Relations between structure and properties in bisphenol A polyester carbonates

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A range of hydroxy-terminated polybisphenol A terephthalate and isophthalate blocks have been prepared with molecular weights 800–5000, which were then coupled with phosgene to give alternating polyester copolycarbonates. These materials have been characterized by their physical, thermal and mechanical properties. The thermal properties have been investigated using differential scanning calorimetry and the glass transition temperatures, specific heats and $\Delta cps'$ (at the T_g) values obtained. A relationship appears to exist between Δcp and the reciprocal molecular weight of the polyester blocks, and the molar ratio of 'ester' to carbonate of the copolycarbonates. A maximum in the glass transition temperature has also been observed in the copolycarbonates, corresponding to a certain 'ester': CO_3 ratio. Tensile mechanical analyses have been performed on cast or moulded films of the copolycarbonates. The terephthalates can give films which extend uniformly but the isophthalates always neck.

INTRODUCTION

In the research, carried out in these laboratories, on the further preparation of block copolymers from polyethylene glycol and different polyarylate blocks[1] we prepared a phosgene linked copolymer of 'bisphenol A' (2,2-bis(4-hydroxylphenyl)propane) terephthalic acid ($\bar{M}n$ 2200) and 8% of polyethylene glycol ($\bar{M}n$ 1500). Stress–strain tests on a cast film of this material showed that it deformed uniformly without necking. We are interested in polymers of this type, since it has been shown both by qualitative arguments[2,3] and experimentally[4,5], that such materials are not subject to crazing in simple tension and may therefore be less prone to the conventional brittle fracture process.

In recent years many attempts have been made to improve on the overall properties of bisphenol A polycarbonate, (BPAPC) by copolymerization of dihydroxy aromatic compounds such as substituted hydroquinones and BPA with dibasic acids like adipic terephthalic and isophthalic acids or their derivatives[6–10]. Domine[11] has reported that a BPA iso/terephthalate (50:50) has valuable mechanical properties. Prevorsek[12] has also investigated BPA for terephthalate copolycarbonates in the ratios ($BPA:TP:CO_3$) 2.0:0.8:1.2 to 2:1.3:0.7 and reported superior scratch resistance, crack resistance, and higher softening points than BPAPC.

In the present work we have prepared various hydroxy-terminated bisphenol A terephthalate and isophthalate blocks with $\bar{M}n$s ranging from ~750–5000 and then coupled them with phosgene to give alternating polyester copolycarbonates. This two stage process made it possible to study both the properties of the bisphenol A polyesters in the low molecular weight range and the properties of the higher molecular weight copolycarbonates coupled by phosgene. In the course of this work we were able to prepare polymers, without including poly(ethylene oxide), which showed very little localization of plastic strain. When deformed in tension after yield they did not form a neck but extended in a nearly uniform way over the parallel length of the test-piece. As indicated above, the polyester–copolycarbonates could be characterized by their ester/carbonate ratio, which can be varied experimentally by changing the polyester block size.

EXPERIMENTAL

Materials

Bisphenol A was from Shell Chemicals UK Ltd. and used without further purification after drying; it had a melting point of 159±1°C.

Phosgene, nitrogen, 1,1,2-2-tetrachloroethane (TCE) and pyridine were purified prior to use by standard procedures. Terephthaloyl chloride (BDH Ltd.) was purified by Soxhlet extraction with dry n-hexane and the pure material was recovered by removal of the hexane. Isophthaloyl chloride was prepared by refluxing isophthalic acid with thionyl chloride and a catalytic amount of pyridine followed by distillation at reduced pressure under N_2 (B. pt 160–165°C at 15 mm Hg).

Polyester synthesis A homogeneous system was used to form the hydroxy terminated polyesters by reaction of an excess of bisphenol A with the appropriate acid chloride, the products and reagents being soluble in TCE. A 10% excess of pyridine, 60°C and 12 h reaction times were employed. The product was recovered by precipitation in excess methanol and washed with 50:50 v/v H_2O:MeOH solution before drying to constant weight in vacuo at 60°C.

Polyester copolycarbonate synthesis Polyester copolycarbonates were prepared by adding phosgene progressively to well stirred solutions of the polyester in TCE, containing a 10% excess of pyridine at temperatures between 25 and 40°C. Phosgene addition was stopped at the required solution viscosity measured on an aliquot

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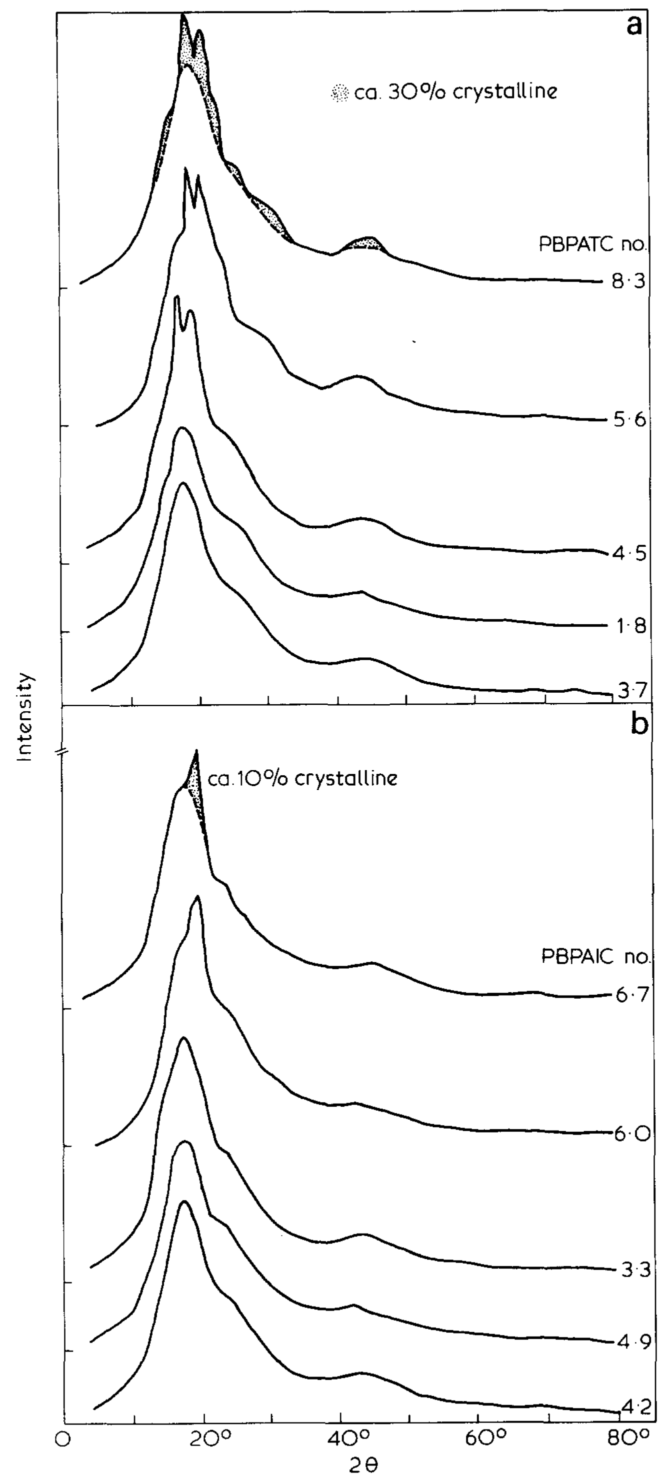

