Impact of H$^+$ Ion Irradiation on Matrimid®. I. Evolution in Chemical Structure

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ABSTRACT: Ion beam irradiation can be used to modify the structure and gas transport properties of glassy polymers. This is the first of two studies that focus on the impact of H$^+$ ion irradiation on the structure and permeation properties of the polyimide Matrimid®. Specifically, the evolution in chemical structure after H$^+$ irradiation over a range of fluences was analyzed using FTIR spectroscopy and dissolution studies. Although H$^+$ ion irradiation at very low ion fluences induced little modification in the chemical structure, irradiation at relatively high ion fluences resulted in crosslinking of the irradiated films. The branched structure of the aliphatic methyl (CH$_3$) was the most sensitive to the H$^+$ ion irradiation. The *para*-disubstituted aromatic ring showed the strongest resistance toward ion irradiation and required fairly high doses to induce degradation. Two potential crosslinking mechanisms related to the degradation of the aliphatic methyl and the benzophenone carbonyl were presented. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2010–2019, 2003

Key words: FTIR; ion beam irradiation; crosslinking; polyimide; gas separation membrane

INTRODUCTION

Gas separation through selective permeation of polymeric membranes is one of the fastest growing branches of separation technology.[1] Over the few past decades, numerous studies have reported on the relationship between gas permeation properties and polymer chemical structure in developing better membrane materials.[2–11] Significant changes in the gas permeation properties of polymers can be induced by subtle changes in chemical structures. The polyimides, isomers 6FDA–6FpDA and 6FDA–6FmDA, are good examples of the effect of structure on transport properties.[9] Although the structure of these two polymers is nearly identical, the two isomers have markedly different transport properties. The *para*-connected polyimide 6FDA–6FpDA has an oxygen permeability that is almost nine times higher than the *meta*-connected 6FDA–6FmDA. Although selective alterations of transport characteristics through chemical synthesis have resulted in improved membrane materials, polymers appear to be reaching an upper bound trade-off between permeability and selectivity.[12] Therefore, the focus of much recent research has been on developing alternative membrane materials and/or postformation

techniques for modification of existing polymeric membranes.[13–30]

There are a number of postsynthesis methods that can be used to modify gas permeation properties of polymers, including thermal treatment,[13,14] fluorination,[15–18] and plasma treatment.[19–21] Ion beam irradiation is a very effect method that has recently been used to modify the selective layer of polymeric membranes.[22–29] In addition, the recently developed plasma immersion ion implantation (PIII)[30] offers many advantages over conventional beamline ion implantation including the ability to implant complex shaped surfaces combined with a lower capital and operating cost. This should allow the use of ion beam irradiation for modifying commercial-size membrane modules.

Whereas for some polymers, ion beam irradiation can significantly increase both permeabilities (for example O$_2$) and permselectivities (for example O$_2$/N$_2$),[23–25] in other cases the effects are much less significant, or there is a decease in both permeabilities and permselectivities.[29] Here there are two interesting subjects: how the chemical structure of the precursor polymer affects the outcome of ion beam irradiation, and how irradiation changes the chemical structure of precursor polymer along with the microstructure and gas transport properties. Both are the current focus of our research group. We will present a study of the effect of H$^+$ ion irradiation on the chemical structure and gas permeation properties of the polyimide Matrimid®. This study focuses on modifications of the chemical structure of Matrimid® induced by H$^+$ ion

irradiation. A second study will focus on evolution in gas permeation properties after H$^+$ ion irradiation.

The modification in chemical structure of polymers induced by ion bombardment has been investigated by numerous groups.[31–34] Davenas et al.[31] and Xu et al.[32] investigated ion-beam–induced chemical and structural modification in polyimide films using infrared spectroscopy (IR). Balanzat et al.[33] used FTIR spectroscopy to study swift heavy ion modification of polyethylene, poly(vinylidene fluoride), and polystyrene. Rajulu et al.[34] studied the mechanism of chemical modification and abstraction of hydrogen, chlorine, C=O, CH$_2$, and CH$_3$ by FTIR analysis of the changes of poly(methyl methacrylate)/poly(vinyl chloride) blend films irradiated by a ^{28}Si ion beam. Although numerous FTIR studies of chemical structure modifications induced by ion bombardment have been reported in the literature, few studies provide detailed quantitative analysis of the evolution in the chemical structure. Detailed information about this chemical structural evolution is critical for understanding the impact of chemical structure on gas transport properties of the irradiated polymer. It is also important for establishing a database on the relationship between chemical structure of precursor polymer, irradiation conditions, and gas transport properties. This work attempts to provide insight into the evolution in the chemical structure of Matrimid$^®$ upon ion beam irradiation.

Polyimides play an ever-increasing role in many applications as the result of a unique combination of superior mechanical, chemical, and thermal properties.[35] In this work, a wide range of H$^+$ ion fluences (from 7×10^{12} to 3×10^{15} H$^+$/cm^2) was used for irradiating Matrimid$^®$. The polyimide Matrimid$^®$ was chosen for the study because it is commercially available and widely used in the industry. It has superior gas permeation properties over those of many commercial polymers for industrially important gas pairs (H$_2$/CH$_4$, O$_2$/N$_2$, etc.). The physical and transport properties of Matrimid$^®$ are also well characterized. The structural evolution was analyzed by FTIR in combination with the dissolution study of the irradiated films. Based on the experimental results, a detailed description of the FTIR spectral evolution after ion beam irradiation and its implication will be presented.

EXPERIMENTAL

Materials

The Matrimid$^®$ was purchased from Ciba Specialty Chemicals Company (Summit, NJ). Methylene chloride (CH$_2$Cl$_2$) was purchased from Fisher Scientific (Pittsburgh, PA). All of the chemicals were reagent grade and used without further purification.

