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SYNTHESIS AND CHARACTERISATION OF ANTIOXIDANT BONDED POLYCARBONATES

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ABSTRACT

The preparation and properties of poly[2,2-bis(4-hydroxyphenyl)propane carbonate] bonded to 1,4-dihydroxyanthraquinone as antioxidant are described. Two types of this product were prepared: one type is bonded to the antioxidant molecules through the chain ends, the other type contains the antioxidant molecules in the chain backbone. The copolymers of antioxidant and 2,2-bis(4-hydroxyphenyl)propane were also prepared and characterised. These copolymers behave as good antioxidants for the polycarbonates and other polymers. The antioxidant-bonded polycarbonates show good thermal stability. The thermal characteristics and the activation energy for the decomposition of these new polymers is also included.

INTRODUCTION

The polycarbonates of 2,2-bis(4-hydroxyphenyl)propane are important commercial polymers. Their thermal properties are of prime importance in processing and application. This polymer undergoes thermal decomposition when it is heated at elevated temperatures [1]. Thus several types of stabiliser have been used with this polymer to improve its thermal stability [2]. In this work we prepared new types of polycarbonate bonded to the antioxidant molecules, i.e. 1,4-dihydroxyanthraquinone. The preparation and characterisation of these polymers are described.

EXPERIMENTAL

Materials

The 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) (I) was a gift from Shell Chemical Ltd. The 1,4-dihydroxyanthraquinone (II) was supplied by Fluka. The two compounds were used as supplied without any further purification. Phosgene, nitrogen and methylene chloride were purified by standard procedures before use.

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TABLE 1

Characterisation and thermal characteristics of the polymers

Sample [a]	$[\eta]$ cm^3 g^{-1}	$\overline{Mv}$ $\times 10^{-3}$	Decomposition Temperature (°C)	dw/dt [b]	Activation energy (kJ mole^{-1})	Antioxidant (Molar %)
1	60.6	34.2	420	0.11	75	
2	37.4	20	425	0.093	148	0.016
3	80.7	51.6	430	0.149	137	0.217
4	26.4	13.1	425	0.129	145	0.046
5	27.9	14.2	425	0.101	128	0.217
6	15.7	6.9	420	0.12	140	0.961
7	26.5	13.1	440	0.17	137	6.41
8	22.9	10.9	450	0.12	126	9.32
9	21.5	10.1	425	0.12	122	12.25
10	20.0	9.3	415	0.132	60	19.32

[a] The samples are: (1), synthetic polycarbonates; (2), (3), synthetic polycarbonates terminated with antioxidant structures; (4–10), synthetic polycarbonates containing the antioxidant structures in the chain backbone as random copolymers.

[b] dw/dt is the rate of decomposition at the decomposition temperature expressed as weight % loss min^{-1}.

Polymerisation

The polymerisation was carried out on a 25 g scale in the emulsion interfacial polymerisation by the procedure described in ref. [3]. Two types of antioxidant-bonded polycarbonates were prepared.

(1) The antioxidant (II) was added to the bisphenol-A (I) before the polymerisation was started. Several polymers were prepared using different molar concentrations of II. The polymers formed were characterised as shown in Table 1.

(2) The antioxidant was added at the end of polymerisation, i.e. five minutes before the polymerisation was ended. In such cases most of the polymer chain would terminate with the antioxidant molecules, because the probability of polymer chains reacting with antioxidant molecules is greater than the probability of condensing two polymer chains with each other due to the great difference in the number of polymer chains and antioxidant molecules. The range of materials prepared and studied are listed in Table 1.

Several batches of poly 2,2-bis(4-hydroxyphenyl)propane carbonate of different molecular weights were also prepared and used for comparison purposes. The molecular weight of these polymers was controlled by varying the polymerisation time, following the procedure used by Adam et al. [4].

Polymer characterisation

The procedures employed were:

(i) viscometry, using Ubbelohde suspended level viscometers at 30 ± 0.01 °C in chloroform solution.

(ii) H NMR spectroscopy and elemental analysis, performed at Prof. Malissa Analytische Laboratories, West Germany.

(iii) Ultra violet and visible spectroscopy. A UV-spectrophotometer (SP 8-100 Pye-Unicam) was used for the determination of the antioxidant concentration in the polymers. Three absorption bands were observed in the UV spectra of the antioxidant-containing polymers, i.e. 330, 475 and 520 nm. The band at 330 nm was used for the quantitative analysis. The molar absorption coefficient for the antioxidant was determined at this wavelength, according to the Beer–Lambert law and was found to be 2476 cm^{-1} l $mole^{-1}$. All the measurements were carried out in chloroform (Fluka spectral type). The concentrations of the antioxidant found in the polymers by UV and elemental analysis are shown in Table 1.