Figure 1 X-ray diffraction patterns for (a), cast PBPAT and (b), PBPAI carbonates (obtained by D. Clarke, R.A.E., Farnborough)

and the polymers precipitated in excess methanol. White fibrous precipitates were filtered, washed with 2M HCl/MeOH (50% v/v) in a Waring blender then washed further with aqueous MeOH (50% v/v) until free from Cl^- ions ($AgNO_3$). The copolymers were dried in vacuo at 60–80°C to constant weight.

Polymer characterization

The following procedures were employed:

(1) *Viscometry* An Ubbelohde suspended level viscometer was used at 25.0 ± 0.01°C on TCE solutions of the polyesters and copolycarbonates, to give limiting viscosity numbers $[\eta]$ $cm^3\ g^{-1}$.

(2) *Vapour pressure osmometry* Number average molecular weights ($\bar{M}n$) were measured with a Perkin-Elmer Hitachi Model 115 instrument using TCE solutions of concentrations 5–15 $g\ kg^{-1}$ at 60 ± 0.2°C. Purified Benzil (*MW* 210) was used to calibrate the instrument.

(3) *Chemical end group analysis* The standard method of HO-determination in polyesters was found to give inconsistent values and instead a variation of this using benzoyl chloride in pyridine with a phenolphthalene endpoint was employed. Although an improvement in accuracy was observed, results were still variable.

(4) *Infra-red* (*i.r.*) A Perkin-Elmer, Model 180, i.r. spectrometer was used. Spectra were run either on KBr discs or thin films as appropriate.

(5) *^1H n.m.r.* Spectra were obtained using a Varian 100 XL spectrometer at 100 MHz using TMS as an internal reference. Samples were run in $CDCl_3$ solutions of TCE solutions as appropriate.

(6) *Density measurements* The densities of the polyester copolycarbonates (cast or moulded films) were measured by flotation in $NaNO_3$ aqueous solutions at 15.6 ± 0.02°C using hydrometers reading to 0.0005 $g\ cm^{-3}$.

(7) *X-ray diffraction* X-ray diffraction patterns were obtained on the same cast films as were used in the density and mechanical analyses on a Picker powder diffractometer using CuKα radiation with a graphite monochromator. Scattered intensities were plotted against Bragg angle and are shown in *Figures* 1*a* and 1*b*. Corrections were made for instrumental background only.

The degree of crystallinity was determined by comparison of crystalline and amorphous scattering maxima but was sensitive to the method of deconvolution adopted. Values were consistent to within 10%.

(8) *Tensile tests* These were performed on an Instron floor model TT-BM on specimens equilibrated at 23 ± 1°C and $40 \pm 5\%$ humidity. The test pieces, BS 2782 1970 301 K type, were cut from cast and moulded films and tested at a nominal strain rate of $3.3 \times 10^{-4}\ s^{-1}$. Each test was averaged over five.

(9) *Preparation of films* Sheets of thickness 0.2–0.4 mm were cast from 90% $CHCl_3$:10% TCE solutions containing PBPAT copolycarbonates (10% v/v) and PBPA1 copolycarbonates (10% w/v) in $CHCl_3$. The films were dried at ambient temperature for 24 h at 30°C in vacuo for 8 h followed by a gradual raising of the temperature to 80°C in vacuo over 12 h and finally drying at 80–90°C in vacuo for a further 24 h. Examination of these cast films by differential scanning calorimetry revealed that the samples had not aged significantly.

The copolycarbonates were also compression moulded at temperatures ~60°C above their glass transition temperatures, i.e. in the range 250–300°C for 1.5 to 2.5 min to form sheets ~1 mm thick. These sheets were quenched from the moulding temperature by quick transference to iced-water and then reheated for a short period, ~0.5 min, at approximately 10° above the glass transition and cooled slowly.

(10) *Thermal analysis* (*d.s.c.*) was performed on a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-2. The temperature was calibrated by standard procedure[13]. The heat of fusion of indium was taken as 28.45 Jg^{-1} in calibrating the thermal response of the instrument.

Table 1

PBPAT Esters [η] cm^3 g^{-1}	$\bar{M}n$ (v.p.o.) (±5%)	Tg (K) ± 2 K	$^1/\bar{M}n \times 10^{-4}$	Δcp(J g^{-1} K^{-1}) ± ~10%
9.7	860	368	11.63	~0.39
14.95	1530	387	6.54	0.23
15.0	1680	402	5.95	0.19
15.3	1820	398	5.50	0.18
16.6	1810	400	5.52	0.19
17.1	1910*	412	5.26	0.20
19.0	2230	410	4.48	0.20
24.2	3170	433	3.15	0.17
25.2	3250*	440	3.08	0.175
26.0	3350	441	2.99	0.14
28.4	3800*	444	2.63	0.15
32.2	5390	450	1.86	0.15
34.9	5500*	454	1.82	0.13
PBPAI Esters [η] cm^3 g$^{-1$}	**$\bar{M}n$ (v.p.o.) (±5%)**	**Tg K (±2 K)**	**$^1/\bar{M}n \times 10^{-4}$**	**Δcp(J g^{-1} K^{-1}) ±10%**
6.9	1200	370	8.33	0.32
8.5	1400	370	7.14	0.30
10.4	1730	402	5.78	0.30
12.3	1960	410	5.10	0.27
14.2	2350	416	4.25	0.27
16.9	2610	420	3.83	0.25

