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SYNTHESIS AND CHARACTERIZATION OF SOME COPOLYCARBONATES OF 2,2-BIS (4-HYDROXYPHENYL)PROPANE (BISPHENOL-A) AND 1,4-BIS(HYDROXYMETHYL) CYCLOHEXANE

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Abstract—Copolycarbonates of Bisphenol-A (BPA) and 1,4-bis(hydroxymethyl)cyclohexane have been prepared. The resulting copolymers have slightly lower glass-transition temperatures than BPA polycarbonate homopolymers. Crystallisation and annealing effects are also reduced. The results are generally similar to those obtained with copolymers of BPA and 1,4-bis(hydroxymethyl)decafluorobicyclo(2,2,1)-heptane [1] but the differences are less marked.

INTRODUCTION

In previous work [1] we showed that the copolycarbonates of 1,4-bis(hydroxymethyl)decafluorobicyclo(2,2,1)heptane and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol-A) have better resistance to annealing and crystallization and have better thermal resistance than the homobisphenol-A polycarbonate. Therefore we decided to investigate whether these effects were due to the presence of fluorine in the comonomer or simply to the incorporation of another monomer. We have therefore made copolymers of 1,4-bis(hydroxymethyl)cyclohexane with bisphenol-A in several molar ratios and have studied their crystallizabilities and annealing behaviours. The mechanical and viscoelastic properties were also investigated. The copolymers were characterized via their molecular weight, chemical structures and thermal properties.

EXPERIMENTAL

Materials

Purified 2,2-bis(4-hydroxyphenyl)propane was a gift from Shell Chemicals U.K. Ltd., 1,4-bis(hydroxymethyl)-cyclohexane (CH) was used as supplied by Ralph Emanuel Ltd. Other chemicals were also used as received; the solvents were purified by standard methods.

Polymerization procedures

The homobisphenol-A polycarbonates and the copolymers (CH copolymers) were made on a 114 g scale in a homogeneous system (mixed solvent) using CH_2Cl_2/C_5H_5N by procedures well established elsewhere [2–4]. Copolymerization in a heterogeneous system proved unsuccessful.

Polymer characterization

Molecular weight. The following procedures were used: (a) *Viscometry.* We used Ubbelohde suspended level viscometers at 25 ± 0.01° to determine the limiting viscosity number $[\eta]$. The solvent was CH_2Cl_2 and the values used in the Mark–Houwink equation [5] are $K = 1.11 \times 10^{-2}$, $\alpha = 0.82$. These values were applied for both the homopolycarbonates and the copolycarbonates so that the values of $\overline{M}_v$ obtained for the copolymers were not very reliable when significant amounts of comonomer were used.

(b) *Gel permeation chromatography* (GPC) involved a Waters Associates analytical instrument fitted with differential refractometry detector; solutions of 2.5 g polymer/dm^3 THF were employed at 25°. Calibration was against polystyrenes.

We found earlier [1] that the GPC results were in reasonable agreement with those found by other techniques, e.g. vapour pressure osmometry. The molecular weight of a copolymer was worked out from the GPC chromatogram by calculating the weight per Å of the extended copolymer chain, using a figure for percentage cyclohexane comonomer calculated from NMR analysis. The results are shown in Table 1.

Infra-red spectroscopy (i.r.) We used a Perkin Elmer 257 grating instrument.

^1H NMR *spectroscopy*. A Perkin–Elmer R12 instrument operating at 60 MHz was employed; samples were run as $CDCl_3$ solutions, with internal TMS standard.

Tensile tests were performed on an Instron floor model TT-BM instrument. The tests were carried out in a controlled environment at 23 ± 1° and at 50 ± 5% relative humidity.

Dynamic mechanical properties were studied on a Rheovibron Direct Reading Dynamic Viscoelastometer Model DDV II.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC 2 machine. The instrument was calibrated before use.

