

FT-Raman Studies of a Range of Polyimides Subjected to High-Energy Radiations at Room and Elevated Temperatures

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ABSTRACT: A range of polyimides have been subjected to electron beam radiolysis at different temperatures. These polyimides were chemically designed to suit space applications, being either transparent or having groups which provide oxidation resistance. The structural changes that occur in the polyimides, when subjected to electron beam irradiation doses up to 18.5 MGy and up to temperatures close to their glass transition temperatures, were studied using FT-Raman spectroscopy. The range of polyimides studied in-

cluded a series of perfluoropolyimides, a silicon-modified polyimide, and Ultem. The changes in the Raman peak intensities of the different groups indicated scission reactions involving the imide rings and ether linkages. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1575–1582, 2006

Key words: FT-Raman; transparent polyimides; e-beam radiolysis; degradation

INTRODUCTION

Polymers used in space and nuclear power plants are constantly exposed to high-energy radiations. Of the polymers utilized in these applications, aromatic polyimides are among the most stable towards radiation damage, and only at high doses/temperatures do they show evidence of any chemical or physical change.^{1–6} In these polyimides, the imide groups provide the linkage between the dianhydride and diamine units, while within these units the aromatic groups can be linked through a variety of groups, including methylene, ether, carbonyl, and isopropylidene.

The concentration of the aromatic groups in the polymer play an important role in determining stability to high-energy radiations and temperature, because aromatic groups provide protection against structural damage.¹ This protective effect is reported to occur via the ability of the aromatic groups to degrade the absorbed energy to heat through their manifolds of vibrational states.^{7,8}

The properties of Kapton and Ultem, two of the best-known and most studied commercial polyimides, have been reported to be little affected by high-energy radiations at relatively low doses at ambient temperature.⁹ Carbon monoxide and carbon dioxide are the principal gases reported to be evolved on radiolysis of Kapton,¹⁰ indicating that radiation damage involves a breakdown of the imide rings. The radiolysis of Ultem at room temperature has also been reported^{5,6,11} to involve imide ring degradation, as well as ether bond scission and reactions at the isopropylidene linkages in this polymer. Ultem also undergoes net crosslinking on radiolysis, but the gel dose is very high (>10 MGy^{5,12}).

Several previous studies have utilized infrared spectroscopy to identify the groups in polyimides, which are the most sensitive to high energy radiation damage on radiolysis at ambient temperature. Long and Long¹¹ have reported the changes in the IR spectrum of Ultem following its exposure to electron beam radiation to very high doses—up to 60 MGy. They observed an increase in the relative intensity of the phenyl C—H band at 3060 cm⁻¹, a decrease in the intensity of the di- and tri-substituted phenyl bands (775–920 cm⁻¹), and an increase in the intensity of the monosubstituted phenyl band (680 cm⁻¹). They concluded that chain scission occurred on radiolysis with the scissions adjacent to the aromatic groups. At 60 MGy, they also observed a decrease in the weak imide band at around 725 cm⁻¹.

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Mishra et al.¹³ found no new IR resonances on electron beam irradiation of an aromatic polyimide (detailed structure unknown) to a relatively low absorbed dose of 23 kGy at ambient temperature, but they reported increases in the relative intensities of some phenyl bands. Fink et al.¹⁴ have also studied the FTIR spectra of a polyimide (detailed structure unknown) following exposure to an ion beam. They concluded that the degradation process occurred in multiple stages. The early stage is characterized by little loss of the oxygen and nitrogen from the polymer, followed by a second stage during which the loss of groups containing these elements is significantly more facile. These observations point to a G-value for breakdown of the imide rings that is dose dependent.

Finally, Lui et al.¹⁵ have reported a study of the γ -radiolysis of a series of aromatic polyimides containing the 6FDA group in the dianhydride units and three or more aromatic groups in the diamine units, with two ether groups and a variety of other linkages. They found no new absorption bands in the IR spectra of the polymers following irradiation to doses of up to 14 MGy at ambient temperature. The molecular weights of the polymers decreased with dose and there was a drastic reduction in the mechanical properties at 14 MGy. At an absorbed dose of 28 MGy the polymers were brittle, with molecular weights in the range 3–7 kg mol⁻¹.

