

Electron irradiation effects on dynamic viscoelastic properties and crystallization behaviour of aromatic polyimides

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High dose rate electron beam irradiation effects on tensile properties, molecular motion and crystallization processes were studied for aromatic polyimides [UPILEX-BOARD (PI-I), LARC-TPI (PI-II), LARC-TPI 1500 (PI-III) and new-TPI (PI-IV)]. The radiation resistances of these polyimides were excellent, i.e. the strength and elongation at break were scarcely affected by irradiation up to 100 MGy. It was revealed from the dynamic viscoelastic measurements that PI-II has a network structure but PI-III is thermoplastic. By irradiation, the shear modulus above the glass transition temperature of PI-I and PI-II was increased. Also, the glass transition of PI-I, PI-II and PI-III shifted to higher temperature. The results from the isothermal crystallization for PI-IV indicated that crystallization is inhibited by irradiation. It was concluded that the polyimides used in this study have excellent radiation resistance and are crosslinked by non-oxidative irradiation.

(Keywords: aromatic polyimides; electron irradiation; tensile properties; molecular motion; isothermal crystallization)

INTRODUCTION

High performance aromatic polymers with skeletons composed of only aromatic units are expected to be the materials used in radiation fields, such as in space and fusion reactor environments. To be able to use materials in such fields, knowledge of their radiation damage and/or resistance is required. We have studied radiation deterioration of aromatic polymers with various chemical structures¹⁻⁴. Our results are summarized as follows: (1) radiation resistance depends strongly upon chemical structure. The order of radiation stability of aromatic units is aromatic imide > diphenyl ether, diphenyl ketone > aromatic amide > bisphenol F > bisphenol A > diphenyl sulphone; (2) radiation resistance is markedly affected by the irradiation environment, for instance, the presence or absence of oxygen during irradiation.

This information will aid the selection of materials to be used in radiation fields, and knowledge of whether radiation deterioration is caused by chain degradation or crosslinking completes the selection process. When the mechanical properties of two polymers deteriorate to the same extent using the same irradiation dose, the selection of a crosslinkable polymer is preferable, because the varying nature of polymeric materials results from the fact that they have high molecular weight.

Generally, whether a polymer undergoes chain degradation or crosslinking is evaluated by molecular weight or gel fraction measurements. These methods cannot be applied to almost all aromatic polymers since they are insoluble in organic solvents. We have attempted to obtain information on chain degradation or crosslinking from the changes in mechanical and dielectric relaxation behaviour for poly(ether-ether-ketone) (PEEK)^{2,3} and poly(4,4'-oxy-di-*p*-phenylene pyromellitic imide) (Kapton)⁴. We have studied four kinds of aromatic polyimides by means of viscoelastic measurement and thermal analysis to discover whether crosslinking or chain degradation occurs during non-oxidative irradiation.

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EXPERIMENTAL

Samples

The polymers used were UPILEX-BOARD® (RB-05, PI-I, Ube Industries Ltd), LARC-TPI® (PI-II, NASA), LARC-TPI 1500® (PI-III, Mitsui Touatsu Chemicals Inc.) and new-TPI® (PI-IV, Mitsui Touatsu Chemicals Inc.). PI-I is a stacking sheet of biphenyl tetracarboxylic acid dianhydride type polyimide UPILEX-R film. PI-II is a polymer obtained from the copolymerization of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3,3'-diaminobenzophenone, and PI-III is a modified polyimide of PI-II. They are non-crystalline polyimides.

PI-IV is a newly developed thermoplastic aromatic polyimide. (The details of the chemical structure have not yet been published.) This polyimide becomes non-crystalline by quenching from the molten state and turns into a semi-crystalline polymer by heat treatment above the glass transition temperature. The thickness of the samples was ~400 μm.

Irradiation and measurements

Specimens shaped into 10 mm width and 100 mm length were irradiated by 2 MeV electrons from a Dynamitron type accelerator in air. The dose rate was measured using a cellulose triacetate film dosimeter (5×10^3 Gy s⁻¹). To prevent an increase in temperature during irradiation, the specimens were wrapped in aluminium foil and attached with conductive adhesive onto a stainless steel irradiation table which was cooled

by a water jacket. With such a high dose rate of irradiation, the surface of the material undergoes radiation oxidation but below the surface the material is not oxidized.

