Spectroscopic analysis of ion-irradiated poly(phenylene sulphide)

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Films of poly(phenylene sulphide) have been irradiated with high energy ions to produce electrically conductive materials. The ions used have been 323 keV Li, 5.6 MeV F, and 50 MeV I. Conductivities between 5.7×10^{-5} S cm^{-1} and 0.7 S cm^{-1} have been observed depending on irradiation conditions. The irradiated polymers have been characterized by infra-red and e.p.r. spectroscopy as well as differential scanning calorimetry (d.s.c.), X-ray diffraction, and scanning electron microscopy. Specular reflectance infrared spectra show the creation of free carriers at higher doses corresponding to increased conductivity. E.p.r. spectra show the existence of free radicals in irradiated films with the concentration generally increasing with dose (up to 4.3×10^{14} ions/cm^2). Because the irradiated layers are much thinner than the complete film samples in these experiments, the differential scanning calorimetry and X-ray diffraction results include contributions from both irradiated and unirradiated regions. Although the d.s.c. suggests increased crystallinity in the irradiated material, X-ray diffraction shows only amorphous material. Possible explanations are discussed. Scanning electron microscopy shows evidence of gas evolution during irradiation.

(Keywords: ion irradiation; poly(phenylene sulphide); conduction; infra-red; electron paramagnetic resonance; differential scanning calorimetry; X-ray diffraction)

INTRODUCTION

Ion irradiation of organic materials is an effective way to produce materials that are highly conductive and stable to ambient conditions. There has been considerable interest in conductive organic materials over the past fifteen years[1], but many of the materials commonly available are not stable to oxygen or moisture. For that reason, ion irradiation is a particularly attractive route to these compounds. Moreover, ion irradiation leads itself to production of conductive patterns on insulating substrates. The technique is effective on many different types of organic materials, including Kapton polyimide[2] and naphthalene tetracarboxylic dianhydride[3]. We chose to investigate poly(phenylene sulphide) (PPS) because it is commercially available, very stable, and readily processed. Furthermore, it is one of the polymers that can be made conductive by chemical doping so that the electrical properties have been thoroughly characterized[4]. The electrical properties of ion irradiated PPS have been described previously by these authors[5] and by Mazurek *et al.*[6].

EXPERIMENTAL

Sample preparation

Films of PPS were prepared from PPS powder (Phillips Petroleum, Ryton, V-1) by melting (300°C) and drawing across an aluminium panel or a quartz slide between 25 μm spacers. The film was quenched in ice water immediately after drawing to prevent crystallization. The result of this procedure was a 25 μm film of PPS on the substrate, which was then cut into pieces of appropriate size for irradiation.

Ion irradiation

A complete discussion of the irradiation experiments is given in a previous paper[5], but will be summarized here for convenience. Irradiation experiments were performed at the Nuclear Physics Laboratory of the University of Pittsburgh using a High Voltage Engineering Corporation Model EN tandem Van de Graaff accelerator. From the information in ref. 7, we arbitrarily selected three ions and energies to cover a wide range of conditions. Those parameters are given in *Table 1* with estimated ranges in PPS[7].

Characterization

Irradiated films were subjected to several analytical techniques. Infra-red spectra were collected in the specular reflectance mode using a Wilkes specular reflectance sample holder on a Perkin-Elmer 1310 infrared spectrophotometer. The aluminium panels on which the films had been cast provided convenient reflective backings. Differential scanning calorimetry (d.s.c.) and X-ray diffraction were carried out on free standing films irradiated with 25 MeV I ions at doses of 1×10^{13} ions/cm^2 to 4.3×10^{14} ions/cm^2. A Perkin-Elmer DSC-2 thermal analyser coupled to a model 3600 data station was used for the thermal analysis. X-ray diffraction of the samples was measured on a Siemens X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron micrographs (SEM) were recorded on a Cambridge Mark IIa SEM. Electron paramagnetic resonance (e.p.r.) spectra were recorded on an IBM–Bruker 200E e.p.r. spectrometer at a frequency of approximately 9.3 GHz at room temperature.

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Table 1 Electrical conductivity of ion-irradiated PPS film

Ion	Energy (MeV)	Energy deposition rate (MeV/mg-cm^2)	Range in PPS dose		Conductivity (S cm^{-1})
			(μm)^a	(10 μ/cm^2)	
Li	0.323	2	12	1×10^{12}	1.7×10^{-9}
				1×10^{13}	1.1×10^{-9}
				1×10^{14}	9.6×10^{-10}
				1×10^{15}	1.4×10^{-9}
F	5.6	13	5	1×10^{12}	1.7×10^{-10}
				1×10^{13}	1.3×10^{-10}
				1×10^{14}	5.7×10^{-9}
				1×10^{15}	5.7×10^{-5}
				5×10^{15}	5.6×10^{-2}
				1×10^{16}	4.6×10^{-1}
I	50	55	11	1×10^{12}	$< 1 \times 10^{-10}$
				1×10^{13}	2.5×10^{-5}
				1×10^{14}	7.0×10^{-2}
I	25	37	6	1×10^{13}	$< 1 \times 10^{-10}$
				1×10^{14}	8.4×10^{-3}
				4.3×10^{14}	2.1×10^{-2}

