Electron Beam Effects on Polymers. III. Mechanical and Thermal Properties of Electron Beam-Irradiated Poly(phenylene Sulfide)

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Synopsis

The effect of electron beam (EB) irradiation on the mechanical and thermal properties of initially amorphous and semicrystalline poly(phenylene sulfide) (PPS) films has been investigated. Irradiations were carried out either in a nitrogen or air atmosphere. Subsequent mechanical testing carried out at 23°C suggested that oxidative degradation occurs in air for high radiation dosages. However, modulus and tensile strength were not greatly affected by irradiation level. Moreover, it was found that elongation by yielding no longer occurs at doses higher than 1000 Mrad for initially amorphous materials and above 500 Mrad for the initially semicrystalline materials. Differential scanning calorimetry (DSC) measurements utilized to determine crystallinity and melting behavior suggest the likely occurrence of some crosslinking with high irradiation levels. Scanning electron microscopy (SEM) of the irradiated PPS surface suggest the possible occurrence of gas evolution—at least for high dosage levels.

INTRODUCTION

Chemical and physical changes of polymers caused by ionizing radiation are of considerable continuing concern because of the utility of polymeric systems in applications where exposure to irradiation occurs. In particular, polymers containing various aromatic rings in the main chain have received much attention. This is because the aromatic character of these polymers tends to make these systems more resistant to radiation damage; therefore, these systems are often utilized in the field of nuclear energy, in outer space, and related applications where potential exposure to high energy radiation exists. The influence of electron beam irradiation on the degradation of tensile properties as well as the general mechanical relaxation of several aromatic polymers has been investigated by Sasuga and others.[1-3] According to the limited studies carried out in air at 23°C, the radiation stability of selected polymers was in the following order: polyimide > PEEK > polyamide > polyetherimide > polyarylate > polysulfone > poly(phenylene oxide). The

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reader should realize that this latter classification is not rigorous, however, and will be system dependent.

Poly(phenylene sulfide) (PPS) is a highly aromatic high-temperature engineering thermoplastic that has a number of beneficial properties.[4] One of its outstanding properties is that it has a particularly strong resistance to chemical (solvent) environments. Recently, films of initially amorphous PPS were irradiated with high energy Li, F, and I ions to produce electrically conductive materials.[5] Based on this study, it was found by differential scanning calorimetry (DSC) that there was some crystallinity induced in the irradiated material. Moreover, results of infrared (IR) and electron spin resonance (ESR) spectroscopies show the creation of free carriers at high doses thereby promoting conductivity and the existance of free radicals in the irradiated material. Similarly, Mazurek et al.[6] reported that ion implantation of arsenic, krypton, and bromine onto thin films of PPS increased the conductivity of the material by up to 12 orders of magnitude. Moreover, infrared spectra of the films before and after implantation showed that crosslinking might have occurred in the implanted films. The response of PPS to electron beam irradiation, however, has not been distinctly investigated.

The objective of the present work is to study the effect of such irradiation on the mechanical and thermal properties of initially amorphous and semicrystalline PPS in the presence of either an air or nitrogen atmosphere.

EXPERIMENTAL

Materials

Amorphous PPS films were kindly supplied by the Phillips Petroleum Company in the form of unoriented amorphous tape having an average thickness of 9×10^{-3} cm and a width of 3.9 cm. Semicrystalline films were prepared by heating these tapes at 120°C for 10 min under vacuum conditions.

Electron Beam Irradiation

Irradiation was performed with an electrocurtain-type accelerator manufactured by Energy Science, Inc. model CB/150/15/180 located in one of the author's (GLW) laboratory. Samples for irradiation were cut into dumbbell shape and exposed to EB irradiation with a dose rate of 50 Mrads/s. The maximum available dose was 20 Mrad per pass, hence, several passes under the electrocurtain were required for higher dose levels. The materials were placed on a stainless steel plate to minimize the rise in the temperature of the samples during irradiation. As will be discussed, however, use of this metal substrate does not inhibit a short-term considerable rise in film temperature at the high dose rate used.

Mechanical Properties

Mechanical tests including tensile strength, elongation and Young's modulus were made at room temperature using an Instron (Model 1122) employing a crosshead speed of 0.5 mm/min. Samples were cut with a die in a dog-bone

shape of initial dimensions (gauge length 10 mm and 2.8 mm in width). Young's modulus was calculated from the initial slope of the stress–strain curves. The yield stress and tensile strength were obtained at the yield point and at break, respectively. The yield and break elongation were calculated on the same basis mentioned above. Dynamic storage and loss moduli (E' and E''), as well as $\tan\delta$ were determined as a function of temperature using an Autovibron Dynamic viscoelastometer. These samples were run from 0°C to 200°C to investigate glass transition (T_g) behavior with a scanning rate of 2°C/min at a frequency of 11 Hz.

