

CRYSTALLINITY MODIFICATION INDUCED IN POLY(PHENYLENE SULFIDE)  
(PPS) FILMS BY ION IRRADIATION

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ABSTRACT

Thin PPS films (2  $\mu\text{m}$  thick) were bombarded with energetic  $^1\text{H}^+$  (300 KeV),  $^4\text{He}^+$  (380 KeV),  $^{10}\text{B}^+$  (350 KeV) and  $^{40}\text{Ar}^{++}$  (700 KeV) ions, with fluences ranging from  $10^{12}$  to  $8 \times 10^{14}$  ions/ $\text{cm}^2$ . The beam current density was 20 nA/ $\text{cm}^2$  in order to avoid sample heating. The modified samples were analysed by differential scanning calorimetry (DSC) and X-ray diffractometry. The DSC results show a decrease in the melting and recrystallization temperatures as a function of the increasing ion fluence. The same tendency is noticed in the enthalpy of fusion and recrystallization. Above a certain fluence, which depends on the bombarding ion, the polymer becomes completely amorphous, and does not show any endotherm peak. The amorphisation process is confirmed by the fact that the X-ray diffraction main peak intensity decreases as a function of the ion fluence, vanishing above a certain fluence value.

Key-words

Polymer irradiation, high energy, degradation, crystallinity, amorphisation, thermal behavior, PPS.

INTRODUCTION

The ion beam bombardment changes drastically the physical and chemical properties of polymeric films. The elastic and inelastic collisions between the energetic incident ion and the target atoms result in a large energy deposition in the polymeric film. The ion beam induced modification on the physical properties and chemical structure of polymeric films can be analysed through different techniques, depending on the relevant parameters to be evaluated [1-5].

The above mentioned effects are being studied in our laboratory for different thermoplastics, and recently in particular for poly(phenylene sulfide), PPS. PPS offers a wide range of technological applications due to its high dimensional stability and relatively low susceptibility to ionizing radiation. Previous work in ion beam modification of PPS was focused mainly in the electrical properties [6-8]. The present investigation reports on preliminary results of ion beam amorphisation process on biaxially oriented PPS thin films. A systematic approach is taken on the morphological changes in PPS caused by nature, energy and fluence of the bombarding ion. Modified samples are characterized by Differential Scanning Calorimetry (DSC) and X-ray Diffractometry (XRD).

EXPERIMENTAL

Commercial grade 2  $\mu\text{m}$  thick PPS films produced by Toray Company, Japan, were mounted in annular aluminium supports. The pristine film degree of crystallinity is of the order of 40% [9], its glass transition temperature,

$T_g$ , around 92  $^{\circ}\text{C}$  and its melting temperature approximately 285  $^{\circ}\text{C}$ . The samples were bombarded by  $^1\text{H}^+$  (300 KeV),  $^4\text{He}^+$  (380 KeV),  $^{10}\text{B}^+$  (350 KeV) and  $^{40}\text{Ar}^{++}$  (700 KeV) ions using the HVEE 400 KV ion implanter at the IFUFRGS, Porto Alegre, in vacuum better than  $10^{-6}$  torr. The ion beam current density was maintained constant and equal to 20 nA/ $\text{cm}^2$  to avoid sample heating. The  $^1\text{H}^+$  and  $^4\text{He}^+$  ions ran through all sample thickness and the  $^{10}\text{B}^+$  and  $^{40}\text{Ar}^{++}$  bombardments were made on both samples sides in order to modify all its thickness [10]. The ion fluences ranged from  $10^{12}$  to  $8 \times 10^{14}$   $\text{cm}^{-2}$ . The differential scanning calorimetry measurements were made in a Perkin-Elmer DSC-4 System. The two complete cycles were performed between 50  $^{\circ}\text{C}$  and 330  $^{\circ}\text{C}$ , using heating and cooling rates of 20  $^{\circ}\text{C}/\text{min}$ . At the beginning of each cycle the temperature was kept constant for 5 minutes.

The X-ray diffraction measurements were performed in a Siemens D-500 equipment using the Cu  $K_{\alpha}$  radiation and a graphite monochromator.