^{a} Calculated from Ref. 7

RESULTS AND DISCUSSION

Considerable work on the characterization of ion-irradiated organic materials has been reported, though work on PPS has been limited to the paper by Mazurek *et al.*[6]. The most complete work has been done at AT&T Bell Labs on perylene tetracarboxylic dianhydride (PTCDA) and nickel phthalocyanine (NiPc) thin fims irradiated with 2 MeV Ar^+ [8,9]. Their results are consistent with the formation of microdomains in which there is loss of chemical structure coincident with the onset on enhanced conductivity. Infra-red, optical, and Raman spectra resemble spectra of amorphous carbon. E.s.c.a. and Rutherford backscattering show an enhanced concentration of carbon in the irradiated region. There is also evidence for the creation of free radicals from e.p.r. spectroscopy, with the maximum occurring at doses near 1×10^{14} ions/cm^2. These films also show the maximum incorporation of oxygen from the air, consistent with reaction with the free radicals. *In situ* mass spectroscopy during irradiation showed evolution of several species, primarily H_2, CO, and CO_2. Other work shows microscopic evidence of gas evolution during irradiation[10]. Although other reports are also consistent with formation of a structure like amorphous carbon[6,11], the electrical properties of these films give a conductivity 2 to 3 orders of magnitude higher than amorphous carbon.

This report will describe the characterization of our irradiated PPS films, which we anticipated to have some properties different from previous work because of the much higher $(dE/dx)_e$ used in our experiments. Techniques of i.r. and e.p.r. spectroscopy, d.s.c., X-ray diffraction and SEM have been applied.

Electrical properties

The electrical properties of these samples have been discussed in detail previously[5], but are summarized here for convenience. Two phenomena occur while the ion is travelling through the polymer: production of 'delta' electrons from the polymer atoms along the ion path, and displacement of polymer nuclei at the end of the ion path. Calculations show that under the conditions of the present work, most ($> 95\%$) of the ion energy is spent in ionization rather than displacement damage during irradiation. Moreover the ratio of displacement damage to ionization damage during the present irradiations is lower than that for lower energy irradiations. Even though there is less displacement damage during the higher energy irradiations, the conductivity of these samples is higher than that of samples irradiated at lower energies. This fact implies that the greater total ionization damage in the present experiments is responsible for the high conductivity. Turning to the bulk charge transport in these materials, the prevailing model for creation of high conductivity by irradiation, essentially a percolation model, proposes the creation of conductive regions during irradiation[3]. As irradiation proceeds, more of these regions are created until there is a continuous conductive pathway through the sample. Continued irradiation creates more conductive regions, increasing the bulk conductivity until saturation of the effect. The magnitude of the conductivity produced by this technique depends primarily on the electronic energy deposition rate $(dE/dx)_e$ of the irradiated species rather than on a chemical effect caused by the irradiated species.

The conductivity of irradiated films used in this work are shown in *Figure 1* and *Table 1*. Lithium-irradiated films showed no effect up to a dose of 1×10^{16} ions/cm^2, probably because of the relatively low $(dE/dx)_e$ of these ions. These ions were not energetic enough to cause sufficient damage to increase the conductivity. Beginning at a dose just below 1×10^{14} ions/cm^2, the fluorine-irradiated films showed a greatly enhanced conductivity. Our work with F-irradiated PPS showed a much higher conductivity than that of Mazurek *et al.* because of the much higher $(dE/dx)_e$ in our experiments. The effect of iodine irradiation was even more pronounced, the conductivity being comparable at an iodine dose of 1×10^{14} ions/cm^2 and fluorine dose of 1×10^{16} ions/cm^2. Our results were consistent with the prediction that conductivity depends primarily on $(dE/dx)_e$.

Infra-red spectroscopy

Infra-red spectroscopy is an excellent method for detection of free carriers in conductive polymers. The presence of free carriers is generally shown by intense, broad absorption in the infra-red, which overwhelms absorptions due to molecular modes. This phenomenon has been observed in many conductive organic systems, including PPS, polyacetylene, and poly(phthalocyanine siloxane)[4,12].

Transmission i.r. spectra were collected by the specular reflectance method on samples deposited on aluminium panels. Results are shown in *Figures 2–4*. The Li-irradiated samples (*Figure 2*) showed no change, regardless of dose. The other materials, in contrast, showed significant changes with ion dose. Spectra of F-irradiated films are shown in *Figure 3* along with the spectrum of 1×10^{12} Li ions/cm^2 sample for comparison. At a dose of 1×10^{13} F ions/cm^2, there was no change in conductivity and no change in the i.r. spectrum. At 1×10^{14} F ions/cm^2, however, there was a slight increase in conductivity, and also an increase in absorption in the i.r. spectrum. The conductivity and i.r. absorption continued to increase with dose until at a dose of 1×10^{16} F ions/cm^2, the conductivity and i.r. absorption have both increased dramatically. Similar results are shown for I-irradiated samples (*Figure 4*), although the effect is less dramatic, possibly because of the lower doses used in those samples. These results are consistent with the creation of free carriers during the irradiation process.