Kapton is more stable towards radiation damage¹⁰ than Ultem because of its higher aromatic group con-

TABLE I
Elemental Composition of UBE-1, UBE-2, PMPD/PDA, and Kapton Expressed as Atom Ratios Relative to Nitrogen

Sample	¹² C	¹⁶ O	¹⁴ N	²⁸ Si	¹⁹ F
UBE-1	10	2	1	0.2	–
UBE-2	10	2	1	–	2
PMDA/PDA	6	2	1	–	–
PMDA/ODA (Kapton)	11	2.5	1	–	–

centration. Hence it has been used extensively in radiation environments. However, despite its low sensitivity to high-energy radiation, its intense brown color is a disadvantage in some applications.¹⁶ Thus, alternative, less-colored polyimides have been developed.^{16,17}

It is important that polymers used in space vehicles, as protective coatings or in nuclear facilities as insulators, etc, are able to retain their properties for an extended lifetime, which may be as long as 20–30 years. Thus, an understanding of the damage which occurs on radiolysis of these materials is of considerable importance. We have previously reported studies on the radiolysis of some “transparent” polyimides^{2–4} in which we have examined the changes in the optical, mechanical, and surface properties of these polymers.

In this study, we examine the sensitivities of several transparent polyimides to high-energy electron beam radiation at room and elevated temperatures and at radiation doses up to 18.5 MGy. FT-Raman spectroscopy was used to monitor the changes in the linking-group concentrations. The polymers have much lower absorbances than Kapton at the maximum density of emitted solar radiation that is at 500 nm.¹⁸

EXPERIMENTAL

Samples

Transparent polyimide films, ODPA/ODA, ODPA/DAB, 6FDA/ODA, were prepared at the NASA-Langley Laboratory, and their structures are shown in Figure 1, along with that of Ultem which was also studied. These polymers are all pale yellow in color.⁴ In addition to these polyimides, the UBE Company, Japan, supplied two other polyimides, labeled UBE-1 and UBE-2, for the study. UBE has not released the structures of these polymers, but their elemental compositions are presented in Table I. One of the polymers contains silicon (UBE-1) to provide resistance to oxidation in the oxygen atom atmosphere of low earth orbit and the other is fluorinated. They are both more colored than the other transparent polyimides and are more colored than Ultem.

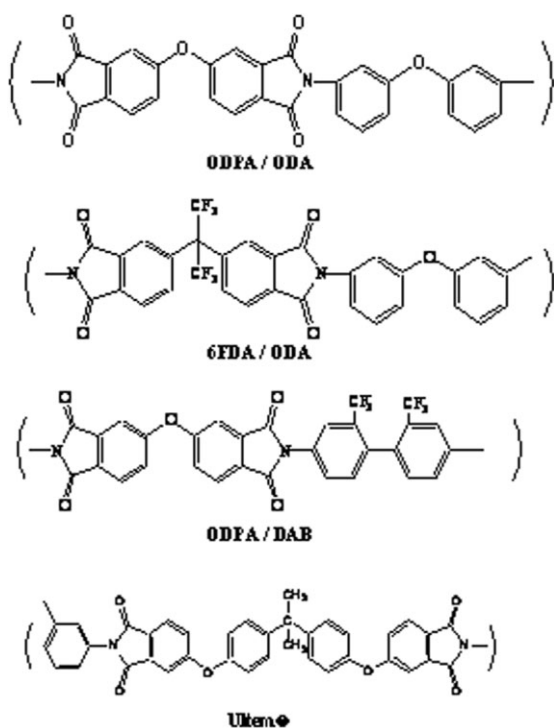


Figure 1 Chemical structures of the transparent polyimides.

The thicknesses of the films were: Ultem, 0.078 ± 0.010 mm; ODPA/ODA, 0.041 ± 0.009 mm; ODPA/DAB, 0.049 ± 0.01 mm; 6FDA/ODA, 0.039 ± 0.007 mm; UBE-1, 0.051 ± 0.008 mm; and UBE-2, 0.049 ± 0.005 mm.

Electron beam radiolysis

The samples were irradiated at the Japan Atomic Energy Research Establishment (JAERI) in Takasaki, Japan using an electron accelerator producing electrons with an energy of 1 MeV and a current of 4 mA. Under these conditions the absorbed doses can be taken to be uniform through the samples.¹⁹

The samples were placed in a custom-made irradiation chamber, which has been described previously,²⁰ and wrapped in an aluminum foil to provide good thermal contact with the thermostatted metal base of the chamber. The temperature of the chamber was controlled via a Chromel–Alumel thermocouple placed in the metal base. The chamber was continuously flushed with helium at ambient pressure and the samples were irradiated to various doses. Following irradiation, the samples were allowed to rest in the chamber to equilibrate to room temperature under helium before being exposed to the atmosphere.

