

Synthesis and Characterization of Some Copolycarbonates of 2,2-Bis(4-hydroxyphenyl)propane and 1,1,1-Trichloro- 2,2-bis(4-hydroxyphenyl)ethane

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ABSTRACT: The monomer 1,1,1-trichloro-2,2-bis(4-hydroxyphenyl)ethane (monomer **II**) was synthesized and purified, and then polymerized with phosgene and 2,2-bis(4-hydroxyphenyl)propane (monomer **I**) in several molar ratios in a mixture of pyridine and chloroform. The molecular weight of polycarbonate could be controlled by small quantities of *p*-cresol. Increasing the quantities of **II** led to a slight reduction in the glass-transition temperature (T_g) of the copolymers. At the same time, the heat stability, as measured thermogravimetrically, was relatively high. Even small quantities of **II** in the copolymer had substantial effect in reducing the tendency to crystallize.

KEY WORDS Copolycarbonate / 2,2-Bis(4-hydroxyphenyl)propane / 1,1,1-Trichloro-2,2-bis(4-hydroxyphenyl)ethane / Glass-Transition Temperature / Heat Stability /

A large number of polycarbonates homopolymers and copolymers have been reported and studied during the past few decades, owing to the interesting properties of this glassy material.¹⁻³

Among the properties of polycarbonates which have recently become of interest may be included the tendency of slow and partial crystallization⁴ and their susceptibilities toward certain organic cracking solvents.⁵

In view of these features, we decided to prepare certain polycarbonate copolymers containing ($-\text{CCl}_3$) polar group, and to study their physical, thermal, and mechanical properties.

EXPERIMENTAL

Materials

The bisphenol-A (**I**) was provided by Shell Chemicals Ltd.; phosgene, nitrogen, chloroform (ethanol-free), and pyridine were purified by standard methods⁶ before use; *p*-cresol (BDH) was used as supplied, and the monomer 1,1,1-trichloro-2,2-bis(4-hydroxyphenyl)ethane was prepared as follows.

In to a three necked flask, equipped with a thermometer, mechanical stirrer, and calcium chloride guard tube were put; phenol (94 g), dehydrated chloral (44.5 cm³), and concentrated H₂SO₄ (2 cm³). The mixture was kept overnight with stirring. The reaction mixture was added to a mixture of ice and water, the precipitate was filtered, and dried followed by crystallization from toluene several times to give a constant melting point product (mp 205°C). The product was characterized by IR, NMR, and elemental analysis (Calcd: C, 52.91%; H, 3.46%; Cl, 33.54%. Found: C, 52.93%; H, 3.49%; Cl, 33.53%).

Polymerization Procedures

Mixed Homogeneous System. Most of the homopolymers including all the copolymers were made on a 25 g scale in a mixed solvent system using CHCl₃-pyridine, by the same procedure described in ref 7.

Heterogeneous System. A series of two-phase polymerizations were carried out by the procedure in ref 7.

Several batches of homopolymers were prepared in

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this system both with and without *p*-cresol as a molecular-weight modifier.

Copolymerization in this system proved unsuccessful, because this system gave "crude copolymers" which certainly contained chlorine as evidenced by elemental analysis, but partial extraction of these materials with chloroform gave fractions which differed greatly in their chlorine contents, showing that these copolymers were not uniform. Further efforts at copolymerization were therefore directed toward the homogeneous system.

The range of materials prepared and used in this study are described in Table I.

In order to allow for the effects of the molecular weight and the chlorine-containing comonomer content upon some of the physical properties of the polymers, a number of bisphenol-A polycarbonates differing in molecular weight were prepared following the method of Adam *et al.*³

Polymer Characterization

The following procedures were employed.

Viscometry. Using a Ubbelohde suspended level viscometer at $25 \pm 0.01^\circ\text{C}$ in chloroform solutions.

Vapour Pressure Osmometer. A KNAUER vapor pressure osmometer (VPO) type 11.15 was used to determine the molecular weights of these polymers in chloroform solutions at 32°C .

Thermal Analysis. The differential thermal analysis (DTA) and thermogravimetry (TG) were performed using a MOM Derivatograph which measures TG, DTA, and DTG spontaneously. This

instrument was calibrated with $\alpha\text{-Al}_2\text{O}_3$ before use. H NMR spectroscopy and elemental analysis have been performed at Analytische Laboratory, Postfach 135, West Germany.

