Radiostability of Polybenzoxazoles. Comparison of Stability of Molecular Ions of Model Compounds in Mass Spectrometry with Resistance of the Polymers to Ionizing Radiations

B. DESPAX, N. PAILLOUS,* and A. LATTES, *Laboratoire des Composés Azotés Polyfonctionnels, E.R.A. au C.N.R.S. n° 264, Université Paul Sabatier, 31400 Toulouse, France*, and A. PAILLOUS, *ONERA-CERTB 2, Avenue E. Belin, 31500 Toulouse, France*

Synopsis

Various benzoxazoles were synthesized and investigated by mass spectrometry. The relative stabilities of their molecular ions were used in the search for radiostable polybenzoxazoles (PBO). The three polybenzoxazoles corresponding to the three bibenzoxazoles previously investigated were irradiated by 900 keV electrons, and their aging was followed in situ by optical measurements. The most radiostable polymer coresponds to the model compound (diphenylbibenzoxazole), which is characterized by the highest degree of conjugation and by the lowest number of fragmentations in mass spectrometry. The resistance of this new polymer to electron irradiation is better than that of Teflon FEP or Kapton H.

INTRODUCTION

The use of polymers under space conditions depends on the stability of their mechanical and optical properties to ultraviolet and ionizing radiations. The investigation of the behavior of thermally stable, transparent polymeric films in space previously led us to search for more photostable polybenzoxazoles (PBO).[1]
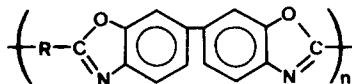
The purpose of the work reported here was to look for the most radiostable polybenzoxazoles. In a first step, model compounds corresponding to the various recurring units of the polymers were investigated by means of mass spectrometry. As a matter of fact, mass spectrometry (as well as irradiations under electron impact) gives rise to the formation of molecular ions:

$$AB \xrightarrow{e^-} AB^{\cdot+} + 2e^-$$

If the fragmentations observed in the materials investigated (model compounds and polymers) are considered to originate mostly from these molecular ions, the

* To whom correspondence is to be sent.

stability of the molecular ions of the model compounds is likely to be analogous to the resistance of the polymers under electron irradiation. Correlations have already been established for the same derivative between the fragmentation processes involved in γ-radiolysis and in mass spectrometry. In the case of alcohols, in particular, the radiochemical yields could be related quantitatively to the percentages of the various mass spectrometry fragmentations.[2]

The data obtained from mass spectrometry led, in a second step, to the synthesis of various polymers whose relative resistance to electron impacts was then tested.

EXPERIMENTAL

Synthesis of Model Compounds

The five model compounds investigated, M_1 to M_5, are monomeric or dimeric benzoxazoles (Table I):   2-adamantylbenzoxazole, M_1; 2-phenylbenzoxazole M_2; 1,3-dimethyl 5,7-di(2-phenyl 4-benzoxazole) adamantane, M_3; 2,2'-diadamantyl 6,6'-bibenzoxazole, M_4; and 2,2'-diphenyl 6,6'-bibenzoxazole, M_5.

Such compounds are usually synthesized by condensation of an aminophenol (or diaminophenol) on a carboxylic derivative.[3-9] However, a new two-step method was developed for the preparation of model compounds M_1 to M_5.[10] o-Aminophenol or diaminophenol (0.01 mol) was first reacted on the acid chloride (0.01 or 0.02 mol) at 0°C for 30 min in anhydrous N-methylpyrrolidone (50 ml) under an atmosphere of dry nitrogen. The mixture was stirred for 30 min, then neutralized by addition of pyridine (0.01 or 0.02 mol) at room temperature. The hydroxamide obtained was then cyclized in situ through thermaldehydratation within the condensation solvent: N-methylpyrrolidone was refluxed for 1 h. The product, which was partly soluble in the solvent, was precipitated with a 50:50 v/v methanol–water mixture, then purified by preparative GLC (silica gel, $d = 2.5$ cm, $h = 25$ cm) and eluted with dichloromethane
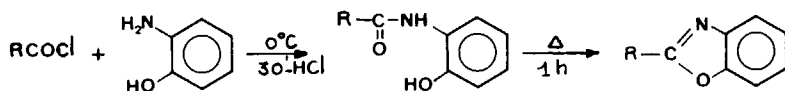
This two-step procedure allowed benzoxazoles to be obtained in yields over 90% (Table I). The yields are much lower when the reaction medium is heated right from the start, since the acid chloride then reacts on both functional groups of aminophenol.