*Values obtained via calibration graph

Table 2

PBPAT Esters	$\bar{M}n$ (v.p.o.) (±5%)	$\bar{M}n$ (n.m.r.)	$\bar{M}n$ (chem end. gp) analysis
	860	1000 ± 50	1200 ± 200
	1530	1500 ± 80	2000 ± 150
	1680	1550 ± 90	2050 ± 150
	1810	2000 ± 150	2700 ± 200
	2230	2400 ± 250	–
	3170	–	–
PBPAI Esters	1200	1400 ± 70	–
	1400	1600 ± 90	1800 ± 200
	1730	1910 ± 140	1980 ± 250
	1960	2130 ± 160	2680 ± 250
	2350	2990 ± 300	3520 ± 350
	2610	2230 ± 160	–

In measuring the glass transition a general procedure was adopted of heating 5–30 mg of the sample, encapsulated in aluminium, at 40K min^{-1} to 20° above the observed melting point, then to quench rapidly to ambient temperatures to produce an amorphous specimen. This was then reheated to just above the glass transition temperature and cooled at 20° min^{-1} to produce a standard glass, ensuring that recrystallization did not occur above the Tg.

The glass transition temperatures were measured on these glasses at various rates of heating and the corrected values obtained by extrapolation to zero rate at constant weight, or alternatively at constant heating rate but for different weights and extrapolating to zero weight.

The temperature dependence of the specific heats were determined for both the glass and the liquid in order that the difference between them at the glass transition temperature ($\Delta cp(Tg)$) could be determined

RESULTS AND DISCUSSION

Polyester block preparation

Polyester molecular weights, up to $\sim 7 \times 10^3$ were found to be satisfactorily controlled by changing the reactant ratios of bisphenol A to acid chloride as described by Flory[14]. Furthermore, by using bisphenol A in excess, accurately bisphenol A terminated polyester blocks have been produced, (as judged by i.r. and n.m.r. spectra). This method was found to be easier to use than that of Riches and Haward[1] which relied on reaction times for controlling block sizes. Details of the blocks prepared are given in *Table* 1.

The n.m.r. derived molecular weights (from the average ratios of five integrations between the bisphenol A protons and the iso- or terephthalate protons) are within experimental error of those obtained by vapour pressure osmometry (*Table* 2). The variability of chemical end group derived molecular weights cannot be due to inaccurate difunctionality since subsequent coupling gave substantially higher molecular weight polyester copolycarbonates. We therefore regard the titrations as suspect.

Vapour pressure osmometry derived number average molecular weights were found and used to construct Mark-Houwink plots of log [η] vs log ($\bar{M}n$) (*Figure* 2). For the range of molecular weight 1–5 × 10^3 the α was 0.74 for 'terephthalates' and ~ 1.1 for the 'isophthalates'. However, it was found that due to the precipitation and washing procedures, an increasing loss of low molecular weight species resulted as the target polyester molecular weight decreased. The polybisphenol A isophthalates were generally more soluble than the terephthalate analogues and so the loss was greater. Since changes in viscosity are less affected by a loss of low molecular weight species than vapour pressure osmometry derived values the actual α values were considered meaningless as far as chain conformation goes.

The viscosity calibration curve was used to determine approximate $\bar{M}n$ values for those polyester molecular weights not determined by vapour pressure osmometry.

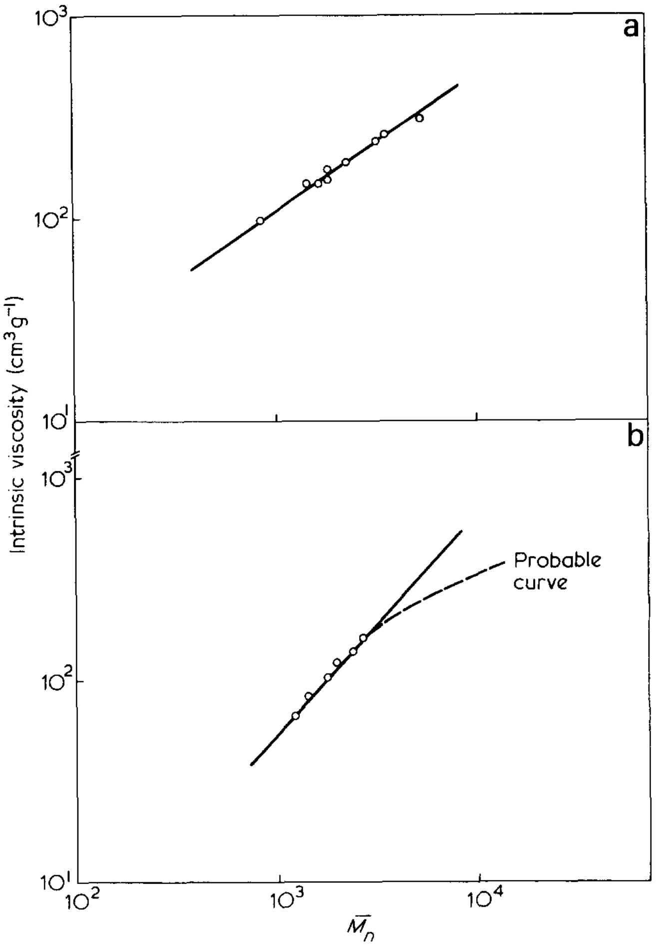

Figure 2 Mark-Houwink plots (log $[\eta]$ v log $\bar{M}n$) for (a), PBPAT and (b), PBPAI esters

The polyester carbonates

The next stage of the synthesis consisted of joining the polyester blocks together with -carbonate linkages introduced by phosgenation of the polyesters in a TCE solution using a pyridine activator. Consequently regularly spaced carbonate linkages were formed in the final polymer and so the ratio of ester molecules to $-CO_3$ was conveniently calculated from the initial polyester $\bar{M}n$ (derived from v.p.o.).

Generally 5% w/v solutions were used as higher concentrations resulted in extremely viscous solutions towards the reaction end point. It was found to be important to use less than a 200% excess of pyridine, otherwise lower molecular weight products resulted and the problems of washing the polymer increased. Pyridinium hydrochloride and pyridine are known to promote degradation at temperatures above 250°C and we also observed this.

Usually the PBPAT and PBPAI copolycarbonates were made with limiting viscosities between 80 and 120 $cm^3\ g^{-1}$. These limits enabled the polymer to extend beyond the tensile yield strain and yet were low enough for the polymers to flow during moulding. A high limiting viscosity resulted in a high melt viscosity under moulding conditions, especially in the PBPATC series, and created problems of bubbles and orientation in the moulded plaques.