Thermal Properties

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC-4 calorimeter equipped with a TADS data station. The melting points of initially amorphous and semicrystalline PPS were determined as a function of radiation dose. A heating rate of 10°C/min was utilized and the determinations were performed under a nitrogen atmosphere. The melting points determined for each sample after irradiation were labeled "first run." After melting the samples at 320°C for 5 min, they were cooled to room temperature and then the melting point was determined again. These data were labeled "second run." These two kinds of data allowed the determination of the effect of electron-beam irradiation on the melting point of PPS (first run), and recrystallization of PPS (second run). Similarly, the heat of fusion was determined from the area under the fusion peak of the DSC scans. The results of melting points and heat of fusion determinations are the average of two measurements per data point.

Scanning Electron Microscope Analysis

The surfaces of initially amorphous and semicrystalline PPS before and after electron-beam irradiation were observed via scanning electron microscopy to look for evidence of damage or gas evolution as a result of EB irradiation. The samples were first metallized by sputter coating and left overnight in a vacuum oven. A scanning electron microscope (Cambridge Stereoscan 200) was utilized for this investigation.

RESULTS AND DISCUSSION

Mechanical Properties

Mechanical response of either initially amorphous or semicrystalline PPS as calculated from the load-elongation curves before EB irradiation show that the elongation occurs by necking. Initially amorphous and semicrystalline PPS were subjected to a radiation dose of 1000 Mrads in the presence of either nitrogen or air. It was found that at this level of electron beam dose, irradiation *in the presence of nitrogen* had little effect on the mechanical properties of either amorphous or semicrystalline PPS. However, when initially semicrystalline PPS was exposed to the same dose in the presence of air, the occurrence of distinct yielding disappeared at dosages above 500 Mrad but

TABLE I
Mechanical Properties of Electron Beam-Irradiated Initially Amorphous and Semicrystalline PPS in the Presence of Oxygen

Radiation dose (Mrad)	Tensile strength (MPa)	Elongation at yield (%)	Young's modulus (GPa)	Tensile strength at break (MPa)	Elongation at break (%)
		Initially amorphous PPS			
Unirradiated	59	3.0	2.1	45	23
500	61	4.7	2.5	46	20
1000	80	4.7	2.5	63	7
		Initially semicrystalline Polymers			
Unirradiated	85	4.9	2.7	70	18
500	90	5.4	2.6	79	9
1000	—	—	2.8	75	4

was still observed for the initially amorphous PPS as shown by the data in Table I.

Figures 1–3 show the effect of electron-beam irradiation on the tensile strength at break, σ_B, Young's modulus, and elongation at break as a function of dose in air for both initially amorphous and semicrystalline PPS, respectively. It is evident that EB irradiation has a distinct effect on the tensile strength of both materials. At low doses there is a tendency for the tensile strength of the initially amorphous PPS to increase up to a dose value of 1500 Mrads after which it rapidly decreases. The increase in tensile strength at lower dose is due to the change in structure from amorphous to that of semicrystalline as a result of rising temperature of the material during the irradiation steps. Although the samples were placed on stainless steel plates, which was expected to minimize the increase in sample temperature during irradiation, it still permitted a considerable rise in the sample temperature due to the rapid energy deposition of the E-beam into the substrate. In fact, using the energy equivalent of 2.4 cal/g per Mrad and a general heat capacity value of 0.4 cal/g per °C, gives a rise in temperature of ~ 6°C/Mrad if adiabatic conditions are assumed. Hence, for a rapid dose of 20 Mrads and for several passes, the material is distinctly brought to temperatures above T_g (85°C) for sufficient time to allow some crystallization to occur before cooling. Indeed, visual inspection of the initially amorphous materials showed the development of turbidity as dosage increased. The use of light transmission through crossed polarizers also supported this view. It is noted that for the initially semicrystalline PPS, the general behavior of the tensile strength decreases with dosage but less so than for the initially amorphous system, thereby suggesting that the crystalline phase is less prone to radiation effects as has been observed for several polymers.

Figure 2 shows the modulus response of initially amorphous and semicrystalline PPS to electron-beam irradiation. As shown, the modulus of initially amorphous PPS seems to increase with increasing dose up to 1000 Mrad. This initial rise is caused by the induced crystallinity from radiation heating. Following the rise, subsequent loss of modulus occurs, suggesting degradation. On the other hand, the modulus of the initially semicrystalline PPS tends to