The structure of compounds M_1 to M_5 was corroborated by their IR spectra recorded on a Beckman IR 20 A spectrophotometer (Table I) as well as by their NMR spectra (Varian T 60, $CDCl_3$, internal reference TMS; Table II).

Polymer Synthesis

The polybenzoxazoles (PBO_1 to PBO_3) corresponding to the model compounds (M_3 to M_5) were synthesized by condensation of a diaminophenol on an acid dichloride.[10] The procedure was analogous to that described above. The polymer was obtained as a film whose thickness is equal to 12 μm and specific mass 1.18 g/cm^3

TABLE I
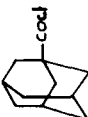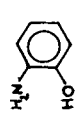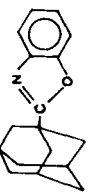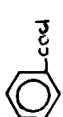Synthesis of the Various Model Compounds
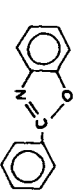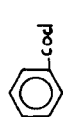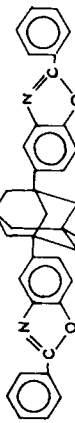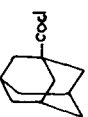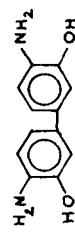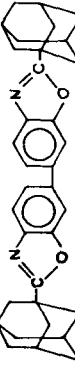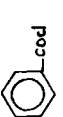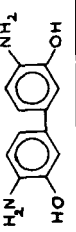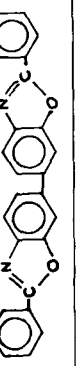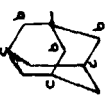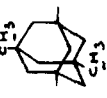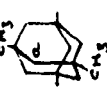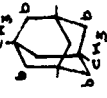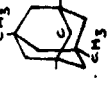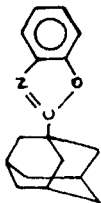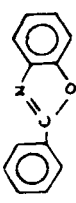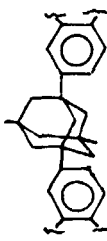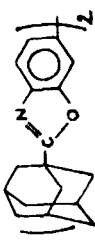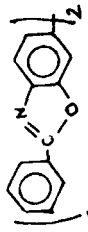
Acid Chloride	Aminophenol	Product	Yield, %	mp, °C	$\nu_{C=N}$, cm^{-1}
			90	102	1625 (CCl$_4$)
			90	103	1620 (CCl$_4$)
			91	100	1620 (CDCl$_3$)
			92	310	1625 (CCl$_4$)
			93	255	1630 (KBr)

TABLE II
NMR Spectra of the Various Model Compounds

Compound						Aromatic systems
	1.8 ppm (s)6(H)	2.12 ppm (s)9(H)				7.22 ppm(m)　4(H) 7.5 ppm(m)
						7.45 ppm(m) 8.12 ppm(m)
			1 ppm (s)6(H)	1.3 ppm (s)2(H)	1.67 ppm (s)8(H)	2 ppm (s)2(H)
						7.22 ppm(s)　7.69 ppm(s) 7.43 ppm(s)　8.2 ppm(m)
	1.85 ppm (s)12(H)	2.28 ppm (s)18(H)				A: 7.76 ppm $J_{AB} = 3.2$ Hz B: 7.51 ppm $J_{BX} = 1.3$ Hz X: 7.69 ppm $J_{AX} = 0.8$ Hz
						7.5 ppm(m) 7.73 ppm(s) 8.16 ppm(m)
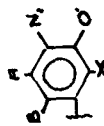
TABLE III
Structure of the Polybenzoxazoles Investigated
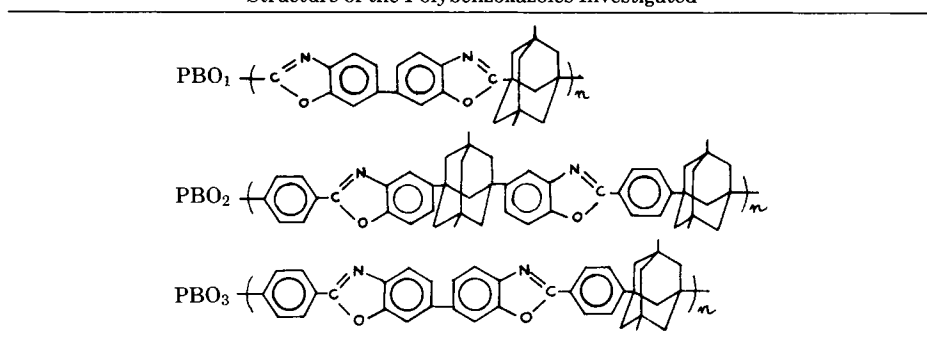
Spectroscopy