Crystallization of Polycarbonate Copolymers. The polycarbonates studied in the present work were all amorphous unless specially treated. However, they were crystallized by hot precipitation from 1,2-dichloroethane solutions,³ treatment with acetone,⁸ and by heating the polymers at 185°C in sealed tubes under a vacuum for 10 days.

Density Measurements. These were carried out on either cast films or fine powders by flotation on a aqueous NaNO_3 solution.

The degree of crystallinity (X_c) was calculated by

$$X_c = \frac{\rho - \rho_A}{\rho_c - \rho_A}$$

The crystalline density (ρ_c) for bisphenol-A polycarbonate was calculated as 1.307 g cm^{-3} from the X-ray structure.⁹

The results obtained by this method may be considered reasonably accurate on comparison with those derived by differential scanning calorimetry and X-ray diffraction.¹⁰ Also it was found that the density due to crystallization of polycarbonates increases linearly with an increase in the heat of transition ΔH_t (Figure 4); ΔH_t can be directly related to the amount of crystallinity by the expression,

$$\% \text{ Crystallinity} = \frac{\Delta H_t}{\text{Heat of fusion } (\Delta H_f)} \times 100$$

Table I. Properties of the main polymers referred in this work

Type of polymer	Mol %		$M_n \times 10^{-3}$, by VPO	$[\eta]$ $\text{cm}^3 \text{ g}^{-1}$	T_g from DTA $^\circ\text{C}$	T_s $^\circ\text{C}$
	By elemental analysis	By NMR				
Polycarbonate of I	—	—	25.9	93.4	155	215
	—	—	12.2	45.6	152	210
	—	—	4.8	28.5	150	210
5% copolymer	4.9	4.6	23.6	90.2	140	210
10% copolymer	9.3	10.0	16.8	59.3	140	215
15% copolymer	14.4	14.3	19.3	74.9	150	215
20% copolymer	19.6	19	13.5	44.1	150	205
50% copolymer	49.7	50	5.2	29.3	140	200

Softening Point Measurements (T_s). The (T_s) of the homopolymers and copolymers was measured by Kofler Hot Bench Thermal Gradient Apparatus type 184 321. This instrument was calibrated with standard pure materials before use.

RESULTS AND DISCUSSION

Thermal Stability of the Copolymers

In order to estimate their thermal stability at high temperatures, it was convenient to employ thermogravimetric analysis; *i.e.*, the sample was heated to a high temperature and changes of weight were observed. Although this method is quite simple to apply, it is necessary to ensure that the copolymers and homopolymers studied are themselves really comparable.

We have noticed in a previous work¹⁰ that the degradation of polycarbonate depends on the active hydrogen present at the chain ends. This leads to an influence from the molecular weight. Thus, it is essential to compare the copolymers with homopolymers of similar molecular weight while studying their thermal stability.

The thermogravimetric technique measures the weight loss of a polymer sample while increasing the temperature at a steady rate ($10^\circ \text{ min}^{-1}$) until the polymer is substantially decomposed (see Figure 1).

From the instantaneous slopes of these curves at different temperatures, we calculated the energy of activation of the decomposition process over the initial 10% weight loss, the results obtained are shown in Table II.

From the DTG thermograms we found the decomposition temperature which is the temperature at which the maximum rate of weight loss takes place. Typical thermograms are shown in Figure 2.

The general features of the thermograms are as follows.

The materials are thermally stable up to about 50 to 100°C above their melting points when they undergo a slightly exothermic weight loss. The weight loss at this temperature increases with increase in the amount of comonomer II in the copolymers; *e.g.*, it is about 0.1, 0.3, 2, 5, 10, and 16.9 for the 5%, 10%, 15%, 20%, 50% and poly[1,1,1-trichloro-2,2-bis(4-phenyl)ethane carbonate] respectively, being due to the loss of hydrogen chloride