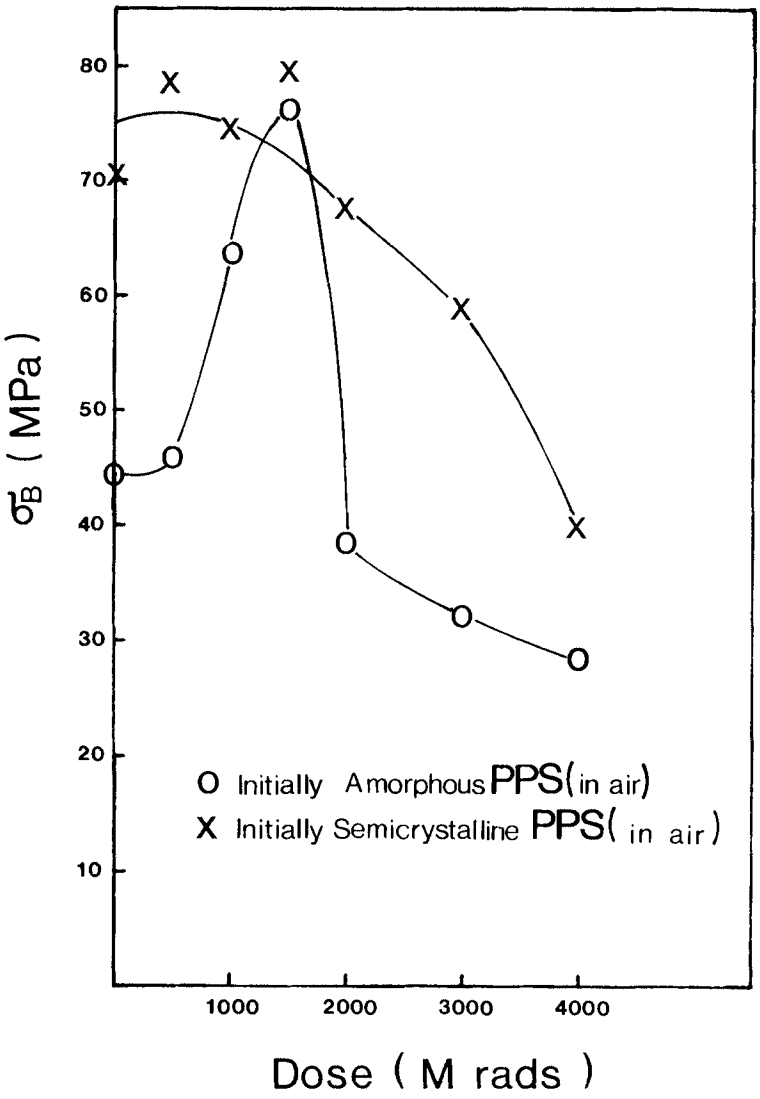


Fig. 1. Effect of electron-beam irradiation in air on the tensile strength of initially amorphous (○) and semicrystalline (×) PPS at different doses.

decrease by increasing dose to 1000 Mrads. Interestingly, this material still maintains a somewhat higher modulus than the initially amorphous material, again suggesting a greater radiation resistance of the crystalline phase.

In Figure 3, it is clear that the elongation at break is very much affected by EB irradiation regardless of whether the initial structure of PPS is amorphous or semicrystalline. One notes that even below about 500 Mrads, there is a considerable decrease in elongation and it nearly plateaus in value above 1000 Mrads. This behavior in elongation at break, together with the deterioration in tensile strength, display the increase in brittleness of the materials. The results are believed to be due to the occurrence of oxidative degradation due to EB irradiation.