The mass spectra of the model compounds were recorded on a Varian Mat 311 A spectrometer equipped with a direct insertion probe; the accelerating voltage was 3 kV, the electron energy was 70 eV, and the emission current 1 mA. The photoelectronic spectra were recorded on a Perkin–Elmer PS 18 spectrometer and calibrated using the $2p_{1/2}$ and $2p_{3/2}$ doublets of argon (15.755 and 15.933 eV, respectively) and xenon (12.127 and 13.427 eV, respectively).

Polymer Irradiation

For electron irradiations, a van de Graaf accelerator was used together with an electron scattering device consisting of a thin (150 μm) aluminum sheet. The samples were introduced in a low-volume cell and irradiated under vacuum (better than 5×10^{-5} torr, using a turbomolecular pump). The samples (2 cm in diameter) were put on a frame which allowed optical measurement of the spectral transmittance of the polymers to be carried out in situ. The electron energy after scattering was 900 keV. The electron flux rate was measured by means of a Keithley electrometer.

RESULTS AND DISCUSSION

MS Investigation of the Model Compounds

The various model compounds (M_1 to M_5) were analyzed by mass spectrometry. The peaks representing a fraction of the total ionic current higher than 3% are listed in Table IV. For the molecular ions, all isotopic ions were considered to be $M^{\cdot+}$. The relative stability of the molecular ions of the various model compounds can be correlated to the relative intensity of the base peak of the spectrum. It can be seen from Table IV that the molecular ions of the dimers are more stable than those of the corresponding monomers:
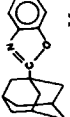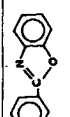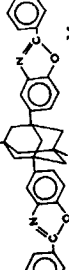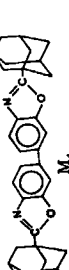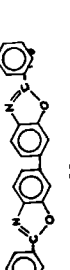
$$M_4(33\%) > M_1 \ (21\%)$$

$$M_5 \ (57.5\%) > M_2 \ (30\%) \text{ and } M_3 \ (30\%)$$

and that the molecular ions are the more stable as they are more conjugated:

$$M_2 \ (30\%) > M_1 \ (21\%)$$

TABLE IV
M S data for the various model compounds[a]

Products	m/e 77	79	81	91	93	94	107	126	135	154	166	167	195	196	197	208	209	253	254	255	300	314	388	389	447	504	505/506	550
M_1	3%	6%	3%	3%	6%		3%		10%					6,5%														
M_2	9%					16%						8%		30%					21%									
M_3	3,5%	10%	3%	3,5%	8,5%		4,5%		10%																			30%
M_4															4,5%	10%	6,5%				9%	4,5%				33%		
M_5	4,5%							11,5%	6%	6%	6%		8% (194)										57,5%					

[a] Fragments whose relative intensity was under 3% are not listed here. The total ionic current is integrated between $m/e = 77$ and $m/e = M$.

$$M_5 \, (57.5\%) > M_4 \, (33\%)$$
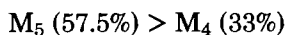
A more detailed investigation of the mass spectra suggests that monomers and dimers undergo analogous cleavages (Table IV).