RESULTS

Typical DSC heating and cooling thermograms corresponding to pristine PPS and samples bombarded with different ions and with different ion fluences are shown in fig. 1-4. It is observed that with increasing ion fluence the melting and the recrystallization peaks are shifted to lower temperatures; also a peak area reduction is quite evident.

Changes on the onset temperatures as function of ion fluence are depicted in fig. 5. Both onset temperatures exhibit a decrease as the ion fluence increases. In order to



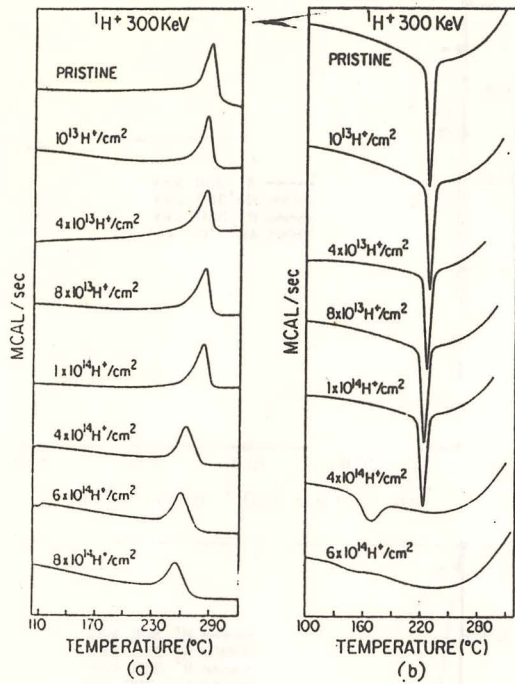


Figure 1. DSC thermograms for  $H^+$  bombarded PPS: (a) heating cycle, 20 °C/min, (b) cooling cycle, 20 °C/min.

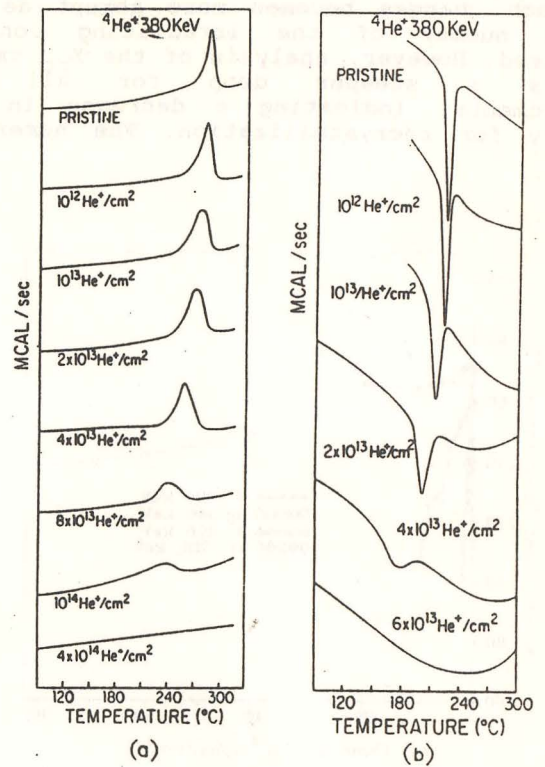


Figure 2. DSC thermograms for  $He^+$  bombarded PPS: (a) heating cycle, 20 °C/min, (b) cooling cycle, 20 °C/min.

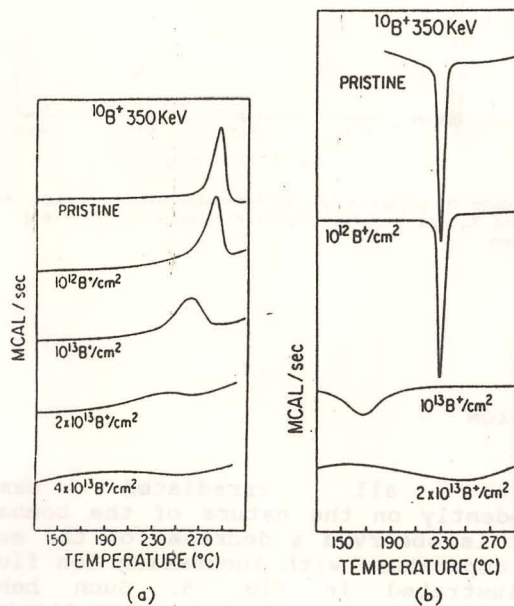


Figure 3. DSC thermograms for  $B^+$  bombarded PPS: (a) heating cycle, 20 °C/min, (b) cooling cycle, 20 °C/min.

