Copolycarbonates derived from bisphenol A phthalates

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Blocked copolymers from aliphatic diacids and diol-terminated aromatic polyester blocks have been prepared and studied. The preparations of such block copolymers with good molecular weights proved difficult, but a final carbonation reaction enabled the preparation of materials with values of [η] above 1.0. The mechanical and thermal properties of these have been studied and reported.

(Keywords: copolymers; copolycarbonates; bisphenol A phthalates; polyester; synthesis; characterization; liquid-crystalline polymer)

INTRODUCTION

Recently there has been considerable interest in the use of crystalline polyesters, particularly those exhibiting liquid crystallinity, within other polymers as structural materials[1], or as process aids[2]. By the same token there has been great interest in amorphous, statistical copolyesters in applications where transparency combined with toughness is of importance[3]. Here, of course, the aim is to avoid the onset of crystallinity, since this will affect optical properties as well as physical and thermal ones, whilst retaining the comparatively strong intermolecular forces.

In this vein we have previously reported[4,5] work in our laboratories on the synthesis and evaluation of block polyesters made by linking together preformed blocks of bisphenol A phthalates with carbonate linkages; the resultant materials showed promise as tough materials since the strong crystallizability of bisphenol A terephthalate in particular could be alleviated by the carbonate linkages, whilst the strong intermolecular (and intramolecular) forces remained. It was also found[6] that the thermal ageing was less than that for comparable materials, and that by careful choice of block length the desired properties could be optimized in a way difficult to achieve otherwise.

We now report on our attempts to extend this work by replacing all or part of the carbonate groups in these materials by other difunctional units, initially dicarboxylic acid residues, so that these would also disrupt the crystalline structures. At the outset of these studies it was hoped to prepare and study a range of materials in which different proportions, up to all, of the carbonate linkages were replaced by several aliphatic acids. However, the full range proved impossible to prepare with reasonable molecular weights, and a fair proportion of carbonate linkages were required for the attainment of good molecular weights. In the same way, the introduction of succinate residues proved impracticable, since the materials synthesized were discoloured; further attempts to proceed with this comonomer were abandoned.

Abbreviated nomenclature

Throughout this paper, the various polymers and oligomers are referred to by simple, self-explanatory codes. Thus, poly(bisphenol A terephthalate) blocks are referred to as PBPAT, such blocks linked together with sebacic residues are called PBPATSe, and such combinations further linked with carbonates are referred to as PBPATSeC. Other keys are I for isophthalates and A for adipates.

EXPERIMENTAL

Synthetic procedures

Bisphenol A (B.D.H.) was recrystallized from toluene before use, and dried at 333 K *in vacuo* for 24 h before use. Terephthaloyl chloride (B.D.H.) was Soxhlet extracted with n-hexane for 10 h; the extracted material was crystallized from this solvent, and carefully dried before use. Solvents were purified by standard methods, and phosgene was purified by bubbling through conc. H_2SO_4 and linseed oil before use. Aliphatic acid chlorides were prepared from the parent acid and thionyl chloride in the usual way[7], using pyridine as acid acceptor/catalyst. Distillation of the products under vacuum gave the materials that were used.

Preparation of poly(bisphenol A terephthalate) (PBPAT) blocks. This is exemplified for the 3:2 material. A 1 dm^3 reaction vessel, fitted with a condenser, a mechanical stirrer, gas inlet tube, a separating funnel and a thermometer, was charged with bisphenol A (30 g); this was stirred slowly under N_2 to grind the crystals, and tetrachloroethane (TCE) (250 cm^3), together with pyridine (41 cm^3), added. The temperature was slowly raised to 45°C, before a solution of terephthaloyl chloride (17.8 g) in TCE (200 cm^3) was added dropwise via the funnel. The funnel was rinsed with TCE (30 cm^3), and the reaction continued for 12 h under N_2. Samples of the

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oligomers were removed from time to time to check the solution viscosity. The oligomeric material was precipitated with methanol from the solution, washed and dried under vacuum.

