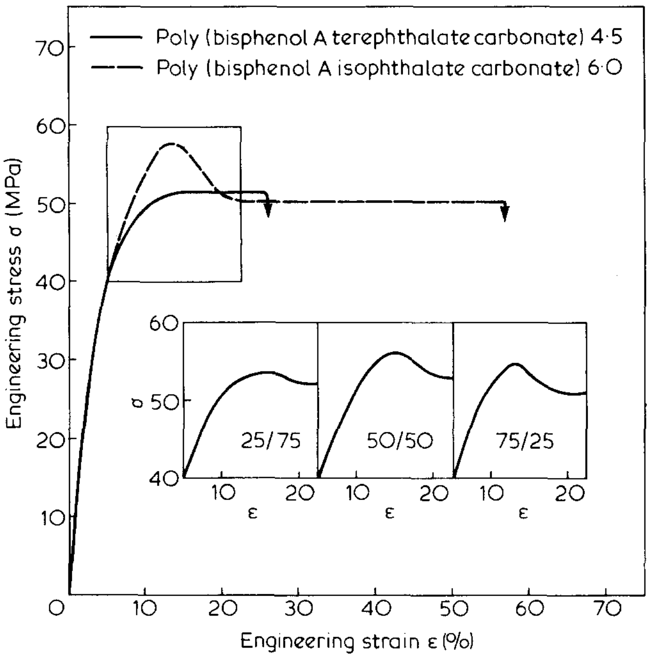

Figure 2 Tensile test results for PBATC and PBAIC, engineering stress (σ) *versus* engineering strain (ϵ)

Table 3 Tensile properties of bisphenol A phthalate copolycarbonates

PBPAI/TC	L.v.n. after moulding ($cm^3 g^{-1}$)	Yield stress (±0.5 MPa)	Yield strain (%)	Fall in stress after yield (%)	Extension to break (%)	Density ($g cm^{-3}$)
25/75	94	52.8	16	1.5	32	1.208
50/50	81	56.5	14	6.4	67	1.2075
75/25	104	54.7	12	7	57	1.2075
Block 50/50	110	54	13	5	58	1.2075
PBPATC 4.5	79	52	~14	0	31	1.21
PBPAIC 6.0	80	57.3	13	8	57	1.207

Strain rate = 3.3×10^{-4} s^{-1}
All values of stress and strain are engineering values

qualitatively similar to those which are able to rotate freely above T_g. Thus with the terephthalate copolycarbonate the polymer chain is assumed to have the most extended configuration which reduces both the tendency to neck and the measured value of ΔC_p.

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