Macromolecules 1991, *24*, 99-105

X-ray, Electron, and Ion Beam Induced Modifications of Poly(ether sulfone)

Giovanni Marletta* and Salvatore Pignataro

*Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6,
95125 Catania, Italy*

András Tóth, Imre Bertóti, and Tamás Székely

*Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences,
H-1112 Budapest, Budaörsi út 45, Hungary*

Balázs Keszler

Research Institute for the Plastics Industry, H-1950 Budapest, Hungária krt. 114, Hungary

Received January 4, 1990; Revised Manuscript Received May 17, 1990

ABSTRACT: The chemical modifications induced by several types of radiation on aromatic poly(ether sulfone) [poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)] have been studied by ESCA. In particular, the effects of soft X-rays (Mg Kα radiation at 1253.6 eV), 1.1-keV electrons, and 1-keV Ar^+ and N_2^+ ions are compared. The following compositional effects are observed: the depletion of sulfur and oxygen with respect to carbon, and the reduction of SO_2 groups to S. This is apparently the first time that the latter process has been observed in high-energy irradiation experiments. The relative importance of these two processes depends on the nature of the projectiles employed. In the case of ion bombardment both processes are enhanced. During ion bombardment the O/S ratio decreases more quickly, and the gradual destruction of the phenyl rings is also observed. On the contrary, when photon or electron beams are used, the oxygen is lost more slowly and the phenyl rings remain almost intact. A reaction mechanism for the radiation-induced reduction of the sulfonyl group is proposed on the basis of the ESCA data.

Introduction

The interaction of "traditional" (γ-rays, energetic electrons and protons) or "nontraditional" (heavy ions of keV or MeV energy) ionizing radiation with polymers is a topic of wide interest for both fundamental and technological reasons.

As to the interest for basic phenomena, we may mention the interest in the peculiar chemistry induced by radiation. The radiation chemistry has been mainly discussed in terms of degradation reactions involving the loss of gaseous products and the irreversible change of the stoichiometry.[1] However, more recent results showed that polymers irradiated with radiation depositing a high density of energy (typically beams of heavy ions) may be characterized as highly reactive systems in which many simple chemical reactions may occur in competition with each other, producing the modification of the functional groups, modification of the polymer backbone, cross-linking, chain scission, etc.[2]

As to the technological importance, we may recall that many of the relevant applications of polymeric materials, as, for instance, applications in aerospace equipment, in fusion reactors, or as resist materials in microelectronics, involve the exposure of these polymers to various ionizing environments. Therefore, it is important to test their response to various types of radiation. On the other hand, according to more recent results, the relevant physical and chemical properties of a polymeric material may be selectively modified by radiation processing. In particular, while photons, electrons, or protons may meaningfully affect the rheological or mechanical properties of polymers,[3] recent work has shown that ion bombardment in the keV or MeV range is particularly effective to induce new electrical, optical, and chemical properties of technological polymers like polyimides, PMMA, PAN, PPO, PPS, etc.[1,2]

Polysulfones are materials of great technological interest due to their applications as polymeric membranes, resists for microelectronics, heat-resistant materials in aerospace applications, matrices for composites, etc. Accordingly, studies have been undertaken on their response to "conventional" radiations like γ-rays, energetic electrons, or MeV protons with the aim of controlling their radiation resistance[4-6] or the modifications induced in their rheological and mechanical properties.[7,8] Furthermore, it has been also shown that ion-beam treatments (in the keV energy range) are very suitable to modify other relevant properties of polysulfones like electrical conductivity or solubility.[9,10]

Problems concerning the use of different types of radiation have been primarily addressed, with the aim of understanding the differences and similarities of the chemical processes induced. This approach has been chosen for the reason that it is more and more evident that different types of radiation may produce different chemical and physical modifications, since the energy deposition mechanisms and in turn the radiation-induced chemical reactions change with the nature and energy of the projectiles.[2]

In particular, in the present paper we compare the chemical modifications induced by soft X-rays, electrons, and ions having energies of the order of keV on a model compound, the aromatic poly(ether sulfone), poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene). X-ray photoelectron spectroscopy (ESCA or XPS) has been used to characterize the composition and the chemical state of the surfaces irradiated in situ. The observed phenomena are discussed in the light of the existing reports on classical radiolysis, and an additional reaction mechanism is proposed.

Further papers will address the relationship between the nature of chemical modifications and the related physical property changes.

0024-9297/91/2224-0099$02.50/0

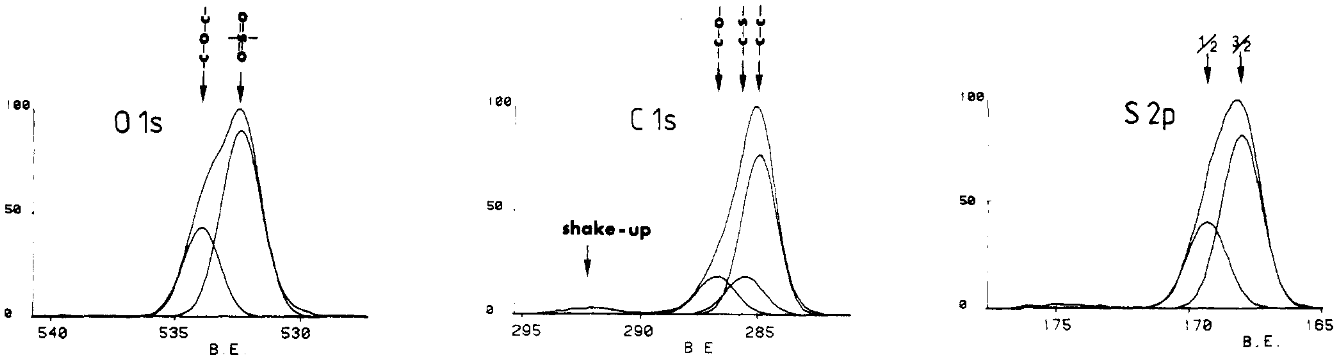


Figure 1. Characteristic photoelectron peaks of the starting PES sample.