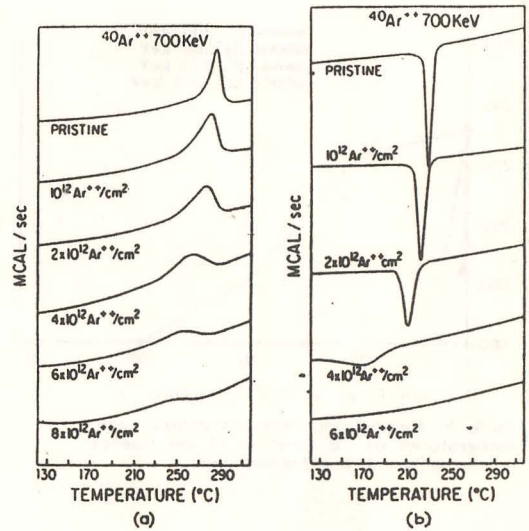


Figure 4. DSC thermograms for  $Ar^{++}$  bombarded PPS: (a) heating cycle, 20 °C/min, (b) cooling cycle, 20 °C/min.

study the crystallinity changes through these thermal cycles, three new quantities are defined as follows. For the heating cycle, a crystallinity index,  $X_f$ , is determined by the ratio between the enthalpy of fusion corresponding to the sample bombarded with a certain ion fluence,  $\Delta H_f$ , and the enthalpy of fusion corresponding to the pristine PPS,  $\Delta H_f^0$ ,

$$X_f = \Delta H_f / \Delta H_f^0,$$

For the cooling cycle a similar parameter,  $X_{rc}$ , is termed recrystallization index. In order to allow a quantitative treatment to the

recrystallizability of the modified polymeric material; a recrystallization factor, is defined by the following equation [11]:

$$F_{rc} = \frac{\Delta H_{rc} / \Delta H_f}{(\Delta H_{rc}^0 / \Delta H_f^0)}$$

The index of crystallinity and recrystallization obtained from the DSC heating and cooling cycles, respectively  $X_f$  and  $X_{rc}$ , are plotted as a function of ion fluence in fig. 6. The crystallinity index  $X_f$  drops slowly for samples bombarded with  $H^+$ ,



but such changes becomes more abrupt as the atomic number of the irradiating ion is increased. However, analysis of the  $X_{rc}$  values reveals a steeper drop for all ion bombardments, indicating a decrease in the ability for recrystallization. The numerical

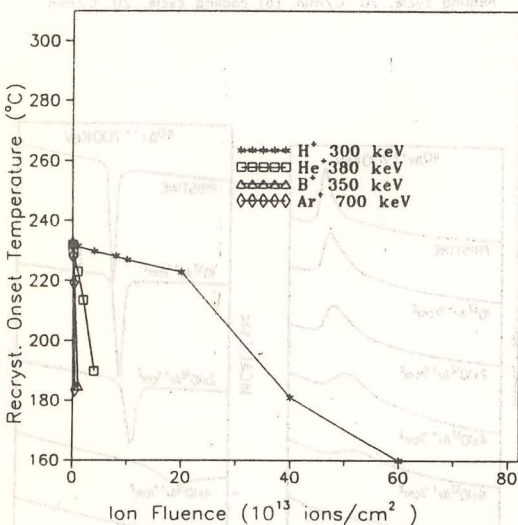
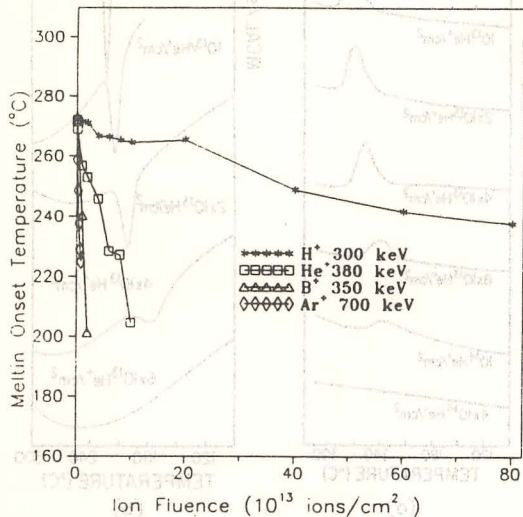


