The properties of equimolar copolycarbonates of bisphenol A with bisphenol S and 1,4-bis(hydroxymethyl)cyclohexane

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Ranges of both alternating and random 1:1 copolycarbonates of Bisphenol-A (2,2-bis(4-hydroxyphenyl)propane) and Bisphenol-S (4,4'-dihydroxydiphenyl sulphone) and of Bisphenol-A and 1,4-dimethanoylcyclohexane have been synthesized in order to test the hypothesis that, other things being equal, a more random structured polymer should exhibit superior thermal ageing characteristics. Studies on these materials' mechanical and thermal properties establish that within each pair they are extremely similar and hence the original hypothesis is disproved.

Keywords Copolymers; alternating; random; polycarbonate; polysulphone; physical ageing; mechanical properties; Bisphenol-A; Bisphenol-S; dimethanoylcyclohexane

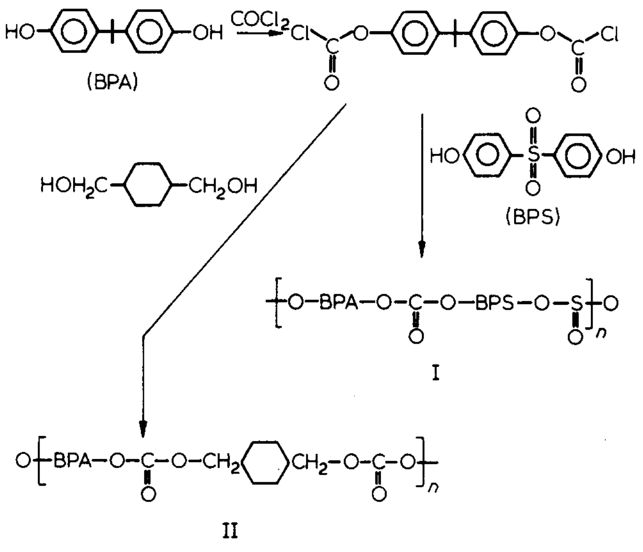
INTRODUCTION

Recently, there has been increasing recognition of the importance of the physical ageing process in polymers[1], and since the effect is generally undesirable, the preparation of polymers with a reduced level of physical ageing would be advantageous. Earlier work[2] carried out in our laboratories showed that the introduction of a comonomer, in quantities of up to 50%, into bisphenol A polycarbonate caused a reduction in this effect. A possible conclusion from this work was that the ageing process might be controlled by the regularity and packing of the polymer chains, and so ways of checking this were sought.

From this starting point, we became interested in the possibility of studying 1:1 copolycarbonates of bisphenol A with another comonomer. We planned to prepare the copolymers in two ways to give copolymers having an irregular and an alternating structure. Bis(4-hydroxyphenyl)sulphone (bisphenol S) and 1,4-dimethylol cyclohexane were selected as suitable comonomers.

In the present work, the irregular or 'random' copolymers were not particularly well defined. The term random was used merely to denote materials synthesized by passing phosgene through a mixture of the two diols under normal[3] polymerization conditions. Not unexpectedly, we found it necessary to employ a deficiency of the more nucleophilic diol in order to approach a 1:1 copolymer. Although we refer to these materials as random, we recognized that they may be tapered or blocky since the nucleophilicities of the amines of bisphenol A and the other component differ considerably. As might be expected, with bisphenol S, the random copolymers were less easy to dissolve than the alternating types and tended to give hazy solutions in some cases.

Synthesis of the alternating materials was much more controlled. In an initial step the bischloroformate of the bisphenol A or the cyclohexadiol was prepared and purified and this was reacted with the other diol in a homogeneous system as in Scheme 1.



Scheme 1

Brief details of the polymerizations are set out in the experimental section, and we discuss here the spectroscopic evidence for the existence of different chain structures.

Because infra-red and ^{1}H n.m.r. show merely that the

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random and alternating materials are similar, without proving that the random materials are truly random or that the others are truly alternating, this evidence comes mainly from ^{13}C n.m.r. However, the ^{1}H n.m.r. results confirmed the elemental analysis results.