RESULTS AND DISCUSSION

Crystallization of polycarbonate copolymers

The polymers used in this study were in their amorphous state (as shown by DSC) unless they were specially treated. Homobisphenol-A polycarbonate can be crystallized in a number of ways, e.g. heating at temperatures above T_g for long time [6], solvent treatment [7] and by precipitation from hot solutions [1]. The last method was used here in studying the

Table 1. Properties of the main polymers referred to in this paper

Type of polymer	M% by NMR	From GPC $\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	T_g (K) from DSC	RV	$[\eta]$ (cm^3/g)	$\bar{M}_v \times 10^{-3}$
1% Copolymer	*	26.4	56.8	2.15	425	170	99	66
2%	*	29.6	62.0	2.10	423	160	107	72
5%	7.3	13.5	29.6	2.19	413	162	54	32
10%	13.3	18.4	45.6	2.48	413	148	80	52
15%	16.4	25.4	48.7	1.92	411	152	94	63
20%	23.3	19.0	56.0	2.94	396	110	58	34
50%	52.9	27.5	50.0	1.82	376	96	97	65
Poly(cyclohexane) carbonate		3.14	6.5	2.07	323	—	31	14

* Method not sensitive enough for such low concentrations.

crystallizability of the homopolymers and the copolymers. The percentage crystallinity was determined by DSC using the heat of fusion of 32.9 cal/g [8] (which was determined from the X-ray diffractometry measurements).

The amount of crystallization achieved was found to be molecular weight dependent. For this reason, we present our results to show the percentage crystallinity measured for a copolymer of a particular molecular weight in such a way that the value can be related to that of similar homopolymer (Fig. 1). Our results show that even small quantities of the CH comonomer have a substantial effect on crystallization.

Glass transition temperature (T_g) *of copolymers*

The T_g's of the homopolymers and the copolymers were estimated from the DSC thermograms. The effects of molecular weight and heating rate were allowed for as before [8]. The comonomer had a significant effect in reducing T_g whether measured on the DSC or from the high temperature relaxation peak of the viscoelastic relaxation curves. The Rheovibron measurements gave values of T_g generally higher than those obtained by DSC (Fig. 2); this can be related to the fact that the DSC measurements were extrapolated to zero heating rate while the Rheovibron measurements were made at 11 Hz.

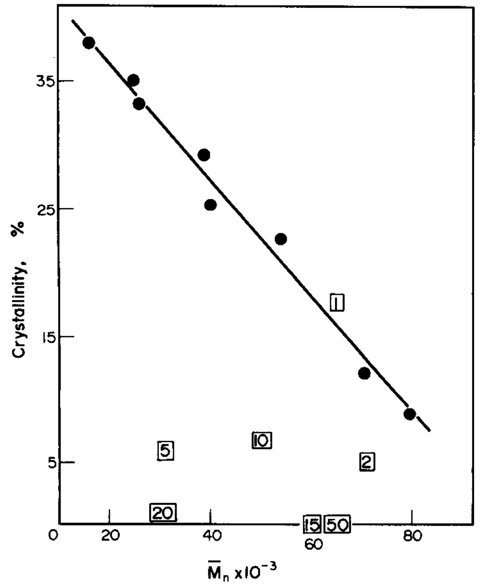

Fig. 1. Crystallinity of the copolymers and homopolymers precipitated from solution. ● Homopolymers. ☐ Copolymers with numbers showing percentage CH comonomers. The homopolymers were synthesized to give a range of molecular weights.

Tensile properties

Tensile experiments were carried out on films cast from 20% methylene chloride solution on to glass plates and progressively dried room temperature for 12 hr then at 35° for 5 hr, and finally at 80° under vacuum. Tensile test-pieces were cut from the films according to BS 2782 (1970) Fig. 301. 12, Method 301K, and tested on the Instron tester under standard conditions. The results are shown in Table 2, which shows that the yield stresses of the CH copolymers fluctuate around 60 ± 2 MN/m^2.

The effect of annealing on the tensile properties of homobisphenol-A polycarbonates has been studied by many authors [9–11], who found that annealing has a great effect on many of the mechanical properties.