Preparation of a mixed ester by a single-stage synthesis. This is exemplified by the preparation of PBPATSe (3:2:1). PBPAT (3:2) was prepared as above, and to the reaction mixture at 30°C sebacoyl chloride (10 cm^3) in TCE (50 cm^3) was slowly added, after which the mixture was stirred for 12 h under N_2. Work-up gave a copolymer of intrinsic viscosity $[\eta]=0.6\,dl\,g^{-1}$.

Preparation of a mixed ester carbonate by a single-stage synthesis. This is exemplified by the preparation of PBPATSeC (3:2:0.8). Hydroxyl-terminated PBPATSe was prepared exactly as above, except that only 8.0 cm^3 of sebacoyl chloride was used in TCE (50 cm^3). After this reaction was completed, phosgene was admitted very slowly[8] to the reaction vessel, at 25°C, with rapid stirring. When the solution became too viscous to stir, a further aliquot (250 cm^3) of TCE was added, and phosgene addition continued to the point where a faint yellow coloration indicated excess. Work-up of these solutions was as follows. The viscosity was reduced by addition of more TCE, and this solution was slowly added to a large excess of either methanol or acetone; this mixture was allowed to stand overnight to permit TCE to diffuse from the coacervate, the solid filtered off and ground in a blender. This powder was washed (three times) with acetone and suspended in hot water for *ca.* 3 h, until free of chloride ions ($AgNO_3$). Drying *in vacuo* at 60°C to constant weight gave a polymer of $[\eta]=2.04\,dl\,g^{-1}$.

Where required, molecular weights were modified by the use of *p*-cresol or acetyl groups as end-stops.

Physical properties

A Perkin–Elmer differential scanning calorimeter, model DSC-2C, was employed as described previously. Samples (15 mg) were used at various heating rates between 2.5 and 40 K min^{-1} in an atmosphere of nitrogen. Temperature calibration was performed using melting points of ultra-pure metals (In, Sn, Pb). Thermal lag corrections were made by extrapolation to zero sample weight at constant heating rate. The calorimeter was calibrated by taking the enthalpy of fusion for In to be $28.4\,J\,g^{-1}$ (ref. 9).

An Instron Materials Tester, TT-BM, floor model, was used for all tensile measurements, using standard dumbell-shaped specimens, effectively $4.2\times 25\,mm^2$, cut from cast films. The average thickness of films was determined by weighing knowing the surface area and densities of the films. Polymer densities were measured by flotation in sodium nitrate solutions, calibrated by hydrometers, at 296 ± 1 K.

The materials were characterized by solution viscometry, in trichloroethane at 298 K. For PBPATC the intrinsic viscosity has been related to molecular weight by the following Mark–Houwink relationships[10,11]:

$$[\eta]=2.16\times 10^{-4}\bar{M}_n^{0.83}$$

$$[\eta]=4.66\times 10^{-4}\bar{M}_w^{0.71}$$

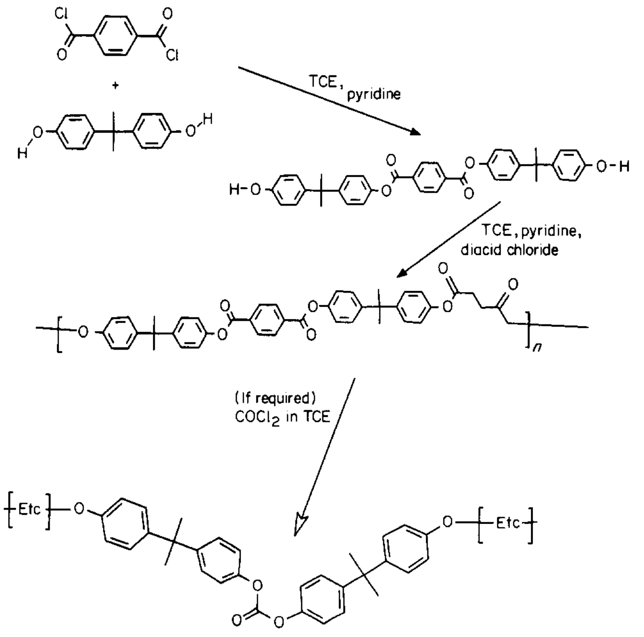
Since the corresponding relationships were not available for the adipate and sebacate copolymers the intrinsic viscosity was used as a guide to molecular weights only.