The copolycarbonates i.r. spectra strongly resemble the initial polyester i.r. spectra but show an additional peak at 1770 cm^{-1} assigned to the -O-CO-O linkage. The normal aromatic ester (-CO-O) peak appears in both cases at 1740 cm^{-1}.

Thermal analysis

Figure 3 shows the d.s.c. thermograms for PBPAT $\bar{M}n$ 1680 and PBPAI $\bar{M}n$ 2350. In the PBPAT esters the original polyesters exhibited a sharp melting peak and no detectable glass transition, showing the material to be

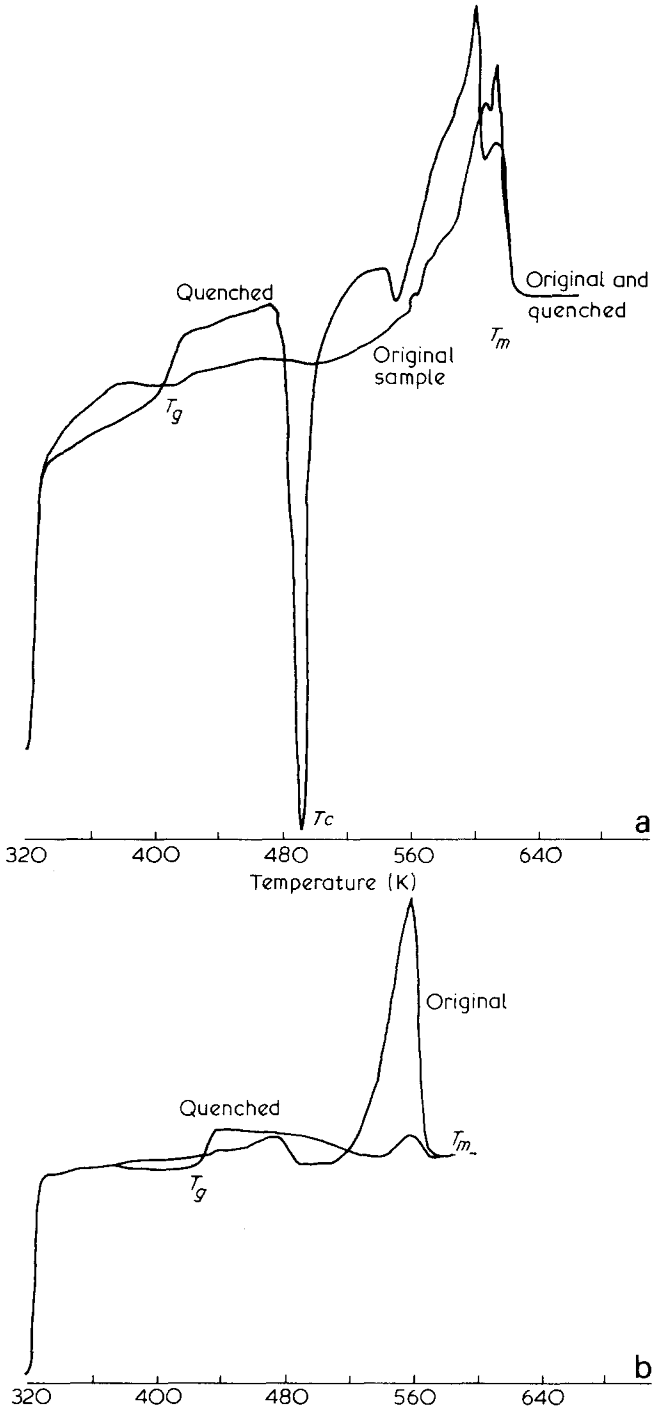

Figure 3 D.s.c. thermograms. (a), PBPAT $\bar{M}n$ 1680; weight = 19.0 mg. (b), PBPAI $\bar{M}n$ 2350; weight = 13.3 mg. Heating rate = 40° min^{-1} and the range = 10 mCal s^{-1} for both cases

Table 3

Ratio ester: CO_3	$[\eta]$ $cm^3 g^{-1}$	*Tg* K ($\pm$2 K)	Δcp($J g^{-1} K^{-1}$) $\pm$10%
Polybisphenol A terephthalate copolycarbonates			
1.8	102	475	0.135
3.7	215	505	0.08
3.7	80	485	0.13
4.0	105	488	0.15
4.0	83	487	0.125
4.5	100	485	0.1
4.5	88	490	0.15
4.5	83	485	0.15
5.6	106	500	0.125
8.3	97	495	0.13
8.8	94	486	0.1
10.0	73	486	0.11
12.0	77	476	0.1
BPAPC 0	73.3	426	0.17
Polybisphenol A isophthalate copolycarbonate			
3.3	117	459	0.19
4.2	92	463	0.18
4.9	88	463	0.20
6.0	80	463	0.23
6.7	81	459	0.24

partially crystalline. The quenched samples were readily crystallised at temperatures around 510K as shown by a large exothermic peak.

The original PBPAI esters again showed no discernible glass transition and melted over a narrow temperature range; however, quenched samples exhibited a well-defined glass transition but crystallization did not develop on subsequent heating. Therefore it is concluded that the PBPAT esters were more easily crystallised than the PBPAI esters.

The values of Tg are shown in *Table* 1. According to Fox and Flory[15] the glass transition temperature, Tg, exhibits a marked dependence on number average molecular weight, $\bar{M}n$, given by the equation $Tg = Tg^0 - K/\bar{M}n$. Errors in Tg values were estimated at ± 2K. The $\bar{M}n$ values were obtained either directly from v.p.o. measurements or from viscosity determinations and the calibration graph. A plot of Tg v $1/\bar{M}n$ gave straight lines for the PBPAT and PBPAI esters (*Figure* 4*a*). For PBPAT esters

$$K = 1.46 \times 10^5$$

$$Tg^0 = 483\text{K}$$

For PBPAI esters

$$K = 1.26 \times 10^5$$

$$Tg^0 = 470\text{K}$$

There were larger errors in determining the Tg values for low molecular weight polyesters ($\bar{M}n < 1000$) because they commenced to degrade rapidly at temperatures significantly above their Tg. This meant the quenching process (heating above the melting point followed by rapid cooling to ambient temperatures) introduced unknown amounts of degradation in the polymer and consequently produced more varied values of the Tg than higher molecular weight polyesters.