The radiation dose rate was measured using strips of cellulose triacetate dosimeter film (CTA). The optical densities of the exposed CTA films were measured relative to an unexposed film using a CTA film reader (FDR-01-NHV, NISSIN-High Voltage, Kyoto, Japan), and the dose rate was calculated from appropriate calibration data. The dose rate at the sample position was ~ 3 kGy s^{-1} .

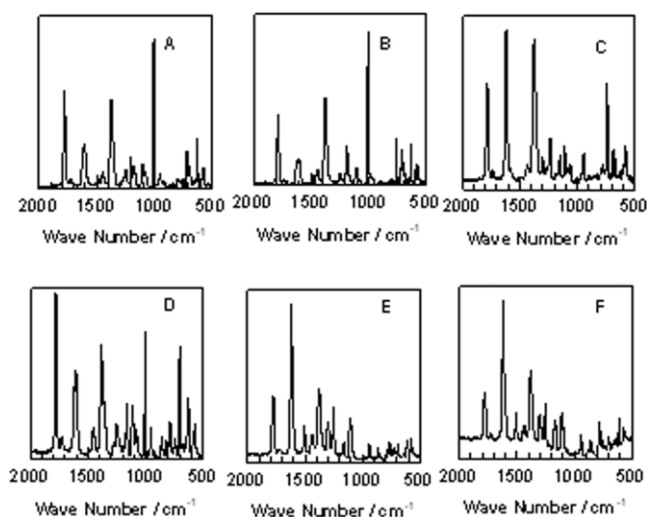


Figure 2 Raman Spectra of (A) ODPA/ODA, (B) 6FDA/ODA, (C) ODPA/DAB, (D) Ultem, (E) UBE-1, and (F) UBE-2.

TABLE II
Assignments for the Peaks of Interest in the Raman Spectra

Frequency (cm^{-1})	Functional group
3148–3044	C—H phenyl
1780	C=O
1655–1590	C=C phenyl
1326–1417	C—N
1004	Ar—O—Ar (in diamine)
740–750	CF ₃
725	Imide

FT-Raman

Raman spectra of the irradiated films were obtained at ambient temperature using a PerkinElmer 2000 spectrometer fitted with a 400 mW, 1064 cm^{-1} laser source. The spectra were accumulated for 50 scans at a resolution of 4 cm^{-1} over the spectral range 500 – 4000 cm^{-1} at ambient temperature.

RESULTS AND DISCUSSIONS

The FT-Raman spectra of the unirradiated polyimides over the wave number range 500 – 2000 cm^{-1} are presented in Figure 2. In addition to the bands shown in Figure 2, all of the spectra contained aromatic C—H bands. The more intense bands of interest in the spectra have been assigned using information available in the literature, and the assignments are presented in Table II. In the spectra the relative intensities of the various peaks for the different polyimides are sensitive to the presence and location of substituents. The band positions for the various stretching vibrations are C—H ≈ 3080 cm^{-1} , C=O at ≈ 1780 cm^{-1} , C=C at ≈ 1620 cm^{-1} , and C—N at ≈ 1380 cm^{-1} . These bands are intense and relatively well resolved in the spectra. The aromatic ring breathing vibration for a meta-substituted phenyl ring is strong in Raman spectra and is found at ≈ 1000 cm^{-1} . Unfortunately, the stretching bands for the ODPA aromatic ether linkages at ≈ 1250 cm^{-1} and the C—F bands at ≈ 1150 – 1300 cm^{-1} overlap other bands, thus inhibiting accurate quantification of small differences in the intensities of these bands. Much of the bending spectral region from 500 to 900 cm^{-1} is also compromised by band overlap.

The shape of the C=C band at ≈ 1620 cm^{-1} varies from polyimide to polyimide, reflecting substitution effects, but the shapes of the other major bands remain similar although the peak positions for the bands do vary slightly.

The chemical structures of UBE-1 and UBE-2

Since detailed chemical structures for UBE-1 and UBE-2 have not been released, the elemental analysis

and Raman spectra of these materials have been used to shed some light on the structures of the polymers. From the elemental analysis of the polymers given in Table I, the ratio of O/N in the two polymers is seen to be 2. This ratio suggests that all of the oxygen and nitrogen atoms are located in the imide groups. Since the oxygen atoms in the imides are present in the two carbonyl groups, the C/N ratios of 10 indicate that there are, on average, eight other carbons per nitrogen atom in the structures. In an aromatic polyimide, the minimum possible number of aromatic carbon atoms per imide ring is six (e.g., for PMDA/PDA where PMDA is pyromellitic dianhydride and PDA phenylene diamine) This number increases by three for each additional aromatic ring in either the dianhydride or diamine of the polymer.