The tensile test was performed on a strip ($10 \times 100 \text{ mm}^2$) using a cross-head speed of 200 mm min^{-1} at room temperature. Elongation at break was determined by dividing the overall displacement by the initial sample length (50 mm). The data used were the average and standard deviation of six specimens.

The mechanical relaxation behaviour of PI-I, PI-II, and PI-III was measured. The measurements were made on strips ($100 \times 10 \times 0.4 \text{ mm}^3$) in the temperature range -160 to 340°C by using a torsion pendulum type apparatus (RHESCA RD 1100 AD) at a frequency of $0.2\text{--}1 \text{ Hz}$. It is well known that the relaxation at the lowest temperature is affected by a trace of absorbed water^{2,5-8}; to remove this effect all specimens were dried on silica gel in a vacuum for 7 days.

Crystallization behaviour of PI-IV was measured by using a differential scanning calorimeter (DSC 7, Perkin-Elmer). The procedure for isothermal crystallization was as follows:

1. the sample was heated to 420°C and held at this temperature for 30 min to completely decay the remaining radicals;
2. the sample was then cooled to 30°C at a rate of $450^\circ\text{C min}^{-1}$, to obtain a non-crystalline sample;
3. heating was continued up to the crystallization temperature at a rate of $100^\circ\text{C min}^{-1}$, and then crystallization occurred isothermally till crystallization was complete. The heating curves were obtained by scanning at a heating rate of $20^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Radiation deterioration

Figures 1-3 show changes in the tensile strength and elongation at break as a function of dose for PI-I, PI-II and PI-III, respectively. The strength and elongation of PI-I decrease with dose, but the elongation remains $>35\%$ of the initial value after irradiation with 120 MGy. The deterioration behaviour of UPILEX-BOARD® is

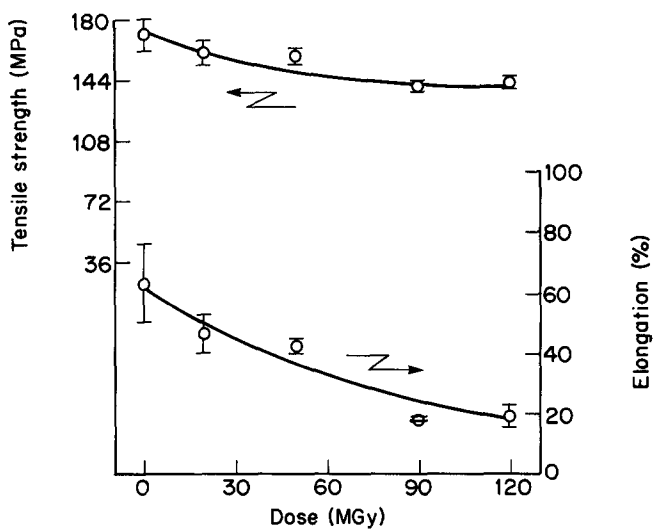


Figure 1 Change in tensile properties of PI-I (UPILEX-BOARD®) on electron irradiation

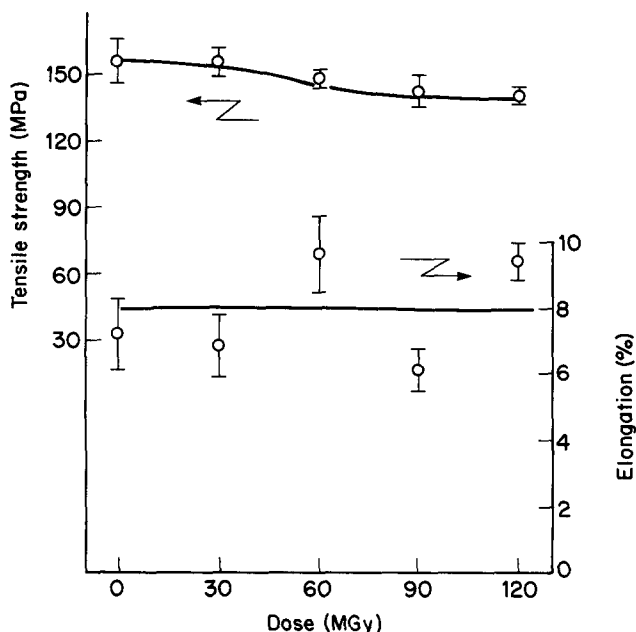


Figure 2 Change in tensile properties of PI-II (LARC-TPI®) on electron irradiation