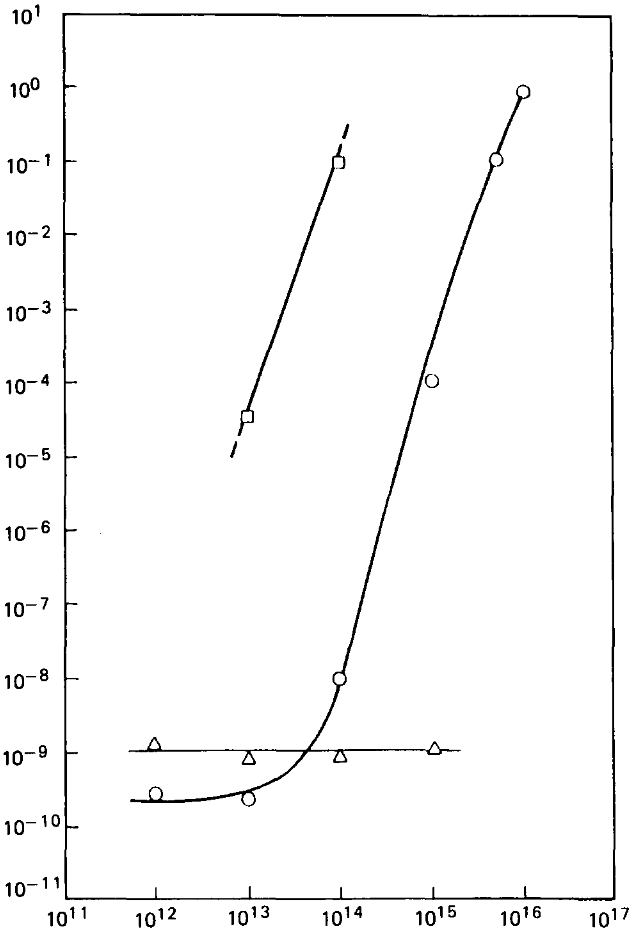

Figure 1 Electrical conductivity of ion-irradiated PPS: (○) 5.6 MeV F, (□) 0.32 MeV Li, (△) 50 MeV I

Electron paramagnetic resonance

Kaplan *et al.*, working with various molecular compounds, have suggested that the conductivity changes are related to the rate of free radical production during the implantation process[3]. As discussed above, ions produce delta electrons along their paths. These electrons engage in further ionization, leading to the production of free radicals in the irradiated layer. The rate of free radical production is proportional to $(dE/dx)_e$. If this rate is low, there is a greater probability that free radicals will interact with unchanged molecules. At higher rates radical–radical interactions become more likely, causing greater changes in the conductivity by increasing the free radical production rate.

The e.p.r. spectrum of conductive organic materials typically shows free carriers, i.e. a free electron g-value near 2.0032. Previous work on e.p.r. spectra of irradiated poly(acrylonitrile) and poly(2,6-dimethylphenylene oxide) have shown a g-value of 2.0025 with a narrow line width, consistent with the existence of free radicals[13]. The ions used were Kr, Br, As, Ar and N at 200 keV with doses from 1×10^{14} ions/cm^2 to 5×10^{16} ions/cm^2. It was found that the unpaired spin concentration increased with dose up to a maximum of approximately 10^{21} spins/cm^3 at a dose of 1×10^{15} ions/cm^2 where saturation occurred. Their lineshape analysis suggested a one-dimensional rather than three dimensional hopping mechanism for charge transport.

In our case, using more energetic ions, we found similar behaviour in the spectra of free-standing I-irradiated films. The samples had been irradiated at 25 or 50 MeV at doses of 1×10^{12} ions/cm^2 to 4.3×10^{14} ions/cm^2. There was no signal in unirradiated films, and the sample