SYNTHESIS

The general method of synthesis followed the pattern of our previous studies[4,5]: short blocks of bisphenol A (tere- or iso-) phthalate were prepared from bisphenol A and the relevant phthaloyl chloride using an excess of diol to ensure that the blocks were uniformly hydroxy-terminated. The materials thus prepared were as close to the theoretical average molecular weights as might have been expected (*Table 1*), and after purification and drying were reacted with a deficit of the appropriate acid dichloride to yield copolymer blocks with considerably increased molecular weights. However, these were not high enough to permit casting of good films, so that mechanical properties and so forth could not be measured. In an attempt to improve on this, a series of materials containing aliphatic acid residues were prepared in such a way as to have them still doubly hydroxy-terminated, and these materials were then treated very cautiously with phosgene to generate the ultimate products for study. This final phosgenation proved to be the key to producing high-molecular-weight materials: as has often proved the case in our laboratories and elsewhere[12], good molecular weights, as evidenced by viscometry, are only attained if the phosgenation is carried out very slowly indeed, so that the final generation

Table 1 Typical polyester block preparations

Block type	Nominal composition	Synthesis temperature	Yield (wt%)	Final intrinsic viscosity ($dl\,g^{-1}$)	Actual (^{1}H n.m.r.) composition
PBPAT	5:4	60	91	0.150	4.86:4.0
	3:2	60	87	0.105	3.02:2.0
	5:4	70	88	1.57	
	3:2	60	92	1.08	
	3:2	50	93	1.07	
PBPAI	3:2	60	72	0.072	
	3:2	60	78	0.085	
	5:4	60	82	0.105	



Scheme 1 General synthetic sequence followed in this work

Table 2 Typical polyester block/ester/carbonate preparations

Block type	Nominal composition	Synthesis temperature (°C)	Yield (wt%)	Final intrinsic viscosity (dl g^{-1})	Actual (^{1}H n.m.r.) composition
PBPATC	5:4:1	30	65	0.78	4.84:4.0
	3:2:1	25	68	0.84	
PBPATA	5:4:1	30	87	0.41	
	5:4:1	30	85	0.47	
	5:4:1	30	82	0.52	
	3:2:1	25	83	0.62	2.85:2.0:0.85
	3:2:1	25	83	0.62	
	3:2:1	25	82	0.70	
PBPATSe	5:4:1	25	81	0.43	
	5:4:1	25	82	0.62	
	5:4:1	25	78	0.52	
	3:2:1	25	85	0.67	3.03:2.0:1.0
	5:4:1	25	82	0.67	
	5:4:1	25	80	0.50	
PBPATAC	3:2:0.5	30	72	0.90	3.27:2.0:0.49
	3:2:0.67	30	75	1.39	3.21:2.0:0.62
	3:2:0.75	30	74	2.10	3.19:2.0:0.75
	3:2:0.8	30	90	1.62	3.16:2.0:0.80
PBPATSe	3:2:0.5	30	60	3.25	3.00:2.0:0.61
	3:2:0.67	30	82	1.10	2.93:2.0:0.67
	3:2:0.75	30	84	1.60	3.00:2.0:0.77
	3:2:0.8	30	75	2.04	2.94:2.0:0.78

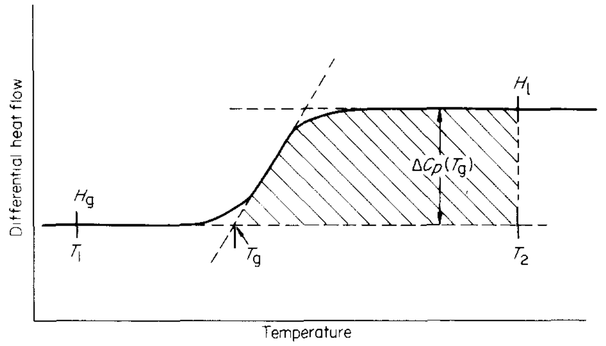


Figure 1 Schematic d.s.c. trace, illustrating the methods used to estimate T_g and C_p. ΔH is the shaded area

of materials bearing only chlorocarbonate tips is postponed as long as possible. The progress of the reaction could be followed in a general way by observing the solution's viscosity as the reaction proceeded: when the viscosity became too high for efficient reaction, the solution was diluted with fresh solvent. Finally, the polymers were end-capped with *p*-cresol before isolation of the polymers.