(iv) Thermal analysis. The thermogravimetry was carried out using a MOM-derivatograph which measures TG, DTG, DTA and temperature simultaneously. The instrument was calibrated before use. The measurements were carried out both isothermally at 300°C, following the procedure used by Askar and Adam [5], and by raising the temperature of the sample at a steady rate (10°C min^{-1}) until the polymer was substantially decom-

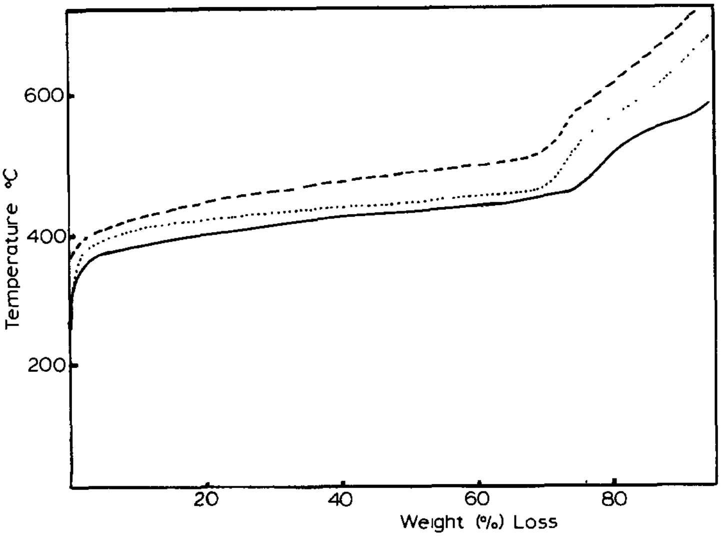


Fig. 1. The thermal stability curves of bisphenol-A polycarbonates. ———, synthetic polycarbonates ($\overline{Mv}$ 34200); ------, synthetic polycarbonates terminated with the antioxidant (0.016 molar %); ······, synthetic polycarbonates containing the antioxidant structures in the chain backbone (0.046 Molar %).

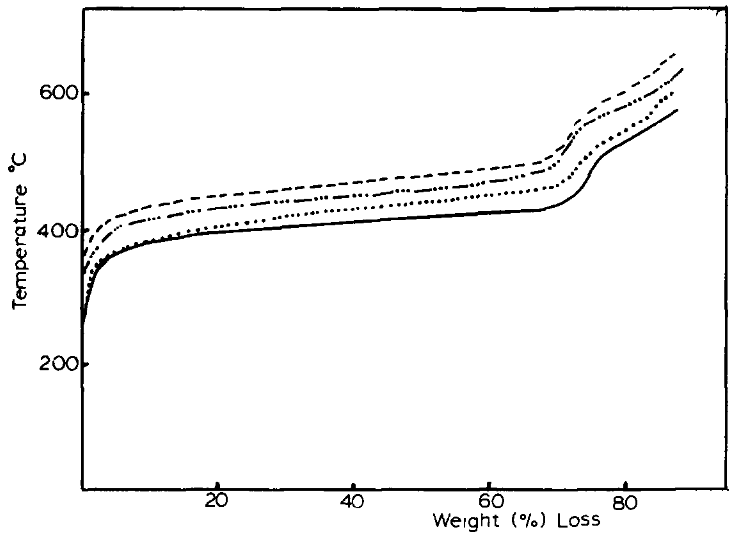


Fig. 2. Typical thermal stability curves of the copolymers prepared from bisphenol-A (I) and 1,4-dihydroxyanthraquinone [antioxidant(II)]. ———, Bisphenol-A poly carbonates; ······, 0.962 Molar % of II; ·—·—·, 19.32 Molar % of II; ------, 6.41 Molar % of II.

posed (Figs. 1–3). The measurements were carried out against standard α-Al_2O_3 in the presence of air.

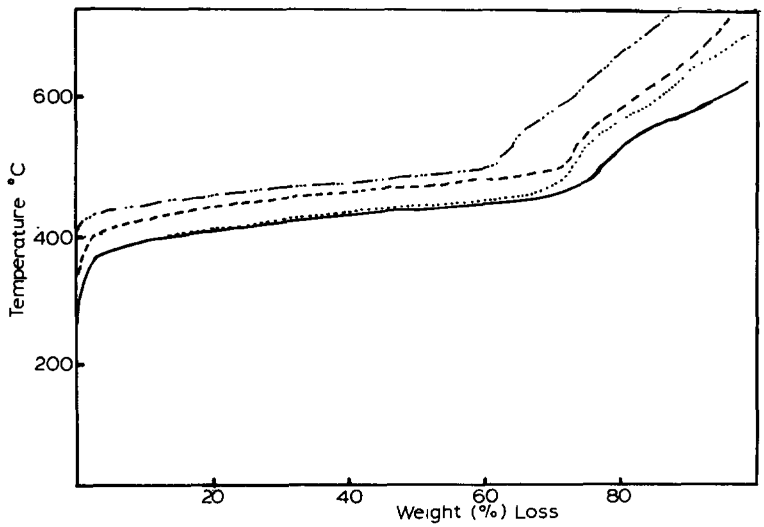


Fig. 3. The effect of addition of poly(1,4-anthraquinone) carbonate on increasing the thermal stability of bisphenol-A polycarbonates. ———, Bisphenol-A polycarbonates; ······, 0.015 Molar % poly(1,4-anthraquinone)carbonate; ------, 0.047 Molar % poly(1,4-anthraquinone) carbonate; ·—·—·, 0.063 Molar % poly(1,4-anthraquinone) carbonate.