A graph of Tg (K) v the molar ratio of 'ester': CO_3 for the PBPAT and PBPAI copolycarbonates is shown in *Figure* 4*b*. A maximum in Tg is observed in the PBPAT copolycarbonate series for a molar ratio of 5–6. This maximum was much less pronounced in the PBPAI copolycarbonate series. Included in *Figure* 4*a* are the values of PBPAT copolycarbonates obtained by Prevorsek[12].

The thermograms of the original copolycarbonates (*Figure* 5) indicate the original materials were partially crystalline but the quenched samples exhibited no tendency to recrystallize on reheating.

Determination of the temperature dependence on the specific heat (cp)

The temperature dependence of specific heat is shown in *Figures* 6 and 7 for a number of PBPAT and PBPAI copolycarbonates from 320–530K. The specific heats of the terephthalate copolycarbonates were greater than the isophthalate analogues but the temperature dependences of the specific heat below the Tg were very similar ($\sim 3.3 \times 10^{-3} \pm 10\%$ Jg^{-1} K^{-2}) bisphenol A polycarbonate values appeared between those of PBPAT and PBPAI polycarbonate with the same temperature dependence. For the 'liquid' polymers (above the Tg) the temperature dependence was $\sim 0.8 \times 10^{-3} \pm 100\%$ $J g^{-1} K^{-2}$.

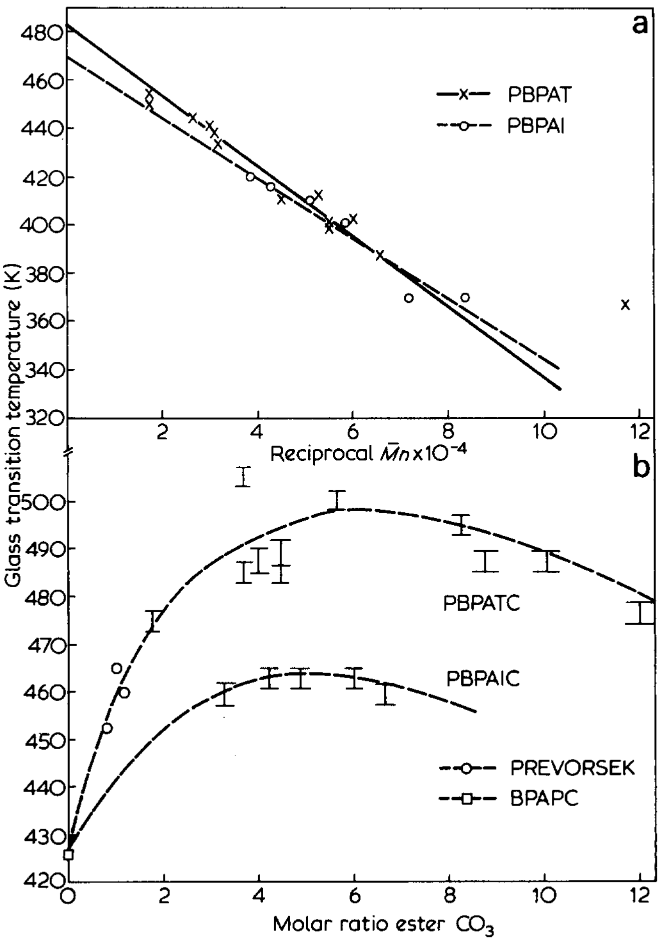

Figure 4a A plot of Tg (K) against $^1/\bar{M}n$ for the amorphous PBPAT and PBPAI esters

Figure 4b A plot of Tg (K) against the molar ratio of 'ester': carbonate for the amorphous PBPAT and PBPAI carbonates

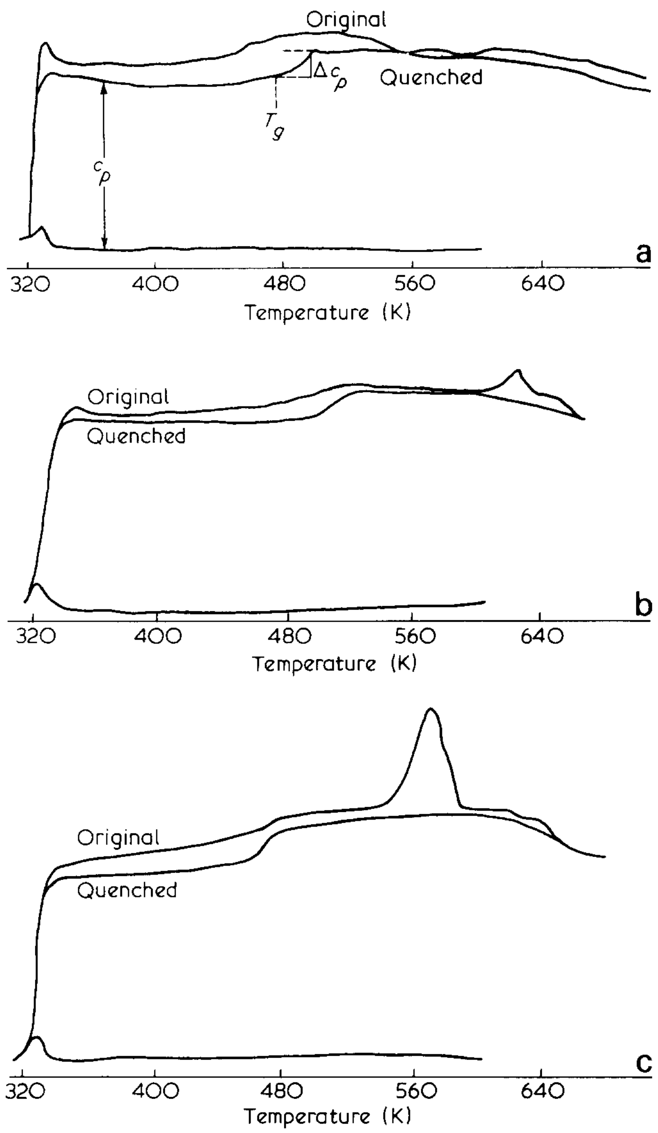

Figure 5 D.s.c. thermograms of (a), PBPATC 1.8 (weight = 6.5 mg; heating rate = 80° min^{-1}, range = 10 mCal s^{-1}); (b), PBPATC 8.3 (weight = 7.3 mg, heating rate = 40° min^{-1}, range = 5 mCal s^{-1}); and (c), PBPAIC 6.0 (weight = 8.1 mg, heating rate = 40° min^{-1}, range = 5 mCal s^{-1})

Δcp *values* $(J\ g^{-1}\ K^{-2})$

Δ*cp* values were obtained simultaneously with specific heat determinations on quenched samples at 20 K min^{-1}. These values varied by as much as ±20% on some repeated samples especially on low molecular weight polyesters. An apparent reciprocal relationship exists between Δ*cp* and molecular weight of the polyester blocks, (see *Figure* 8*a*) but specific heats are temperature dependent and some part of this dependence may reflect the variation of the glass transition temperatures. The limiting Δ*cp* value corresponding to the infinite *MW* for PBPAT was 0.11 J g K^{-1} and PBPAI 0.21 J g^{-1} K^{-1}.

