

A novel depolymerization route to phosphorus-containing oligocarbonates

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Abstract

The interaction of poly[2,2-bis(4-hydroxyphenyl)propanecarbonate] (PC) with phosphonic acid dialkyl esters [(RO)₂P(O)H, where R_YCH₃ or CH₃CH₂] or with phosphoric acid triethyl ester (CH₃CH₂O)₃P(O) was studied. Treatment of PC pellets with phosphonic acid dialkyl esters at 160°C or with triethyl phosphate at 180°C yielded phosphorus-containing oligocarbonates. The structure of the phosphorus-containing oligocarbonates was studied by ³¹P NMR, ¹H NMR and ¹³C NMR spectroscopy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Depolymerization; Phosphorus-containing oligocarbonate

1. Introduction

The development of a new synthetic route for synthesizing phosphorus-containing oligomers is an important direction in phosphorus chemistry, as these materials are widely used for the modification of polymers [1–4]. Oku et al. have developed a highly efficient alkali-catalyzed methanolysis of PC to bisphenol A and dimethyl carbonate [5]. It was shown that the ester interchange reaction between PC and low molecular mass carbonates results in the formation of telechelic oligocarbonates [6].

Recently we reported [7–11] a highly efficient method for polyurethane depolymerization using reactive low molecular mass organophosphorus compounds. We anticipate that this unique method can be applied to polycarbonate. This paper describes a novel route to the synthesis of phosphorus-containing oligocarbonates by reacting PC with phosphonic acid dialkyl esters or triethyl phosphate. We anticipate that phosphorus-containing oligocarbonates could be used as precursors for the modification of polymers such as polyurethanes, polypropylene, unsaturated resins, and glass fibers, improving flame retardancy, thermal stability, and adhesion.

2. Experimental

2.1. Materials

PC based on bisphenol A pellets (2 mm thickness and

3 mm length with $M_n = 41,290$ and $M_w = 62,490$) were supplied by Bayer AG, Germany. Dimethyl phosphonate and diethyl phosphonate were purchased from Fluka (Catalog no. 41,439 and 32,449). Triethyl phosphate was purchased from Aldrich (Catalog no. 24,089-3). All compounds were used without further purification.

2.2. General procedure for depolymerizing PC

2.2.1. Depolymerization by dimethyl phosphonate

Into a three-necked flask equipped with a stirrer, thermometer and reflux condenser 5 g (0.02 mol on the basis of repeating monomer unit in the polymer) PC pellets and 25 g (0.23 mol) dimethyl phosphonate were placed. The depolymerization proceeded at 160°C. After 5 h the reaction mixture was cooled to 60°C and vacuum (1.10^{-2} mm Hg) was applied to remove the unreacted dimethyl phosphonate. The resulting solid product was dissolved in CH₂Cl₂ and precipitate from MeOH. The precipitate was filtered and dried at 40°C for 1 h in vacuo (1.10^{-2} mm Hg). Additional depolymerization experiments were performed for 10 h (**1b**) and 15 h (**1c**). The resulting products **1a**, **1b**, and **1c** were characterized by ³¹P, ¹H and ¹³C NMR spectroscopy. ³¹P NMR (CDCl₃): 10.62 (dq, ³J(P, H) = 12.5 Hz, ¹J(P, H) = 704.0 Hz). ¹H NMR (CDCl₃): 1.52 (s, CH₃–C), 3.75 (d, ³J(P, H) = 12.2 Hz, P–OCH₃), 3.80 (s, C(O)OCH₃), 6.61–6.96 (m, bisphenol A aromatic H), 6.77 (d, ¹J(P, H) = 704.0 Hz, P–H). ¹³C{H} NMR (CDCl₃): 31.6 (CH₃–C), 43.2 (CH₃–C–), 52.5 (P–OCH₃), 53.5 (C(O)OCH₃), 115.4, 121.0, 128.6, 148.5, 149.0 (bisphenol A aromatic C), 152.9 (C_YO), 154.4 (C(O)OCH₃).

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Table 1

GPC analyses of PC* and phosphorus-containing oligocarboxates (PC*—pure polycarbonate: $M_n = 41,300$; PD = 1.51)

Reaction time (h)	Phosphorus-containing oligocarboxates					
	1		2		3	
	M_n	PD	M_n	PD	M_n	PD
5	4600	1.31	4956	1.26	11500	1.61
10	4213	1.18	2850	1.11	5970	1.38
15	3700	1.12	2800	1.04	5460	1.36

2.2.2. Depolymerization by diethyl phosphonate

The depolymerization was conducted as in the case of dimethyl phosphonate, with diethyl phosphonate.