The reaction sequence followed is set forth in *Scheme 1*; a selection of the materials prepared are shown in *Table 2*, together with their inherent viscosities, their expected compositions (from the reaction stoichiometries) and their actual compositions as estimated from ^{1}H n.m.r.

PROPERTIES

Thermal analysis

The thermal analyses of the various materials prepared in this study were performed to investigate their crystallizability, the variation of the glass transition temperatures, T_g, with composition, and the change in heat capacity at the glass transition temperature, $\Delta C_p(T_g)$, since this parameter determines[13] the extent of physical ageing that can be induced.

In typical d.s.c. traces for PBPATSC in the range 370–490 K, only a single glass transition is displayed, at around 420 K. No other transitions were observed below the decomposition temperature. Crystallization could not be induced in any of these copolymer samples, although it was carefully sought by extended heating at temperatures between 450 and 600 K—the anticipated melting point range. Films cast from solution were also amorphous with respect to density changes and glass transition measurements by d.s.c. The materials were thus considered to be non-crystalline.

The glass transition temperatures, T_g, were measured adopting the procedure of Richardson and Savill[14]. The area, ΔH in *Figure 1*, above the calorimeter baseline between the two temperatures T_2 and T_1 was evaluated by integration of the data. Clearly,

$$\begin{aligned}\Delta H &= H_{l,T_2} - H_{g,T_1}\\ &= (H_l^\circ - H_g^\circ) + \Delta C_p(T_2 - T_1)\end{aligned}$$

where H_g and H_l are the enthalpies of glass and liquid respectively, and superscript ° refers to standard conditions. Measurement of the temperature dependence of the individual specific heats enables ΔC_p to be evaluated, and hence $H_l^\circ - H_g^\circ$.

Since at the glass transition temperature:

$$H_g(T_g) = H_l(T_l)$$

it follows that

$$H_g^\circ + aT_g + \frac{b}{2}T_g^2 = H_l^\circ + AT_l + \frac{B}{2}T_l^2$$

Using the above values for $(H_l^\circ - H_g^\circ)$, T_g values were obtained. This analysis gave T_g values some 1–3 K below those determined by extrapolation of the onsets of the glass transition, as shown by the broken lines in *Figure 1*. The glass transitions thus obtained were corrected for thermal lag by extrapolation to zero sample size, and these corrected values were used in subsequent analyses.

The glass transition has kinetic properties, and the observed T_g varied both with heating and with cooling rates. Accordingly, a standard procedure was adopted to quench all the samples at 160 K min^{-1} through the glass transition. Over a limited measuring range of 1–2 decades in rate, the dependence of the glass transition temperature upon rate is adequately described[15] by an Arrhenius relationship, and plots of log(cooling rate) against T_g^{-1} were linear and corresponded to an activation energy for glass formation of 550 ± 50 kJ mol^{-1} for the PBPATC copolymers. This compares favourably with similar values[16] obtained previously for polycarbonate.