The relevant feature of the ^{13}C n.m.r. measurements on these materials occurs in the aromatic region of the spectrum. The alternating materials showed chemical shifts and only the number of signals compatible with the assumed structure. On the other hand, the random polymers showed much more complicated spectra with up to twice as many visible peaks. This confirms both the random (or irregular) chain structure of these materials and the more ordered, and by implication alternating, structure assumed for the ordered syntheses.

EXPERIMENTAL

Materials

Purified 2,2′-bis(4-hydroxyphenyl)propane (bisphenol A) was a gift from Shell Chemicals UK Ltd: bisphenol S, 4,4′-dihydroxydiphenyl sulphone, supplied by Aldrich Chemical Co. at 98% purity was purified further as in ref. 4. 1,4-Bis(hydroxymethyl)cyclohexane was used as supplied by the same company. The solvents were purified by standard methods and bisphenol A chloroformate was prepared as in refs 5 and 6.

Polymerization procedures

The BPA–BPS and BPA—CH copolymers were both prepared in a homogeneous system using $C_2H_4Cl_2/C_5H_5N$ as a mixed solvent. Copolymerization in a heterogeneous system always gave low molecular weight polymer in the BPA–BPS system.

Polymer characterization

^{1}H n.m.r. measurements were carried out with instruments at 60 and 100 MHz, ^{13}C spectra were obtained at 25 MHz on a JEOL instrument, and i.r. measurements by Perkin–Elmer 180 grating spectrometer. Differential scanning calorimetry (d.s.c.) was performed using a Perkin–Elmer DSC 2 instrument.

Molecular weight

Number average molecular weights were measured by vapour pressure osmometry in $CHCl_3$ using a Knauer instrument. Calibration was with cetyl alcohol.

Limiting viscosity number $[\eta]$

The viscosities of alternating copolymers were measured in trichloroethane. The random copolymers did not dissolve completely in this solvent and DMF was used. It was shown with the alternating polymer that the values of $[\eta]$ were identical in the two solvents.

Tensile tests

These were carried out on an Instron floor model TT-BM machine. Films were cast from $CHCl_3$ and dried at room temperature for 20 h and then for 15 h at 50°, 90° and 120°C in a vacuum. Tensile test pieces were cut according to BS 2782 (1970), figure 30, method 301 K.

Annealing

Samples were annealed in ovens in air, for the times stated, before testing.

RESULTS AND DISCUSSION

Details of the polymers obtained are given in *Tables 1* and *2*. A plot of log $\bar{M}_n$ against log $[\eta]$ including both types of BPS copolymer, according to the Mark–Houwink equation $[\eta] = KM^{\alpha}$ indicated a value of α greater than unity (1.4) indicative of a rod-like configuration in solution. However, in view of the small number of points and the dependence of the slope on the two extreme measurements we would not attach significance to the actual figure, though α was clearly high.

The average compositions of all the polymers were reasonably constant, the proportion of BPS being within the range $53.5 \pm 2.6\%$ and for the dimethylol cyclohexane copolymers $51.5 \pm 2.0\%$. It was therefore thought appropriate to look for differences between the two types of material by plotting the value of T_g against $1/[\bar{M}_n]$ as shown in *Figure 1*. It will be seen that a line may reasonably be drawn through all the points, which implies no significant difference between the two types of copolymer. A similar conclusion applies to the four results for the dimethylol cyclohexane copolymers given in *Table 2*.

Physical ageing of the copolymers[6-10]

The ageing behaviour of the two types of copolymers was measured by integrating the heat capacity temperature plots between two fixed temperatures, one in the glass region and one in the liquid, chosen to be away from the transition. The difference between this area and that obtained from a rapidly quenched specimen (cooling rate 300K min^{-1}) was taken to be a measure of the ageing endotherm ΔH_a. The value of the change increased progressively with log (time of ageing) and the ageing

Table 1 Properties of the BPA–BPS random and alternating copolymers

Type of copolymer	%M (BPA) by n.m.r.	$[\eta]$ ($cm^3 g^{-1}$)	T_g (K) by d.s.c.	$\bar{M}_n \times 10^{-3}$ by v.p.o.
Random 1	53.5	43	453	12.0
2	53.7	31	437	–
3	52.6	35	441	8.5
Alternating 4	54.7	84	451	13.3
5	53.3	57	449	12.9
6	56.1	40	433	–
7	54.2	96	457	26.6

Viscosities are measured in TCE (alternating ones) and DUF (random ones) solvents