Figure 5. Melting and recrystallization onset temperatures as a function of ion fluence for the different bombardment ions.

values for  $X_f$ ,  $X_{rc}$  and  $F_{rc}$  are shown in Table I.

Figure 7 shows the crystallinity and recrystallization indexes as a function of energy fluence. Energy fluence is a measure of the average energy deposited per repeating unit of the polymeric chain, regardless how this energy is deposited [12].

The PPS X-ray diffractograms corresponding to nonbombarded and bombarded samples at several ion fluences are shown in fig. 8. As can be seen the main diffraction peak area decreases continuously with increasing ion fluence, confirming the gradual reduction in the samples crystallinity.

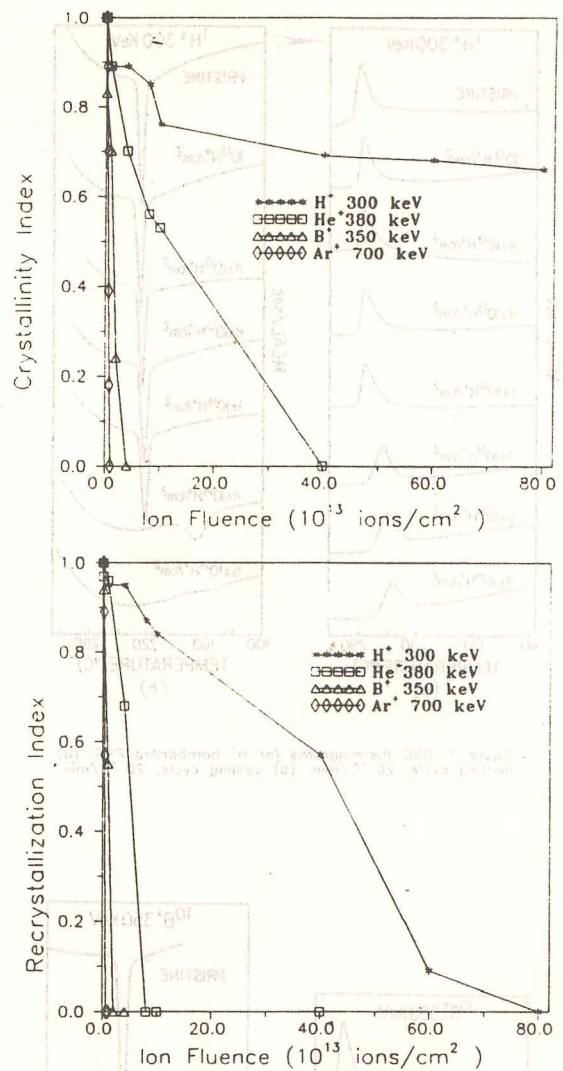


Figure 6. Crystallinity and recrystallization indexes,  $X_c$  and  $X_{rc}$ , as a function of ion fluence for different ions.

## DISCUSSION

For all irradiated samples, independently on the nature of the bombarding ion, it is observed a decrease on the melting onset temperature with increasing ion fluence, as illustrated in fig. 5. Such behavior reveals a reduction on the crystallinity of the biaxially oriented PPS samples, which can be related to the increasing number of defects in the polymeric crystallites induced by the ion energy deposition. Further analysis of the thermograms, (fig. 1a-4a), indicates a relative broadening, followed by a small decrease of the area of the melting endotherm peak; thus revealing a reduction on the number of crystalline aggregates as well as becoming less morphologically homogeneous. Additional support to this behavior is given by the analysis of the recrystallization thermograms, as depicted in fig. 1b-4b, since lower temperatures are required to form crystalline aggregates as ion fluence is increased. Also, these aggregates are formed in smaller amounts and are less homogeneous on their morphological characteristics, leading to broader and less intense recrystallization exotherm peaks.