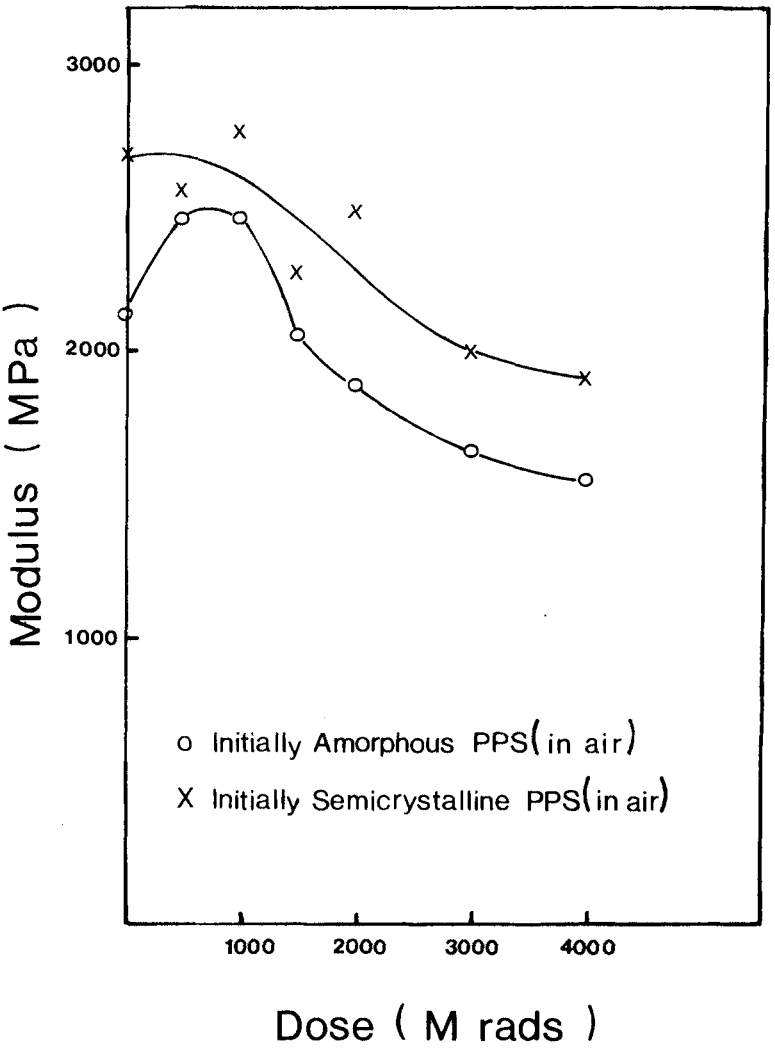


Fig. 2. Effect of electron-beam irradiation in air on the modulus of elasticity of initially amorphous (○) and semicrystalline (×) PPS at different doses.

Dynamic Mechanical Properties

Figure 4 shows typical curves of the logarithm of storage modulus as a function of temperature obtained for initially amorphous PPS before and after irradiation to 1500 Mrads. It is observed that before irradiation, initially amorphous PPS shows a decrease in the modulus at about 90°C indicating the onset of the glass transition temperature of PPS. Following this drop, the modulus increases at about 120°C as a result of crystallization. The glass transition and crystallization temperatures observed by the change in storage modulus are in good agreement with the values obtained by differential scanning calorimetry shown later in Figure 5. Furthermore, the irradiated PPS does not present the typical decrease in modulus at the glass transition temperature as seen in the unirradiated PPS, but there is a slight decrease in

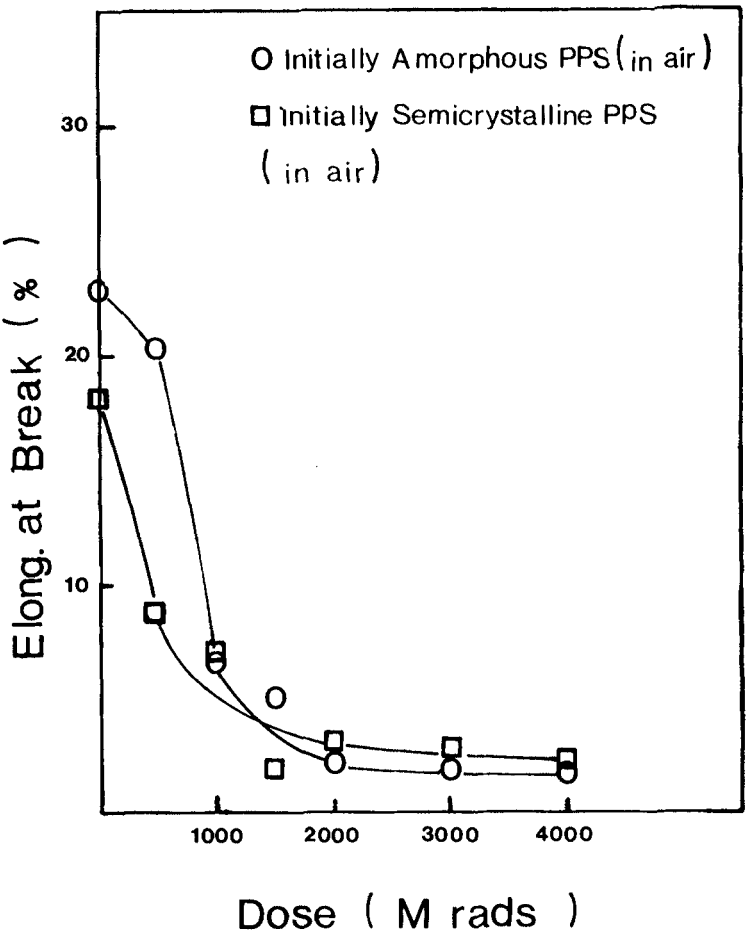


Fig. 3. Effect of electron-beam irradiation in air on the elongation at break of initially amorphous (○) and semicrystalline (□) PPS at different doses.

modulus noticed at 115°C. As discussed earlier, this difference is attributed to the fact that with a sufficient irradiation dosage, the initially amorphous PPS crystallizes and hence the modulus drop at T_g is no longer as distinct.