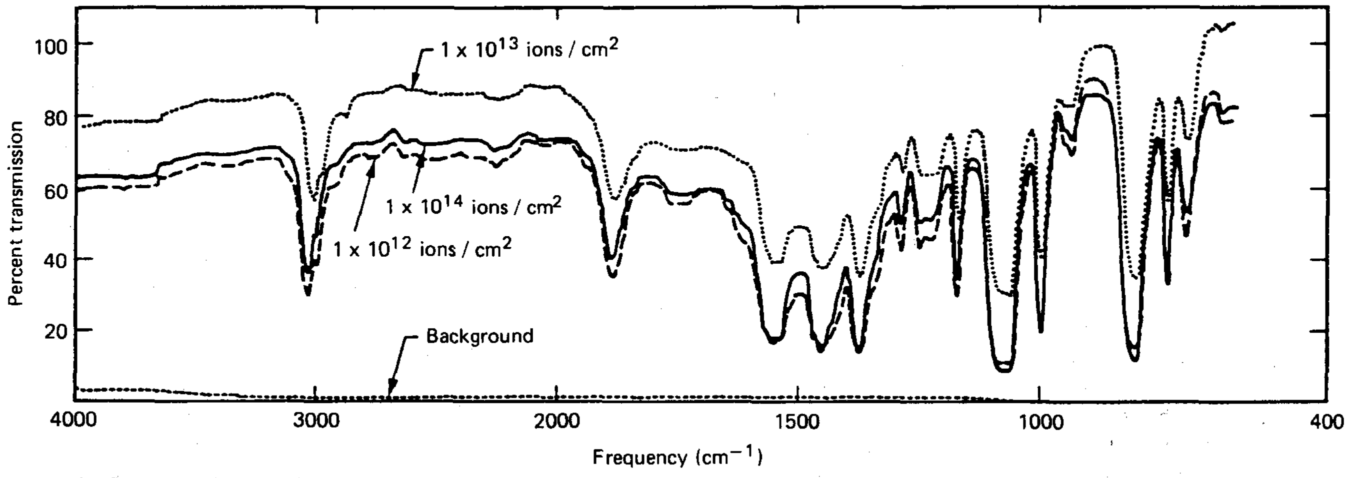

Figure 2 Specular reflectance i.r. spectra of Li-irradiated PPS

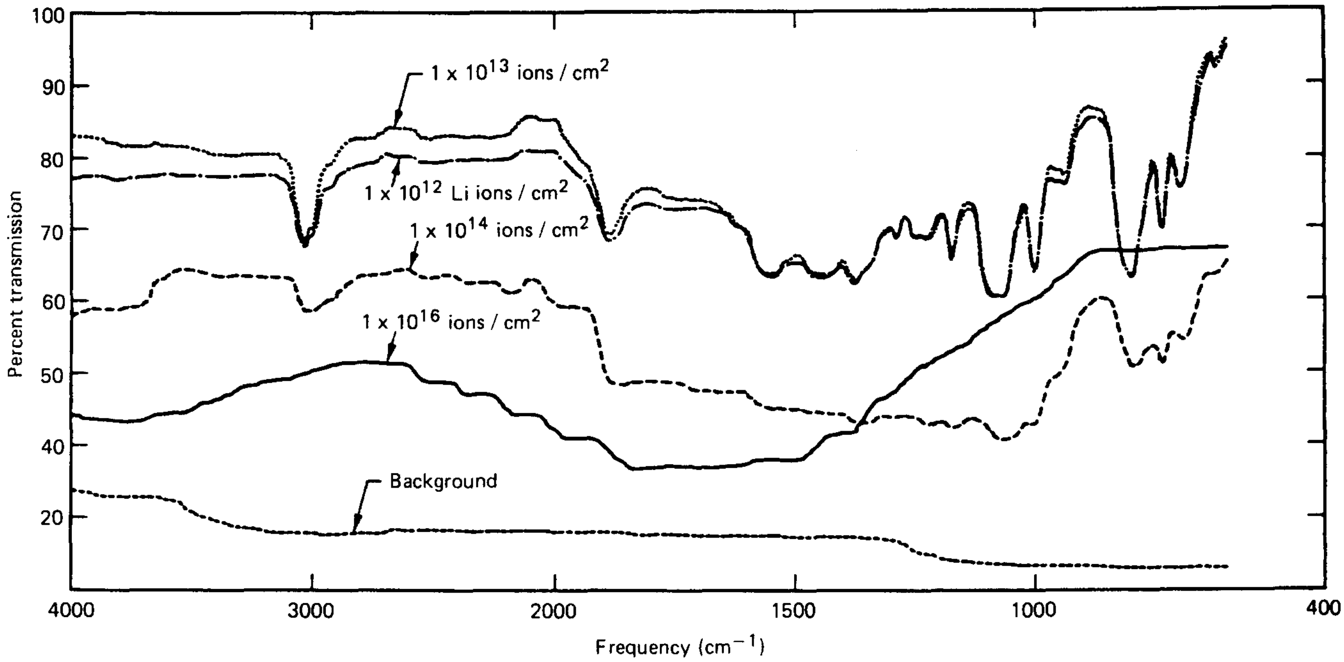

Figure 3 Specular reflectance i.r. spectra of F-irradiated PPS compared with 1×10^{12} Li ions/cm^2 irradiated PPS

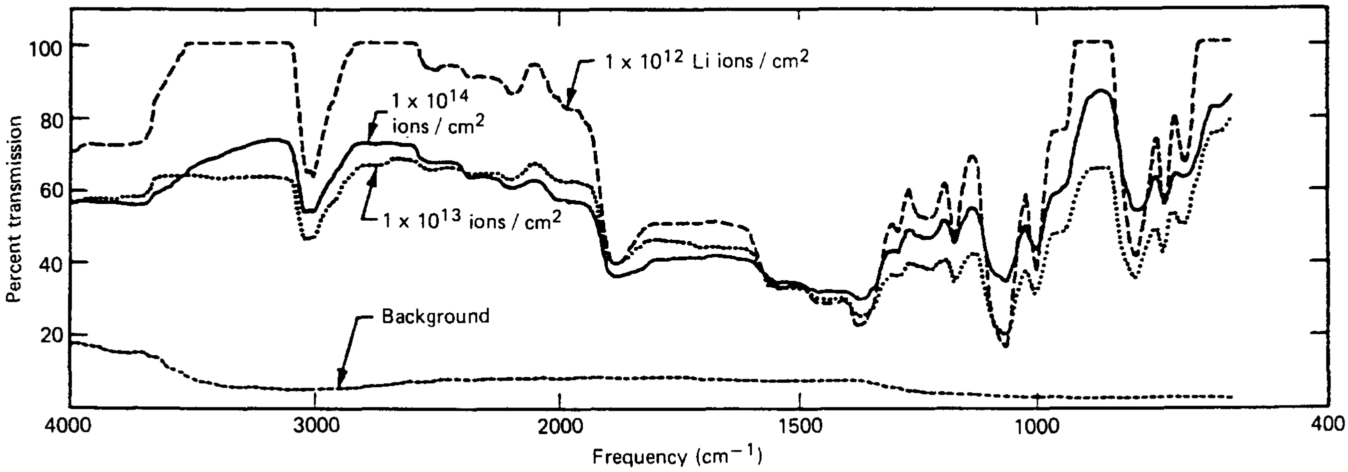

Figure 4 Specular reflectance i.r. spectra of I-irradiated PPS compared with 1×10^{12} Li ions/cm^2 irradiated PPS