Table 2 Properties of BPA—CH random and alternating copolymers

Type of copolymer	%M (BPA) by n.m.r.	$[\eta]$ ($cm^3 g^{-1}$)	T_g (K) by d.s.c.	$\bar{M}_n \times 10^{-3}$ by v.p.o.
Random 1	52.3	87	375	15.8
Alternating 2	50.7	93	372	17.7
3	53.5	62	370	12.0
4	49.5	89	476	15.8

Viscosities are measured in TCE solvent. In annealing experiments by d.s.c. and Instron, random 1 and alternating 2 samples are used

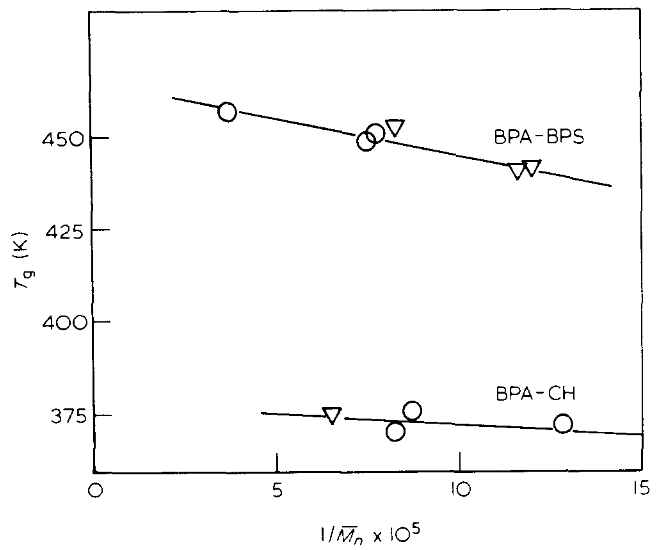

Figure 1 A plot of T_g against $1/\bar{M}_n$ for the four types of copolymer discussed in this paper: ○, randon copolymers; ▽, alternating copolymers

process, at a fixed temperature T_a, followed the kinetic relationship:

$$(1-\Delta H_t/\Delta C_p.\Delta T)=A\log(Bt/\tau)$$

where A and B are effectively constants for the system, τ is the relaxation time for the ageing process, $\Delta T=T_g-T_a$, and ΔC_p is the heat capacity difference between liquid and glass at T_g. Clearly, $\Delta C_p.\Delta T$ represents the maximum value which ΔH can achieve at equilibrium.

In the present study, plots of $(1-\Delta H/\Delta C_p.\Delta T)$ against log (time) were linear, as shown by *Figures 2a* and *2b* for the BPS copolymers and *Figures 3a* and *3b* for the CH polymers; these indicate that there is very little difference between the materials prepared in different ways. Indeed, the relaxation time, τ, obtained by linear extrapolation to zero of $(1-\Delta H/\Delta C_p.\Delta T)$ did not vary substantially between materials, but depended only on the value of ΔT (see *Figure 4*). This clearly demonstrates that little is lost or gained by chain regularity in terms of physical ageing, albeit some small effects may be present. The maximum extent of physical ageing is thus primarily determined by the product $\Delta C_p.\Delta T$ and this in turn by chain structural units and by the increase in chain flexibility above T_g. In conformity with this notion, no marked variation was observed between the copolymers.

The energetics of the ageing process have usually been found to be similar to those of glass formation, as determined by the glass transition's dependence on rate of cooling. Accordingly, physical ageing is here considered to be an extension of the glass forming process, which is temperature dependent, to very slow rates at the ageing temperatures.

Activation energies have been measured for the copolymers (*Table 3*) but, within the large errors in these, no