Dense film preparation

Freestanding dense films were used for FTIR analysis and dissolution studies. A solution of 5–7 wt % Matrimid$^®$ in methylene chloride was used for dense film formation. A specific volume of polymer solution (5–10 mL) was poured on top of a 4-in. polished silicon wafer, which was fixed on a spin coater (P-6000 Spin Coater from Specialty Coating System) and was spun at 400–700 rpm for about 6 min. The cast film was immediately masked with aluminum foil and immersed in water for removal from the wafer. Finally, the sample was dried in a vacuum oven overnight at 80°C to remove residual solvent. All film thicknesses measured using a digital micrometer were between 4.5 and 5.5 μm.

H$^+$ ion beam irradiation

Ten freestanding dense films were irradiated with H$^+$ ions at 450 keV using a Tandem Accelerator at the University of Western Ontario, London, Ontario, Canada. All of the irradiation was performed at room temperature within a vacuum chamber at a pressure less than 1.9×10^{-7} Torr. To avoid overheating of the sample, a low-beam current density (<1 μA/cm^2) was used. The incident beam was perpendicular to the surface of the samples. The incident energy of irradiation was determined using a well-known program titled The Stopping and Range of Ion in Matter (SRIM)[36] to ensure that the entire thickness of the film was modified. The irradiation fluences were varied from 7×10^{12} to 3×10^{15}/cm^2.

Fourier transform infrared spectroscopy (FTIR)

FTIR was used to study the evolution of the chemical structure of Matrimid$^®$ after irradiation with H$^+$ ion beam. All the measurements were performed using a Nicolet FTIR 5DV spectrometer (Nicolet Analytical Instruments, Madison, WI) at the Instrument Center of the University of Toledo. Each sample was measured at the same condition before and after ion irradiation to monitor any changes of the spectrum induced by the irradiation. The absorption of a species is Gaussian in nature. A Gaussian function was used to fit the curves for each band with the area under each band determined by integrating the Gaussian function.[37,38]

For FTIR analysis, the sizes of the relevant functional bands were determined by the areas under the peaks. To minimize complications from the overlapping "tail" of the neighboring bands, each characteristic band was isolated from its neighbors. Sigma$^®$ software was used for the Gaussian function curve fitting to decompose each band.

Dissolution studies

The set of dense films used for FTIR study was subsequently used for dissolution measurements. A small

TABLE I
Impact of Ion Fluence on Dissolution of the Irradiated Matrimid®R Films in Solvent Methylene Chloride[a]

Ion fluence (H^+/cm^2)	Results
7×10^{12} to 1×10^{13}	Completely dissolved
5×10^{13} to 3×10^{14}	Partially dissolved
6×10^{14} to 3×10^{15}	No noticeable dissolution

[a] Placed in excess of methylene chloride at room temperature.

piece of each sample was immersed in an excess volume of methylene chloride in a small tube at room temperature and sealed to observe the dissolution. Methylene chloride is a commonly used solvent for polyimides and easily dissolves Matrimid® within minutes. The tubes were stored in a refrigerator at around 4–6°C for 1 month and observed again.

RESULTS AND DISCUSSION

Dissolution of the irradiated films

The dissolution results for the H^+ ion irradiated samples are summarized in Table I. At very low fluences (up to 1×10^{13} H^+/cm^2), the irradiated films were completely dissolved in methylene chloride, so that ion irradiation resulted in no noticeable crosslinking of the Matrimid®. At medium ion fluences (ranging from 5×10^{13} to 3×10^{14} H^+/cm^2), the irradiated films were partially dissolved in methylene chloride, indicating that ion irradiation resulted in the partial crosslinking of Matrimid®. As the ion fluence was increased to 6×10^{14} H^+/cm^2 and beyond, the irradiated samples became totally insoluble and were highly crosslinked.

FTIR analysis of Matrimid® modified by H^+ irradiation

FTIR spectrum of virgin Matrimid®

The chemical structure of Matrimid® is shown in Figure 1. Figure 2 represents a typical spectrum of the virgin Matrimid® film obtained at room temperature in the range of 400 to 4000 cm^{-1}. For all of the virgin films, the IR spectra were consistent with Matrimid® spectra reported in the literature.[39,40] As shown in Figure 2, four bands, which are located at 1778, 1725, 1374, and 1096 cm^{-1}, respectively, are generally accepted as being characteristic of the imide group of Matrimid®. The 1778 and 1725 cm^{-1} bands are most commonly attributed, respectively, to symmetric [denoted $\nu^{C=O(s)}$] and asymmetric stretching [denoted $\nu^{C=O(as)}$] of carbonyl groups coupled through a five-membered ring, which are identified as the imide I band in Figure 2. The band at 1370–1380 cm^{-1} is attributed to the axial stretching mode of CNC (imide II) [denoted $\nu^{CNC(II)}$]. The absorption at 1070–1140

cm^{-1} is assigned as the transverse stretching mode of CNC group (imide III) [denoted $\nu^{CNC(III)}$].

In the spectrum of Matrimid®, there is another band at about 1676 cm^{-1} that belongs to the benzophenone carbonyl C=O stretching vibration [denoted $\nu^{C=O(b)}$]. This carbonyl group absorbs at a lower wavenumber than the carbonyl group of the imide moiety (1778 and 1725 cm^{-1}) because of its high conjugation with phenyl group that causes a delocalization of the π-electron of the carbonyl group. Delocalization reduces the double-band character of the carbon to the oxygen, which results in a lower absorption frequency.[39]

In addition, CH stretching vibration of the methyl group at 2960–2860 cm^{-1} [denoted $\nu^{C—H}$] and the semicircle stretching vibration of the *para*-disubstituted phenyl group at 1512 and 1488 cm^{-1} [denoted $\nu^{C=C(aromatic)}$] are characteristic bands of Matrimid®. Table II summarizes the infrared band assignments of Matrimid®. The numbers shown in Table II, which correspond to characteristic infrared peaks in the spectrum, are also shown in Figure 2 to facilitate reading of the spectrum. The evolution in each of these bands after H^+ ion beam irradiation are discussed in this report.