Thermal Properties

Figure 5 shows a DSC scan for an amorphous unirradiated PPS sample. The typical thermal transitions of the amorphous polymer are observed. First is the T_g of PPS at ~ 85°C, followed by a crystallization peak with its maximum at 130°C, and finally a melting transition, T_m, that peaks at 278°C. Figures 6 and 7 present plots of the melting point of the irradiated samples as a function of radiation dose for initially amorphous and semicrystalline PPS, respectively. The melting points have been defined as the maximum in the crystallization peak as shown in Figure 5. It is observed that the melting point of initially amorphous PPS decreases from 276°C for unirradiated to ~ 270°C at 4000 Mrads. (Recall it crystallizes during the DSC scans.) Similarly, the

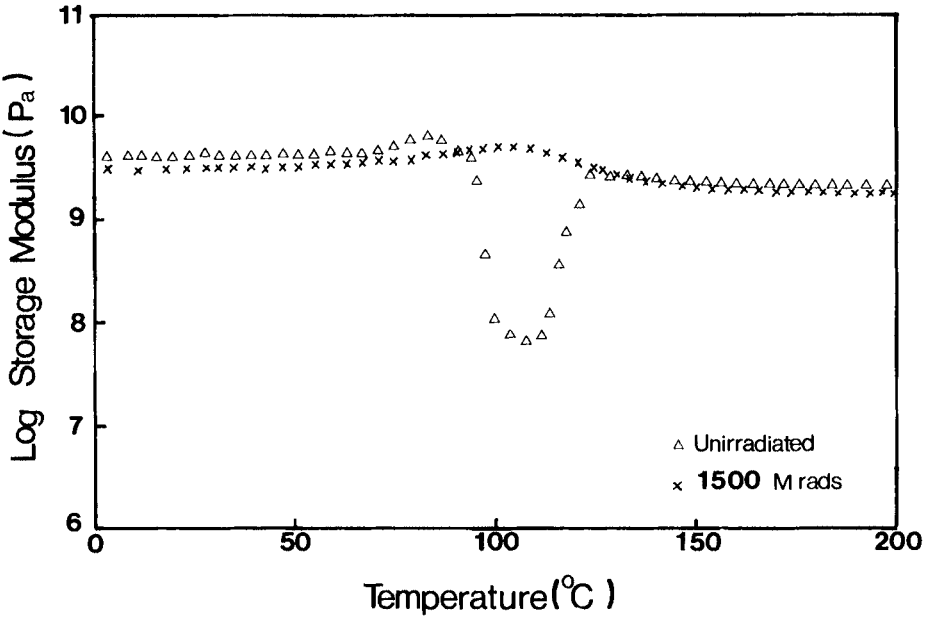


Fig. 4. Plot of storage modulus as a function of temperature for initially amorphous PPS before (△) and after (×) exposure to an electron-beam dosage in air of 1500 Mrads.

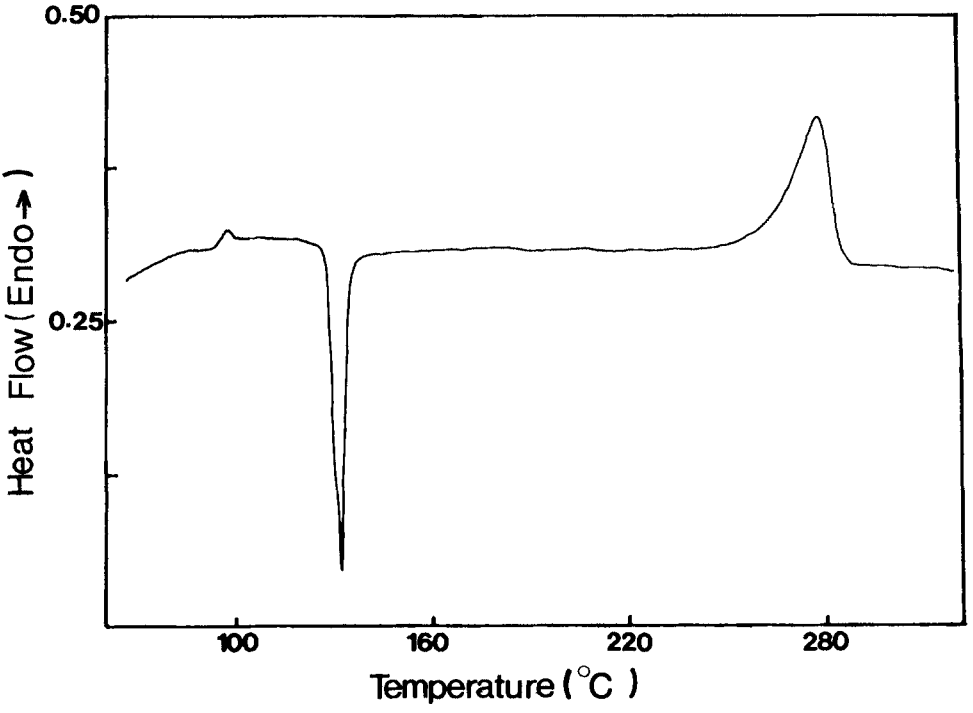


Fig. 5. Differential scanning calorimetry (DSC) trace of unirradiated initially amorphous PPS.