Experimental Section

Aromatic poly(ether sulfone) [poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)] (hereinafter denoted as PES) received from ICI (Victrex 100P) was studied in the form of foils or films cast from *N*-methylpyrrolidone onto a 6 × 6 mm sample holder made of gold. Exposure to beams of X-rays, Ar^+ ions, or N_2^+ ions and the related XPS analysis were performed in situ using a Kratos XSAM 800 electron spectrometer equipped with a Kratos Macrobeam ion gun system. The electron irradiation treatments as well as the related XPS analysis were also performed in situ in a Kratos ES 300 electron spectrometer, equipped with a Kratos electron gun, operating with 50–5000-eV electron beams at variable currents (between 100 nA and 100 μA). The beams were rastered over the sample area to ensure the whole of the specimen was uniformly treated with ions or electrons. The absence of the N 1s peak in the spectra reflected lack of residual solvent in the films studied.

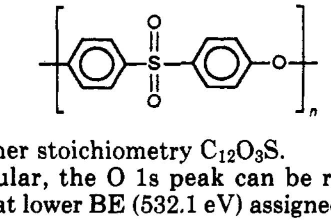
The XPS spectra were referenced to the main component of the C 1s peak of PES at 284.8 eV of binding energy (BE). After the irradiation treatments, in which the BE of the most reduced hydrocarbon-like component is expected to be slightly shifted toward lower values, the referencing was performed assuming that the S 2p component pertaining to the sulfone group (at 168.0 eV of BE) was not shifted. The irradiation treatments generally resulted in a small shift of all the peaks (up to ca. 0.6 eV) toward higher KEs, implying an increased conductivity of the modified surfaces.

For studying the X-ray beam effects, Mg Kα radiation (1253.6 eV) was used with an estimated fluence of 1×10^{12} photons cm^{-2} s^{-1}.[11] The electron irradiation was performed by using an electron beam of 1.1 keV with a current density of 0.7 $\mu A\ cm^{-2}$ (i.e., 4×10^{12} electrons $cm^{-2}\ s^{-1}$). During the ion bombardments 1-keV Ar^+ or N_2^+ beams were employed, with current densities of 1.1 or 1.4 $\mu A\ cm^{-2}$, respectively (i.e., 7×10^{12} or 9×10^{12} ions $cm^{-2}\ s^{-1}$).

Data acquisition and data processing were performed partly by using the Kratos DS 300 data system running on a DEC LSI 11/23 computer and partly by using routine programs on a HP-1000 computer. The Shirley-type nonlinear background subtraction was used. The overlapping peaks were resolved by the peak synthesis method based on Gaussian peaks.[12]

Results

The O 1s, C 1s, and S 2p peaks of PES are shown in Figure 1. The peak synthesis and the assignment of the components have been performed according to literature data.[13-17] The reported spectra refer to low exposure to X-rays, for which the atomic ratios obtained from the XPS peaks reflect quite well the stoichiometry of the repeat unit



with monomer stoichiometry $C_{12}O_3S$.

In particular, the O 1s peak can be resolved into a component at lower BE (532.1 eV) assigned to the oxygen present in the SO_2 groups and a component at 533.8 eV assigned to the ether-type oxygen. The ratio of the two components is slightly different from that expected (2.4:1 instead of 2:1). This may be diagnostic of some H_2O adsorption on the PES surface. Also the C/S atomic ratio is slightly higher than that expected for the ideal stoichiometry (13.2:1 instead of 12:1), this being diagnostic of the presence of some hydrocarbon contamination on the polymer surfaces. However, at variance with previous reports concerning PES and other polysulfone systems,[15] no traces of reduced sulfur were observed on the surfaces studied under the conditions of low exposure to X-rays. (The two components shown in Figure 1 are assignable to the S $2p_{1/2}$ and the S $2p_{3/2}$ levels.)

The irradiation of PES samples with X-rays, energetic electrons, or ion beams in the vacuum environment of the XPS apparatus is found to damage severely the chemical structure of PES. The nature of the chemical modifications induced by irradiation depends qualitatively and quantitatively on the type of irradiation applied.

First, having X-rays as the excitation beam in the XPS analysis, we examined the effect of prolonged X-irradiation on the chemical structure of PES. Figure 2 shows the modifications observed at increasing times of exposure for the O 1s and S 2p bands of PES. The main effect is that a new component is created on the S 2p region by X-irradiation at the BE of the sulfide group (163.8 eV).[13-15,17] This component reaches the intensity of ca. 20% of the total S 2p band after a relatively long irradiation time (ca. 5 h). Simultaneously with the appearance of this reduced S 2p component, the O 1s component pertaining to the sulfone groups decreases in intensity with respect to the ether-type O 1s component. In addition, the losses of sulfur and oxygen are observed with respect to carbon. The variations in the concentrations of C, O, and S (expressed in atomic percent) are reported in Figure 3. The composition after 5 h of irradiation corresponds to the rough formula $C_{20.2}O_{3.9}S$ in contrast to the initial monomer formula.