Our present results show that the CH copolymers were less affected by annealing than the homopolycarbonates. However, in studying annealing effects, allowance might be necessary for differences in T_g, since the most sensitive annealing temperatures would be lower for the copolymers than for the homopolymers. Nevertheless, it will be seen from Fig. 3 that the homopolycarbonate and the CH copolymers

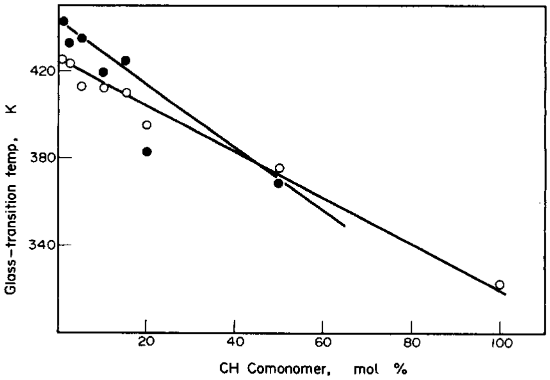

Fig. 2. Glass-transition temperature of copolymers. ● Measured by the Rheovibron. ⊙ Measured by DSC.

Table 2. Mechanical properties of the copolymers

% CH copolymer	Tensile yield stress (MN/m²)*	Elongation (%) at break	$\overline{M}_n \times 10^{-3}$
Bisphenol-A	61		
polycarbonate	61.3	158	
1% Copolymer	59.0	220	26.4
2%	58.0	200	29.6
5%	62.5	180	13.5
10%	61.6	210	18.4
15%	58.7	200	25.4
20%	59.0	>160‡	19.0
50%	61.3	>170‡	27.5
Poly (CH) carbonate†		Brittle‡	3.1

* Each value is the average of five tests which agree within ±1 MN/m².

† The brittle film show a marked DSC melting peak at 80°.

‡ The neck was not propagated to the whole length of the specimen.

show the same differences in annealing response over a wide range of temperatures. The effect of copolymer composition was also examined by annealing a series of materials for a standard time viz. 130° for 48 hr. The results are depicted in Fig. 4, which shows the relative increase in yield stress, $\Delta\sigma/\sigma_0$, due to the treatment, plotted against composition. The CH copolymers with a high proportion of CH comonomer are not shown in this figure because the annealing temperature is rather close to their individual T_g's.

Study of annealing effects by DSC

The influence of annealing in causing an endothermic peak in the differential scanning calorimeter at T_g has also been known for some time [12–14]. These peaks therefore can be taken as an alternative means of studying annealing effects, as distinct from measurements of yield stress. Again, we studied materials similar to those used in previous sections and in Figs. 3 and 4. Figure 5 shows the annealing behaviour of homobisphenol-A polycarbonate compared with the 15% CH copolymer.

The results are analogous to those observed with yield stress; in other words, the copolymers are much less affected by annealing than the homopolymers. The effect of comonomer content under constant annealing conditions, shown in Fig. 6, demonstrates that the introduction of the comonomer also reduces the effects due to annealing as measured by DSC.

Measurements of dynamic mechanical properties, details of which can be found elsewhere [4], exhibited the following points of interest:

(a) The α-relaxation peak, which occurs at the glass-transition region remains sharp for all the copolymers, suggesting that they have a reasonably random structure. The α-peak moved to a lower temperature with increasing CH comonomer content.

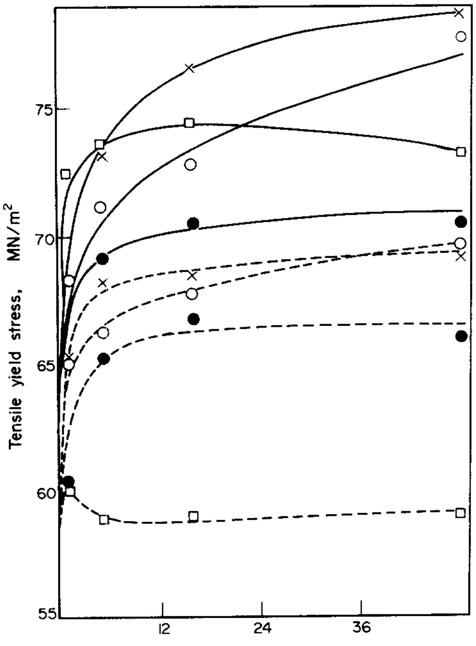

Fig. 3. Effect of annealing below T_g on the tensile yield stress of homopolycarbonate (——) and the 15% copolymer (----). ×, 130°. ○, 120°; ●, 110°; □, 140°.