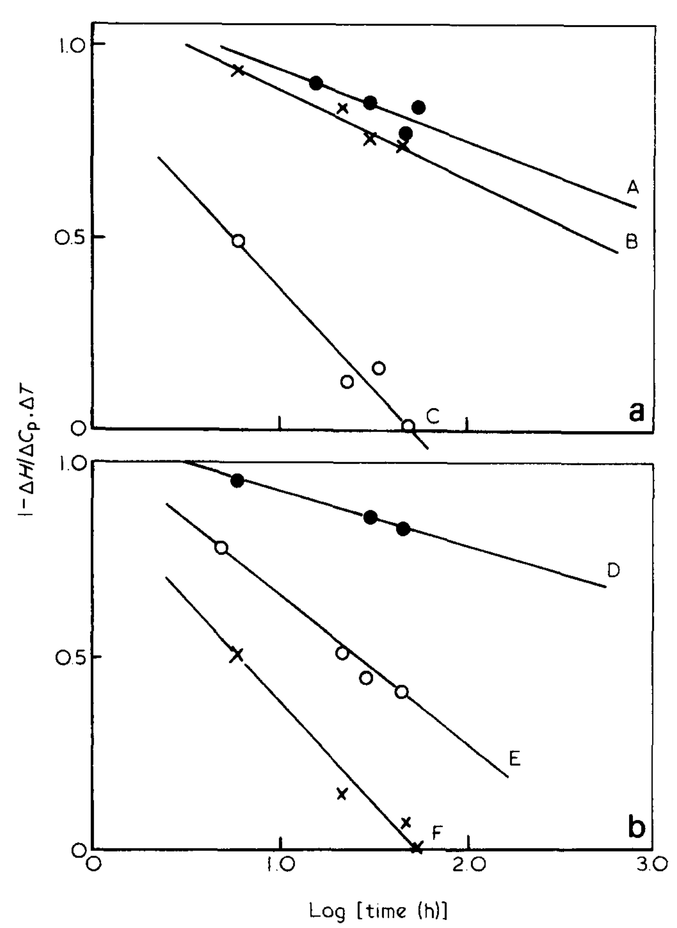

Figure 2 Ageing behaviour of BPA–BPS copolymers: (a) A, 130°C; B, 138°C; C, 150°C. (b) D, 138°C; E, 145°C; F, 156°C

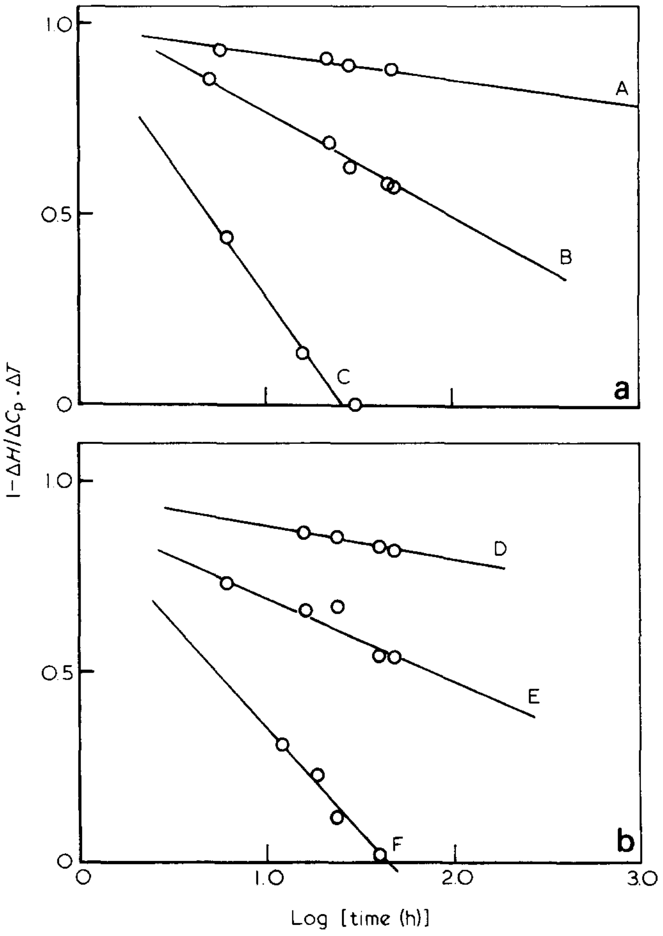

Figure 3 Ageing behaviour of BPA–CH copolymers: (a) A, 68°C; B, 78°C; C, 88°C. (b) D, 67°C; E, 82°C; F, 92°C