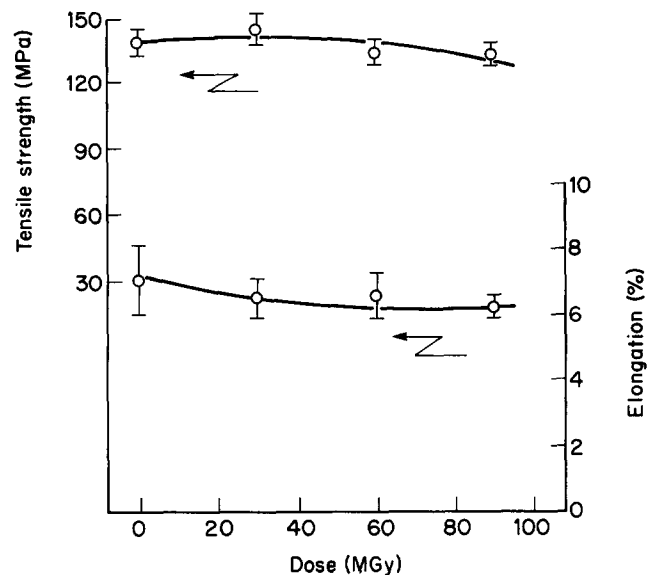


Figure 3 Change in tensile properties of PI-III (LARC-TPI 1500®) on electron irradiation

similar to that for UPILEX-R® film^{1,4}. The strength of PI-II and PI-III decreases slightly with dose but elongation is scarcely affected by irradiation. Consequently, these three polyimides have excellent radiation resistance. It has also been reported that PI-IV shows excellent radiation resistance⁹.

Radiation effects on mechanical relaxation

Figure 4 shows the temperature dependence of the mechanical loss (logarithmic decrement) of PI-I unirradiated and irradiated with 90 MGy. Three discrete relaxation peaks are observed. These molecular processes are referred to as γ , γ' and β relaxations from low to high temperature. The γ relaxation appearing at the lowest temperature can be attributed to the local motion of chains in the glassy state⁵⁻⁸. By irradiation, the γ peak temperature is unchanged but its magnitude is increased.

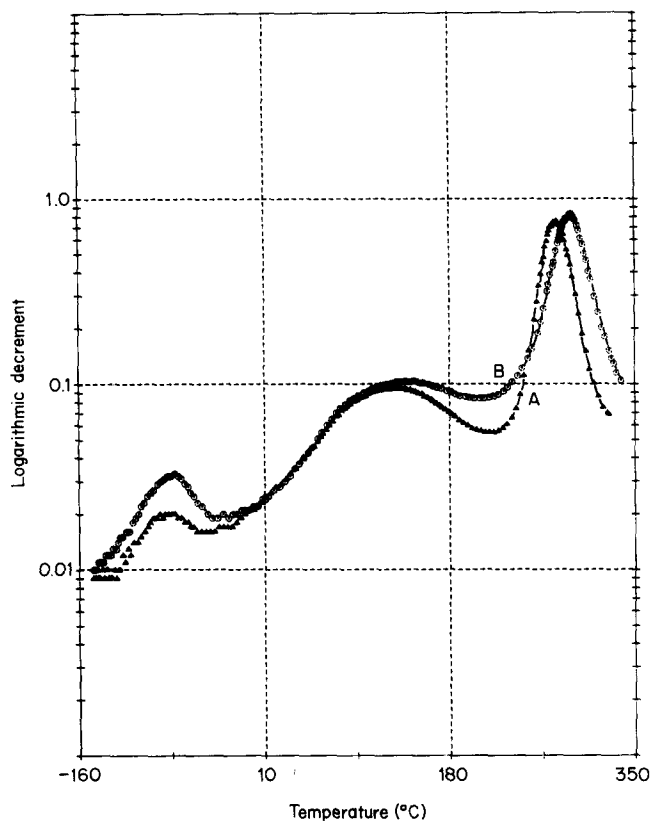


Figure 4 Change in logarithmic decrement of PI-I (UPILEX-BOARD®) on electron irradiation: A, unirradiated; B, irradiated with 90 MGy