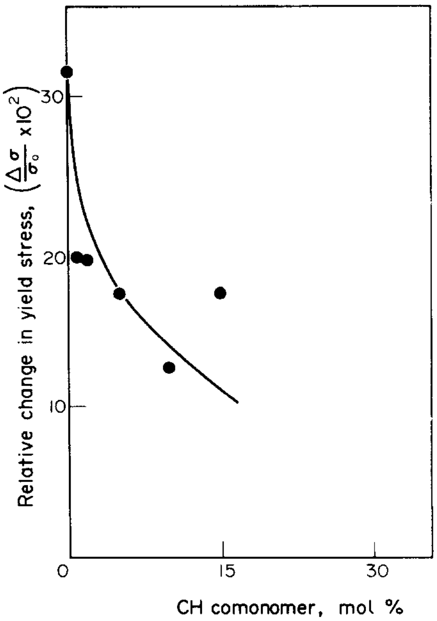

Fig. 4. Relationship between copolymer composition and the relative change in yield stress due to annealing (heated at 130° for 48 hr).

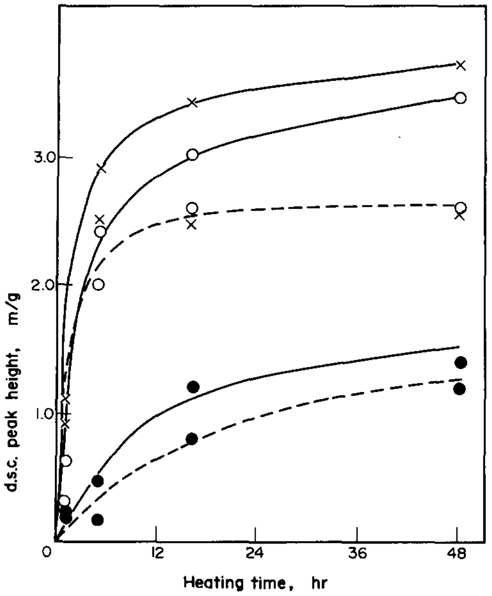

Fig. 5. The effect of annealing time and temperature on DSC peak height for homobisphenol-A polycarbonate (——) and 15% copolymer (– – – –). ×, 130°; ○, 120°; ●, 110°.

(b) Two low temperature (β) peaks were observed with the homopolymer and with the copolymers. The size of the higher temperature peak decreases with increasing CH content in the copolymer and its position moves from −10 to +30°.

(c) The low temperature peak does not change much in size, although its position changes in a way similar to the higher temperature β peak i.e. it rises from −110 to −70° with the copolymer containing 50% of the CH comonomer.

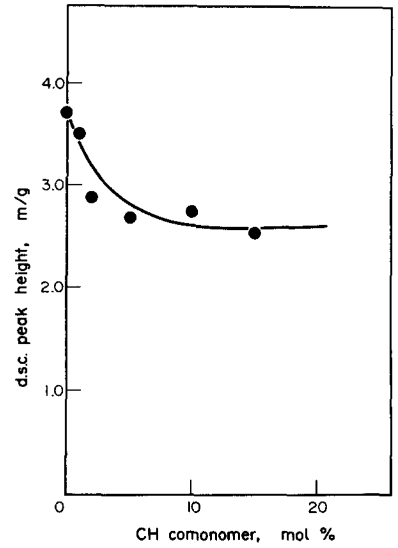

Fig. 6. Effect of the CH comonomer on the DSC peak height developed by heating at 130° for 48 hr.

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