PC pellets 5 g (0.02 mol), diethyl phosphonate 25 g (0.18 mol). The final products 5 h (**2a**), 10 h (**2b**), and 15 h (**2c**) were characterized by ^{31}P , ^1H and ^{13}C NMR spectroscopy. ^{31}P NMR (CDCl_3): 8.88 (dt, $^3J(\text{P}, \text{H}) = 7.8$ Hz, $^1J(\text{P}, \text{H}) = 698.9$ Hz). ^1H NMR (CDCl_3): 1.34 (t, $^3J(\text{H}, \text{H}) = 7.0$ Hz, POCH_2CH_3), 1.63 (s, $\text{CH}_3\text{-C}$), 4.07–4.12 (m, $\text{C}(\text{O})\text{OCH}_3$ and POCH_2CH_3), 6.60–7.01 (m, bisphenol A aromatic H), 6.80 (d, $^1J(\text{P}, \text{H}) = 700.5$ Hz, P–H). $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3): 16.5 ($\text{CH}_3\text{CH}_2\text{OC}(\text{O})$), 16.8 (POCH_2CH_3), 31.5 ($\text{CH}_3\text{-C}$), 43.2 ($\text{CH}_3\text{-C-}$), 62.8 (P– OCH_2CH_3), 65.5 ($\text{C}(\text{O})\text{OCH}_2\text{CH}_3$), 115.0, 121.8, 128.4, 148.0, 149.0 (bisphenol A aromatic C), 152.8 ($\text{C}_\text{Y}\text{O}$), 155.0 ($\text{C}(\text{O})\text{OCH}_2\text{CH}_3$).

2.2.3. Depolymerization by triethyl phosphate

The depolymerization was conducted as in the case of dimethyl phosphonate, using triethyl phosphate.

PC pellets 5 g (0.02 mol), triethyl phosphate 25 g (0.03 mol). The depolymerization proceeded at 180°C . The unreacted triethyl phosphate was removed by vacuum (1.10^{-2} mm Hg) at 90°C . The resulting products 5 h (**3a**), 10 h (**3b**), and 15 h (**3c**) were characterized by ^{31}P , ^1H and ^{13}C NMR spectroscopy. ^{31}P NMR (CDCl_3): 2.25 (quintet, $^3J(\text{P}, \text{H}) = 7.9$ Hz). ^1H NMR (CDCl_3): 1.34 (t, $^3J(\text{H}, \text{H}) = 7.04$ Hz, $\text{CH}_3\text{CH}_2\text{OC}(\text{O})$), 1.35 (t, $^3J(\text{H}, \text{H}) = 7.0$ Hz, POCH_2CH_3), 1.68 (s, CH_3C), 4.06–4.17 (m, $\text{C}(\text{O})\text{OCH}_3$ and POCH_2CH_3), 6.59–7.02 (m, bisphenol A aromatic H), $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3): 16.5 ($\text{CH}_3\text{CH}_2\text{OC}(\text{O})$), 16.7 (POCH_2CH_3), 31.6 ($\text{CH}_3\text{-C}$), 43.2 ($\text{CH}_3\text{-C-}$), 64.4 (P– OCH_2CH_3), 64.5 ($\text{C}(\text{O})\text{OCH}_2\text{CH}_3$), 115.5, 121.0, 128.6, 148.9, 149.6 (bisphenol A aromatic C), 152.8 ($\text{C}_\text{Y}\text{O}$ and $\text{C}(\text{O})\text{OCH}_2\text{CH}_3$).

2.3. Characterization

2.3.1. GPC

Molecular weight of the oligomers was determined relative to polystyrene standard by GPC in THF as the eluent on a Waters 244 instrument, equipped with Ultrastaygel columns of 100, 100, 500, 500 Å.

2.3.2. NMR

^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer using tetramethylsilane as internal standard in CDCl_3 solvent. ^{31}P NMR spectra were recorded on a Bruker 300 MHz spectrometer with chemical shifts reported in ppm relative to external 85% H_3PO_4 in CDCl_3 .

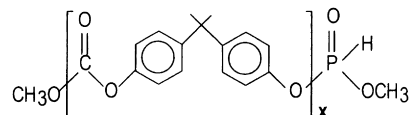
2.3.3. Thermogravimetric analysis (TGA)

A Perkin–Elmer TGS-2 thermogravimetric analyzer was used for the degradation measurement. It was carried out at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. Sample size was 5 mg.

