

## **Poly(arylenecarbonate)s oligomers by carbonate interchange reaction of dimethyl carbonate with bisphenol-A**

### **FAB-MS evidence for the nature of end groups in the oligomers\***

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### **SUMMARY**

Fast atom bombardment mass spectrometry (FAB-MS) has been used to identify oligomers with different end groups obtained by the carbonate interchange reaction of bisphenol-A with dimethyl carbonate and the partial methanolysis of poly(bisphenol-A carbonate)s. Based on the FAB-MS data, a reaction pathway for the formation of compounds in the synthesized oligomers is proposed.

### **INTRODUCTION**

Synthesis of poly(arylenecarbonate)s by the carbonate interchange reaction of dimethyl carbonate with bisphenol-A is of significant interest as a nonphosgene route to aromatic polycarbonates(1). A large number of patent disclosures describe the synthesis of such oligomers which can be subjected to postpolycondensation to yield high molecular weight polymers(2-6). It is generally recognized that the structure of oligomers play a key role in determining the efficiency of the polymer forming reactions. However, there are no attempts in the literature to structurally characterize the oligomers formed.

In continuation of our work in the area of carbonate interchange reaction of phenols(7) and bisphenols(8) with dimethyl carbonate, we have examined the reaction of bisphenol-A with dimethyl carbonate in presence of several catalysts under various reaction conditions(9). Selected oligomers obtained with organotin catalysts were subjected to Fast Atom Bombardment Mass Spectrometer(FAB-MS) and mass spectral pattern were compared with oligomers generated by the controlled methanolysis of poly(arylenecarbonate)s. FAB-MS analysis of the end groups present in the oligomers provides valuable insights into the nature of oligomer forming reactions and relative reactivity of oligomers. This paper reports the results of this study.

### **EXPERIMENTAL**

**Materials:** Dimethyl carbonate (DMC) (Aldrich, USA) was distilled using one foot fractionating column and stored over 4<sup>0</sup>A molecular sieves. 4,4' Isopropylidenediphenol (bisphenol-A, BPA) (Aldrich, USA) was recrystallized from toluene. Di-n-butyltin oxide (FASCAT-4201, M & T chemicals,Rahaway, NJ) was used as received. 1,3-diphenoxytetrabutyl distannoxane was prepared according to the literature procedure(10).

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### Synthesis of oligocarbonates:

(a) *by the reaction of BPA with DMC*: BPA and DMC (BPA:DMC = 2) were reacted in the temperature range of 110-240°C using di-n-butyltin oxide and 1,3 diphenoxytetrabutyl distannoxane as catalysts using procedures similar to that described for phenols(7). The oligocarbonates (A,B) were purified from unreacted BPA by washing with cold alkali at room temperature. The crude product was dissolved in chloroform and carefully precipitated from petroleum ether and dried in vacuo.

(b) *by partial methanolysis of poly(arylcarbonate)s*: 0.1g of poly(bisphenol-A carbonate) (PC) (M.W = 25,000) was dissolved in 20 mL of chloroform and 3 mL of freshly prepared 1N solution of HCl in methanol were added. The mixture was allowed to react at room temperature for 120 h, after which the solvent was evaporated and the residue dried in vacuo.

**Analysis:** Melting points were determined in open capillary tubes using melting point apparatus (Campbell Electronics, India) and are uncorrected. The <sup>1</sup>H NMR spectra of oligomers were recorded in CDCl<sub>3</sub> solvent on a Bruker 200 MHz instrument. The molecular weights of oligomers (A,B) were determined using Knauer, West Germany vapour phase osmometer, using chloroform solvent at 35°C. GPC of oligomers were performed using a Waters 150C instrument in THF (0.3 %) at 30°C. styragel column bank of 100,200,500, 10<sup>3</sup>,10<sup>4</sup>, 10<sup>5</sup> Å were used. FAB-MS were performed on a double focusing Kratos MS 50S mass spectrometer, equipped with the standard FAB source and DS 90 software.

## RESULTS AND DISCUSSION

FAB-MS has emerged as a powerful tool for the characterization of low molecular weight oligomers(11-16). The technique provides information on oligomer structures, monomer sequence distribution and copolymer composition. For polymers prepared by condensation method FAB-MS offers significant advantages over NMR for molecular characterization.

In the present study oligomers synthesized by carbonate interchange reaction of BPA with dimethyl carbonate as well as by methanolysis of poly(arylcarbonate)s were examined by FAB-MS. The particulars of the synthesized oligomers A,B used in the study are shown in Table 1.

