Polymer Bulletin 21, 483-488 (1989)

Polymer Bulletin

Sequencing an aromatic copolycarbonate by partial ammonolysis and FAB-MS analysis of the products

Giorgio Montaudo[1],* Concetto Puglisi[2], and Filippo Samperi[2]

[1]Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria, 6,
I-95125 Catania, Italy
[2]Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, Consiglio Nazionale delle Ricerche,
Viale Andrea Doria, 6, I-95125 Catania, Italy

SUMMARY

Fast atom bombardment mass spectrometry (FAB-MS) has been used to identify the low molecular weight compounds produced in the partial ammonolysis of an essentially alternating copolycarbonate containing resorcine and Bisphenol A (BPA) units.
The FAB-MS spectra allow to identify sequences with an exactly alternating structure. Furthermore, some spurious sequences containing blocks of 2-4 consecutive BPA units are detected.

INTRODUCTION

There is currently a great interest in obtaining information on the sequence arrangements of comonomer subunits in condensation copolymers, since the latters cannot be easily sequenced by current methods, including 13C-NMR. Mass spectrometry is able to look at the mass of individual molecules in a mixture and it is therefore an interesting alternative to NMR.

Recently, we have used fast atom bombardment mass spectrometry (FAB-MS) to identify the oligomers formed in the photolysis [1], hydrolysis [1,2] and methanolysis [3] of several copolyamides and copolyesters. The results obtained yielded detailed information about the structure and sequence of the copolymers investigated, and have established the basis for a new and straightforward method of sequencing multicomponent condensation copolymers having large comonomer subunits.

We wish to report here a novel case: the problem of cheking the sequence of an aromatic copolycarbonate (III) which, based on the synthetic route adopted (Eq.1), should have had an exactly alternating structure.

I II III Eq.1

---

*To whom offprint requests should be sent

Instead, the FAB-MS analysis of the partial ammonolysis products allowed to ascertain the presence of spurious sequences containing from two to four consecutive units of Bisphenol A carbonate in the copolymer, a result which might have escaped the scrutiny of other techniques.

EXPERIMENTAL

Copolycarbonate Synthesis - BPA bis chloroformate (m.p. 92°C) was shown by MS not to contain higher bis chloroformate oligomers. Comonomers I and II were dissolved in dichloromethane and water, respectively. Triethylamine was added in stoichiometric amount, and a phase transfer agent tricapryl methylammonium chloride (Aliquat 336) was also added as catalyst. The reaction was run at 0°C in a Waring blender and, after work up, the copolymer obtained was measured an intrinsic viscosity of 0.13.

Mass Spectrometry - A double focusing Kratos MS 50S equipped with the standard FAB source and a DS 90 data system was used to obtain mass spectra. The FAB gun (ION TECH) was operated with 7-8 kV xenon beam. The instrument was scanned from m/z 1800 to 60, with a scan rate of 10 s/decade. Accelerating voltage was 8 kV. Cesium and rubidium iodide (50/50 w/w) were used for computer calibration. The resolution was 2000.

A drop of the ammolyzed copolymer solution was placed on the copper target-end of the direct insertion FAB probe and mixed with 3,nitro-benzyl alcohol. Peak intensity values shown in mass spectra, computed after subtraction of the contribution from the liquid matrix, represent the average of five separate mass spectra.

GPC Analysis - A Waters 6000A apparatus equipped with four columns (micro) Styragel (in the order 1000, 500, 10000 ,100 A pore size) was used. A differential refractometer Model R 401 from Waters was used as detector. The analysis were performed at 25°C in tetrahydrofuran (THF) at a flow rate of 0.8 mL/min.

In Figure 1 are reported the GPC traces of untreated and treated samples of copolymer (III) with piperidine (ratio 10:1 on a molar basis) in THF at 25°C for 1 hour. The GPC traces show a molecular weight decrease and the appearance of several oligomers peaks in the sample subjected to partial ammonolysis.

RESULTS AND DISCUSSION

Polycarbonates are known to undergo quite easily to ammonolysis at room temperature and the latter reaction has been also used to synthesize some copoly(urethane-carbonates) [4,5].

In our approach, we have used FAB-MS to identify the products formed in the partial ammonolysis of copolymer III, (Eq.2).