3. Results and discussion

3.1. Depolymerization of PC by dimethyl phosphonate

It has been found that the interaction of PC with dimethyl phosphonate or diethyl phosphonate at 160°C , or with triethyl phosphate at 180°C results in decrease of the PC molecular weight. The ^{31}P NMR spectrum of the final product shows that the signal at 10.62 ppm presents a doublet of quartets with $^3J(\text{P}, \text{H}) = 12.5$ Hz and $^1J(\text{P}, \text{H}) = 704.0$ Hz. This signal can be assigned to the phosphorus atom in product **1**.



1

1a - $x = 18$

1b - $x = 16$

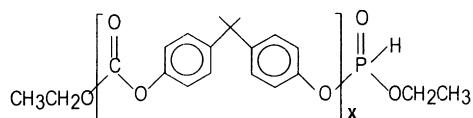
1c - $x = 14$

The structure of product **1** was confirmed by ^1H and ^{13}C NMR spectroscopy (see Section 2). In the ^1H NMR spectrum of the reaction product there are signals at $\delta 6.77$ ppm, doublet with $^1J(\text{P}, \text{H}) = 704.0$ Hz which can be assigned to the P–H proton and at 3.75 ppm, doublet with $^3J(\text{P}, \text{H}) = 12.2$ Hz which is characteristic for the CH_3 protons of the methoxy group, bonded to the phosphorus atom. These results clearly reveal that the phosphorus atom is bonded to a proton and one methoxy group (the signal in the ^{31}P NMR spectrum presents a doublet of quartets). On the other hand, the singlet at 3.80 ppm in the ^1H NMR spectrum and the signal at 53.50 ppm in the $^{13}\text{C}\{\text{H}\}$ NMR spectrum confirm the existence of the $\text{CH}_3\text{O-C}(\text{O})\text{-O}$ group.

3.2. Depolymerization by diethyl phosphonate

The data from the ^{31}P , ^1H and $^{13}\text{C}\{\text{H}\}$ NMR (see Section 2) show that the interaction of PC with diethyl phosphonate yielded phosphorus-containing oligocarboxate **2**. The ^{31}P NMR spectrum of the final product shows that the signal

at 8.88 ppm presents a doublet of triplets with $^3J(\text{P}, \text{H}) = 7.8 \text{ Hz}$ and $^1J(\text{P}, \text{H}) = 698.9 \text{ Hz}$ and can be assigned to the phosphorus atom in product **2**.



2

2a - $x = 19$

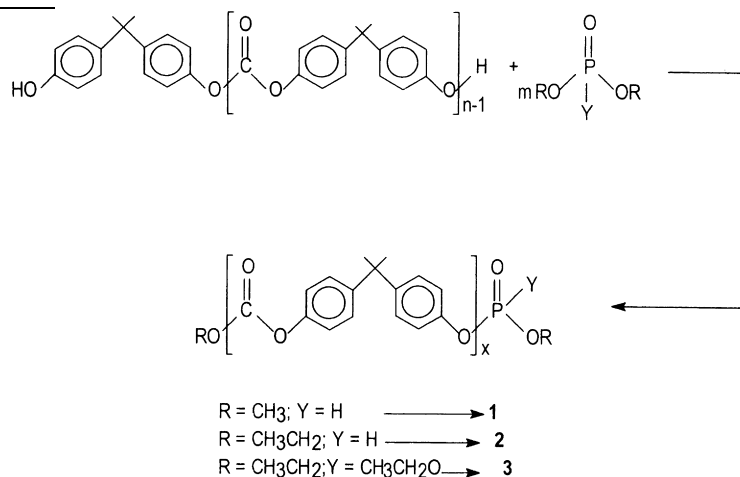
2b - $x = 11$

2c - $x = 11$

weight decreases with increasing reaction time. The initial breakdown is rapid. The molecular weight strongly decreases for the first 5 h reaching a molecular weight near to the final value. Longer reaction time reduced polydispersity (PD).

3.5. Reaction mechanism

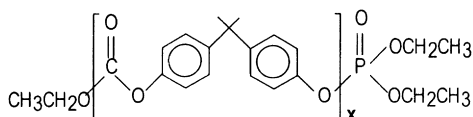
The phosphorus-containing oligocarbonates **1**, **2** and **3** result from an interchange reaction which depolymerizes PC in the presence of low molecular mass phosphorus compounds (Eq. (1)).



Data from ^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectroscopy confirm the structure of product **2**.