TABLE I - Crystallinity and recrystallization indexes  $X_f$  and  $X_{rc}$ , as well as recrystallization factor  $F_{rc}$  results extracted from DSC for  $H^+$ ,  $He^+$ ,  $B^+$  and  $Ar^{++}$  bombarded samples.

Fluence	$X_f$	$X_{rc}$	$F_{rc}$
PRISTINE	1.00	1.00	1.0
$10^{13} H^+$	0.89	0.95	1.0
$4 \cdot 10^{13}$	0.89	0.95	1.0
$8 \cdot 10^{13}$	0.85	0.87	1.0
$10^{14}$	0.76	0.84	1.0
$4 \cdot 10^{14}$	0.69	0.57	0.8 $\rightarrow \phi_c$
$6 \cdot 10^{14}$	0.68	0.09	0.1
$8 \cdot 10^{14}$	0.66	0.00	0.0 $\rightarrow \phi_a$
$10^{12} He^+$	1.00	0.97	1.0
$10^{13}$	0.89	0.96	1.0
$4 \cdot 10^{13}$	0.70	0.68	0.9 $\rightarrow \phi_c$
$8 \cdot 10^{13}$	0.56	0.00	0.0
$10^{14}$	0.53	0.00	0.0
$4 \cdot 10^{14}$	0.00	0.00	0.0 $\rightarrow \phi_a$
$10^{12} B^+$	0.83	0.94	1.0
$10^{13}$	0.70	0.55	0.8 $\rightarrow \phi_c$
$2 \cdot 10^{13}$	0.24	0.00	0.0
$4 \cdot 10^{13}$	0.00	0.00	0.0 $\rightarrow \phi_a$
$10^{12} Ar^{++}$	1.00	1.00	1.0
$2 \cdot 10^{12}$	0.89	0.89	1.0
$4 \cdot 10^{12}$	0.70	0.57	0.8 $\rightarrow \phi_c$
$6 \cdot 10^{12}$	0.39	0.00	0.0
$8 \cdot 10^{12}$	0.18	0.00	0.0
$10^{13}$	0.00	0.00	0.0 $\rightarrow \phi_a$

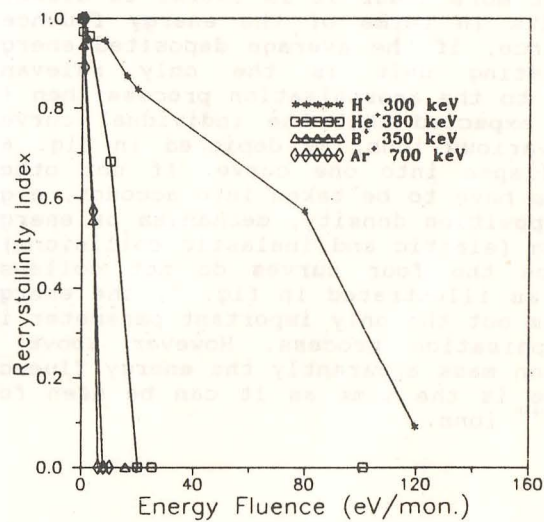
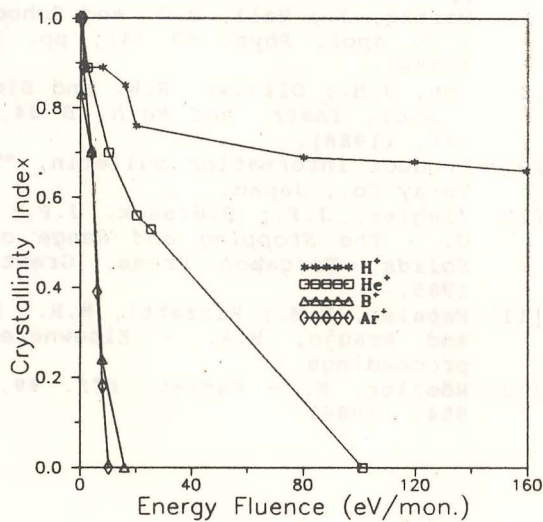


Figure 7. Indexes of crystallinity and recrystallization,  $X_f$  and  $X_{rc}$ , as a function of ion energy fluence for the different ions.