Thus the elemental analysis suggests that UBE-1 and UBE-2 are either substituted PMDA/PDA or copolymers or blends with the polymer chains comprised principally of PMDA and PDA. Inoue et al.²¹ of the UBE Company, have reported studies on polyimide copolymers noting their chemical resistance in corrosive environments.

The proposed composition of UBE-1 and UBE-2 is supported by the appearance of two carbonyl bands in the Raman spectra of UBE-2 (see Fig. 2), indicating that two dianhydrides may be present, and by the more intense coloration of these polymers compared to the other polyimides studied here. The Raman spectrum of UBE-1 has a small band at $\approx 2900\text{ cm}^{-1}$ consistent with the presence of aliphatic C—H groups, but no corresponding band is present in UBE-2, which is fluorinated. In addition, the presence of the band at 1505 cm^{-1} in the spectra for both UBE-1 and UBE-2 is consistent with the presence of PMDA units,^{18,22} and the absence of a band at $\approx 1000\text{ cm}^{-1}$ indicates that the aromatic groups are not meta-substituted. Unfortunately, the locations of the groups containing silicon and fluorine in UBE-1 and UBE-2 respectively, have not been identified.

Radiolysis studies at ambient temperature

Following general similarity of the electron-beam radiolysis to the photoinduced changes, one can expect substantial role of the anharmonic electron-phonon anharmonicity in these polymers. This is shown for polymers with similar combination of the chemical bonds using nonlinear optical methods.²³ This anharmonicity may lead to substantial electron charge transfer, manifesting in charge density redistribution and changes to the FTIR-Raman modes, manifesting in broadening of the corresponding FTIR-Raman spectra.

The previous FTIR studies of the radiolysis of polyimides at ambient temperature, along with the studies on gas evolution,¹⁰ have identified the imide rings in

the polyimides as the main focus of the radiation chemistry, particularly at high doses. Since the C=C, C=O, and C—N groups in the polyimides are Raman sensitive, Raman spectroscopy provides an excellent tool with which to monitor imide degradation. However, the bands for C—H and C—F stretching are relatively weak by comparison, so that the loss of these groups is less easily monitored by Raman spectroscopy.

The changes in the relative areas of the absorption bands (ΔA) for the groups of interest in the spectra can be quantified using the following equation:

$$\Delta A = \frac{[A_{\text{group}}/A_{\text{phenyl}}]_{D=D} - [A_{\text{group}}/A_{\text{phenyl}}]_{D=0}}{n_{\text{group}} \times [A_{\text{group}}/A_{\text{phenyl}}]_{D=0}}$$

Here A_{group} = the area of the band for the functional group under consideration; A_{phenyl} is the area of the aromatic C=C band at $\approx 1620\text{ cm}^{-1}$, which has been used as the reference peak; D is the radiation dose, and n_{group} is the number of linkages in the polymer repeat units which contribute to the band (e.g., 4 for C=O, 6 for C—N and C—F). By indexing the areas to the aromatic band, which was considered to be the most stable towards radiation damage, any laser intensity or sample thickness variations are taken into account. In addition, expressing ΔA as the ratio of the change in the relative band intensity to that at zero dose eliminates any contributions from Raman scattering factors. Thus, a negative value of ΔA for a particular band (linkage or group) is indicative of a decrease in the concentration of that group relative to that of the phenyl groups present in the polyimide.

On radiolysis of the polyimides, the relative intensities of the C=O, C—N, and C—H bands were found to change with increasing dose. In Figure 3, a set of typical results for ΔA versus dose are shown for ODPA/ODA following radiolysis at room temperature. The figure shows that the values of ΔA for the C—H, C=O, and C—N stretching vibrations appear to increase slightly with dose up to a dose of 9.25 MGy, but between 9.25 and 18.5 MGy the values decrease. However, the changes up to 9.25 MGy are within the accuracy of the peak area measurements, indicating that the radiation has little effect on the phenyl and imide groups in ODPA/ODA at room temperature up to a dose of 9.25 MGy. Ultem showed a behavior similar to that of ODPA/ODA at room temperature. The behaviors of these polymers agrees with the observations of Liu et al.¹⁵ and Fink et al.¹⁴ over this dose range, with little effect of the radiation on the polymer structure at low dose, but a more significant effect at doses around 20 MGy.