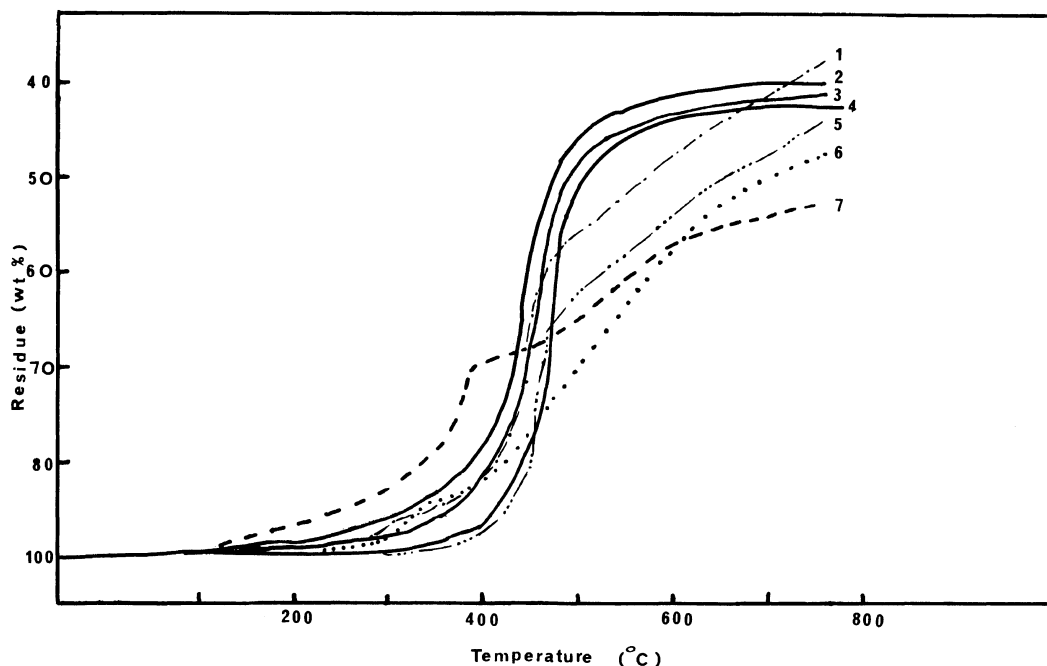
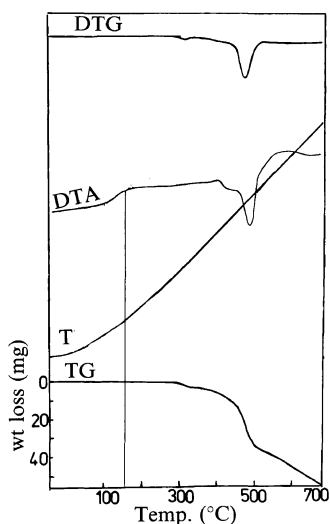


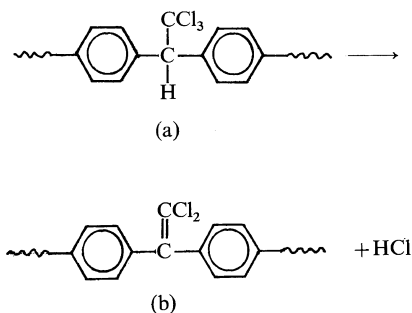
Figure 1. Weight losses by thermal decomposition of different polycarbonates and copolymers. 1, 20% copolymer; 2, polycarbonate homopolymer ($M_n=4800$); 3, polycarbonate ($M_n=12200$); 4, polycarbonate ($M_n=25900$); 5, 5.5% copolymer; 6, 50% copolymer; 7, polycarbonate of II.

Table II. Thermal stability characteristics of the homopolymers and copolymers from the thermal decomposition curves

Type of polymer	$M_n \times 10^{-3}$	Decomposition temp		Activation energy
		°C		kJ mol^{-1}
Polycarbonate of I	25.9	480		75 ± 10
	12.2	475		70 ± 10
	4.8	470		65 ± 10
5% II copolymer	23.6	470		75 ± 10
10% II copolymer	16.8	480		80 ± 10
15% II copolymer	19.3	480		70 ± 10
20% II copolymer	13.5	468		90 ± 15
50% II copolymer	5.2	450		180 ± 15
Polycarbonate of II	3.6	250 and 450		45 ± 5