Similar effects may be detected when the polymer surfaces are irradiated with electrons of 1.1 keV. The energy and the dose rate of the electron beam were chosen to be comparable with the parameters of the X-irradiation (see Experimental Section). Also in this case, the main effects consisted in the formation of a reduced sulfur species at the same BE of that observed during X-irradiation (see bottom part of Figure 4) and in the partial loss of sulfur and oxygen (Figure 5). The rough formula corresponding to the highest exposure is $C_{20.5}O_4S$; i.e., it is very close to that reported above for the highest irradiation time with X-ray photons. The comparison of the structure of the S 2p band for e^--irradiated (Figure 4, 120 min) and for X-irradiated (Figure 2, 140 min) surfaces suggests that electrons are significantly more effective than X photons in producing the reduced sulfur

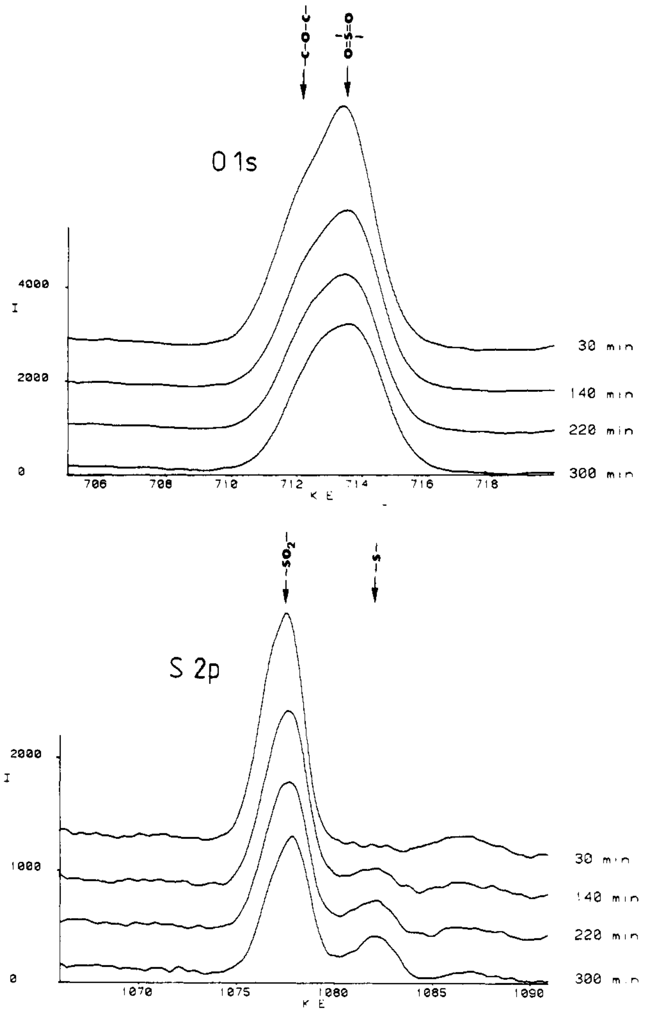


Figure 2. Effect of X-irradiation.

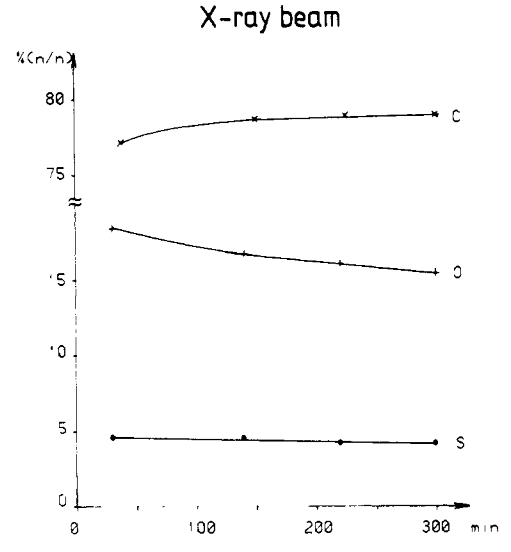


Figure 3. Surface composition of the X-irradiated PES.

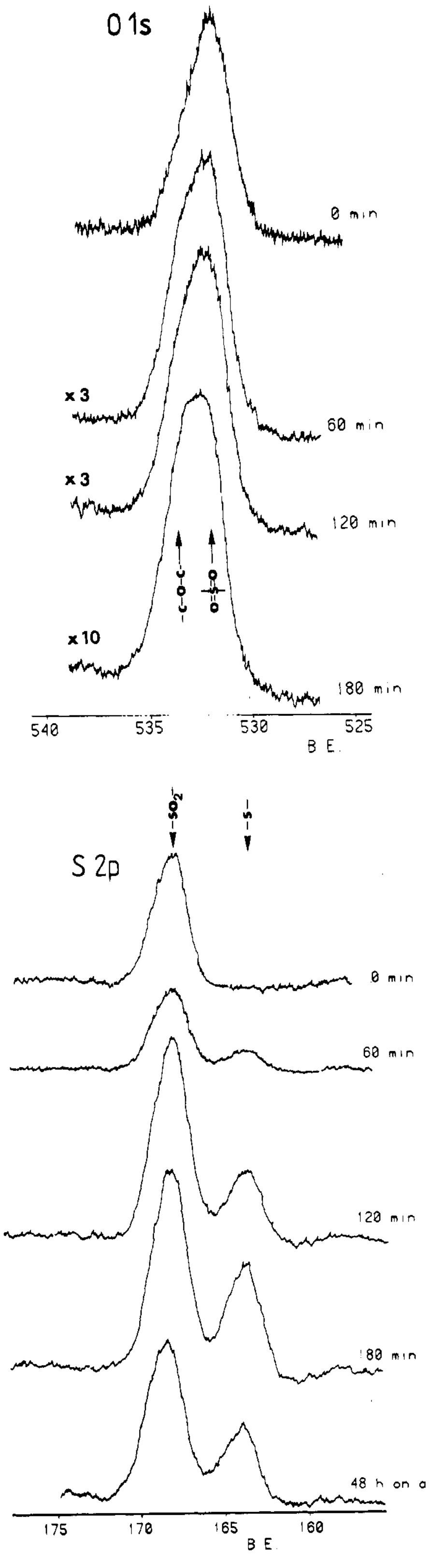


Figure 4. Effect of electron irradiation.