Evolution of FTIR spectra after H^+ ion beam irradiation

Typical FTIR spectra of the Matrimid® films irradiated with H^+ at ion fluences ranging from 7.0×10^{12} to 3.0×10^{15} H^+/cm^2 are shown in Figure 3. No changes were evident in the FTIR spectra of the Matrimid® after ion irradiation at ion fluences below 5×10^{13} H^+/cm^2. There is a general gradual decrease in the intensities of the absorbance bands of most characteristic functional groups for the fluence range from 6×10^{14} to 3.0×10^{15} H^+/cm^2. This would indicate that significant bond breaking occurs at the methyl, phenyl ring, carbonyl, and CNC of the imide moiety at and above ion fluences of 6×10^{14} H^+/cm^2. The aliphatic methyl CH_3 (2960–2860 cm^{-1}) with the branched structure appears to be the most susceptible to the H^+ ion irradiation because it has the fastest rate of decay with ion fluence.

To better investigate the effect of ion fluence on modification of the chemical structure, the normalized areas of the characteristic absorption bands of Matrimid® were calculated and are plotted as a function of ion fluence in Figures 4 and 5. The normalized
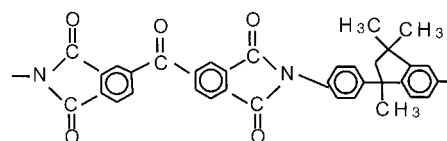

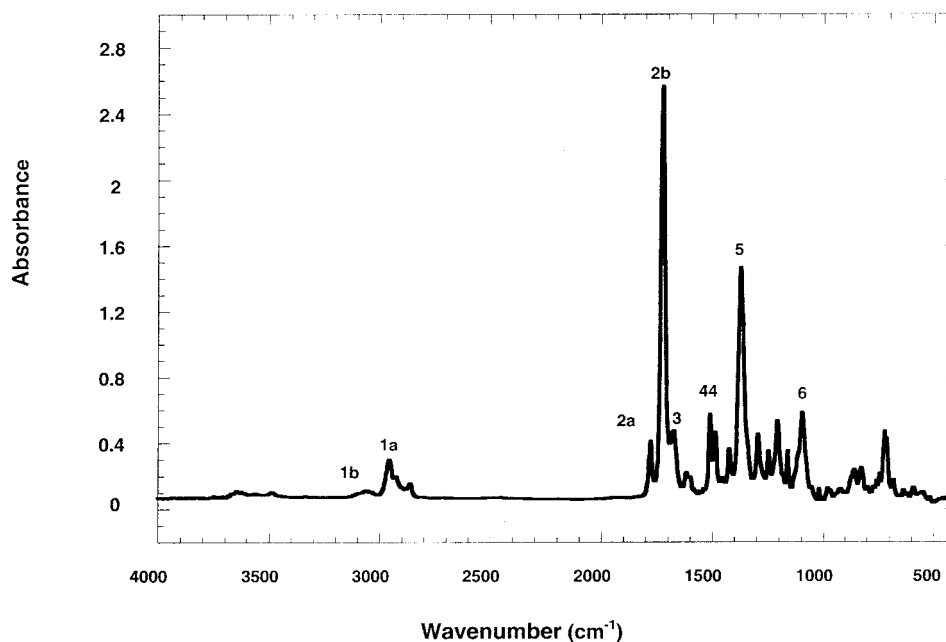**Figure 1** Chemical structure of monomer unit of Matrimid® repeat unit.

Figure 2 FTIR spectrum of virgin Matrimid$^\circledR$ recorded at room temperature. The numbers shown in the figure, which correspond to different characteristic IR peaks, are listed in Table III.

area is defined as the ratio of the area of the band of the Matrimid$^\circledR$ after ion irradiation (A) to the area of the band of the virgin Matrimid$^\circledR$ (A_0).

The normalized areas of three bands attributed to the imide group as a function of ion fluence are shown in Figure 4. For the lower ion fluences (below 3×10^{14} H$^+$/cm^2), the three bands corresponding to the imide group—the imide I C=O stretching mode (i.e., 1778 and 1725 cm^{-1}), the imide II axial CNC stretching mode (i.e., 1374 cm^{-1}), and the imide III transverse CNC stretching mode (i.e., 1096 cm^{-1})—were unaffected by ion irradiation. At a fluence of 3×10^{14} H$^+$/cm^2, slight decreases in each of the normalized areas were observed, which indicates that ion irradiation at this fluence resulted in measurable degradation of the imide group. At higher fluences, there was a sharp decrease in the normalized area.

The normalized areas of the aliphatic methyl stretching mode—the benzophenone C=O stretching mode, the imide I C=O stretching mode, and the

aromatic stretching mode of the *para*-disubstituted phenyl group as a function of ion fluence—are presented in Figure 5. To avoid overcrowding in the figure, the normalized areas of the other two bands of the imide group (i.e., 1374 and 1096 cm^{-1}) are not shown as a function of ion fluence because their rates of decrease with ion fluence were very similar to that of the imide I C=O (see Fig. 4). At an ion fluence of 5×10^{13} H$^+$/cm^2, only the normalized area of the aliphatic methyl CH$_3$ band decreases with ion fluence, whereas the other three functional groups remain unchanged. As discussed above, H$^+$ ion irradiation at an ion fluence of 5×10^{13} H$^+$/cm^2 resulted in the partial crosslinking of the irradiated Matrimid$^\circledR$. Degradation of the methyl bond (CH$_3$) may have contributed to the partial crosslinking of the Matrimid$^\circledR$ after H$^+$ ion irradiation at ion fluences up to 5×10^{13} H$^+$/cm^2.