By contrast with the intensity changes for the imide bands, the ΔA values for the ring breathing vibrations of the meta-substituted phenyl groups, the aromatic

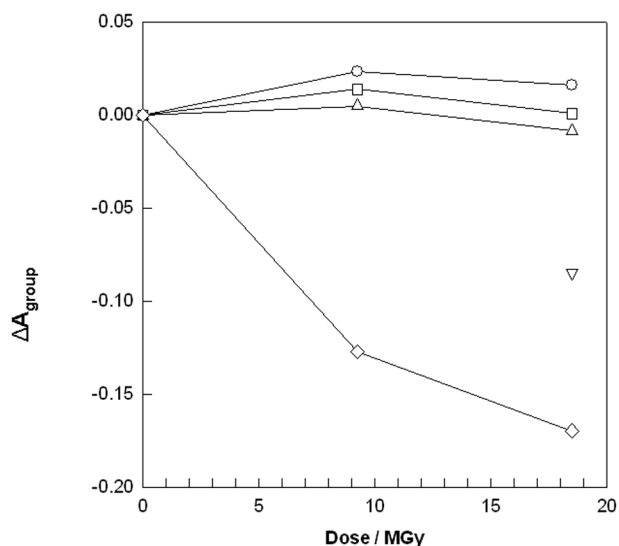


Figure 3 ΔA_{group} versus radiation dose for radiolysis of ODPA/ODA at room temperature. (○) C—H; (□) C=O; (△) C—N; (◇) Ar—O diamine; (▽) Ar—O diacid.

ether groups in the ODA units of ODPA/ODA, fall continuously with increasing dose (see Fig. 3). Thus, up to a dose of 18.5 MGy, the ODA ether units are the major centers for radiation damage in ODPA/ODA, and not the imide groups. The relative intensity of the aromatic ether band at $\approx 1240 \text{ cm}^{-1}$ also falls with dose (see Fig. 3), but by less than that for the ODA band at $\approx 1000 \text{ cm}^{-1}$, perhaps indicating that the ether linkage in ODPA is less sensitive to radiation damage than that in ODA. However, it should be noted that quantification of this ODPA ether band is prone to significant error arising from band overlap and the much greater half-width of this band in the spectra compared with the band at 1000 cm^{-1} , for example.

In a previous study,¹⁹ we reported a decrease in the elongation and stress at break for radiolysis of ODPA/ODA at room temperature. The Raman spectra indicate that scission of the polymer chains at the ether linkages is principally responsible for these changes in mechanical property. This observation is consistent with the fact that cleavage of one ether bond in the repeat unit of the polymer will lead to a reduction in the polymer molecular weight, whereas at least two bonds must be broken in an imide unit to produce a corresponding decrease.

When ODPA/ODA is irradiated at room temperature, a small peak grows into the Raman spectrum at 2988 cm^{-1} , as demonstrated in Figure 4. A similar peak was also found to grow with increasing dose in the spectra of 6FDA/ODA and Ultem, but this band was not observed to grow in for the other polymers. A similar small peak can be observed to grow in the FTIR spectra reported by Lui et al.¹⁵ (their Fig. 6) for an irradiated 6FDA-based polyimide which contains

Ar—O diamine linkages. This peak has been assigned to a C—H stretch in a nonaromatic structure. Since ODPA/ODA and 6FDA/ODA contain no aliphatic protons initially, such structures can only be formed by a loss of some aromatic groups. Nonaromatic groups could be formed following scission of an aromatic ether bond if, for example, one of the radical fragments of bond scission reacted with an adjacent aromatic group in the polymer to form a cyclohexadiene-type structure. However, cyclohexadiene-type structures have not been observed⁵ in the ^{13}C -NMR spectra of Ultem following γ -radiolysis to a high dose at room temperature. Alternatively, nonaromatic structures could be formed as a result of phenyl ring opening reactions on radiolysis. The formation of aliphatic structures, with an overall loss of double bonds, could explain the small initial increases in the relative band areas for the imide groups in the spectra of the polymers following radiolysis at room temperature.