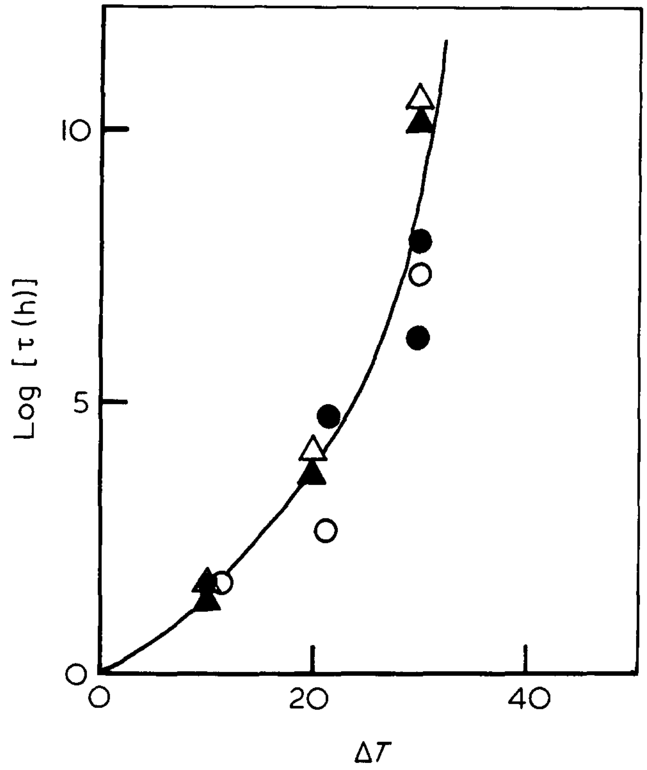

Figure 4 Dependence of log (relaxation time) upon degree of supercooling: ●, BPA–BPS alternating; ○, BPA–BPS random; ▲, BPA–CH alternating; △, BPA–CH random copolymers

Table 3 Ageing characteristics

		T_g (K)	ΔC_p (mcal g^{-1} K^{-1})	ΔE_{act} (kcal mol^{-1})
BPA–CH	Random	375	20 ± 1	200 ± 20
	Alternating	371	21 ± 1	200 ± 50
BPA–BPS	Random	441	22 ± 1	210 ± 40
	Alternating	433	18 ± 1	200 ± 60

difference was seen between the various copolymers, despite the measured differences in T_g of 80°C.

Similarly, the absolute changes, with ageing, in enthalpy and yield stress for all four copolymers were very similar, although the yield stresses of the BPS copolymers were about double those of the CH materials.

Further, although the observed enthalpic changes on ageing are not comparable with previous studies on copolymers of BPA, the changes in yield stress *are*, and in each case they are significantly lower than those reported for homopolymers prepared in a similar way. In this connection the behaviour of the 15[10] and 50% CH copolymers are quite comparable.

The final conclusion from this work must be that the original thesis of 'beneficial randomness', i.e. that a more disordered chain would age less severely than its more ordered equivalent, must be dismissed as a working hypothesis. This is consistent also with studies yet to be reported on polypropene, poly(vinyl chloride) and poly(ethylene terephthalate), in which it has been observed that the extent of ageing is determined by ΔC_p, ΔT and ΔE_{act} alone. These parameters do not change substantially on copolymerization and, for a given series of copolymers, rates of ageing will only show marked dependence on ΔT.

REFERENCES

1 Struik, L. C. E. 'Physical Ageing in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
2 Adam, G. A., Parsons, I. W. and Haward, R. N. *Polymer* 1975, **16**, 433
3 Adam, G. A., Haward, R. N. and Parsons, I. W. *Eur. Polym. J.* 1976, **12**, 299
4 McGrath, J. E., Ward, T. C., Shchor, E. and Wnuk, A. J. *Polym. Eng. Sci.* 1977, **18**, 647
5 Koleshnikov, S., Smirnova, O. V., Nikitayev, A. K. and Gladyschev, V. M. *Polym. Sci. USSR* 1970, **12**, 1617
6 Colter, R. J., Matzuer, M. and Kuirkjy, R. P. *Chem. Ind.* 1965, 791
7 Schnell, H. *Makromol. Chem.* 1962, **1**, 57
8 Clark, J. R. U.S. Patent 3 551 501, 1970
9 Kolenikov, H. S., Smirnova, O. V., Nikitayev, A. K. and Kuzina, S. I. *Polym. Sci. USSR* 1968, **10**, 296
10 Adam, G. A., Hay, J. N., Parsons, I. W. and Haward, R. N. *Polymer* 1976, **17**, 51