component at 163.8 eV. Indeed, the intensity of this component reaches ca. 35% of that of the whole S 2p band for e$^-$-irradiated samples versus 20% for the X-irradiated samples at a similar chemical composition. Accordingly, the sulfone-type oxygen component in the O 1s band is reduced in intensity, and at the highest exposure employed it has about the same intensity as the ether-type component (Figure 4, 180 min). The reduction of the sulfone groups seems to be irreversible: on exposure of the electron-bombarded sample to the atmosphere for 48 h, no reoxidation of the sulfide takes place (Figure 4).

Finally, we studied the modifications induced by ion beams on the PES surfaces. Ar$^+$ and N$_2^+$ ions at energies of 1 keV and typical dose rates of (7–9) × 10^{12} ions/cm^2 were used in order to have beam parameters roughly comparable to those used in X-ray and electron irradiations. The main effects are qualitatively similar, but strikingly different from a quantitative point of view. Indeed, (1) the sulfide-like component becomes predomi-

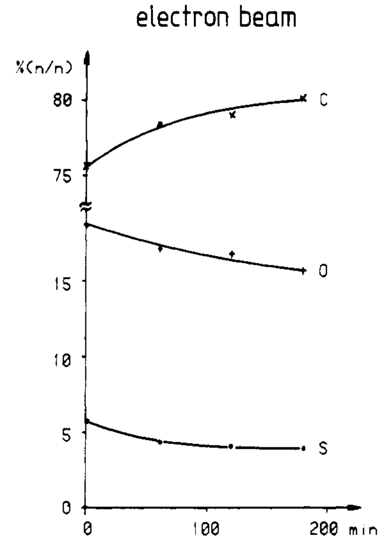


Figure 5. Surface composition of the electron-irradiated PES.

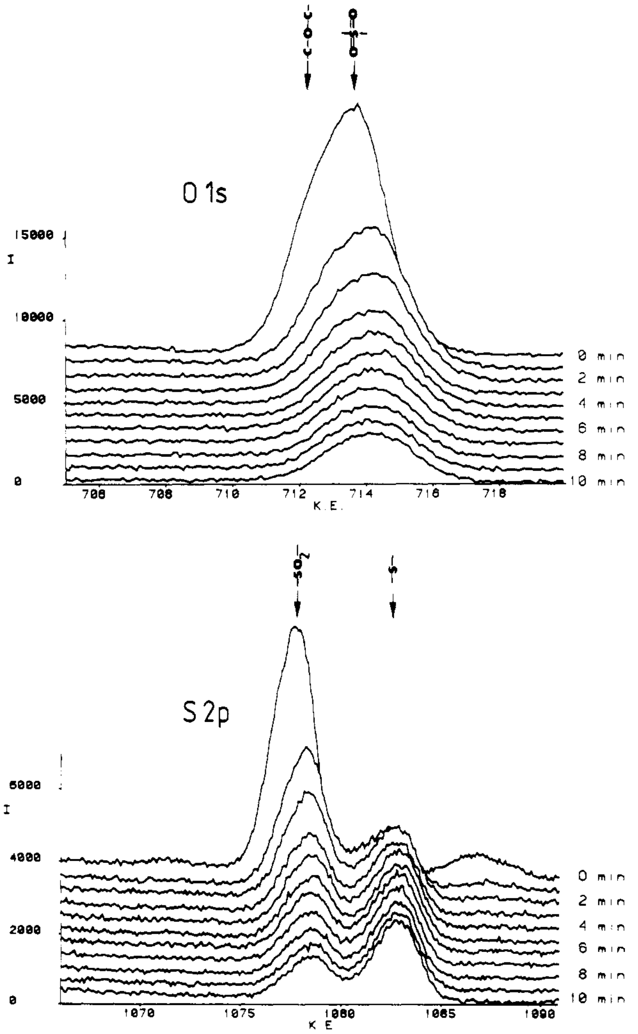


Figure 6. Effect of Ar^+ ion bombardment.

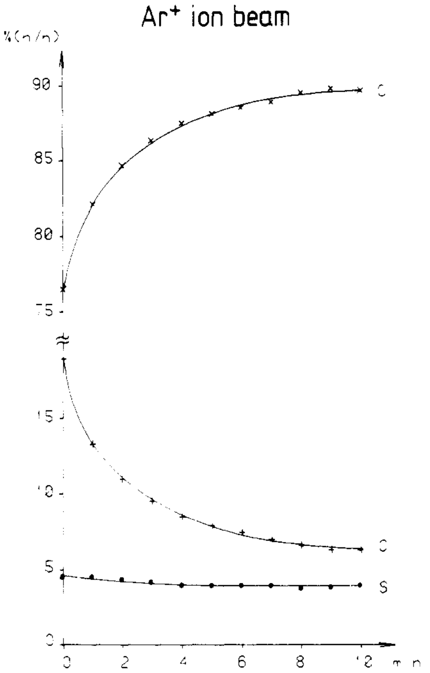


Figure 7. Surface composition of the Ar^+ ion bombarded PES.