The dependence of Δ*cp* on the molar ratio of 'ester' CO_3 for the PBPAT and PBPAI copolycarbonates is depicted in *Figure* 8*b*.

For the PBPAT copolycarbonates the values generally decrease from ~0.17 J g^{-1} K^{-1} (the value obtained from quenched bisphenol A polycarbonate $[\eta] = 73.3\ \text{cm}^3\ \text{g}^{-1}$) to ~0.085 J g^{-1} K^{-1} for a PBPAT copolycarbonate with a ratio of 10. In the PBPAI copolycarbonate series the Δ*cp* values increased with increasing molar ratio of isophthalate:CO_3 from the bisphenol A polycarbonate value of 0.17 to 0.25 J g^{-1} K^{-1} for a ratio of 7.0. However the values depicted in *Figure* 8*a* would suggest that Δ*cp* would decrease from 0.25 to 0.21 J g^{-1} K^{-1} for a pure polybisphenol A isophthalate of high molecular weight.

The decreasing Δ*cp* values in the PBPAT copolycarbonate series as the ester:CO_3 ratio increases is believed to reflect the increasing chain stiffness mainly caused by a decreasing molar content of bisphenol A. Conversely in the PBPAI copolycarbonate series the increasing Δ*cp* values with increasing isophthalate:CO_3 ratio may be due to the increasing isophthalate content in the polymers.

Mechanical properties

The results of the tensile tests are given in *Tables* 4 and 5.

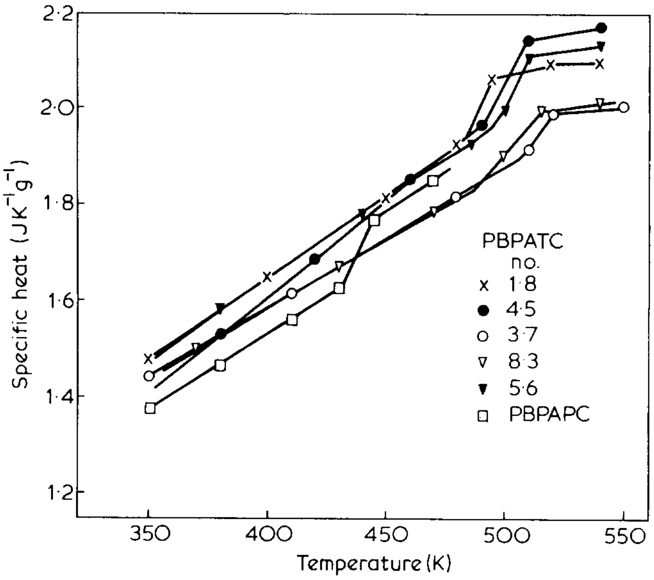

Figure 6 The temperature dependence of the specific heat of amorphous PBPAT carbonates

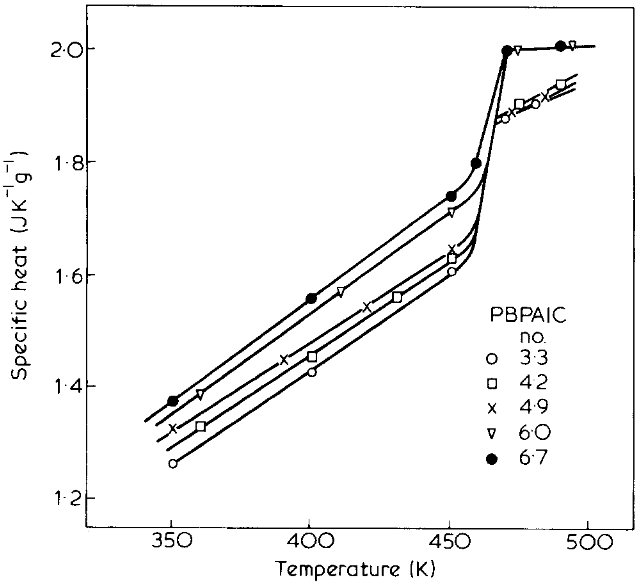

Figure 7 The temperature dependence of the specific heat of amorphous PBPAI carbonates

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Dr. M. J. Richardson of the National Physical Laboratory kindly agreed to check our results on two typical polymers from *Figures* 6 and 7. Within experimental error his results were the same as ours.

Polybisphenol A terephthalate copolycarbonates PBPATC

(1) *Cast films* The well-dried cast films were shown by d.s.c. and viscosity determinations not to have undergone significant amounts of thermal or physical ageing as a result of the drying process.

The values in *Table* 4 and *Figure* 9*a* illustrate that the engineering yield stresses of the PBPATC's are essentially similar, irrespective of the ester:CO_3 ratio, at ~57 MPa. However, there were marked differences in their post yield behaviour between polymers of different ester:CO_3 ratios. PBPATC 1.8 exhibited a 2% fall in engineering stress after yield which was concurrent with the formation of a stable neck. There was no observed fall in engineering stress after yield for PBPATC 3.7 ($[\eta]=80$ or 215 $cm^3\ g^{-1}$) and the polymers extended 'almost' uniformly. Thereafter, it was observed that increasing the ester:CO_3 ratio gradually increased the value of the fall in engineering stress after yield and a necking mode of extension was re-established (see *Figure* 11). D.s.c. and X-ray data on the PBPATC cast films showed the films were amorphous up to an ester:CO_3 ratio of 3.7 whereas PBPATC's 4.5, 5.6 and 8.3 contained degrees of crystallinity c.a. 15–30%. The effect of crystallinity on the mechanical properties has been reported[16,17]. Generally, an increase of crystallinity in polymers leads to an increase in the values of the yield stresses. Two theories have been postulated: first, the crystallites act as cross-links by tying segments of many molecules together, secondly, the crystallites have much higher moduli compared to the amorphous parts so they behave as rigid fillers in an amorphous matrix[17]. The partial crystallinity of PBPATC's 4.5, 5.6 and 8.3 would imply that the values of the yield stresses of these cast films would be lower if the films were rendered amorphous.