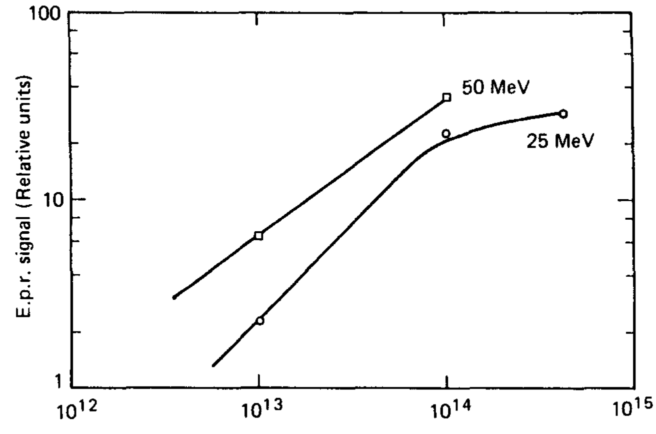

Figure 5 E.p.r. signal vs. dose for I-irradiated PPS films at 25 MeV and 50 MeV

irradiated at 1×10^{12} ions/cm^2 showed only a very weak resonance. The other samples all showed a strong, narrow (4 g half-width–half-maximum) resonance line at a *g*-value of 2.0033 ± 0.0003, consistent with the existence of organic free radicals. Qualitatively the e.p.r. signal strength increased with dose up to 1×10^{14} ions/cm^2 and then started to show saturation (*Figure 5*). This observation was also reported by Wasserman *et al.*[13] and Venkatesan *et al.*[8]

Thermal analysis

Differential scanning calorimetry (d.s.c.) measurements were made on several of the I-irradiated samples, and the results are shown in *Figure 6*. These films had been cast on quartz substrates by rapid quenching from the melt and were easily removed after irradiation. Before irradiation the films were amorphous and show the characteristic transitions observed in such films: glass transition (T_g) at 88°C; crystallization (T_c) at 128°C; and melting (T_m) at 282°C [14]. Crystallized films show only the melting transition. As the irradiation proceeded, the two lower temperature transitions decreased in size considerably until they were completely gone when the dose was up to 4.3×10^{14} I ions/cm^2 sample. The heats of the transitions are given in *Table 2*. Heating above 120°C is reported to cause crystallization[14] and the d.s.c. results

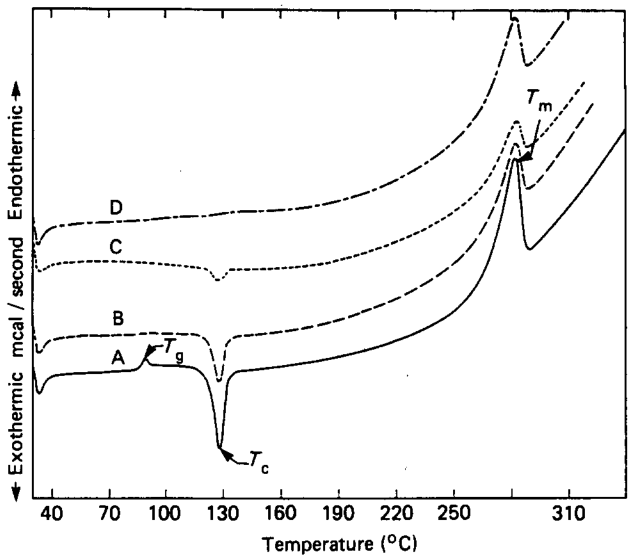

Figure 6 Differential scanning calorimetry of PPS films: (A) unirradiated; (B) 1×10^{13} I ions/cm^2; (C) 1×10^{14} I ions/cm^2; (D) 4.3×10^{14} I ions/cm^2

Table 2 Heats of transition of I-irradiated PPS from d.s.c. experiments

Dose (ions/cm^2)	Heat of transition (cal/g)	
	Crystallization (128°C)	Melting (282°C)
Unirradiated	4.62	9.51
1×10^{13}	3.99	7.91
1×10^{14}	1.95	9.07
4.3×10^{14}	–	8.15

were consistent with that report. The d.s.c. trace suggests that there are additional crystals being formed in the sample above 128°C. Crystal formation could account for the greater amount of heat released at melting than at crystallization in the amorphous sample.

There were two layers of approximately equal thickness in these samples: irradiated and unirradiated. If the unirradiated layer were not affected by the experiment, it would still be amorphous, and we would expect to see the lower temperature transitions in the d.s.c. scans of the irradiated samples. The results in *Figure 6* suggest crystallization of that layer since only the PPS crystalline melting transition is observed in the irradiated films. In fact, because the heat of melting in the heavily irradiated sample is comparable to that in the starting material, the irradiated region may also be predominantly crystalline PPS. If it were amorphous or a different crystalline material, the heat of transition at T_m should be reduced by approximately half compared with the starting material. These results thus suggest substantial crystallization of both irradiated and unirradiated regions of the polymer films during irradiation, which could be caused simply by heating or by structural rearrangement. Although the samples were maintained near room temperature during irradiation, localized heating cannot be ruled out, particularly with a quartz substrate which has a lower thermal conductivity than does aluminium.