The critical ion fluence, which is defined as the fluence at which a noticeable decrease in normalized area can be observed, can be determined from Figure

TABLE II
Characteristic Absorbance Bands for the Polymer Matrimid$^\circledR$R in the Range 400–4600 cm^{-1}

Number	ν (cm^{-1})	Band assignment
1a	2960–2860	CH stretching of methyl
1b	3062	Aromatic CH stretching
2a	1778	Symmetric C=O stretching (imide I)
2b	1725	Asymmetric C=O stretching (imide I)
3	1676	C=O stretching of benzophenone carbonyl
4 and 4′	1512 and 1488	C=C stretching of *para*-disubstituted aromatic ring
5	1374	CNC axial stretching (imide II)
6	1096	CNC transverse stretching (imide III)
7	3450–3500	OH stretching
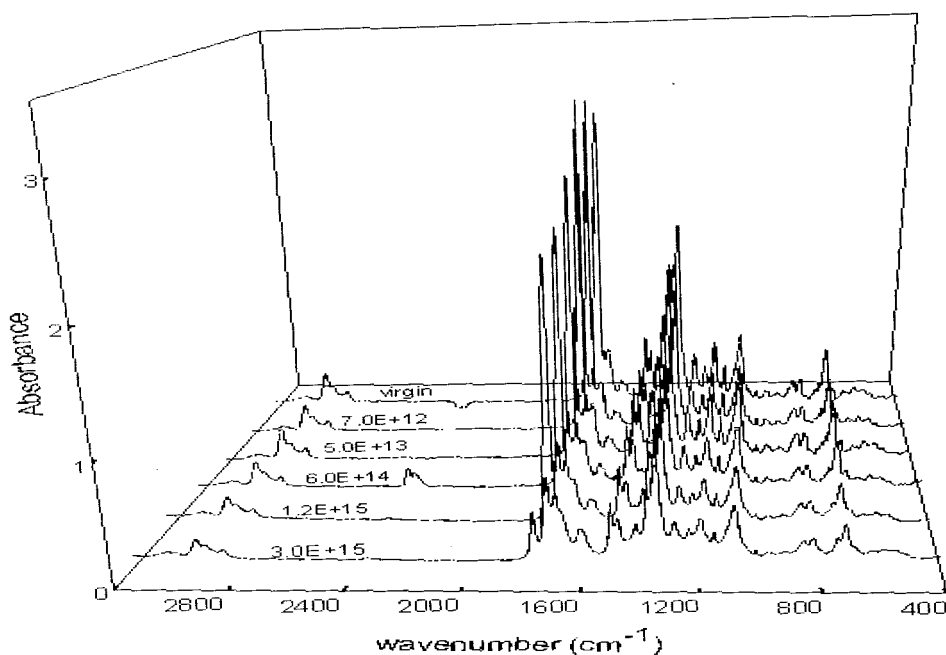
Figure 3 FTIR spectra for Matrimid® films irradiated with 450 keV H^+ ions of ion fluence ranging from 7×10^{12} to 3×10^{15} H^+/cm^2.

5. The values are listed in Table III. Of these functional groups, the *para*-disubstituted aromatic ring exhibits the slowest decay and the strongest resistance to ion irradiation because its critical ion fluence is the highest. Only at relatively high ion fluences was the *para*-disubstituted aromatic ring affected by ion irradiation. Additionally, at 6×10^{14} H^+/cm^2, significant decreases in the normalized areas of the other three functional groups (the aliphatic methyl CH_3, the benzophenone $C=O$, and the imide I $C=O$) were observed. As noted earlier, this ion irradiation fluence is the point at which the irradiated films were totally insoluble. Therefore, a relatively high fluence of H^+ ion irradiation was needed to achieve a high level of crosslinking. Regarding transformation of the aromatic ring after ion beam irradiation, many possible
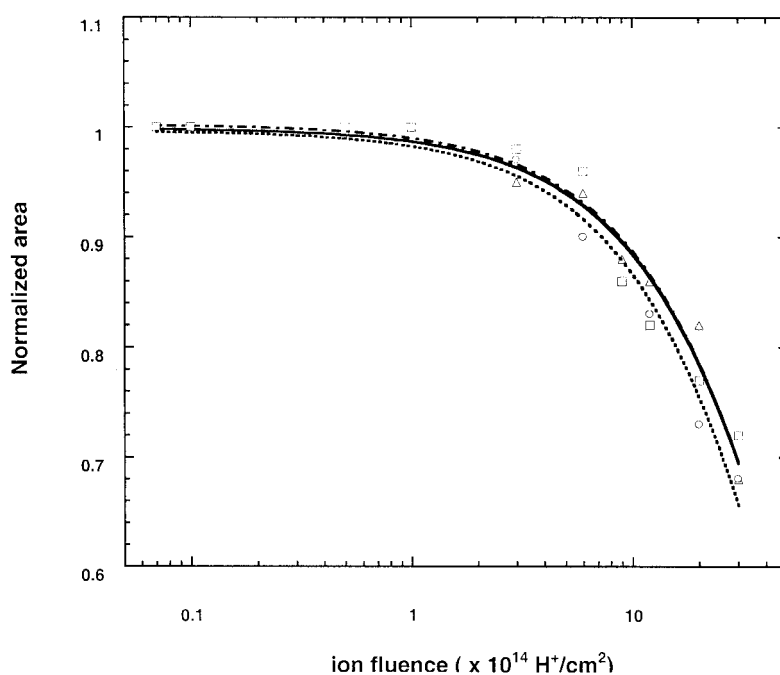