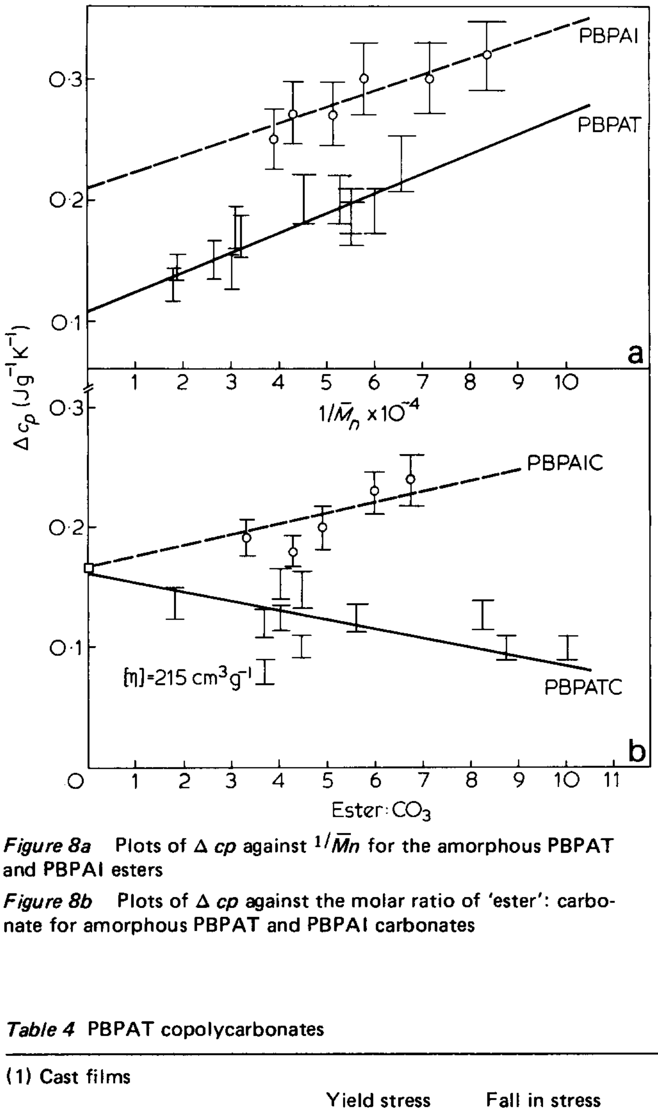

Figure 8a Plots of Δ *cp* against $1/\bar{M}n$ for the amorphous PBPAT and PBPAI esters

Figure 8b Plots of Δ *cp* against the molar ratio of 'ester': carbonate for amorphous PBPAT and PBPAI carbonates

(2) *Moulded specimens* The number of test specimens obtained by compression moulding at ~60°C above the glass transition temperature was limited due to problems of degradation and high melt viscosities. Generally yellow transparent plaques were produced and d.s.c. and X-ray analyses showed that all the moulded specimens were amorphous. Examination under crossed polars also showed no or little presence of orientation. A final specimen viscosity value of $\geqslant 70\ cm^3\ g^{-1}$ was found necessary for the material to extend beyond the yield strain.

The moulded PBPATC's 4.0 ($[\eta]=80\ cm^3\ g^{-1}$) and 4.5 ($[\eta]=79\ cm^3\ g^{-1}$) both diffusely necked after yield with no detectable fall in engineering stress. Observations on the broken test pieces revealed no signs of crazing or stress-whitening but this may not be significant by itself.

PBPAI copolycarbonates (PBPAIC)

(1) *Cast films* The cast films of PBPAIC 3.3, 4.2 and 4.9 were shown by d.s.c. and X-ray diffraction traces to be completely amorphous and transparent whereas PBPAIC's 6.0 and 6.7 were partially crystalline (~10% by X-ray) and white. The maximum observed engineering

Table 4 PBPAT copolycarbonates

Ester: CO_3	$[\eta]$ $cm^3\ g^{-1}$	Yield stress (±0.5 MPa)	Fall in stress after yield (%)	Yield strain (%)	Ultimate extension %	Ultimate strength (MPa)	Density ±0.0005 g cm^{-3}
(1) Cast films							
1.8	102	56	2	14	30	56	1.2075
3.7	80	58	0	~14	85	61	1.216
3.7	215	53	0	~15	52	55	1.2075
4.5	88	56.5	1–2	14	60	56	1.215
5.6	106	56	3	13.5	60	57	1.215
8.3	94	56	3	14	60	60	1.217
BPAPC (0)	73	57	13	6	170	53	1.204
(2) Moulded films (Stabilized with *p*-cresol ends)							
4.0	80	56.7	0	~14	47	61	1.208
4.5	79	52	0	~14	31	56.5	1.210

All values of stress and strain are engineering values
Initial strain rate = $3.3 \times 10^{-4}\ s^{-1}$

Table 5 Polybisphenol A isophthalate copolycarbonates

Ester: CO_3	$[\eta]$ cm^3 g^{-1}	Yield stress (±0.5 MPa)	Fall in stress after yield (%)	Yield strain (%)	Ultimate extension (%)	Ultimate strength (MPa)	Density (g cm^{-3})
(1) Cast films							
3.3	117	57	19	8	32	47	1.240
4.2	92	57.5	17	8	41	52	1.243
4.9	88	58.8	16	9	56	53	1.245
6.0	81	62.2	20	7	36	52	1.255
6.7	81	59.2	17	8	39	52	1.248
(2) Moulded films							
3.3	100	54.5	9	12	86	53	1.208
4.2	90	55.8	10	13	64	51	1.2075
4.9	85	56.2	10	13	88	56	1.2075
6.0	80	57.3	8	13	57	52	1.207
6.7	80	56.7	10	13	82	56.7	1.207