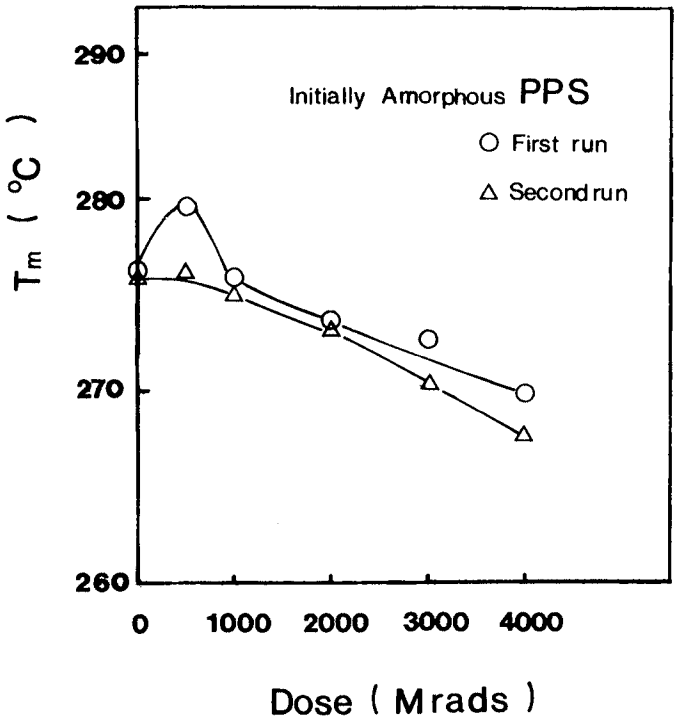


Fig. 6. Effect of electron-beam irradiation in air on the melting point of initially amorphous PPS. (○) First run; (△) second run.

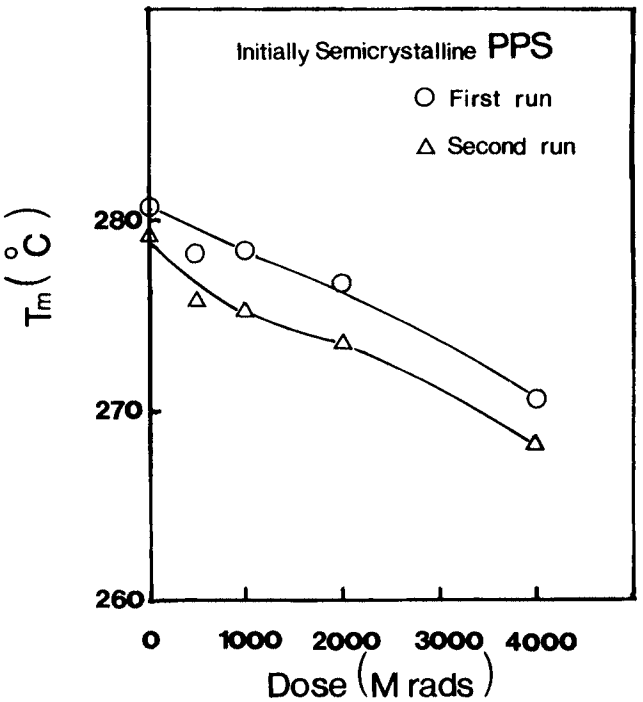
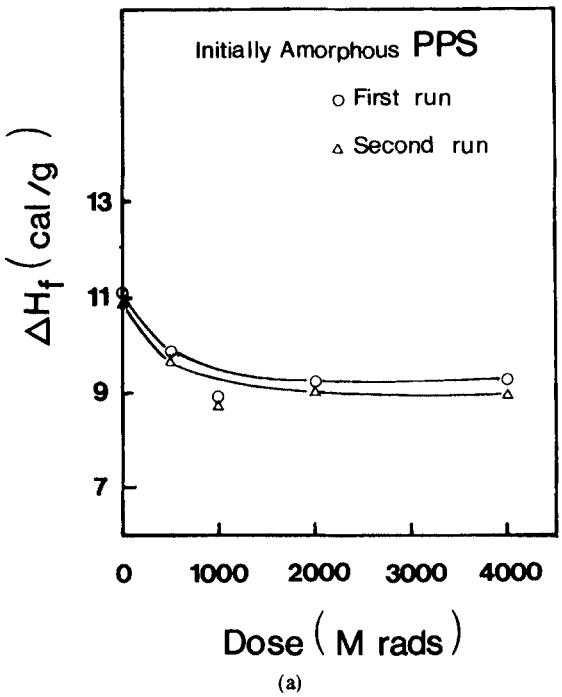