Table 1. Characterization of synthesized oligocarbonates

Oligomer code	Melting point (°C)	Dp <sup>a</sup>	Mn (VPO)
A	90	6.4	1071
B	78	3.3	686

<sup>a</sup>calculated by NMR from the integration of carbomethoxy and hydroxyl groups to isopropylidene/aromatic protons.

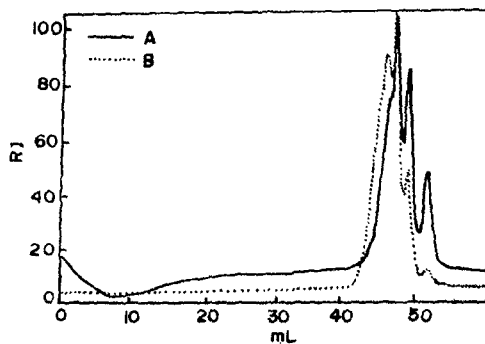


Fig. 1. GPC traces of synthesized oligocarbonates A and B

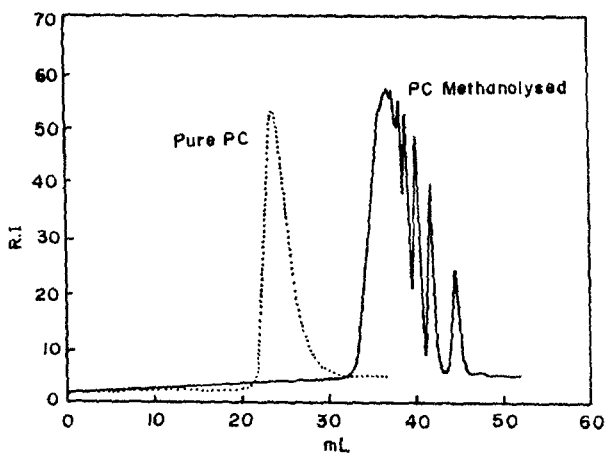


Fig. 2. GPC traces of pure Poly(bisphenol A carbonate) (M.W. = 25,000) and methanolyzed 120 h at room temperature

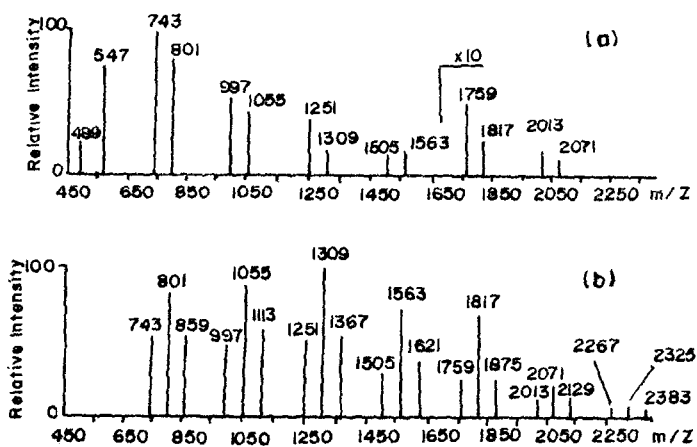
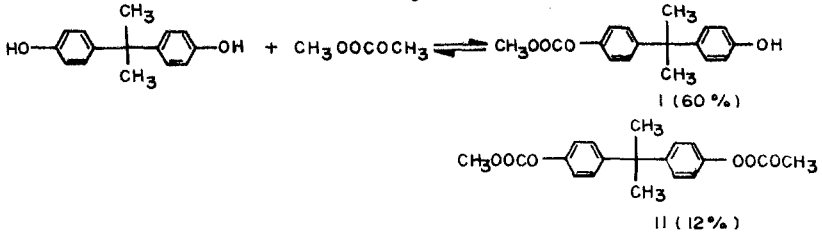
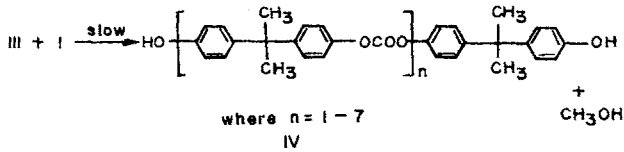
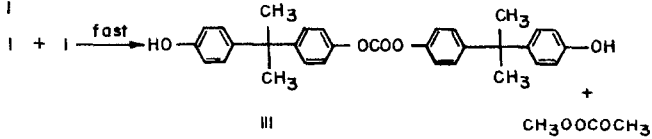


Fig. 3. FAB-MS spectra of oligocarbonates obtained a) by synthesis b) by methanolysis of Poly(bisphenol A carbonate)