3.3. Depolymerization by triethyl phosphate

Like dimethyl and diethyl phosphonate, the interaction of triethyl phosphate with PC leads to the expected phosphorus-containing oligocarbonate **3**. The structure of **3** was determined by ^{31}P , ^1H and ^{13}C NMR spectroscopy (see Section 2).



3

3a - $x = 45$

3b - $x = 23$

3c - $x = 21$

The assignments of the chemical shifts of phosphorus, carbon atom and protons of degraded products are based on the data published by M. Crutchfield et al. [12] and Kalinowski et al. [13].

3.4. GPC analyses

The GPC analyses show (Table 1) that the molecular

3.6. Thermogravimetric analysis

Thermal degradation of the phosphorus-containing oligocarbonate was analyzed with TGA. Fig. 1 shows the thermal gravimetric (TG) curves of PC and the aforementioned oligomers under a nitrogen atmosphere. The TG curves show that phosphorus-containing oligocarbonates degrade at a lower temperature than pure PC. Phosphorus-containing oligocarbonate **1a** degrades at lower temperature than **2a**, **3a**, **3b** and **3c**. The phosphate end group in **3a**, **3b** and **3c** provides a better thermal stability than the phosphonate end group. Table 2 shows the weight losses at 500°C . It can be seen that PC loses 55%, **1a**—45%, **2a**—35%, **3a**—10%, **3b**—22%, and **3c**—20%. These data indicate that the presence of phosphorus in the oligocarbonates improves their thermal stability at higher temperature. TGA analysis shows that the char yield at 850°C increases in the order:

$\text{PC}(12.8\%) < \mathbf{2a} (23.6\%) < \mathbf{3b} (23.8\%) < \mathbf{3c} (25\%)$

$< \mathbf{3a} (26\%) < \mathbf{1a} (28.2\%)$

Obviously, phosphorus is an effective char former. The char yield value is important for the flame resistance of the materials. It can be converted into the limited oxygen index (LOI), using the van Krevelen equation [14]:

$\text{LOI} = 17.5 + 0.4 \times \text{CR}$

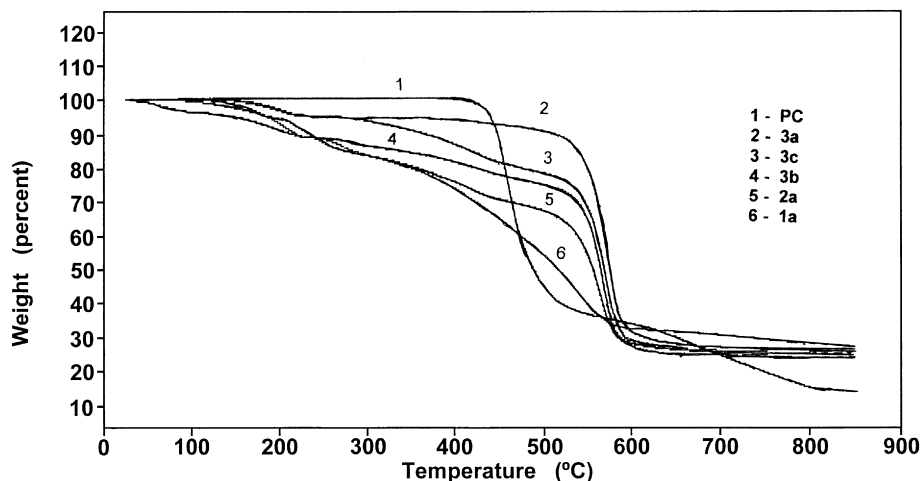


Fig. 1. TGA thermograms of PC and phosphorus-containing oligocarboxates in nitrogen atmosphere.

Table 2
Weight losses of PC and phosphorus-containing oligocarboxates at 500°C

Materials	Weight loss (%)
PC	55
1a	45
2a	35
3a	10
3b	22
3c	20

where CR is the char yield (wt%) at 850°C under a nitrogen atmosphere from the TGA measurement. These data indicate that phosphorus-containing oligocarboxates **1** and **2** and organophosphate **3** have better nonflammability property compared with pure PC.

4. Conclusions

Phosphorus-containing oligocarboxates were synthesized by depolymerizing PC with low molecular organophosphorus compounds. The presence of phosphorus in the oligocarboxates improves their thermal stability at higher temperature. The results obtained allow consideration of

the exchange reaction as an alternative to simple depolymerization of polycarbonate waste products. The method presented aims at contributing towards the solution of global problems like environment preservation and conservation of natural resources.

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