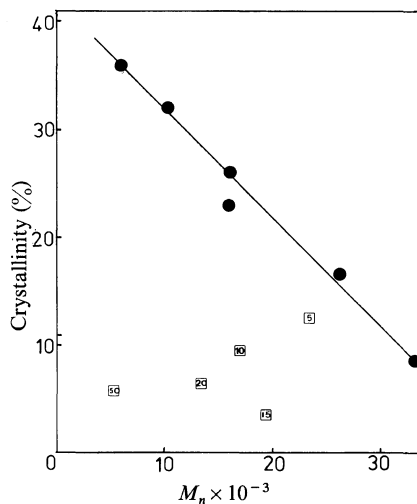
**Figure 2.** Typical thermograms for the copolymers (15%) obtained from the MOM Derivatograph.

according to the following mechanism.



Thus structure (b) is more stable than (a), as was confirmed by Adam *et al.* in previous work.^{11,12} The product undergoes further decomposition at relatively high temperatures (see Table II).

In the case of poly[1,1,1-trichloro-2,2-bis-(4-phenyl)ethane carbonate] the decomposition takes place in two stages: the first, at 250°C where the HCl elimination occurs and the second stage, at 450°C.

**Figure 3a.** Crystallinity of the copolymers and homopolymers precipitated from solutions. The homopolymers were synthesized to give a range of molecular weights: ●, homopolycarbonate from ref 3; □, copolycarbonates with numbers showing percentages of **II**.

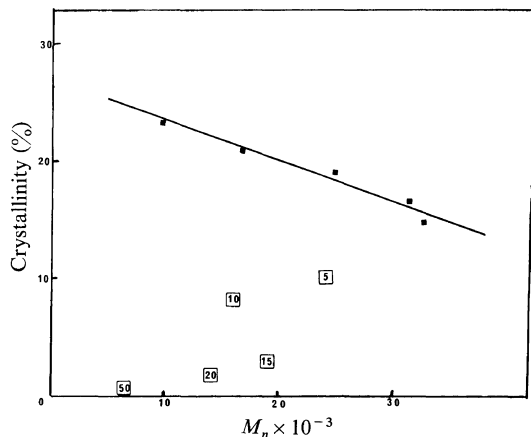


Figure 3b. Crystallinity of the copolymers and homopolymers heated at 185°C for 10 days: ■, homopolymers; □, copolymers with numbers showing percentages of II.

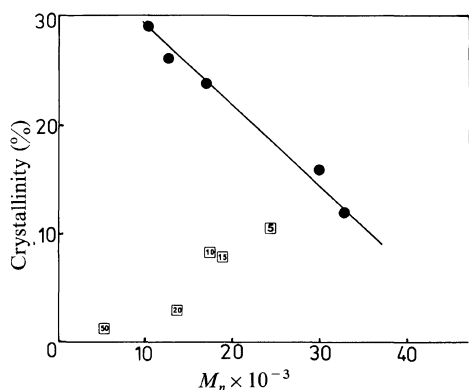


Figure 3c. Crystallinity of the copolymers and homopolymers treated with acetone for 48 hours at 25°C: ●, homopolymers; □, copolymers.

Glass Transition Temperature

The effect of introducing II on the glass transition temperature of the copolymers was not very large. Nevertheless, the comonomer did have a slight effect in reducing T_g (see Table I). A similar effect was noticed on the softening temperature.

Crystallizability of Polycarbonate Copolymers

Since the degree of crystallization achieved with a

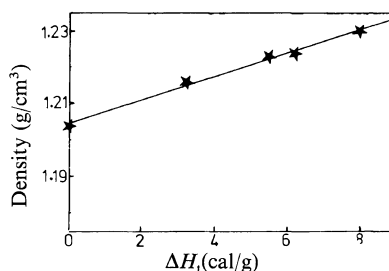


Figure 4. The relationship between the density increase due to crystallinity, and heat of transition ΔH_t .

particular treatment depends on the molecular weight of the homopolymers¹⁰ it is essential to show the percentage of crystallinity measured for the copolymers of particular molecular weights in such a way that the values can be related to those of similar homopolymers (Figure 3). It will be seen that even small quantities of the comonomer II have a substantial effect on crystallization.

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