The T_g values for the various samples, as determined by d.s.c., are listed in *Table 3*. These values are clearly dependent on composition, although the exact nature of this dependence is obscured by the dependence of T_g on the reciprocal of molecular weight, i.e.

$$T_g = T_g^\circ + \frac{A}{M_n}$$

and wide variations in intrinsic viscosity are present. Allowances for this were made by using a relationship

Table 3 T_g and ΔC_p values for the copolyester/carbonate polymers

	Polymer type	Nominal composition	$[\eta]$ ($dl\,g^{-1}$)	$T_g{}^a$ (K)	T_g (K)	$T_g^{\infty\,b}$ (K)	ΔC_p ($J g^{-1} K^{-1}$)
	PBPATC	3:2	0.84	474	470	485	1.20
Adipate esters	PBPATAC	3:2:0.5	0.90	446	444	459	1.40
		3:2:0.67	1.39	445	441	451	1.40
		3:2:0.75	2.10	442	439	447	1.45
		3:2:0.80	1.62	439	435	444	1.45
Sebacate esters	PBPASeC	3:2:0.67	1.10	418	415	427	1.45
		3:2:0.75	1.60	417	414	420	1.50
		3:2:0.80	2.04	413	410	416	1.65

[a] Extrapolated value, see text

[b] $T_g^\infty = T_g + 13.5/\eta_{sp}$

Table 4 Effect of heating rate on the measured specific heat (C_p) of PBPTASeC (3:2:0.75)

	Heating rate ($K\,min^{-1}$)	Specific heat ($J g^{-1} K^{-1}$) 380 K	385 K	390 K	395 K	400 K	405 K	410 K
Below T_g	10	1.60	1.63	1.65	1.66	1.69	1.73	1.76
	5	1.54	1.56	1.58	1.60	1.61	1.63	1.65
	2.5	1.52	1.53	1.55	1.56	1.57	1.59	1.60

	Heating rate ($K\,min^{-1}$)	Specific heat ($J g^{-1} K^{-1}$) 440 K	445 K	450 K	455 K	460 K	465 K	470 K
Above T_g	10	2.03	2.06	2.08	2.09	2.12	2.11	2.16
	5	1.89	1.90	1.91	1.93	1.94	1.96	1.97
	2.5	1.81	1.83	1.84	1.84	1.86	1.87	1.88

Table 5 Thermograms of PBPATAC of different adipate contents

Temperature (K)	Specific heat ($J g^{-1} K^{-1}$) PBPATAC 3:2:0.25	PBPATAC 3:2:0.51	PBPATAC 3:2:0.75	PBPATAC 3:2:0.8
381	–	1.58	–	–
385	–	1.63	–	–
390	1.60	1.65	1.65	1.66
395	1.63	1.66	1.69	1.69
400	1.65	1.69	1.71	1.71
405	1.68	1.73	1.73	1.74
410	1.70	1.74	1.75	1.76
415	1.77	1.75	1.78	1.79
420	1.79	1.78	1.81	1.82
425	1.82	1.81	1.83	1.85
430	1.84	1.83	–	1.87
435	1.90	1.86	1.90	1.90
440	1.92	1.89	1.91	1.95
445	2.03	1.93	1.99	2.06
450	2.06	1.98	2.08	2.11
455	2.07	2.08	2.12	2.13
460	2.08	2.11	2.14	2.15
465	2.10	2.12	2.16	2.17
470	2.12	2.14	2.18	2.19
475	2.17	–	2.21	2.22
485	2.17	2.20	2.25	–
490	2.18	2.23	–	–
494	2.21	2.24	–	–

derived[1] for PBPATC polymers, i.e.

$$T_g = T_g^\circ + 13.5\frac{\eta}{c}$$

from which the T_g° values shown in the table were obtained. These values showed a linear dependence on the composition of the aliphatic component, which could be reasonably extrapolated to the T_g° value for PBPATC.

Specific heat measurements

Specific heats were measured using sapphire[17] as an internal standard, and correcting for the d.s.c. baseline. The values obtained outside the glass transition region were dependent on both sample size and heating rate, owing to thermal lag (see *Table 4*). Extrapolation to zero rate was adopted to determine the values of the specific heats of the various copolyesters outside the glass transition region. These values are listed (*Table 5*). Kinetic effects ruled this out as a valid method in the region of the glass transition. From plots of these values the change in specific heat at the thermodynamic glass transition, $\Delta C_p(T_g)$, was determined. The value of $\Delta C_p(T_g)$ is a measure of the increased numbers of modes of rotation that are associated with the glass transition. It can be seen from *Table 5* that there is an increase of $\Delta C_p(T_g)$ with the number of CH_2 units in the aliphatic dicarboxylic chain, presumably associated with increased flexibility due to the methylene sequences. This increase goes hand in hand with a decrease in T_g, as shown in *Figure 2*.