In the adamantyl series (M_1 and M_4), the predominant cleavages correspond to the formation of either an adamantyl ion ($m/e = 135$) or phenyl ions $C_6H_5NO^+$ ($m/e = 107$), $C_6H_5O^+$ ($m/e = 93$), $C_6H_5N^+$ ($m/e = 91$), $C_6H_7^+$ ($m/e = 79$), and $C_6H_5^+$ ($m/e = 75$).

In the phenyl series, the cleavages mainly correspond to the loss of a carbonyl group (either from the monomer itself or from the dimer cleavage products) and to the formation of phenyl or diphenyl ions. These cleavages are analogous to those reported for benzoxazole[11] whose fragmentation is characterized by a loss of CO and HCN. As the mass spectrum of benzoxazole is identical with that of 2-cyanophenol, it was postulated that benzoxazole first underwent an isomerization and that the fragmentations observed were those of 2-cyanophenol.[11] Such an isomerization is however unlikely in the case of phenylbenzoxazole.

With a few exceptions, the main fragmentations are practically of the same nature and relative importance for the monomers and their corresponding dimers. However, the monomers give rise to more numerous fragmentations of low relative intensity which may be due to the participation of other kinds of fragmentations.

The fragmentations of model compound M_3 are more complex than those of the other model compounds; they cannot be directly correlated to those of phenylbenzoxazole or of its dimer.

Interpretation

The above data show that the conjugation in the molecule brings about a greater stability of the molecular ion. This effect can be accounted for by different phenomena:

(1) The aromaticity can, in particular, increase the number of the possible ionized states, thus allowing a better energy transfer toward the most stable ions. This point is in agreement with the lower number of fragmentations in the more highly conjugated compounds.

(2) The dissociation energy of a molecular ion is the higher the more highly conjugated this ion is. Its potential energy diagram is then characterized by a deeper trough. Besides, as the increase in the conjugation enhances the energy of the highest orbital occupied, the ionization potential of these molecules should be lower.

The occurrence of a correlation between the conjugation of the molecule and its ionization potential was ascertained by means of the photoelectronic spectra of model compounds M_1 to M_5. The assignment of the various values of the ionization potentials to the various molecular orbitals was derived from the data previously obtained for benzoxazole.[12] The order of the molecular orbitals was assumed to be the same as in benzoxazole. The data listed in Table V clearly show that the first ionization potential of the π orbital is the lower the more highly conjugated the molecule is.

It has been argued that, in general, the effect of substituent on the ionization potential IP is more pronounced than on the appearance potential AP. In the same way here, the difference AP $-$ IP must be increased by the conjugation that

TABLE V
Ionization Potentials (eV) of the Model Compounds[a]

M_1	8.45 (π)	8.99 (π)	9.82 (nN)	10.08 (π)	11 (π)
M_2	8.35 (π)	9.07 (π)	9.42 ($\pi\varphi$)	9.87 ($\pi\varphi$)	10.30 (nN)
M_3	8.05 (π)	8.57 (π)	9.55		
M_4	7.80 (π)	8.78 (π)	9.56	10.10	
M_5	7.70 (π)	8.56 (π)	8.90 ($\pi\varphi$)	9.36 ($\pi\varphi$)	9.96 (nN)

[a] π is the molecular orbital π delocalized on the benzoxazole ring, $\pi\varphi$ is the molecular orbital π delocalized on the aromatic ring, and nN the nonbinding orbital σ localized on the nitrogen atom.

would explain that the fraction of molecular ions with insufficient energy to decompose is more important.

Investigation of the Degradation of Polybenzoxazoles under Electron Irradiation

The polymers corresponding to the dimeric model compounds M_3, M_4, and M_5 were simultaneously irradiated by electrons whose energy was 900 keV; the electron flux density was 4.4×10^{11} e/cm^2 s. The polymers were selected in view of their possible use as coatings, which have to be transparent to solar radiation outside the atmosphere, so their aging was followed mainly by measuring in situ their optical transmittance. Figure 1 shows the changes in the UV-visible transmission spectra of the various polymers for electron fluences of 2.2×10^{14}, 1.1×10^{15}, 2.2×10^{15}, 4.4×10^{15}, and 8.8×10^{15} e/cm^2. The behavior of FEP Teflon, which is a transparent polymer widely used in space technology, was assessed under the same conditions. These data clearly show that aging mainly impairs the transmission in the UV range.