If the ODA units in ODPA/ODA are replaced by DAB units, the vulnerability of the imide groups to radiation damage increases for radiolysis at room temperature (see Fig. 5). This increase in the sensitivity of the imide units may be rationalized in terms of the greater rigidity of the DAB units compared to the ODA units and the potential for any fluorine atoms released from the DAB units to undergo secondary chemistry. In our previous study of the mechanical properties of the polyimides,¹⁹ we observed that both ODPA/ODA and ODPA/DAB undergo ductile failure, and that the decrease in the tensile modulus for ODPA/DAB is greater than for ODPA/ODA following radiolysis at room temperature. These observations would be consistent with greater overall main-chain scission of ODPA/DAB during radiolysis, as shown to be the case through the Raman study.

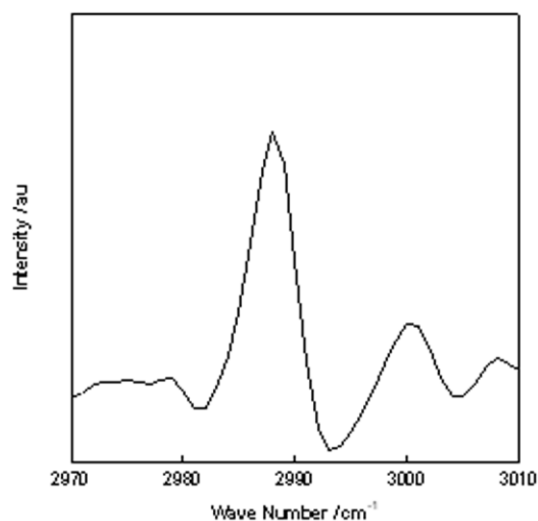


Figure 4 The Raman spectrum of the species which appears on radiolysis of ODPA/ODA at room temperature.

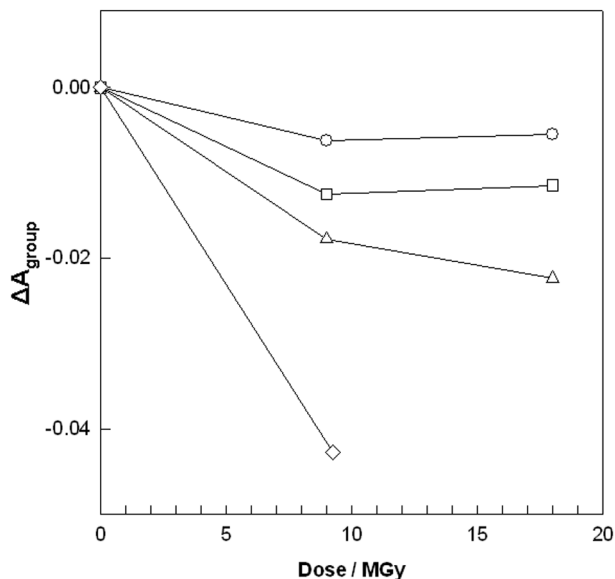


Figure 5 ΔA_{group} versus radiation dose for radiolysis of ODPA/ODA at room temperature. (○) C—H; (□) C=O; (△) C—N; (◇) C—F.

When the ether linkage in the dianhydride unit of ODPA/ODA is replaced by the fluorinated isopropylidene linkage in 6FDA/ODA, both the C=O and C—N groups in the polymer are more vulnerable to radiation damage than the corresponding groups in ODPA/ODA and ODPA/DAB (see Fig. 6). However, it is again the ether linkages which are the most susceptible to bond scission, with ΔA for the Ar—O bonds being almost twice that for these bonds in ODPA/ODA. In our study of the material properties

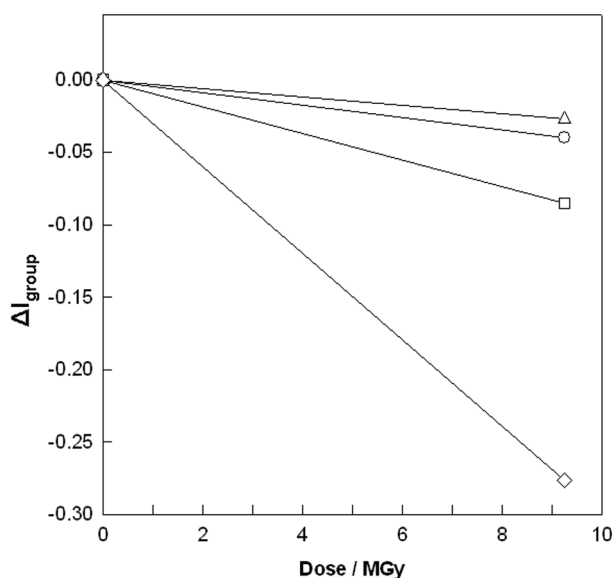


Figure 6 ΔI_{group} versus radiation dose for radiolysis of ODPA/ODA at room temperature. (○) C—H; (□) C=O; (△) C—N; (◇) Ar—O diamine.