X-ray diffraction

X-ray diffraction of I-irradiated samples was also recorded and compared to amorphous and crystalline unirradiated films. Previous work with PPS has shown that the polymer crystallizes in an orthorhombic unit cell with parameters $a = 8.67$ Å, $b = 5.61$ Å, $c = 10.26$ Å[15]. Crystallization is caused by heating above 200°C in air. We used the same samples that had been subjected to d.s.c., thus the films were amorphous before irradiation, and contained irradiated and unirradiated layers of approximately equal thickness. X-ray diffraction patterns of I-irradiated films were identical to that of an amorphous film (*Figure 7*) and showed none of the reflections due to crystalline PPS. Since these films contain only weakly diffracting atoms, and the irradiated layers are thin, we cannot be sure that these diffraction patterns were truly representative of diffraction from the irradiated layer. Electron diffraction experiments are planned since the electron beam should have a much more shallow depth, and thus be more effective at sampling the irradiated region. Until we make those measurements, we cannot resolve the apparent conflict with the d.s.c. results. One possibility is that the crystallites are quite small, so they would show a heat of fusion in the d.s.c., but they lack sufficient long range order to produce a crystalline X-ray diffraction pattern. A previous electron diffraction study[9] of irradiated PTCDA showed that the crystallinity of the initial film diminished considerably during irradiation beginning at a dose near 1×10^{12} Ar ions/cm^2. The films were completely amorphous at doses above 1×10^{14} Ar ions/cm^2. In fact, the electron diffraction pattern was similar to that of amorphous carbon.

Scanning electron microscopy

Scanning electron micrographs of F-irradiated films are shown in *Figures 8* and *9*. Unirradiated films are very smooth with occasional imperfections of the type shown in *Figure 8a*. These imperfections are small (1–2 μm) and appear as cavities in the film surface. As the ion dose increased, there was some evidence of gas evolution in the films, shown by large bubbles (10 μm) under the surface (*Figure 8c* and *9a,b*) and possible burst bubbles as well (*Figure 9c*). These results are consistent with those of other workers who have reported H_2 evolution in irradiated samples as shown by mass spectroscopy during irradiation[16]. SEM photographs of Ar-irradiated (40–

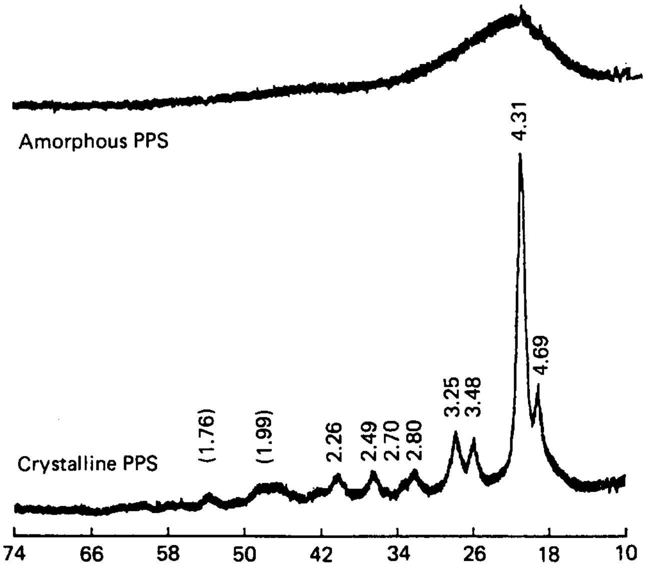

Figure 7 X-ray diffraction patterns of crystalline and amorphous PPS. Interplanar *d* spacings indicated in Å