$\Delta C_p(T_g)$ is also an important parameter in that it is a measure of the maximum change[13] that can be measured in the physical ageing of the polymer by d.s.c. We have observed[18] that the extent of physical ageing, x_t, measured by the ageing endotherm, ΔH_t, is given by:

$$x_t = \frac{\Delta H_t}{\Delta C_p \Delta T}$$

and at equilibrium, $\Delta H_{max} = \Delta C_p \Delta T$. Here, ΔT is the undercooling for the quenched glass transition temperature. Thus, a polymer will not be observed to age by calorimetry if ΔC_p is zero. This was observed to be the case for the rigid-rod polymer n-butyl nylon-1[19].

The specific heat has its origins in the molecular structure of the polymer, and to a first approximation

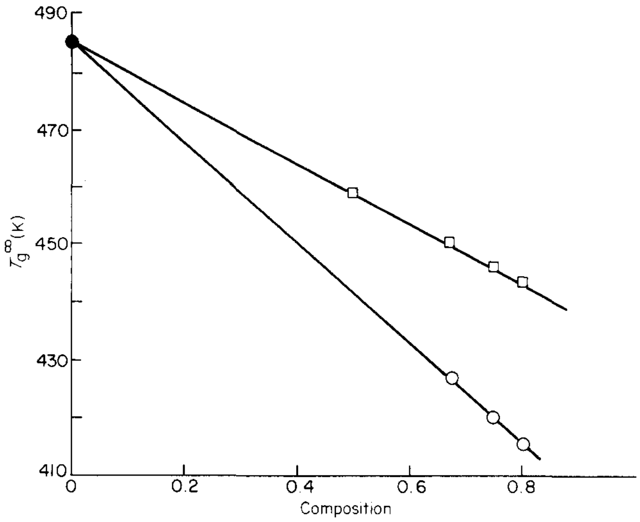


Figure 2 T_g^∞ *versus* composition of copolymers, namely the mole ratio of aliphatic acid residue to (acid + carbonate) in the copolymer: (□) PBPATAC; (○) PBPATSeC; (●) PBPATC 3:2

each grouping along the chain contributes additively to the overall molar heat capacity C_p. Accordingly, we can attribute contributions to the bisphenol A residue, and to the terephthalate and aliphatic acid residues, in proportion to their concentrations in the polymer:

$$C_{p,M}=\frac{x_{\mathrm{bpa}}C_{p,\mathrm{bpa}}}{M}+\frac{x_{\mathrm{T}}C_{\mathrm{T}}}{M}+\frac{x_{\mathrm{A}}C_{\mathrm{A}}}{M}$$

the linear increase in specific heat with composition of the aliphatic ester, keeping the bisphenol A/terephthalate ratio constant at 3:2, is consistent with the above interpretation.

Mechanical properties

Only solvent-cast films were extensively studied, and then after considerable drying to remove solvent, since the moulded specimens exhibited a lower yield stress by as much as 10–20 MPa. The viscosities of the moulded films were reduced by as much as 25%, and so oxidative degradation was assumed to have taken place. The stress–strain curves of the moulded materials exhibited deformation and essentially uniform drawing with little or no strain hardening before failure.

Solution-cast films exhibited a higher yield stress, but extensive drying was essential to develop the highest yield stress. Drying at 285 K for 24 h was finally chosen as producing optimum results.

The elongation–stress plots in each case exhibited a very diffuse neck on yield, with little drop in load (≃5–10%) as the neck forms. Strain hardening follows immediately after neck formation, and is apparent in the stress–strain curves. The samples are essentially drawing uniformly. All the samples exhibited marked strain-rate effects; see *Figure 3* for an example. The yield stress, and yield drop on neck formation, as well as ultimate yield stress and elongation are listed in *Table 6* for the various samples as a function of composition. Whilst in any particular series there is no marked variation between the samples, there is a general increase in the elongation at fracture.