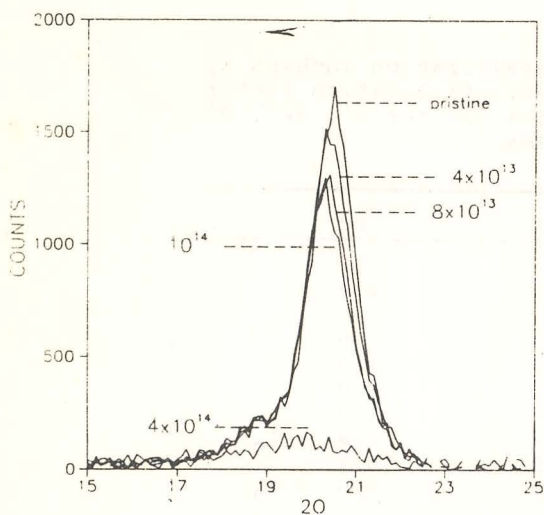


Figure 8. Main X-ray diffraction peak corresponding to several different  $\text{He}^+$  bombardment fluences.

At Table I, comparison of the melting enthalpies of PPS samples irradiated with  $4\text{--}8 \times 10^{14} \text{ H}^+/\text{cm}^2$  reveals no sharp difference in their values. However, the recrystallization process indicates for these same samples a strong broadening of the exotherm peak, with an abrupt change of this thermal event at  $4 \times 10^{14} \text{ H}^+/\text{cm}^2$  fluence. Indicating that at this fluence the polymeric material lost its ability for recrystallization. This fluence is called the critical ion fluence,  $\phi_c$ . For fluences higher than  $\phi_c$ , the polymeric material shows a morphology strongly dominated by an amorphous phase. For every bombarding ion a similar behavior is observed. A new quantity is defined for the heating process when no endotherm peak is observed for an irradiated sample, the quantity is termed amorphisation fluence,  $\phi_a$ . These quantities,  $\phi_c$  and  $\phi_a$ , depend on the energy deposition process and fluence of the bombarding ion in the polymeric material and on the nature of the ion. To make this point more clear it is useful to discuss our results in terms of the energy fluence. For instance, if the average deposited energy per repeating unit is the only relevant parameter to the amorphisation process then it would be expected that the individual curves for the various ions, as depicted in fig. 6, would collapse into one curve. If not other parameters have to be taken into account, e.g. energy deposition density, mechanism of energy deposition (elastic and inelastic collisions), etc. Since the four curves do not collapse into one as illustrated in fig. 7, the energy fluence is not the only important parameter in the amorphisation process. However above a certain ion mass apparently the energy fluence dependence is the same as it can be seen for  $\text{B}^+$  and  $\text{Ar}^{++}$  ions.

The PPS crystallinity reduction with increasing ion bombardment fluence is confirmed by the decrease in the main X-ray diffraction peak area as a function of the ion fluence. Above  $4 \times 10^{14} \text{ He}^+/\text{cm}^2$  the X-ray results indicate the complete samples amorphisation.

## CONCLUSIONS

Bombardment of energetic ions like  $^1\text{H}^+$ ,  $^4\text{He}^+$ ,  $^{10}\text{B}^+$  and  $^{40}\text{Ar}^{++}$ , on PPS thin films alters the polymer morphology (crystalline regions) by the generation and accumulation of structural defects. This process, as monitored by DSC and X-ray diffractometry, develops smoothly up to a certain critical ion fluence. Beyond that, abrupt changes are observed leading to a completely amorphous material. This critical ion fluence depends on the nature of the incident ion. The deposited energy per polymer chain repeating unit by the ion is not the only important parameter in the amorphisation process. Apparently the energy deposition density and the kind of energy deposition process are also important parameters.

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