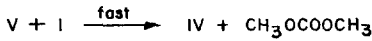
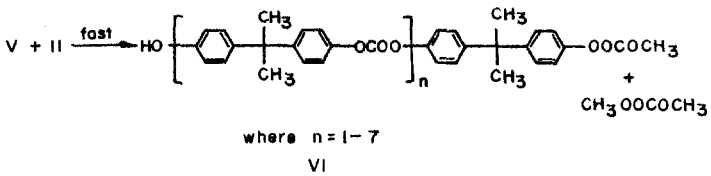
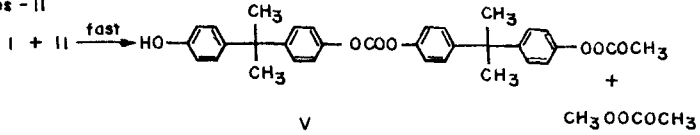
Scheme-1 Reaction pathway for the formation of oligocarbonates



Series-I



Series-II



Series-III

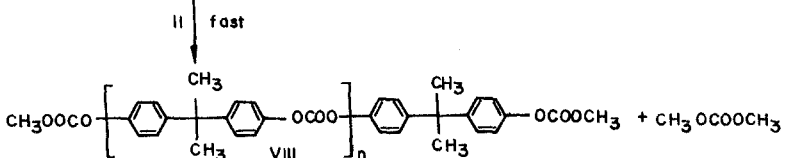
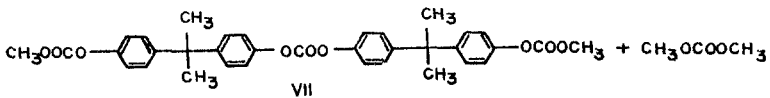
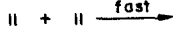


Table 2. (+)FAB-MS spectral data of oligocarbonates obtained by synthesis and methanolysis

Oligocarbonates	Lithiated molecular ions (n)
$\text{HO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\left[\text{COO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}\right]_n-\text{H}$	489(1), 743(2), 997(3) 1251(4), 1505(5), 1759(6) 2013(7), 2267(8)
$\text{HO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\left[\text{COO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}\right]_n-\text{COOCH}_3$	547(1), 801(2), 1055(3) 1309(4), 1563(5), 1817(6) 2071(7), 2325(8)
$\text{CH}_3\text{OOCO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\left[\text{COO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}\right]_n-\text{COOCH}_3$	859(2), 1113(3), 1367(4) 1621(5), 1875(6), 2129(7) 2383(8)

A typical GPC of the two oligomers is shown in figure 1. In figure 2 are reported the GPC traces of PC and that of the 120 h methanolysed sample of PC, which shows the presence of series of low molecular weight oligomers. The FAB-MS spectra of the two sets of oligomers (figure 3) were recorded using 3-nitrobenzyl alcohol as matrix doped with LiCl and they appear as lithiated pseudomolecular ion (MLi)<sup>+</sup>. The structure of the molecular ions observed in the mass spectra in figure 3 are assigned in Table 2. The oligomers obtained by synthesis show two series of oligomer structures. One series comprises of terminal hydroxyl groups with DP = 1-7. The other series consist of one terminal hydroxyl and one terminal methyl carbonate end groups with DP = 1-7. On the contrary, oligocarbonates obtained by methanolysis of poly(arylcarbonate)s show three series of oligomer structures (Table 2). Over and above the two series found for oligocarbonates obtained by synthesis, the oligomers obtained from methanolysis show a third series consisting of two methyl carbonate groups.

This interesting difference between the two sets of oligomers can be explained on the basis of relative reactivities of the compounds in the individual oligomer series. Methanolysis which involves random scission of the carbonate linkages can be expected to produce all the three series of oligomers. However, the complete absence of oligomer bearing two terminal carbonate groups in the synthesized product indicates the high chemical reactivity of such oligomers which prevents their accumulation among the reaction products (Scheme 1).

We had earlier observed that mono-methylcarbonate of bisphenol- A (I) was far less reactive to chain growth polymerization compared to bis-methylcarbonate of bisphenol- A (II). This was evidenced by facile polymerization of II to high molecular weight poly(arylenecarbonate)s whereas I resulted in the formation of low molecular weight poly(arylenecarbonate)s with low yields (17). Also in the first step carbonate interchange reaction between BPA and DMC, I is

formed as the major product(60%) with II(12%) as the minor product (18).However, on account of the substantially higher reactivity of II, it disappears fast to produce the second series of oligomers. Thus, oligomers of series III never accumulates during the reaction.

### ACKNOWLEDGEMENT

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