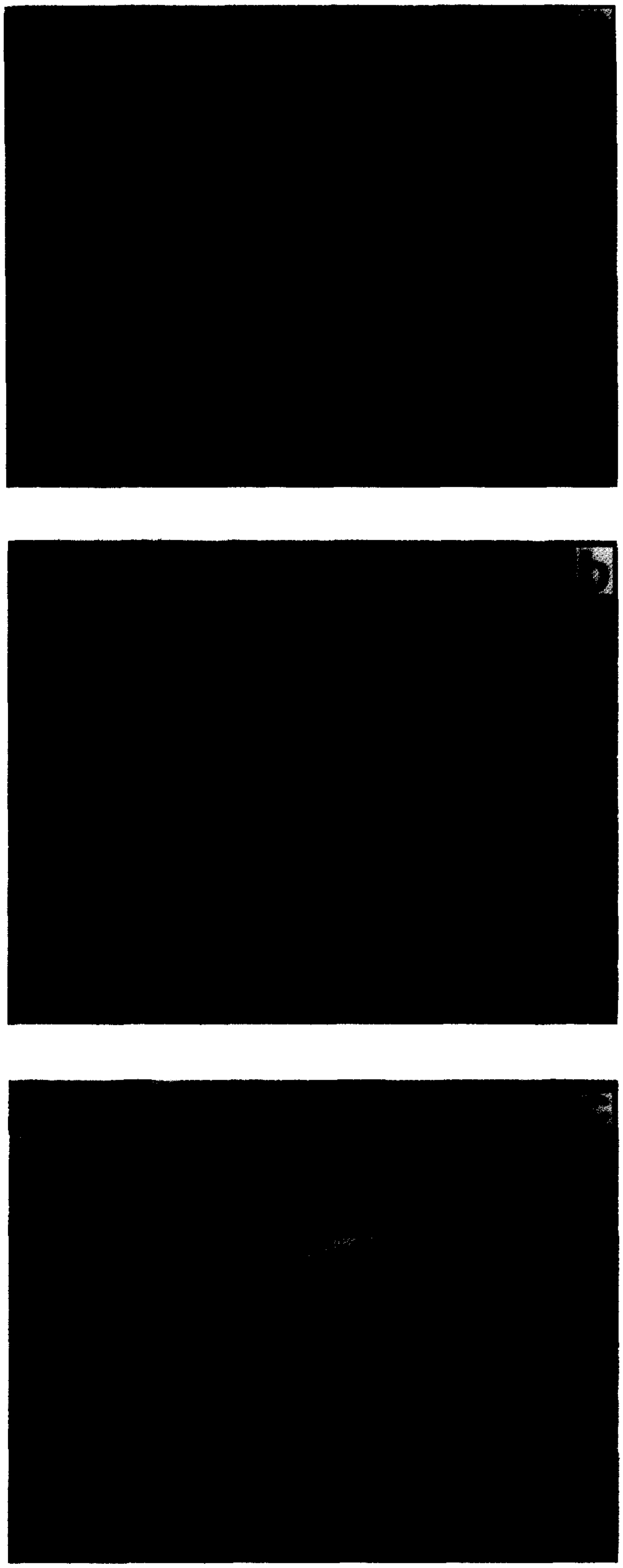

Figure 8 SEM photographs of PPS films: (a) unirradiated; (b) 1×10^{13} F ions/cm^2; (c) 1×10^{14} F ions/cm^2

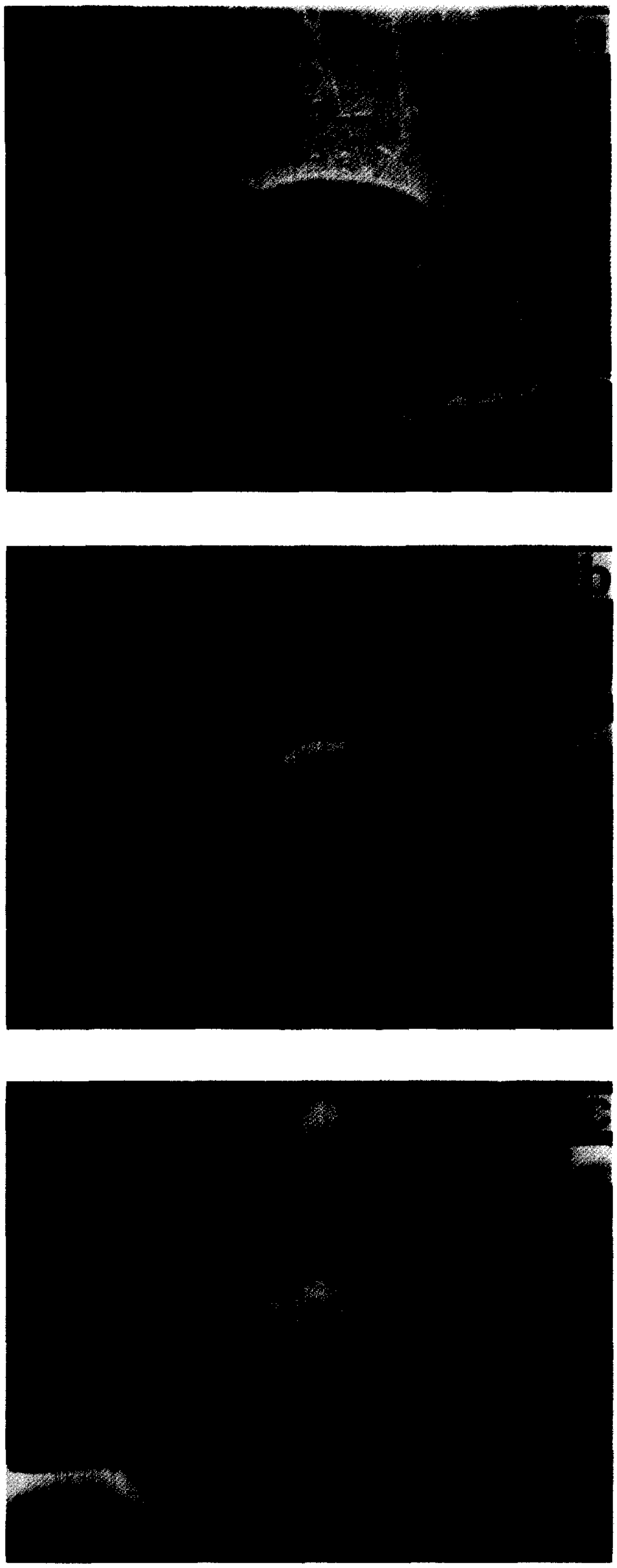

Figure 9 SEM photographs of PPS films: (a) 1×10^{15} F ions/cm^2; (b) 1×10^{16} F ions/cm^2; (c) 1×10^{16} F ions/cm^2