To assess the overall aging of the polymers, their transmittance was integrated over the whole solar spectrum (T_s) before (T_{s_1}) and after (T_{s_2}) irradiation. The solar transmittance T_s is defined by the equation

$$T_s = \sum_{\lambda=250nm}^{2500nm} T(\lambda)\,E(\lambda)\,\Delta\lambda \Big/ \sum_{\lambda=250nm}^{2500nm} E(\lambda)\,\Delta\lambda$$

where $E(\lambda)$ is the spectral solar irradiance, and $T(\lambda)$ is the spectral transmittance.

The lowest relative variation of transmittance was observed for the most highly conjugated polymer (Table VI).

As to bibenzoxazole (M_4 and M_5), the relative stability order found for the molecular ions of the model compounds holds for the corresponding polymers. PBO$_2$ is less stable than PBO$_3$ in the same way as M_4 is less stable than M_5. The occurrence of an adamantyl ring between benzoxazole recurring units (PBO$_1$

TABLE VI
Solar Transmittances Before (T_{s_1}) and After (T_{s_2}) Irradiation Fluence of 8.8×10^{15} e/cm^2

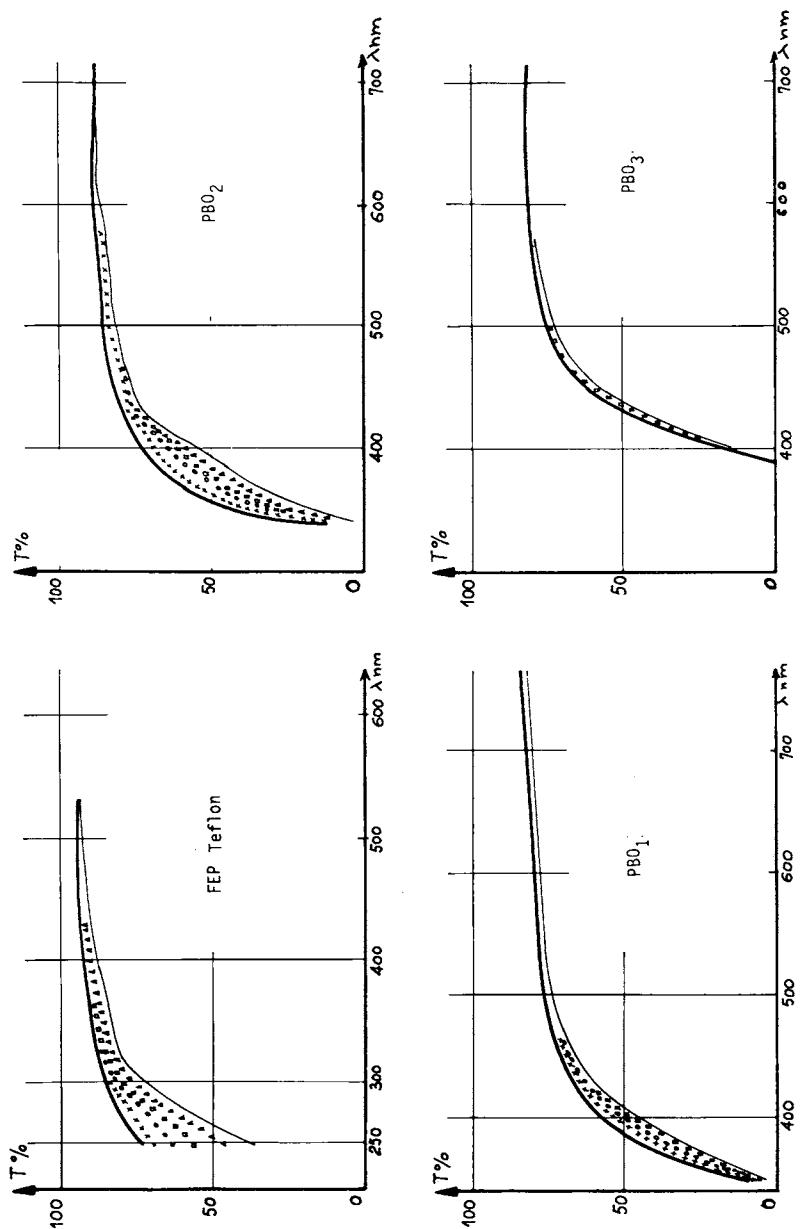|	T_{s_1}, %	T_{s_2}, %	$\Delta T_s/T_{s_1}$
PBO$_1$	76.42	74.15	2.97
PBO$_2$	84.65	81.15	4.13
PBO$_3$	71.9	71.05	1.18