Fig. 7. Effect of electron-beam irradiation in air on the melting point of initially semicrystalline PPS. (○) First run; (△) second run.

melting point of initially semicrystalline PPS decreases from 281°C for unirradiated material to 271°C after a dose of 4000 Mrads. In addition, PPS irradiated in the amorphous state shows a lower melting point than that irradiated in the initially semicrystalline state. Also, upon recrystallization after melting (second run), the melting point is further depressed for both irradiated PPS that initially had been in either the amorphous or in the semicrystalline state. This indicates that the ability of the polymer to recrystallize is decreased by the earlier electron-beam irradiation. Since the melting point is an indication of the crystallite size and perfection, a decrease in the melting point implies a smaller crystallite size and/or a less perfect crystal formed after irradiation. Two possible explanations can be forwarded, the first would consider a chain scission mechanism; i.e., a decrease of molecular weight due to irradiation. This is in accordance with previous studies performed on the crystallization behavior of PPS which showed that the melting point of PPS decreases with decreasing molecular weight.[7] The second argument implies the occurrence of branching and/or possibly crosslinking. Previous studies have indicated that branching decreases the melting point of PPS.[8] Moreover, it has been reported that curing or crosslinking of PPS decreases the crystallizability of PPS, i.e., its ability to crystallize.[9] Crosslinking of thin films of PPS upon ion implantation has been previously suggested by Mazurek et al.[6] While either argument (or both) might be applicable to our data, the small increase in T_m and ΔH_f (see below) suggests that if crosslink-



(a)

Fig. 8. Heat of fusion (ΔH_f) or initially amorphous and semicrystalline PPS as a function of radiation dosage in air: (a) initially amorphous, (○) first run; (△) second run; (b) initially semicrystalline. (●) First run; (○) second run.

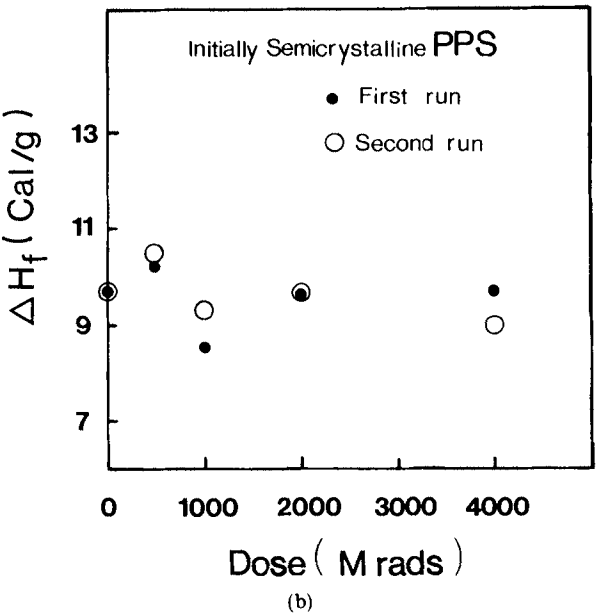


Fig. 8. (*Continued from the previous page.*)

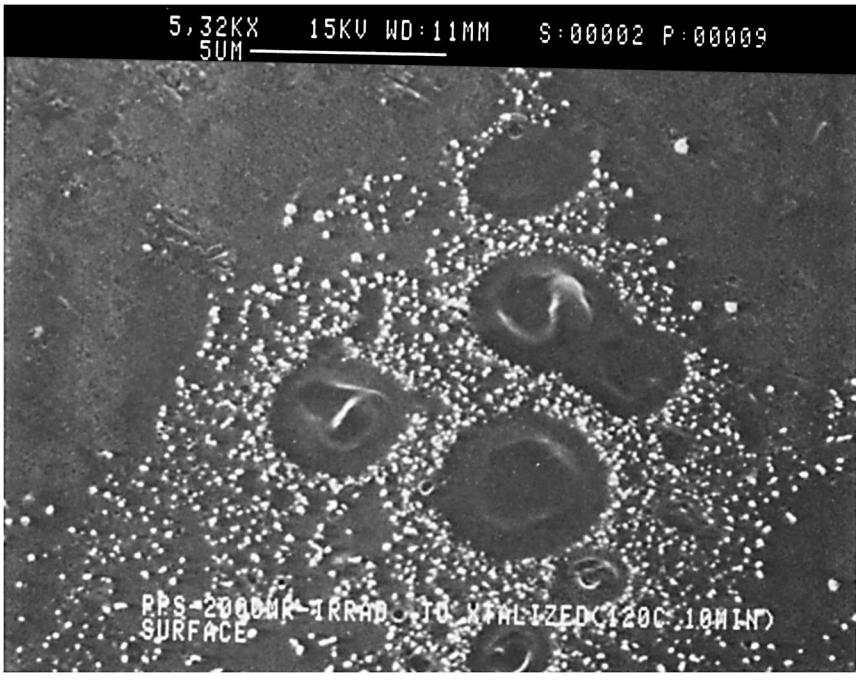
ing occurs, it is not extreme even at these high dosages and, for this reason, gel fractions were not measured.