nant at very low irradiation times (Figure 6), corresponding to fluences lower than those employed with X-rays or electrons; (2) the ion-irradiated surfaces are more depleted in sulfur with respect to carbon (Figure 7) than in the case of X-rays or electrons); and (3) the total oxygen is drastically depleted with respect to the case of X-rays or electrons: the O/S atomic ratio is 1.6 after 10 min of ion bombardment, while it is respectively 3.9 and 4.0 for X-ray- and e^--irradiated surfaces at the steady state. Accordingly, the sulfidic component of the ion-irradiated samples is ca. 40% of the whole S 2p band with an O/S ratio of 2.6, while in the case of electron irradiation an O/S ratio of 4 corresponded to a 35% conversion into sulfide.

The rate of decrease of the C 1s shake-up satellite (reflecting the unsaturation) depends upon the projectile: in the case of ion irradiation this satellite is quickly destroyed, while it remains almost constant in intensity during X-ray and e^- irradiation (Figure 8). The decrease of this satellite, as it is widely reported in literature,[11,16] indicates a severe alteration of the phenyl rings (e.g., destruction or cross-linking). On the other hand, we can also exclude, in the case of ion irradiation, the formation of a graphite-like structure which is characterized by a well-defined π-plasmon satellite at 7 eV from the C 1s peak.[2,9] It is noteworthy that the different behavior of the shake-up satellite occurs at a similar degree of sulfur loss. This difference in the behavior of the shake-up satellite can be considered diagnostic of the occurrence of another degradation mechanism, mainly involving the direct fragmentation of the phenyl rings due to a large collisional (impulse transfer) energy deposition term.

Irradiation with N_2^+ does not change substantially the situation with respect to the Ar^+ irradiation. In this case, however, a rapid incorporation of chemically bonded nitrogen is observed, which practically does not affect the overall compositional trends (Figures 9 and 10). Indeed, the rough formulas obtained for Ar^+- and N_2^+-irradiated samples at steady state are very close, being respectively $C_{22.5}O_{1.6}S$ and $C_{23.1}O_{1.6}N_{1.3}S$.

Our results may be summarized as follows:

(a) The SO_2 group is partially transformed into a sulfide-like group in each case.

(b) During each type of irradiation a partial loss of sulfur occurs in competition with its reduction.

(c) Ion beams are much more efficient in producing the observed effects than X-rays or electrons. In particular, during ion bombardment the O/S ratio decreases more quickly.

(d) The phenyl rings are heavily damaged by ion irradiation.

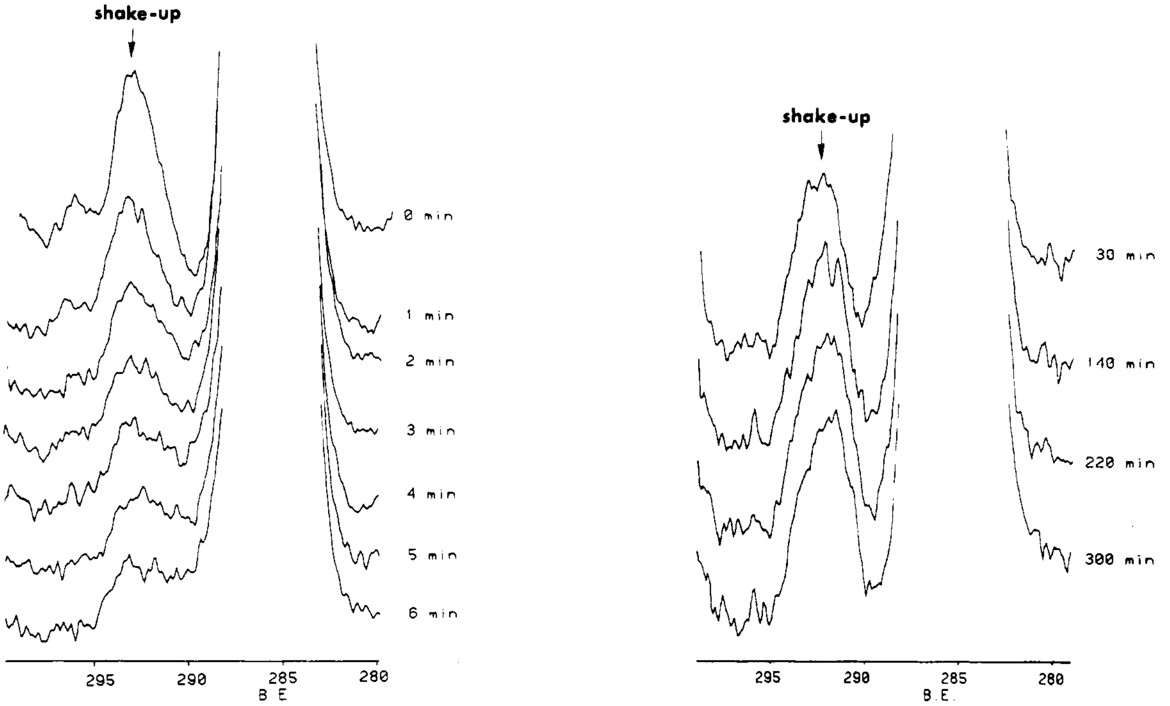


Figure 8. Evolution of the C 1s shake-up satellite during X-ray and Ar$^+$ ion irradiation.