Figure 4 Normalized areas of three bands corresponding to the imide groups as a function of ion fluence for Matrimid® irradiated with 450 keV H^+ ions (CNC 1374, △; CNC 1096, ○; and imide $C=O$, □).
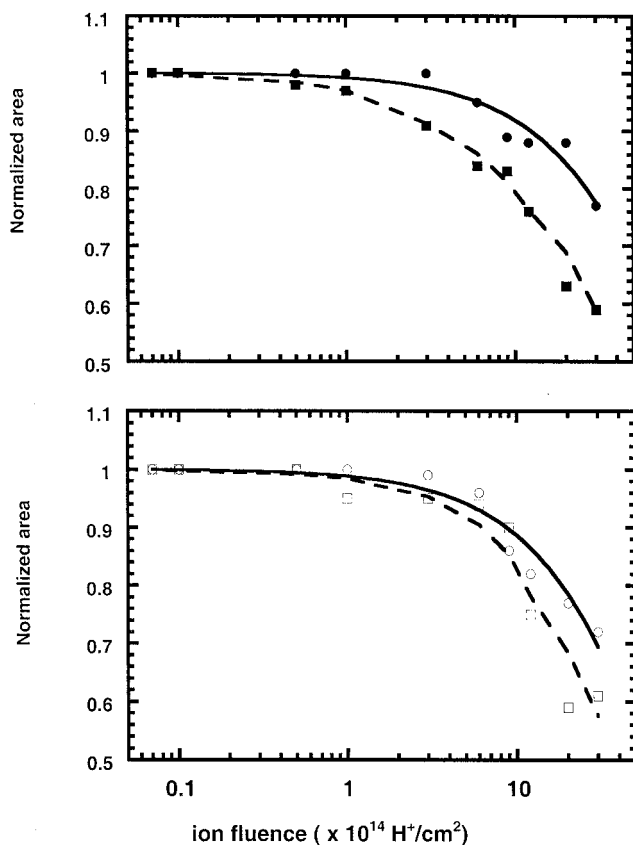
Figure 5 Normalized areas of the characteristic absorption bands attributed to the aliphatic methyl CH$_3$ (■), the benzophenone C=O (□), the imide I C=O (○), and the *para*-disubstituted aromatic ring (●), versus ion fluence for Matrimid$^®$ irradiated with 450 keV H$^+$ ions.

Figure 6 Potential reaction mechanism attributed to the cleavage of the branched structure of aliphatic methyl (CH$_3$) during H$^+$ ion irradiation of Matrimid$^®$.

mechanisms have been reported in the literature, including the production of unsaturated bonds,[31,33,41–44] carbonization, and graphitization.[31,35,45,46] However, the formation of conjugated double bonds by opening of the aromatic ring is the most likely, as reported by several groups.[33,42,43]

Potential mechanisms of chemical evolution induced by H$^+$ irradiation

Mechanism for earlier stage crosslinking

Irradiation of polymers results in outgassing (or gas emission), crosslinking, and/or main chain scission.[34,39,47–49] Generally, a branched structure is a
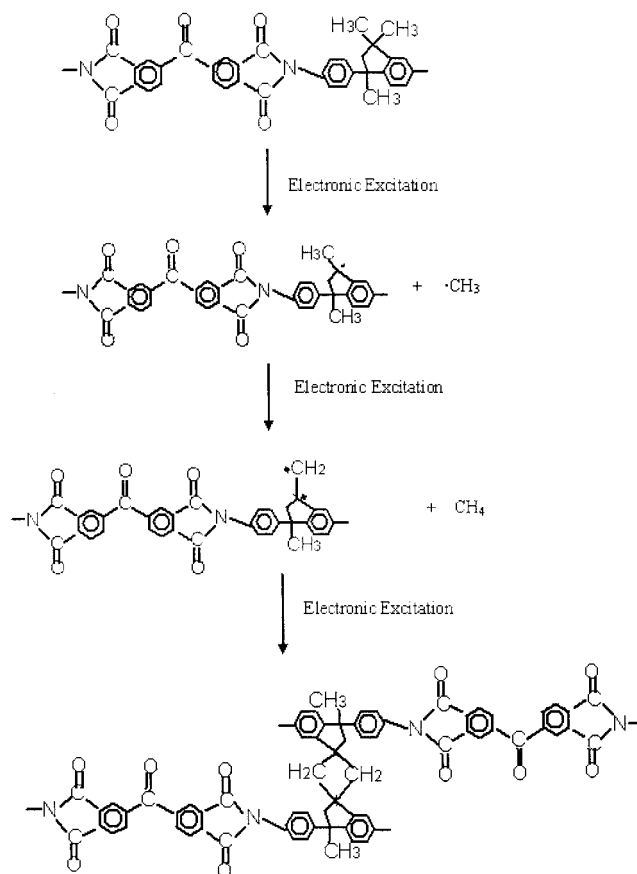
weak point under ion irradiation.[47,48] Moreover, several groups have demonstrated that the chemical structure of emitted gases closely corresponds to that of the side groups in the repeat units.[34,39,47–49] For example, methane was formed by the cleavage of the bond between the side chain and the tertiary carbon atom after polypropylene (PP) [–(CH$_2$–CH(CH$_3$))$_n$–[was irradiated with ^{58}Ni$^+$ ion at very high energy, where electronic energy loss was predominant.[39] Polyethylene without a side chain produces mostly H$_2$; polypropylene with a CH$_3$ side chain produces H$_2$ and CH$_4$; polybutene [–CH$_2$–CH(CH$_2$CH$_3$)–] with an ethyl side chain (–CH$_2$–CH$_3$) produces mostly ethane.[47] Also polyisobutylene [–(CH$_2$–C(CH$_3$)$_2$)$_n$–] has two