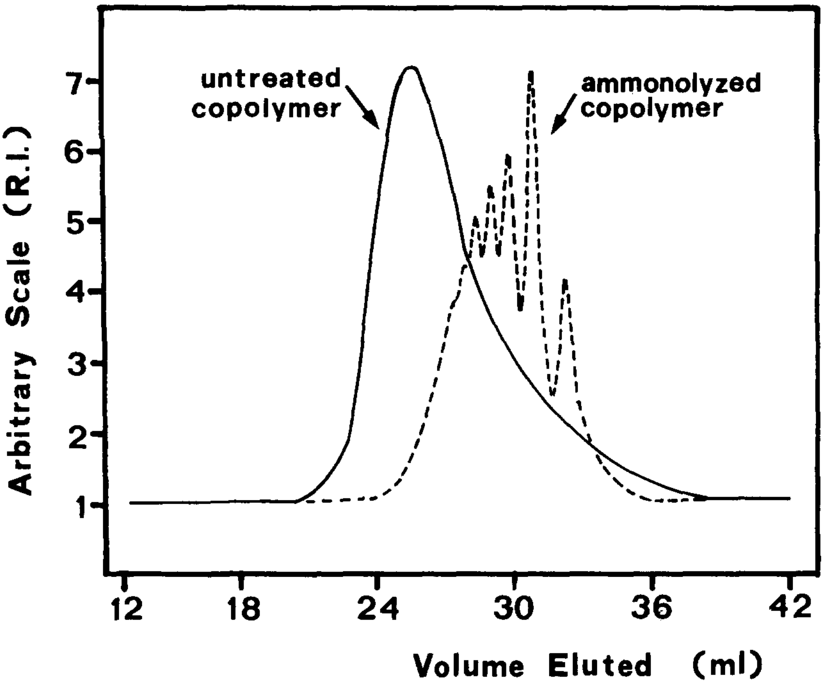
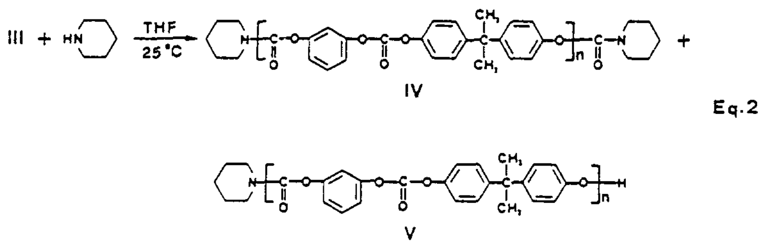


Figure 1 - GPC traces of untreated and treated samples of Poly(resorcine-co-BPA carbonate) with piperidine.



Eq.2

Copolymer III was treated with piperidine (ratio 10:1 on a molar basis) in THF at 25°C for 1 hour, and the FAB mass spectrum of the mixture of products obtained according to Eq.2 was taken using 3-Nitrobenzyl alcohol as the liquid matrix.

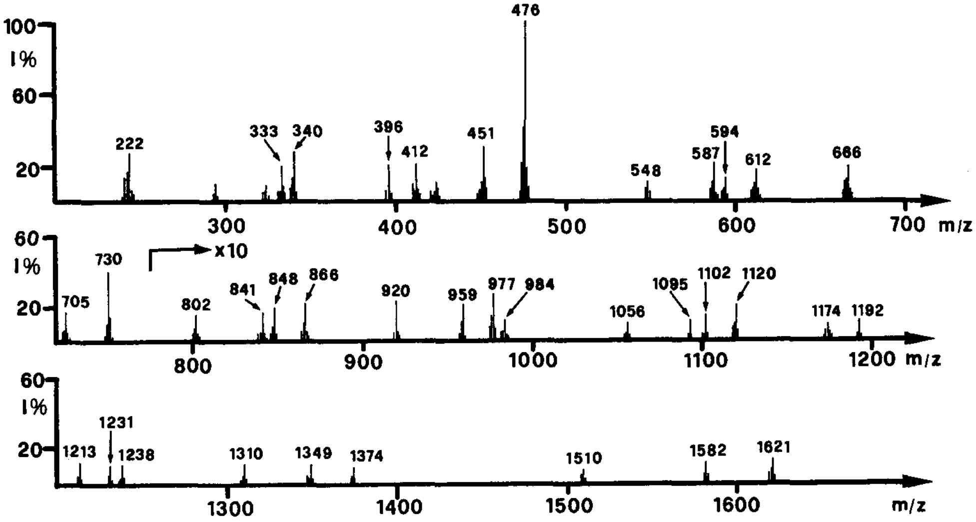


Figure 2 -FAB spectrum of the compounds obtained in the partial ammonolysis of copolycarbonate III with piperidine.