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

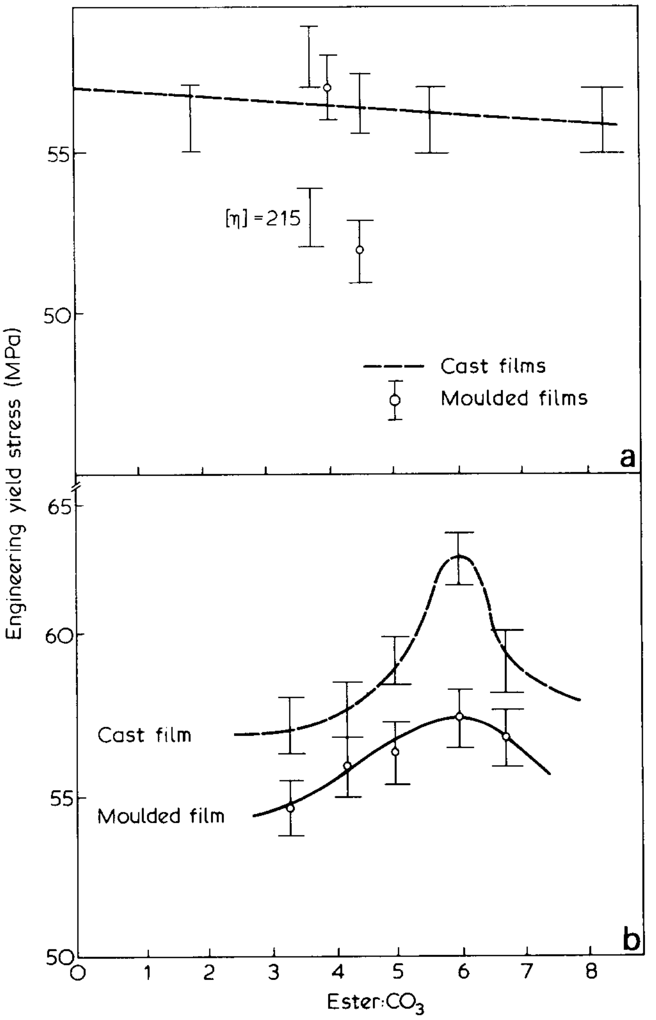

Figure 9 Plots of engineering yield stress against the molar ratio of 'ester': carbonate for cast and moulded PBPAT, (a) and PBPAI, (b), carbonates

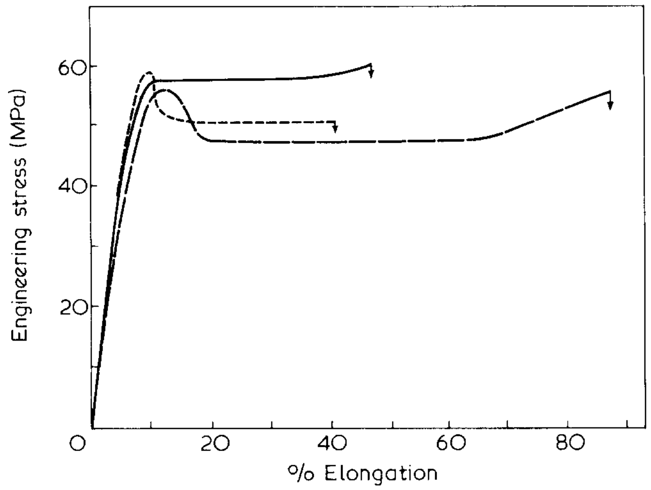

Figure 10 Tensile stress–strain curves of moulded PBPATC 4.0 (——), cast PBPAIC 4.2 (· · · · ·) and moulded PBPAIC 4.9 (— — — —). Strain rate = 3.3×10^{-4} s^{-1}

yield stress corresponding to an isophthalate:CO_3 ratio of 6 (see *Figure 9b*) may be the result of crystallinity.

All the PBPAIC cast films appeared to neck in a similar fashion but PBPAIC 3.3 exhibited stress-whitening in the necked portion whereas PBPAIC's 4.2 and 4.9 did not and remained clear. The necked portions of PBPAIC 6.0 and 6.7 appeared to be almost transparent but this was difficult to judge due to the initial weakness of the film and may simply be due to thinning of the material in the necked region.

(2) *Moulded films* The PBPAIC polymers were easily moulded at 250°C with little molecular weight degradation to produce clear, colourless amorphous plaques. The engineering yield stresses of all the moulded PBPAIC's were below their analogous cast films and again a maximum observed engineering yield stress was recorded for a polymer of ester:CO_3 ratio ~6 (*Figure 9b*). Compression moulded thick specimens of BPA polycarbonate were reported by Morgan and O'Neal[18] to have greater tensile yield stresses than the thinner cast films. Compared to the cast films, the moulded specimens exhibited approximately 50% lower falls in engineering stress after yield, 50% increased yield strains and a 100% increased ultimate elongations.

The necked portions of all the pulled, moulded PBPAIC specimens remained transparent up to fracture. In some cases the necks propagated throughout the waist portion of the dumbbell realizing ultimate extensions of about 90% and appeared insensitive to changes in the isophthalate:CO_3 ratio within ±5%.

Haward and Thackray[19] proposed a model associating

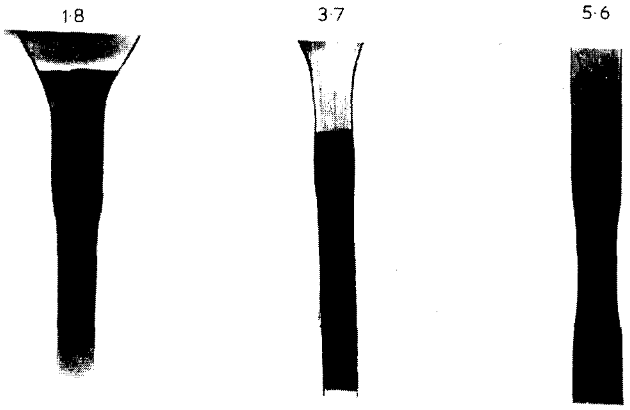

Figure 11 Cast films. Limiting viscosity numbers (cm^3 8^{-1}) 1.8–102; 3.7–80; 5.6–106. A higher viscosity polymer (2.15) with a ratio of 3.7 gave no necking at all

yielding and strain hardening with the straightening of molecules in a random configuration as in rubber elasticity. Argon[20] similarly proposed a model of yielding based on the idea of the straightening of the number of kinks or 'natural hinges' in polymer molecules. Where the molecules are already in a near linear configuration strain hardening would be expected to set in at low strains and a rapid rise in the true stress after yield setting in at low strains may prevent a necking mode of extension from taking place, as in cellulose derivatives.

As the bisphenol A content decreases in the PBPATC polymers the polymer chains would be expected to become more linear, hence one might expect (from the models proposed by Haward and Argon) the 'chances of uniform extension' to improve. According to this view, the 'linearity' of the PBPATC polymers should be a contributing factor to the diffuse deformation of PBPATC 3.7, (cast) and 4.0 and 4.5 moulded films, in tension (*Figures* 10 and 11).

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