TABLE III
Critical Ion Fluences for Several Functional Groups of Matrimid®R Under 450 keV H$^+$ Ion Irradiation

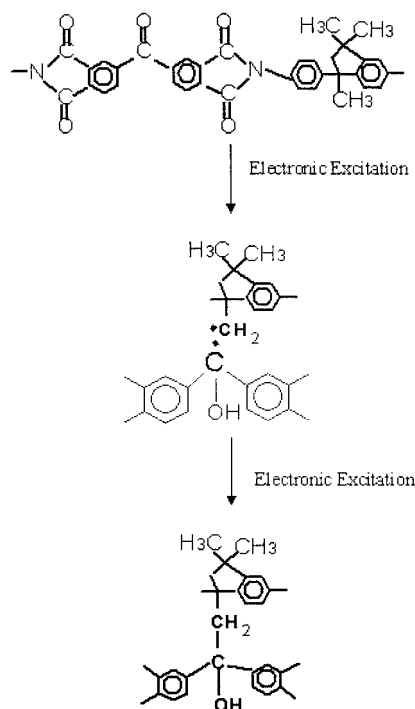| Functional group	Critical ion fluence (H$^+$/cm^2)
CH stretching of aliphatic methyl	5×10^{13}
C=O stretching of benzophenone carbonyl	1×10^{14}
C=O stretching of imide I carbonyl	3×10^{14}
C=C stretching of *para*-disubstituted aromatic ring	6×10^{14}

Figure 7 Potential crosslinking reaction mechanism attributed to the benzophenone C=O during H⁺ ion irradiation of Matrimid®.

methyl groups on the same carbon and mostly methane is released.[48] In vinyl polymers such as poly(vinyl chloride) and poly(vinylidene difluoride), HCl and HF were emitted.[49] Therefore, it is probable that methane was released when Matrimid®, which has two CH_3 on the same carbon atom, was irradiated with H⁺ at 450 keV, where the predominant mechanism of energy loss is once again electronic. H⁺ ion irradiation may

cause the formation of a radical methyl CH_3 and macromolecular radical along the Matrimid® backbone. Finally, hydrogen abstraction of macromolecular radicals by methyl radicals, which occurs only on a neighboring chain CH_3, could lead to a crosslink formation with the release of methane. Therefore, a possible reaction mechanism, which is attributed to the cleavage of the branched structure of the aliphatic methyl (CH_3) during the ion irradiation of Matrimid® with H⁺ ions, is shown in Figure 6.

Mechanism of crosslinking involved with benzophenone C=O

A decrease in the normalized area of the benzophenone C=O band was observed at ion fluences of 1×10^{14} H⁺/cm² or greater. As ion fluence is increased from 1×10^{14} to 3×10^{15} H⁺/cm², the normalized area of the benzophenone C=O band decreases from 0.96 to 0.60 (see Fig. 5). At fluences up to 5×10^{13} H⁺/cm², the presence of crosslinking in the irradiated film might be attributed to the cleavage of the branched structure of aliphatic methyl CH_3. At higher fluences, degradation of the benzophenone C=O may also contribute to the presence of crosslinking in the irradiated Matrimid® films. The crosslinking mechanism of benzophenone-containing polymers including polyimides under UV irradiation has been reported in detail.[50–53] For UV-induced crosslinking, the presence of the benzophenone moiety and suitable hydrogen donors along the polymer backbone are required.[50,51,53] Matrimid® has both benzophenone and hydrogen donor (aliphatic methyl CH_3) reactive groups that are similar to the polyimides reported in the literature. Therefore, the crosslinking of the Matrimid® after H⁺
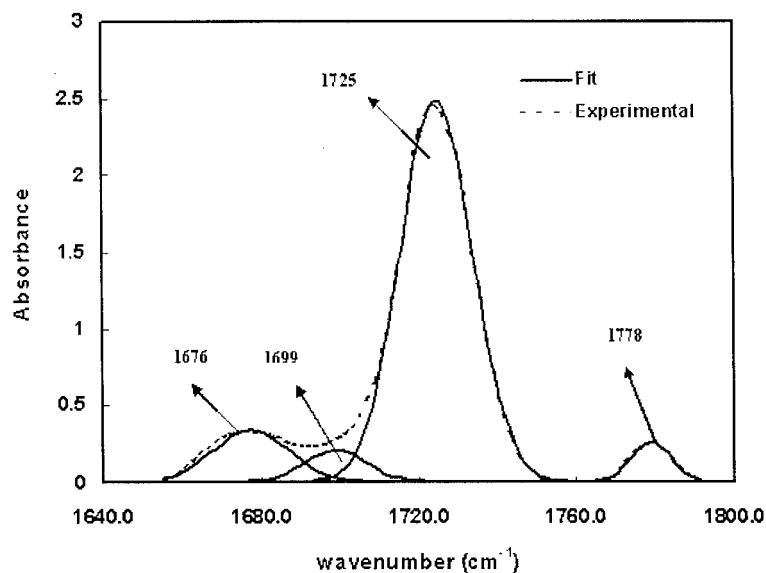

Figure 8 Curve-resolved infrared spectrum of virgin Matrimid® film, recorded at room temperature in the range from 1650 to 1800 cm⁻¹.

ion irradiation may result partially from degradation of the benzophenone C=O. A proposed crosslinking mechanism involving benzophenone C=O is shown in Figure 7 and is based on a mechanism reported in the literature for UV-induced crosslinking of similar polyimides.[50–53] Upon H$^+$ ion irradiation, the benzophenone was excited to its singlet state followed by intersystem crossing to the triplet state. The triplet benzophenone can abstract hydrogen from a donor, generating two radicals that subsequently couple and form a crosslink between chains. As for the hydrogen donor, the single aliphatic methyl CH$_3$ group is more likely to be the hydrogen donor than the gemdimethyl CH$_3$ groups because of steric effects. Because the efficiency of crosslink formation at the benzophenone C=O reactive sites is low, usually on the order of 0.03,[51] it is difficult to observe a change in OH stretching vibration in FTIR.