1500 keV) photoresist films have shown similar bubbling, which was interpreted as trapping of argon gas in the films[10]. The doses were 1×10^{14} ions/cm^2 to 1×10^{17} ions/cm^2. It was found that the thickness of the irradiated region exceeded that of unirradiated areas at doses above 1×10^{16} ions/cm^2. Moreover, there could have been solvent evaporation of polymer sublimation due to localized heating in addition to generation of gases from the irradiation process. Since our PPS films were prepared from the melt and are stable well above 300°C, we would expect any bubbles in the irradiated specimens to be the result of gas evolution from the film during irradiation, rather than trapped solvents or polymer sublimation.

CONCLUSION

Films of poly(phenylene sulphide) have been irradiated with high energy Li, F, and I ions to produce electrically conductive materials. The irradiated polymers have been characterized by infra-red and e.p.r. spectroscopy as well as differential scanning calorimetry, scanning electron microscopy, and X-ray diffraction. Results of infra-red and e.p.r. spectroscopies were consistent with the creation of free radicals during irradiation. The increase in number of free radicals corresponded to increased dose of ions and increased bulk conductivity. Although d.s.c. suggested increased crystallinity in the irradiated material, X-ray diffraction showed the same samples to be amorphous. Until we record electron diffraction patterns from the samples, we will be unable to resolve the apparent conflict. The samples contained both irradiated and unirradiated layers, and X-ray scattering from the irradiated layer may have been weak. Scanning electron microscopy showed evidence of gas evolution during irradiation. In general these irradiated films had spectroscopic properties quite similar to those of films irradiated at much lower energies.

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REFERENCES

1 Seymour, R. B. Ed. 'Conductive Polymers', Plenum Publishing Corp., New York, 1981

2 Hioki, T., Noda, S., Sugiura, M., Kakeno, M., Yamada, K. and Kawamoto, J. *J. Appl. Phys.* 1983, **43**, 30

3 Kaplan, M. L., Forrest, S. R., Schmidt, P. H. and Venkatesan, T. *J. Appl. Phys.* 1984, **55**, 732

4 (a) Shacklette, L. W., Elsenbaumer, R. L., Chance, R. R., Eckhardt, H., Frommer, J. E. and Baughman, R. H. *J. Chem. Phys.* 1981, **75**, 1919; (b) Clarke, T. C., Kanazawa, K. K., Lee, V. Y., Rabolt, J. F., Reynolds, J. R. and Street, G. B. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 117; (c) Schoch, Jr., K. F., Chance, J. F. and Pfeiffer, K. E. *Macromolecules* 1985, **18**, 2389

5 Bartko, J., Hall, B. O. and Schoch, Jr., K. F. *J. Appl. Phys.* 1986, **59**, 1111

6 Mazurek, H., Day, D. R., Maby, E. W., Abel, J. S. Senturia, S. D., Dresselhaus, M. S. and Dresselhaus, G. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 537

7 Way, K. Ed. 'Nuclear Data Tables', Academic Press, New York, 1970, 7(3–4)

8 Venkatesan, T., Forrest, S. R., Kaplan, M. L., Schmidt, P. H., Murray, C. A., Brown, W. L., Wilkens, B. J., Roberts, R. F., Rupp, Jr., L. and Schonhorn, H. *J. Appl. Phys.* 1984, **56**, 2778

9 Lovinger, A. J., Forrest, S. R., Kaplan, M. L., Schmidt, P. H. and Venkatesan, T. *J. Appl. Phys.* 1984, **55**, 476

10 Bello, I., Carter, G., Knott, K. F., Haworth, L., Stephens, G. A. and Farrell, G. *Rad. Effects* 1985, **89**, 189

11 Venkatesan, T., Forrest, S. R., Kaplan, M. L., Murray, C. A., Schmidt, P. H. and Wilkens, B. J. *J. Appl. Phys.* 1983, **54**, 3150

12 (a) Diel, B. N., Inabe, T., Lyding, J. W., Schoch, Jr., K. F., Kannewurf, C. R. and Marks, T. J. *J. Am. Chem. Soc.* 1983, **105**, 1551; (b) Fincher, Jr., C. R., Ozaki, M., Heeger, A. J. and MacDiarmid, A. G. *Phys. Rev. B Condens. Matt.* 1979, **B19**, 4140

13 Wasserman, B., Dresselhaus, M. S., Braunstein, G., Wnek, G. E. and Roth, G. *J. Electron. Mat.* 1985, **14**, 157

14 Brady, D. G. *J. Appl. Polym. Sci.* 1976, **20**, 2541

15 Tabor, B. J., Magre, E. P. and Boon, J. *Eur. Polym. J.* 1971, **7**, 1127

16 Wasserman, B., Dresselhaus, M. S., Braunstein, G., Wnek, G. in 'MRS Symposium on Ion Implantation and Ion Beam Processing Materials', (Eds. G. K. Hubler, O. W. Holland, C. R. Clayton and C. W. White), Materials Research Society, Boston, 1983, p 423