The heat of fusion, ΔH_f, provides another important piece of information. Figure 8 shows the heat of fusion of irradiated PPS as a function of dose. For initially semicrystalline PPS, irradiation does not seem to produce any systematic variation in ΔH_f. In addition, there is no difference in ΔH_f obtained in the first or second heating. However, the heat of fusion for initially amorphous PPS presents a clear trend. The ΔH_f decreases from 11.0 cal/g for the unirradiated PPS to 9.0 cal/g at 1000 Mrads. Irradiation to doses of 4000 Mrads does not appear to decrease ΔH_f any further. Also, there is no difference in ΔH_f obtained from the first or second heating. The heat of fusion is, of course, proportional to the crystalline content of a semicrystalline polymer. Therefore, these data indicate that irradiation of initially amorphous PPS only slightly decreases the crystalline content achievable during a DSC scan at 10°C/min, suggesting a lower radiation resistance of the amorphous phase. Previous investigations on the crystallization behavior of PPS[7] have shown that lower molecular weight PPS ($\langle Mw \rangle$ = 24,000) presents a higher heat of fusion than higher molecular weight PPS ($\langle Mw \rangle$ = 63,000) for the same thermal treatment. Furthermore, it was observed that the introduction of branches[8] or crosslinking[9] in PPS decreases the heat of fusion. Consequently, the present data on heat of fusion seem to indicate the occurrence of branching and possibly very light crosslinking upon irradiation of amorphous PPS rather than a decrease in molecular weight.

Scanning Electron Microscopy (SEM) Tests

Scanning electron micrographs of unirradiated and EB (2000 Mrads) irradiated PPS surfaces are shown in Figure 9. These samples were crystallized at

(a)



(b)

Fig. 9. SEM micrographs of the surface of initially semicrystalline PPS. (a) unirradiated PPS and (b) PPS irradiated in air to 2000 Mrads.

120°C for 10 minutes. As shown in Figure 9(a), the unirradiated surface is relatively smooth with small size (less than 1 μm) imperfections. However, the surface of a PPS film irradiated at 2000 Mrads shows some evidence of gas evolution [Fig. 9(b)], as indicated by random porelike structures. These are somewhat consistent with results previously reported as H_2 evolution in the irradiated PPS samples.[10] Our results suggest an off-gasing caused by chemical changes induced by radiation. While the extent of change was not investigated in depth, it was noted that the infrared spectrum (not shown) of the materials showed no significant change after exposure to high irradiation dosage. This indirectly suggests that little chemical change occurs at these dosage levels. This, of course, is in agreement with the results presented earlier (little change in T_m, ΔH_f, etc.). Our earlier suggestion of some partial oxidative degradation would still be reasonable to apply to these observations. If solution nuclear magnetic resonance (NMR) could be applied, possibly a more complete answer could be provided, however, as pointed out earlier, this technique has not been utilized due to the inability of obtaining a sufficiently good solution at temperatures where NMR spectra can be obtained.

CONCLUSIONS

Initially amorphous and semicrystalline films of PPS have been exposed to high doses of electron-beam radiation in either air or nitrogen atmosphere. The electron-beam-irradiated materials were evaluated by mechanical tests, dynamic mechanical tests, differential scanning calorimetry, and scanning electron microscopy. Irradiation results in the presence of nitrogen revealed no noticeable change in mechanical or thermal properties of PPS at least up to 1000 Mrads. On the other hand, at the same level of dosage in air instead of nitrogen, the data show change in both the mechanical and thermal properties. In general, based on the experimental results obtained from mechanical tests several points can be stated:

1. Elongation at break is much more affected by electron-beam irradiation than the other stress–strain properties reported.
2. At higher doses (4000 Mrad), the initially amorphous PPS loses about 62% of its original tensile strength while the initially semicrystalline PPS loses about 57%.
3. Initially amorphous PPS is more susceptible to damage than initially semicrystalline PPS upon electron-beam irradiation as determined from mechanical properties as well as DSC results.
4. In general, PPS shows considerable resistance to degradation by electron-beam radiation—at least under the irradiation conditions addressed here.
5. Scanning electron microscopy observations of the surfaces of PPS irradiated at high dosage suggest the occurrence of gas evolution following high dosages of irradiation.

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