Rearrangement of imide carbonyl of Matrimid$^®$ after H$^+$ ion beam irradiation

Figure 8 shows an expanded spectrum from 1650 to 1800 cm^{-1} of the virgin Matrimid$^®$ films that was transferred into a curve fitting using four Gaussian bands. There are three major bands attributed to the benzophenone C=O at 1676 cm^{-1}, the asymmetric stretching C=O at 1725 cm^{-1}, and the symmetric C=O at 1778 cm^{-1}, which are distinct and obvious. However, it appears that there is one other band envelope at about 1699 cm^{-1}. Moreover, curve fitting used in the restricted C=O region for 10 virgin Matrimid$^®$ films indicated that four Gaussian bands are necessary to fit the experimental data well. Interchain imide has frequently been proposed as side products in imidization.[54,55] However, it cannot be readily identified by FTIR because of a very low concentration. The band at 1699 cm^{-1}, which is difficult to observe independently in the FTIR spectrum of virgin Matrimid$^®$ (Fig. 2), may correspond to overlapping of CO–NR–CO and Aryl–CO–OH of the interchain imide. This assignment can be further verified by the presence of a weak peak around 3540–3500 cm^{-1} attributed to OH stretching vibration[56] as shown in the FTIR spectrum of the virgin Matrimid$^®$ (Peak 7 in Fig. 2).

Figure 9 shows the expanded spectra from 1650 to 1800 cm^{-1} of the Matrimid$^®$ films irradiated at ion fluences of 6×10^{14} [Fig. 9(a)], 9×10^{14} [Fig. 9(b)], and 2×10^{15} H$^+$/cm^2 [Fig. 9(c)], which are analogous to the virgin spectra shown in Figure 8. A comparison of Figure 8 and Figure 9 shows that the band at 1699 cm^{-1} became broader and the intensity of this band increased as ion fluence increased from 6×10^{14} to 2×10^{15} H$^+$/cm^2. In addition, the intensity of the imide I C=O at 1725 cm^{-1} decreased with increasing ion fluence. Finally, there was a slight shift of the band at 1699 cm^{-1} to 1708 cm^{-1} at ion fluences up to 6×10^{14}
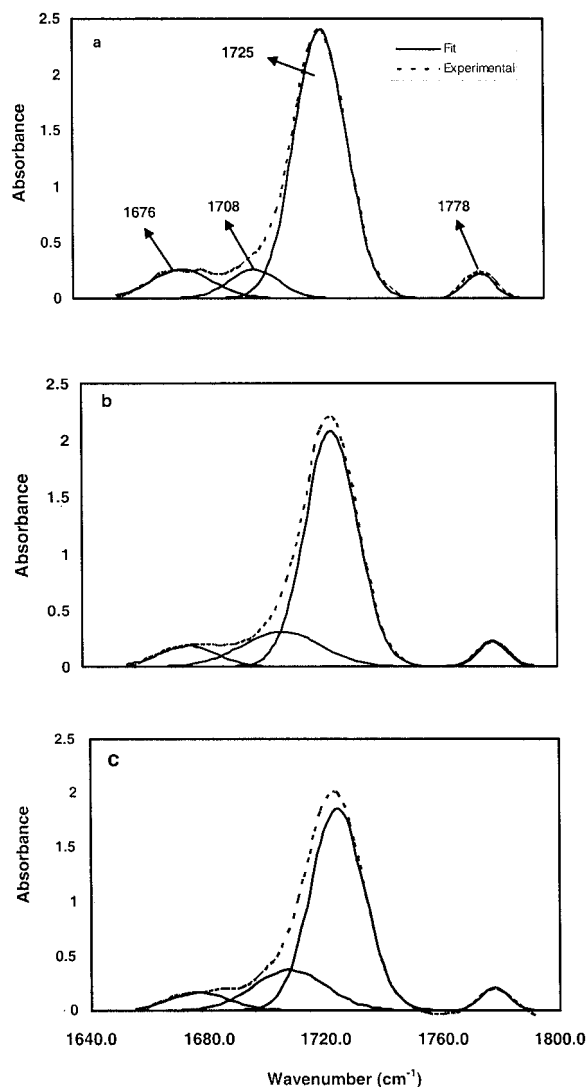

Figure 9 Curve-resolved infrared spectra of Matrimid$^®$ films irradiated with H$^+$ ion at ion fluence of 6×10^{14} (curve a), 9×10^{14} (curve b), and 2×10^{15} H$^+$/cm^2 (curve c), recorded at room temperature in the range from 1650 to 1800 cm^{-1}.

H$^+$/cm^2. Therefore, H$^+$ ion irradiation destroys the imide group and leads to the rearrangement of the imide C=O. This would transform the imide C=O into a new kind of C=O that could result in a shift in the peak at 1699 cm^{-1}.

To further investigate H$^+$ ion irradiation–induced rearrangement of the imide C=O, the difference infrared spectra of the irradiated Matrimid$^®$ films are given in Figure 10. The difference infrared spectra were generated by digitally subtracting the spectra of virgin Matrimid$^®$ films from those of corresponding irradiated Matrimid$^®$ films on a 1 : 1 basis assuming no change in thickness of the samples after irradiation.