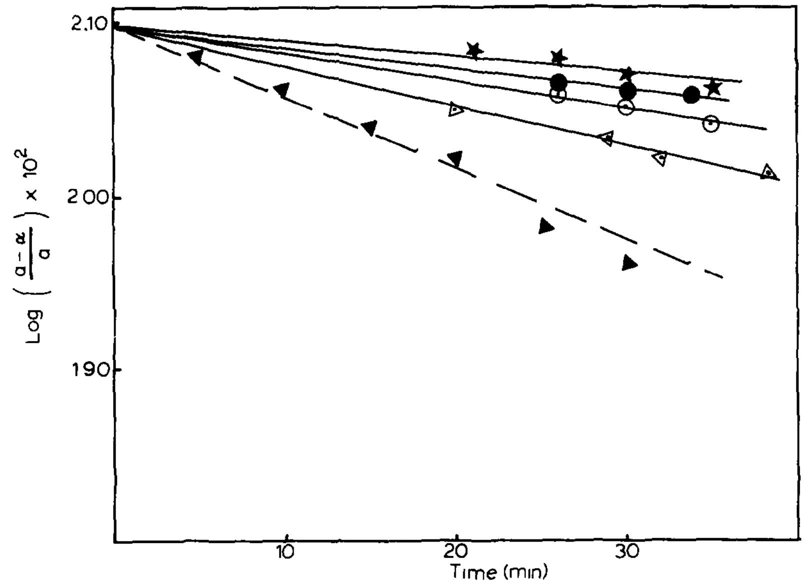
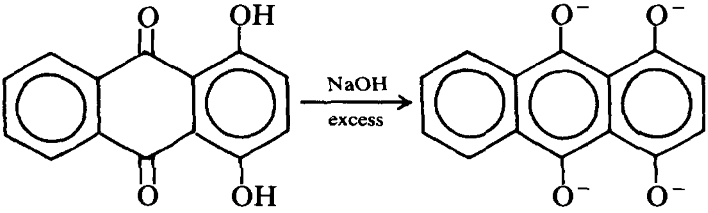


Fig. 4. Typical isothermal weight loss curves at 300°C for the polymers. ★, Polycarbonate terminated with the antioxidant(2); ⊙, polycarbonate terminated with the antioxidant (3); △, copolymer (6) of bisphenol-A and antioxidant; ●, copolymer (7) of bisphenol-A and antioxidant; ▲, bisphenol-A polycarbonates ($\overline{Mv}$ = 62000).

RESULTS AND DISCUSSIONS

The bonding of antioxidant molecules to the polymer chains was checked by UV and by an extraction technique. An extraction technique was used because the antioxidant dissolves in methanol while the polycarbonate does not. Analysis before and after the extraction procedure yielded the same analysis data for several polymer samples.

One of the critical factors in the polymerisation reactions was the pH of the polymerisation medium because the antioxidant molecules can undergo polymerisation by either the hydroxy groups and/or the quinone groups which can enolise according to the reaction



This was controlled by adding sodium hydroxide solution dropwise during the polymerisation because it was found that when the sodium hydroxide solution was added in one portion, a cross-linked polymer was obtained and a gel was formed within the first five minutes.

The thermogravimetric analysis results show that when the polymer chains are bonded to the quinonic structure of the antioxidant the thermal stability of the products are improved even at very low molar concentrations of antioxidant (0.016 Molar %) (see Fig. 1).

The thermal stability of the bisphenol-A polycarbonate increases when the polymer chains are terminated with the quinonic structures (Fig. 1). This result supports the chain-end mechanism assumed for the decomposition of polycarbonate.

The presence of antioxidant structures in the polymer chain backbone produces a less effective antioxidant than their presence at the polymer chain ends (Figs. 1, 2).

On the other hand, we found that the copolymers of (I) and (II) and polycarbonates of (II) behave as good stabilising agents for polycarbonates (Fig. 3) and other polymers [6].

From the instantaneous slopes of the isothermal curves at different temperatures, we calculated the energy of activation for the decomposition process over the initial 15% weight loss. The results obtained are shown in Table 1. Typical isothermal curves are shown in Fig. 4. The activation energy values for the antioxidant-containing polymers are greater than those of bisphenol-A polycarbonates (both synthetic and stabilised commercial products) (125 kJ mole^{-1} [1]).

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