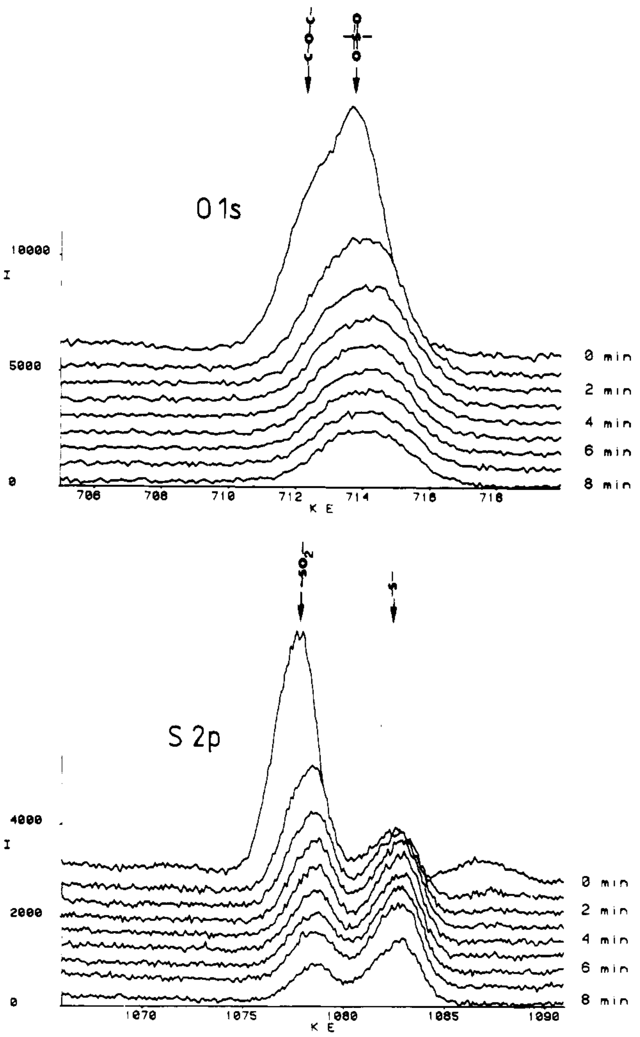


Figure 9. Effect of N$_2^+$ ion bombardment.

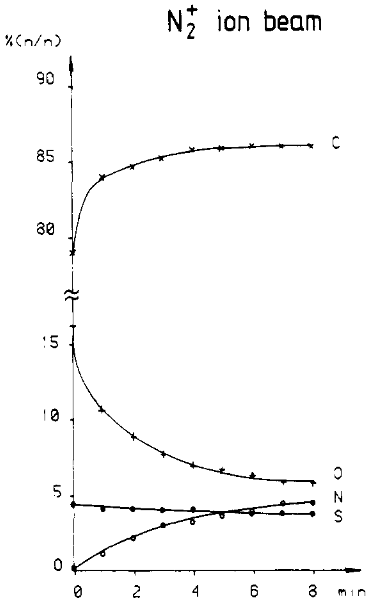


Figure 10. Surface composition of the N$_2^+$ ion bombarded PES.

Discussion

The results are not entirely explainable in terms of the current knowledge of radiation-induced phenomena in PES. Indeed, the reduction of the sulfone group to a sulfide-like entity and the extensive damage of the aromatic rings are not reported in the current literature describing the effects of γ, e$^-$, and proton irradiation on poly(ether sulfones).[4-8] The main findings reported in the literature are as follows: (a) radiation-induced degradation occurs through the loss of SO_2; (b) chain cleavage arises at C–S or C–O sites, forming few types of related radicals; (c) the aromatic rings in the chain are suggested as increasing greatly the radiation resistance of aromatic poly(ether sulfones). Also, there is a general agreement than ionizing radiations like γ-rays and energetic electrons act in a very similar way on aromatic polysulfones. The first chemical damage step in aromatic polysulfones is agreed to involve the homolytic cleavage of one of the two C–S bonds present in the monomer unit of the polymers. Such a process is proposed to produce two radicals as fragments, the benzenesulfonyl and the residual phenyl radical.[6,8] The further evolution of the system should lead to the cleavage of the second C–S bond, with the simultaneous elimination of the SO_2 group, which in the particular case of γ-irradiation is the major trapped product.[5] Another possible degradation mechanism is proposed to involve the scission of an ether linkage, yielding a phenoxy radical, which has been indeed inferred on the basis of ESR measurements.[4] The relaxation of the system in this case is suggested to occur through the H abstraction from a phenyl ring producing a final OH group. Finally, a third process involving the attachment of "hot" hydrogen atoms to a phenyl ring has been proposed based on the ESR evidence for cyclohexadienyl radical.[4]

Also the effects induced by 3-MeV protons were found to be consistent with the above results and their interpretation. Furthermore, several direct experimental indications are reported on the formation of phenoxy radicals (responsible for the formation of OH groups) and arylsulfonyl radicals.[8]

The processes summarized above, and in particular those reported for SO_2 loss, are also proposed to explain the products of thermal degradation.[18]

None of the cited papers reports the reduction of SO_2.

In a somewhat different case, the reduction of the sulfone group to a sulfide-like group has been reported for UV-irradiated bisphenol A polysulfone.[17] According to these authors, not only a partial reduction is detected together with a moderate loss of the total sulfur but also the phenyl rings are observed to be stable to irradiation, at variance with the drastic destruction observed when the UV irradiation of bisphenol A polysulfone is performed in oxygen.[19] No mechanism is proposed to explain the sulfone reduction.