In Figure 10, a noticeable positive peak at about 1708 cm^{-1} and the negative peak at 1725 cm^{-1} are observed in the C=O region for all of the difference spectra. Based on the above discussion, the negative
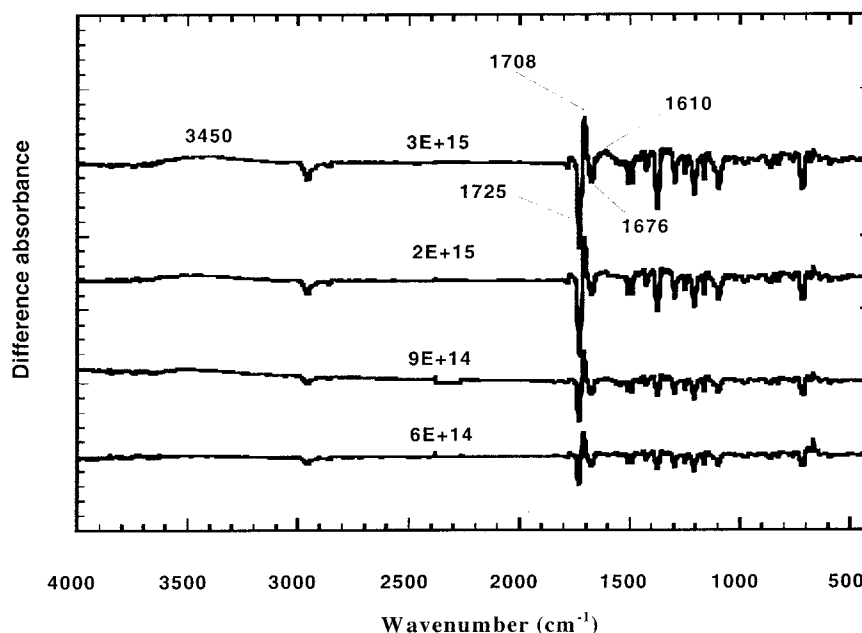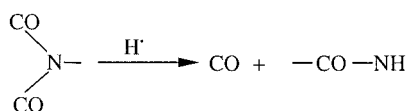
Figure 10 Difference FTIR spectra between irradiated Matrimid® films and corresponding virgin Matrimid® films.

peak at 1725 cm^{-1} can be attributed to breaking of the imide C=O band at 1725 cm^{-1} induced by irradiation. Further, the positive peak at 1708 cm^{-1} is attributed to the formation of the new C=O band at 1699–1708 cm^{-1} and shift of the absorption peak at 1699 cm^{-1} to 1708 cm^{-1}. For higher ion fluence (at or beyond 9 × 10^{14}), the negative peak at 1725 cm^{-1} is observed and it decreased faster than the positive peak at 1708 cm^{-1} increased, suggesting the formation of the C=O at 1708 cm^{-1} only at the expense of some of imide C=O. Additionally, the NH stretching vibration is observed as a weak band at 3450 cm^{-1} and the C=O band characteristic of the amide group (–CO–NH–)[55,57,58] appears as a weak positive peak around 1610 cm^{-1} when the ion fluence is greater than 9 × 10^{14} H$^+$/cm^2. Broadening and weakening of the NH band at 3450 cm^{-1} are attributed to the hydrogen bonding between the NH group and the carbonyl group. All results may be attributed to transformation of the imide C=O at high dose into two kinds of C=O, one of which belongs to the amide group (–CO–NH–). The transformation of the imide C=O into the amide group C=O during ion irradiation has been reported in the literature and the following degradation reaction mechanism was proposed[58,59]:

$$
\begin{array}{c}
\text{CO} \\
\diagdown \\
\text{N–} \xrightarrow{\text{H}^{\boldsymbol{\cdot}}} \text{CO} + \text{–CO–NH} \\
\diagup \\
\text{CO}
\end{array}
$$

where H$^{\boldsymbol{\cdot}}$ denotes a radical produced by the ion irradiation. The method of imide C=O transformation into the C=O at 1699–1708 cm^{-1} cannot be confirmed here. A detailed comparison of the impact of ion irra-

diation on several structurally similar polyimides will be included in a future submission.

CONCLUSIONS

A series of freestanding Matrimid® films was irradiated with 450 keV H$^+$ ions at fluences ranging from 7 × 10^{12} to 3.0 × 10^{15} H$^+$/cm^2. FTIR and dissolution studies were used to probe the effect of H$^+$ irradiation on the chemical structure of the Matrimid® films. FTIR analysis of the samples after ion irradiation indicated that the aliphatic methyl (CH$_3$) bond and the benzophenone C=O were more sensitive to ion irradiation and began to degrade at ion fluences of 5 × 10^{13} and 1 × 10^{14} H$^+$/cm^2, respectively. The imide groups and the *para*-disubstituted aromatic ring were both more resistant to ion beam irradiation and began to degrade at ion fluences of 3 × 10^{14} and 6 × 10^{14} H$^+$/cm^2, respectively. At very low ion fluences (below 5 × 10^{13} H$^+$/cm^2), H$^+$ ion irradiation resulted in little or no crosslinking of the Matrimid® samples so that the irradiated films could be totally dissolved in solvent. For ion fluences of 5 × 10^{13} H$^+$/cm^2, ion irradiation led to degradation only of CH$_3$ which contributed to the partial crosslinking of the irradiated Matrimid® films. Also the benzophenone C=O may provide reactive sites for H$^+$ ion irradiation-induced crosslinking. For higher ion fluences (≥6 × 10^{14} H$^+$/cm^2), both the degradation of the *para*-disubstituted aromatic ring and the rapid degradations of CH$_3$, benzophenone C=O, and the imide groups, which contributed to the high level of crosslinking of the irradiated Matrimid®, were observed. In addition, H$^+$ ion irradiation of ion fluence higher than 9 × 10^{14} H$^+$/cm^2

appears to result in the transformation of the imide I C=O to a polyamide.

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