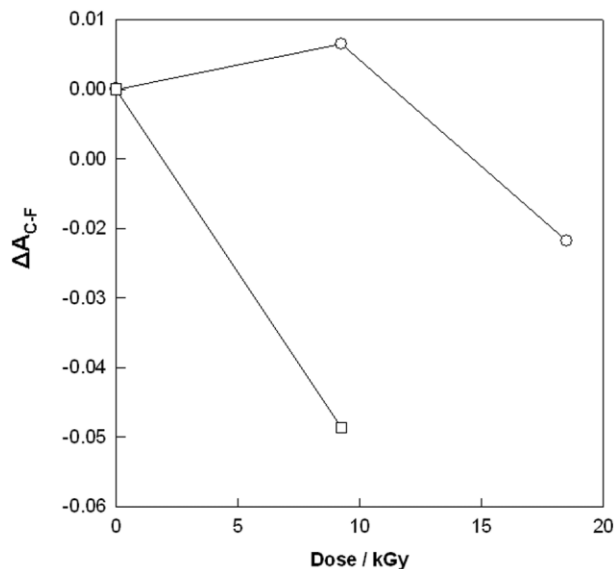


Figure 7 ΔA_{CF_3} versus radiation dose for radiolysis of (○) ODPA/DAB and (□) 6FDA/ODA at room temperature.

of 6FDA/ODA,¹⁴ we observed that it undergoes brittle fracture, indicating that the polymer chains are more rigid than its ODPA counterpart. In addition, the change in the tensile modulus on radiolysis of 6FDA/ODA was significantly greater than that for ODPA/ODA. The greater rigidity of the copolymer chains and the breakdown of the —CF₃ groups may account for the observed enhanced bond scission for the 6FDA-based polyimide.

The trifluoromethyl bands near 750 cm⁻¹ can be used to monitor the breakdown of these groups in both ODPA/DAB and 6FDA/ODA. Figure 7 shows that the C—F bonds in the trifluoromethyl groups degrade substantially on radiolysis, with the groups associated with the fluorinated isopropylidene units of 6FDA being more sensitive to degradation than those attached directly to the aromatic rings in DAB. While a breakdown of the fluorinated isopropylidene groups could lead directly to main chain scission in the 6FDA based polymer,^{5,6} it is less likely that a loss of the fluoromethyl groups in DAB would lead to a decrease in the chain length, since they are attached to a phenyl ring. These aromatic groups would also be expected to provide some protection for the trifluoromethyl groups against radiation degradation in ODPA/DAB.

The changes in the relative peak areas for C=O and C—N peaks relative to those for C=C for UBE-1 and UBE-2 on radiolysis at room temperature were small, even at a dose of 18.5 MGy, and were within the anticipated errors in the area measurements. The small area changes no doubt arise as a result of efficient degradation of absorbed energy by the aromatic groups in UBE-1 and UBE-2, which provide a measure of radiation protection for the imide and other linking

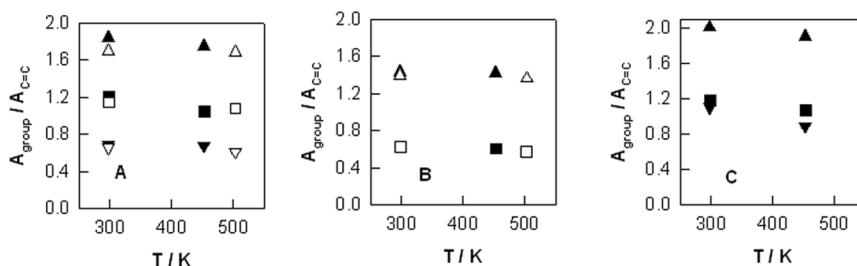


Figure 8 $A_{\text{group}}/A_{\text{C=C}}$ versus temperature for radiolysis of (A) ODPA/ODA; (B) ODPA/DAB; (C) 6FDA/ODA. (\square) C=O; (Δ) C=N; (∇) Ar-O diamine. Filled symbols 9.25 MGy; open symbols 18.5 MGy. (An estimate of the error in measurement of the peak areas is \tilde{n})

groups in the polymers. In this respect the behaviors of these two polymers are similar to the behavior of Kapton,^{9,10} which is much less sensitive to radiolysis than Ultem. The protective effect of neighboring aromatic groups is known to occur through both in-chain and interchain processes, which may explain why polyimides with a propensity to form higher donor-acceptor concentrations, and so are more colored, are less sensitive to radiation.