Comparing our results with the published data, we suggest that the reaction mechanism proposed so far for γ, e^-, and proton irradiation experiments is basically valid also for the chemical changes observed for X or e^- irradiation in the present work. Our experimental findings indicate, however, that, in the radiation-induced chemistry of aromatic polysulfones, the decomposition route involving the SO_2 elimination occurs in competition with at least another main reaction channel, consisting of the reduction of the sulfone groups to sulfide ones. Consequently, a satisfactory mechanism should be proposed to explain this entirely new process. Some further routes in the modification mechanism should also be considered to account for the fact that the aromatic system is destroyed with high efficiency in the case of ion bombardment.

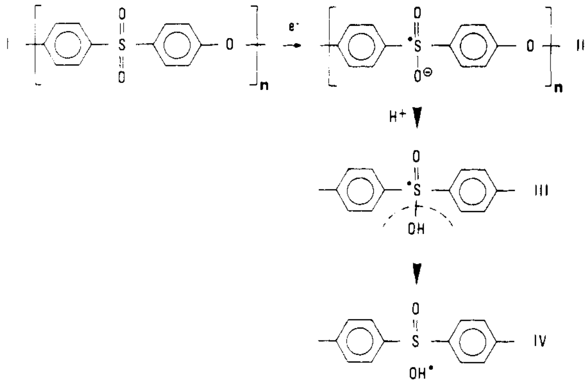
At the present stage of the study some steps in such a mechanism may be proposed based on the chemical information in the ESCA spectra.

A reduction mechanism for the SO_2 group to S necessarily involves the cleavage of two $S{=}O$ bonds. This process may be thought to occur in competition or as a consequence of the C–S bond cleavage, which is proposed to be the primary event for SO_2 elimination.[8]

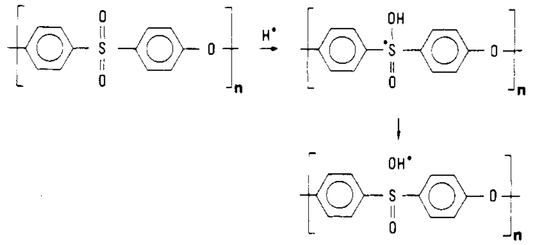
The first possibility is that the $S{=}O$ bond cleavage is promoted by the presence of reducing species produced during the irradiation. The most probable such species are e^- and $H^\bullet$, which are known to be produced in huge quantites during irradiation. In the first case, an e^- may be trapped in a π-orbital of the SO_2 group,[20] producing a charged intermediate that reacts according to Scheme I. Alternatively, an $H^\bullet$ radical may react similarly with SO_2 producing directly an $SOOH^\bullet$ group that is further reacted according to Scheme II.

A different possibility may be proposed in analogy to the Fries mechanism for photoinduced degradation of polycarbonates.[21] This mechanism is based on the primary formation of a radical site on a phenyl ring adjacent to the sulfone group and on the subsequent scission-and-isomerization process reported in Scheme III.

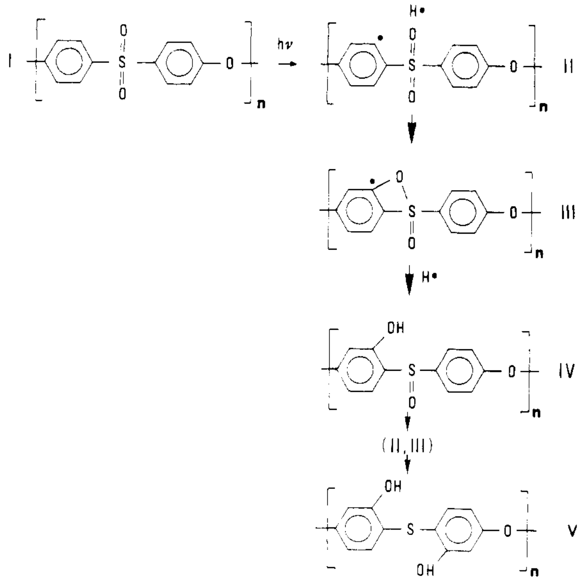
Scheme I



Scheme II



Scheme III



In fact, the following can be inferred from the present ESCA data:

(a) Intermediate sulfoxide groups may be present in low concentration. The S 2p peak of this group occupies an intermediate position between those of sulfone and sulfide.[16] Since no effort was made to cool the samples during the irradiation, the very low intensity of this peak component can be explained by the thermal instability and reactivity of organic sulfoxides.[22]

(b) The oxygen coming from the sulfone group is partly transferred to carbon sites as ether or as OH groups, reflecting that the reduction of the sulfone group should not necessarily be followed by a complete elimination of oxygen or oxygen-containing species, but these species may react according to a Fries-like mechanism.

Finally, we note that in the case of ion bombardment the reduction of the sulfone group may also be promoted by the destruction of the aromatic backbone, so that it may proceed by a pathway additional to those depicted in Schemes I–III.

The qualitative differences observed between the effects of X-rays and electrons and those of ions also suggest that different types of projectiles may induce different chemical processes with different "damage cross sections". Low-keV ions, in particular, are known to produce direct and random fragmentation of the polymer chains, due to the so-called "nuclear term" of the energy deposition process of the ions. On the other hand, the characteristic modification depths as well as the energies deposited per unit volume of the different types of projectiles of the same energy are strongly different. In particular, the mean projected range of 1-keV Ar^+ in PES can be estimated to be 45 Å with a mean deposited energy of ca. 35 $eV{\cdot}Å^{-1}$ (ca. 5 $eV{\cdot}Å^{-1}$ of which is deposited by electronic interaction).[23] The mean projected range of 1.2-keV electrons is estimated to be of the order of 1300 Å with a mean deposited energy of 2.5 $eV{\cdot}Å^{-1}$, while for 1.25-keV photons the corresponding estimated values are ca. 50 000 Å and 0.05 $eV{\cdot}Å^{-1}$.[24] Therefore, these data account for the strong quantitative differences (e.g., the rate of reduction of SO_2) between the effects of different types of projectiles, while some qualitative chemical differences (e.g., destruction of the phenyl rings) depend upon the energy deposition mechanisms.