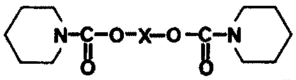
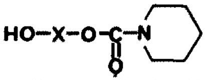
The FAB spectrum, reported in Figure 2, is constituted essentially by the molecular ions of the compounds generated in the ammonolysis. It shows structurally significant peaks up to 2000 daltons (the cut-off of our magnet), allowing to characterize the structure of copolycarbonate III. Structural assignments for the peaks identified are reported in Table I.

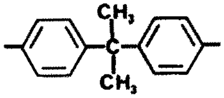
From the inspection of data in Table I, it appears that the partial ammonolysis products allow to identify sequences with an exactly alternating structure up to the heptamer level (peak at m/z 1621, Table I). This result indicates that copolymer III does actually possesses an alternating structure. However, several peaks present in the FAB spectrum in Fig.2 do correspond to spurious sequences containing blocks of two, three and four consecutive units of bisphenol A (Table I). The amount of consecutive (block) units can be estimated to about 10% (based on the relative intensities of peaks in Fig.2). This result appears to indicate that a sizeable portion of bisphenol A bischloroformate was hydrolyzed during the course of the polymerization reaction, yielding bisphenol A and/or monochloroformate which reacted further and was included in the copolymer, thus altering its sequence. The absence of blocks containing consecutive resorcinol units confirms the above conclusion.

The impressive simplicity and informative power of this method of structural characterization and copolymer sequencing, should be stressed once again.

In fact, to the best of our knowledge, there are no methods available in the literature to determine the sequence of condensation copolymers. Up to present, the exactly alternating structure of copolymers synthesized has been assumed on the basis of the synthetic method adopted, without the possibility of obtaining a reliable analytical proof.

TABLE I Protonated molecular ions of the compounds detected in the FAB-MS analysis of the compounds obtained by partial ammonolysis with piperidine of poly(resorcine-co-BPA carbonate).

		
X	MH^+	MH^+
-Ph-	333	222
-BPA-	451	340
-BPA-O-CO-O-Ph-	587	476
-Ph-O-CO-O-BPA-O-CO-O-Ph-	---	612
-BPA-O-CO-O-Ph-O-CO-O-BPA-	841	730
-BPA-O-CO-O-Ph-O-CO-O-BPA-O-CO-O-Ph-	977	866
-BPA-O-CO-O-Ph-O-CO-O-BPA-O-CO-O-Ph-O-CO-O-BPA-	1231	1120
-BPA-O-CO-O-Ph-O-CO-O-BPA-O-CO-O-Ph-O-CO-O-BPA-O-CO-O-Ph-	---	1256
-BPA-O-CO-O-Ph-O-CO-O-BPA-O-CO-O-Ph-O-CO-O-BPA-O-CO-O-Ph-O-CO-O-BPA-	1621	1510
-BPA-O-CO-O-BPA-	705	594
-BPA-(-O-CO-O-BPA-)$_2$	959	848
-BPA-(-O-CO-O-BPA-)$_3$	1213	1102
-Ph-(-O-CO-O-BPA-)$_3$	1095	984
-Ph-(-O-CO-O-BPA-)$_4$	1349	1238
-Ph-(-O-CO-O-BPA-)$_4$O-CO-O-Ph-	---	1374

BPA =  , Ph = 

ACKNOWLEDGMENT

This work was carried out under partial financial support from the Italian Ministry of Public Education and Consiglio Nazionale delle Ricerche.

REFERENCES

1. G. Montaudo, E. Scamporrino, D. Vitalini, **Macromolecules, 22,** xxx, (1989).
2. G. Montaudo, E. Scamporrino, D. Vitalini, **Polymer, 30,** xxx (1989).
3. A. Ballistreri, D. Garozzo, M. Giuffrida, G. Impallomeni, G. Montaudo, **Macromolecules, 22,** xxxx (1989).
4. V. S. Foldi, T. W. Campbell, **J. Polym. Sci., 56,** 1 (1962).
5. S. Foti, M. Giuffrida, P. Maravigna, G. Montaudo, **J.Polym.Sci.,Polym.Chem.Ed., 21,** 1583 (1983).

Accepted March 2, 1989 C