Radiolysis studies at elevated temperatures

The effect of radiolysis temperature on the extents of degradation of ODPA/ODA, ODPA/DAB, and 6FDA/ODA are demonstrated in Figure 8. In the figure the peak areas for the groups of interest in the Raman spectra of the polymers, relative to those for C=C groups in the spectra, are plotted against the radiolysis temperature for doses of 9.25 and 18.5 MGy.

The figure shows that for each of the polymers the relative Raman peak areas decrease for radiolysis at higher temperatures, indicating that the extent of degradation is higher at the higher temperature. A similar behavior was found for Ultem and UBE-1 and UBE-2, as demonstrated in Figure 9. However, the extent of the decrease in the relative peak areas for all of the groups were smaller for the latter two polymers than for Ultem and the other three polyimides, undoubtedly because of the higher level of protection by the aromatic groups in UBE-1 and UBE-2. This protective

effect of aromatic groups apparently provides stabilization even at high radiolysis temperatures.

For ODPA/ODA, ODPA/DAB, 6FDA/ODA, and Ultem the decreases in the relative peak areas generally fall in the range 2–10%, with the percentage change for the C=O peaks greater than those for the C=N peaks for each of the polymers. Decreases in the relative areas of peaks for the aromatic ether units of 8–10% were observed for ODPA/ODA, 6FDA/ODA, and Ultem, again indicating that the ether linkages are the most vulnerable to radiation damage.

Thus, for radiolysis at temperatures close to, but less than glass transition temperature (T_g), the dose dependencies for radiolysis of all of the polymers indicate a small extent of degradation up to a dose of 18.5 MGy. Thus, even at a dose 18.5 MGy at relatively high temperatures of 450–500 K, a clear majority of the imide and ether linkages (at least 85%) remain intact. So, these polyimides, including the transparent polyimides, continue to display very acceptable material properties over these high dose-high temperature ranges.

SUMMARY

The radiation sensitivities of three transparent polyimides have been compared with that of Ultem and two other polyimides with higher aromatic group concentrations. These sensitivities have been investigated at room temperature and at temperatures approaching

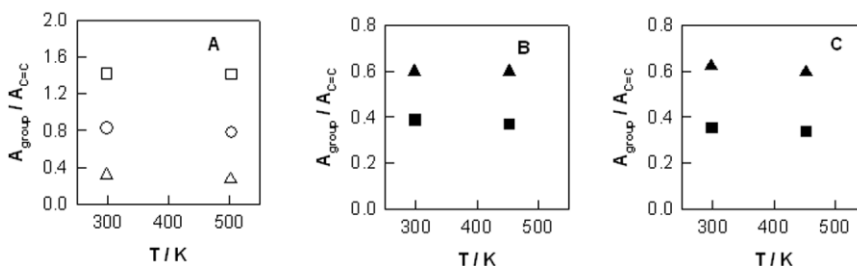


Figure 9 $A_{\text{group}}/A_{\text{C=C}}$ versus temperature for radiolysis of (A) Ultem; (B) UBE-1; (C) UBE-2. (A) ODPA/ODA; (B) ODPA/DAB; (C) 6FDA/ODA. (\circ) C-H; (\square) C=O; (Δ) C=N. Filled symbols 9.25 MGy; open symbols 18.5 MGy.

the T_g s of the polymers. The differences in the behaviors of these polyimides have been rationalized in terms of the chemical structures of the polymers.

All of the polymers studied exhibited only small changes in their chemical structure following radiolysis to 18.5 MGy over a range of temperatures between 298 and 503 K. The ODPa and 6FDA polymers were shown to undergo main chain bond scission on radiolysis, and the aromatic ether linkages were shown to be the most vulnerable of the linking groups present. Their overall radiation sensitivity was found to be similar to that of Ultem. In the polymers containing trifluoromethyl groups, irradiation resulted in a loss of these functional groups, but those groups attached directly to the aromatic rings were less sensitive. The two polymers containing a higher concentration of aromatic groups, UBE-1 and UBE-2, exhibited only small changes in their chemical structure compared to the other polyimides studied following radiolysis over the dose and temperature range studied.

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