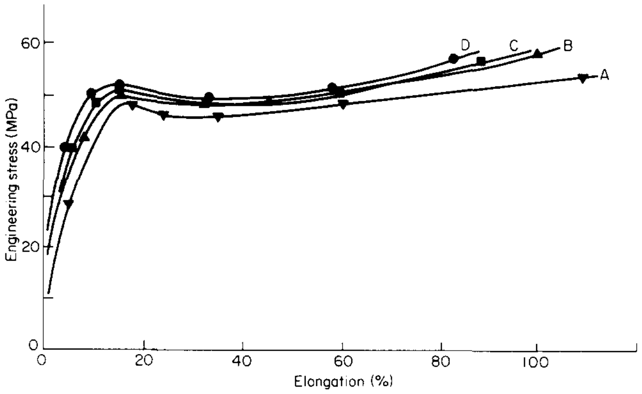


Figure 3 Effect of increasing strain rate on the stress–strain behaviour of PBPATSeC 3:2:0.8. Strain rates: (A) 3.3×10^{-4}; (B) 1.67×10^{-3}; (C) 3.3×10^{-3}; (D) 8.3×10^{-3}

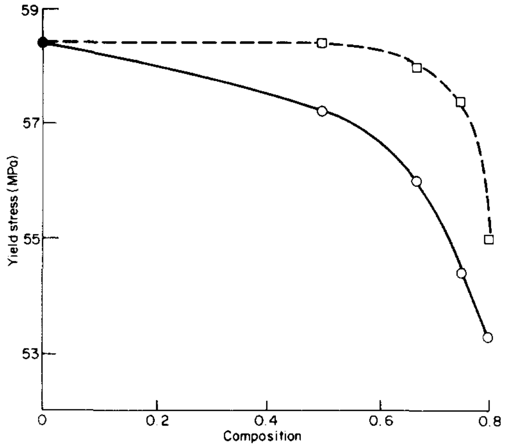


Figure 4 Effect of increasing aliphatic content on the yield stress of the copolymers, composition being plotted as mole ratio of aliphatic acid residue to (acid + carbonate) in the copolymer: (□) PBPATAC; (○) PBPATSeC; (●) PBPATC 3:2

Table 6 Yield behaviour of copolycarbonates described in this work

Composition	Yield stress (MPa)	Yield drop (%)	Yield strain (%)	Ultimate elongation (%)	Ultimate strength (MPa)
BPA:TPC:A					
3:2:0.5	58.4	3.5	12	50	59.0
3:2:0.67	58.0	4.0	12	60	64.2
3:2:0.75	59.4	8.5	14	35	53.7
3:2:0.8	55.0	8.5	14	70	57.2
BPA:TPC:Se					
3:2:0.5	57.2	2.0	14	60	62.9
3:2:0.67	56.0	4.0	14	75	60.2
3:2:0.75	54.4	5.0	14	75	57.3
3:2:0.8	53.3	7.0	14	86	57.0

The samples are all tough ductile materials under the conditions of the tests, but the fracture energy increases with ratio of ester to carbonate owing to increased elongation to fracture. The yield stresses were high, comparable with BPAPC alone. Strain effects were evident in that yield stress (σ_y) increased logarithmically with strain rate ($\dot{\varepsilon}$), consistent with the Eyring equation[20]:

$$\frac{\partial\sigma_y}{\partial\ln\dot{\varepsilon}}=2\frac{kT}{v}$$

The apparent activation volume v was found to be 6.8 nm^3.

The effect of incorporating increasing amounts of aliphatic ester into the copolymers is summarized in *Figure 4*. The yield stress is not substantially altered until high ratios (0.5) are exceeded, but it decreases rapidly thereafter. The glass transition, on the other hand, is substantially reduced (by as much as 50–80 K). It would seem that incorporation of substantial amounts of copolyesters into the structures can be advantageous in lowering the processing temperature without substantially altering the mechanical properties.

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