Conclusions

The irradiation of aromatic poly(ether sulfone) by various ionizing beams has been studied by ESCA, and some of the radiation induced processes have been identified. In particular, the sulfone groups are dramatically affected by irradiation with low-keV projectiles, which are shown to produce both the depletion of the SO_2 and its reduction to a sulfide-like form. The latter reaction was previously unknown for irradiation with γ-rays, electrons, and protons.

On the basis of the ESCA data new reaction pathways additional to those of the known degradation mechanism are proposed. The available evidence suggests that the reduction process may occur through the formation of a sulfoxide intermediate and that oxygen may partially be transferred from the sulfone groups to the carbon backbone either directly to the aromatic rings (in the case of X-ray or electron irradiation) or to the complex network produced by the destruction of the aromatic rings (in the case of ion irradiation).

Acknowledgment. The financial supports from the CNR and MURST (Italy) and from the Hungarian Research Fund (OTKA-46/1988) are gratefully acknowledged. We thank Roger Kelly (IBM Research Division) for critically reading the manuscript and valuable remarks.

References and Notes

(1) Venkatesan, T.; Calcagno, L.; Elman, B. S.; Foti, G. In *Ion Implantation in Insulators*; Arnold, G. W., Mazzoldi, P., Eds.; Elsevier: Amsterdam, 1987; p 301.

(2) Marletta, G. *Nucl. Instrum. Methods B* **1990**, *46*, 295.

(3) Reichmanis, E.; O'Donnell, J. H., Eds. *The Effects of Radiation on High-Technology Polymers*; American Chemical Society: Washington, DC, 1989.

(4) Lyons, A. R.; Symons, M. C. R.; Yandell, J. K. *Makromol. Chem.* **1972**, *157*, 103.

(5) Brown, J. R.; O'Donnell, J. H. *J. Appl. Polym. Sci.* **1975**, *19*, 405.

(6) Brown, J. R.; O'Donnell, J. H. *J. Appl. Polym. Sci.* **1979**, *23*, 2763.

(7) Sasuga, T.; Hayakawa, N.; Yoshida, K. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 529.

(8) Coulter, D. R.; Smith, M. V.; Tsay, F.-D.; Gupta, A.; Fornes, R. E. *J. Appl. Polym. Sci.* **1985**, *30*, 1753 and references therein.

(9) (a) Marletta, G.; Pignataro, S.; Oliveri, C. *Nucl. Instrum. Methods B* **1989**, *39*, 773. (b) Marletta, G.; Pignataro, S.; Oliveri, C. *Nucl. Instrum. Methods B* **1989**, *39*, 792.

(10) Loo, J. A.; Wang, B. H.; Wang, F. C.-Y.; McLafferty, F. W. *Macromolecules* **1987**, *20*, 698.

(11) Tòth, A.; Bertòti, I.; Székely, T.; Mohai, M. *Surf. Interface Anal.* **1985**, *7*, 282.

(12) Proctor, A.; Sherwood, P. M. A. *Anal. Chem.* **1982**, *54*, 13.

(13) Dwight, D. W.; McGrath, J. E.; Wightman, J. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1977**, *18*, 123.

(14) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 791.

(15) Gardella, J. A., Jr.; Ferguson, S. A.; Chin, R. L. *Appl. Spectrosc.* **1986**, *40*, 224.

(16) Kaul, A.; Udipi, K. *Macromolecules* **1989**, *22*, 1201.

(17) Munro, H. S.; Clark, D. T. *Polym. Degrad. Stab.* **1987**, *17*, 319.

(18) (a) Davis, A. *Makromol. Chem.* **1967**, *128*, 242. (b) Ehlers, G. F. L.; Fish, K. R.; Powell, W. R. *J. Polym. Sci.* **1969**, *A1* (7), 2955.

(19) Munro, H. S.; Clark, D. T. *Polym. Degrad. Stab.* **1985**, *11*, 225.

(20) Pignataro, S. *Chim. Ind. (Milan)* **1975**, *57*, 25.

(21) Schnabel, W.; Kiwi, J. In *Aspects of Degradation and Stabilization of Polymers*; Jellinek, H. H. G., Ed.; Elsevier: Amsterdam, 1978; Chapter 5, p 195.

(22) Eigenmann, K.; Farooq, S. *Angew. Chem.* **1975**, *87*, 635.

(23) Biersack, J. P. In *Ion Beam Modification of Insulators*; Mazzoldi, P., Arnold, G., Eds.; Elsevier: Amsterdam, 1987; p 301.

(24) (a) ICRU Report 37, "Stopping Powers for Electrons and Positrons"; International Commision on Radiation Units and Measurements: Bethesda, MD, 1984. (b) Biggs, F.; Lighthill, R. "Analytical Approximation for X-ray Cross Section III", SAND 87-0070; Sandia National Laboratory: Albuquerque, NM, 1988.

Registry No. PES, 25667-42-9; Ar^+, 7440-37-1; N_2^+, 7727-37-9.