Fig. 1. Variations of the transmittance of the various polymers under electron irradiation (900 keV) for a fluence of zero (—), 2.2×10^{14} e/cm^2 (×), 1.1×10^{15} e/cm^2 (O) 2.2×10^{15} e/cm^2 (□), 4.4 $\times 10^{15}$ e/cm^2 (△), and 8.8×10^{15} e/cm^2 (—).

corresponds to M_3) gives rise to a different behavior: the aging of PBO_1 under irradiation was markedly less pronounced than that of PBO_2, which could not be expected from the comparison between M_3 and M_4. Since the fragmentations of M_3 observed in mass spectrometry were quite different from those observed for bibenzoxazoles, it is understandable that polymer radiolysis leads to different, fragmentation types and therefore to a differing discoloration.

The radiostability of PBO_3 as a whole is nevertheless quite satisfactory. It is superior not only to that of Teflon FEP, as we can see on Figure 1, but also to that of a polyimide, Kapton H, as well. (Kapton H is a transparent polymer which is widely used in space.) Under similar conditions of irradiation (fluence 8.8×10^{15} e/cm^2), the transmittance variation $\Delta T_s/T_s$ for Kapton H was 5.6%.[12] The degradation of PBO_3 is therefore five times slower than that of Kapton H.

CONCLUSIONS

The correlation between the molecular ions of the model compounds (bibenzoxazoles) and the radiostability of the corresponding polymers yields an interesting approach in the search for radiostable polymers. It can only be applied to products that belong to closely related series (bibenzoxazoles in the present case). These investigations led to the synthesis of the polymer PBO_3, whose optical and mechanical properties as well as its thermal stability are particularly interesting. Furthermore, as to its stability to ionizing radiations, this new polymer has proved to be competitive with commercial polymers such as Teflon and Kapton.

References

1. B. Despax, A. Paillous, N. Paillous, and A. Lattes, *J. Polym. Sci., Part A*, **18**, 593 (1980).

2. (a) R. A. Basson, *J. S. Afr. Chem. Instr.*, **22**, 63 (1969); (b) R. A. Basson and H. J. Van der Linde, *J. Chem. Soc. A*, 1618 (1969).

3. R. M. Gitina, G. I. Braz, V. P. Bazov, and A. Ya. Yakubovich, *Vysokomol. Soedin*, **8**(9), 1535 (1966).

4. A. Landerburg, *Ber.*, **9**, 1524 (1876).

5. R. Brodersen, and W. Herrmann, Ger. Pat. 886,745 (1953).

6. P. W. Hein, R. J. Alheim, and J. J. Leavitt, *J.A.C.S.*, **79**, 427 (1957).

7. Y. Imai, I. Taoka, K. Uno, and Y. Iwakura, *Macromol. Chem.*, **83**, 167 (1965).

8. W. W. Moyer Jr., C. Cole, T. Anyos, J. Polym. Sci. Pt. A 3 (6), 2107 (1965).

9. G. L. Genkins, A. M. Knevel, and C. S. Davis, *J. Org. Chem.*, **26**, 274 (1961).

10. G. G. Bellman, A. M. Groult, and J. H. Arendt, Ger. Offen. 2,330,452 (1974).

11. A. Maquestiau, Y. Van Haverbecke, C. DeMeyer, and R. Flammang, *Org. Mass. Spectr.*, **9**, 149 (1974).

12. G. Guimon, G. Pfister-Guillouzo, G. Salmona, and E. J. Vincent, *J. Chim. Phys.*, **75**, 9 (1978).

13. A. Paillous, D.E.R.T.S., CR 03.48.72 (1972).