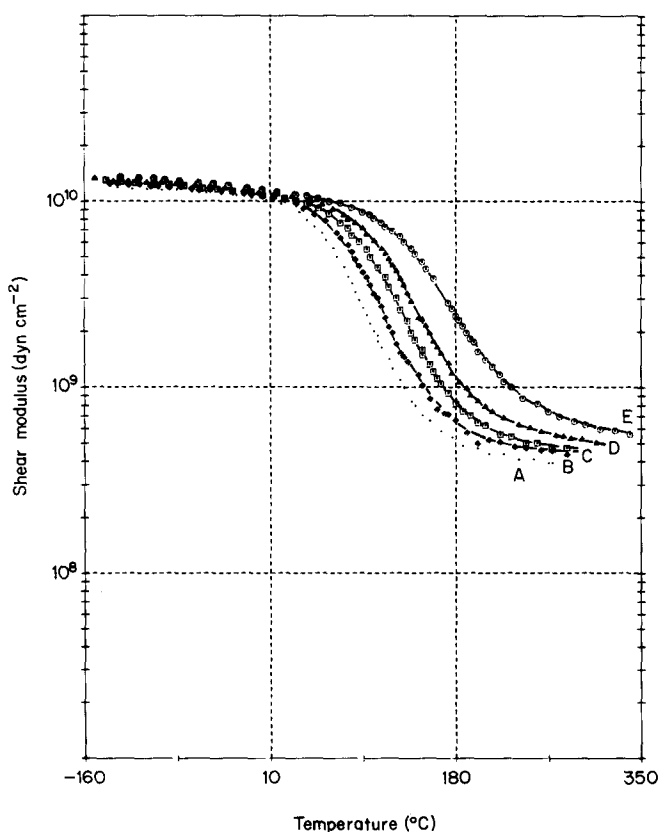


Figure 5 Change in shear modulus versus temperature curves on irradiation with various doses for PI-I (UPILEX-BOARD®): A, unirradiated; irradiated with B, 30 MGy; C, 60 MGy; D, 90 MGy; E, 120 MGy

The magnitude of the γ relaxation is strongly affected by traces of absorbed water⁵⁻⁸, so that details cannot be discussed here.

The β relaxation peak shifts to higher temperature on irradiation. Figure 5 shows the temperature dependence of the shear modulus of PI-I in the β relaxation region. The shear modulus decreases sharply at the β relaxation temperature, so the β relaxation can be attributed to the molecular motion of chains during the glass transition. The shear modulus becomes a constant value above the glass transition temperature. This phenomenon is often observed in crosslinked polymers due to a network structure. Since PI-I is a non-crystalline polymer, the fact that the modulus is constant above the glass transition temperature indicates that UPILEX-BOARD® has a network structure. This network structure is formed during preparation.

Furthermore, the glass transition shifts to higher temperature and the modulus above the glass transition temperature increases with dose. It can be concluded that crosslinking density is increased by high dose rate electron irradiation. Consequently, it is concluded that UPILEX-BOARD® (UPILEX-R) is further crosslinked by non-oxidative irradiation.

The shear modulus of unirradiated PI-II and PI-III in the β relaxation region is shown as a function of temperature in Figures 6 and 7. The modulus versus temperature curve of the unirradiated PI-II is almost the same as that of PI-I, i.e. the modulus above the glass transition temperature is constant. This shows that crosslinking has occurred during preparation and LARC-TPI® is not an entirely thermoplastic polyimide. In contrast, the modulus of PI-III decreases sharply with temperature above the glass transition temperature,

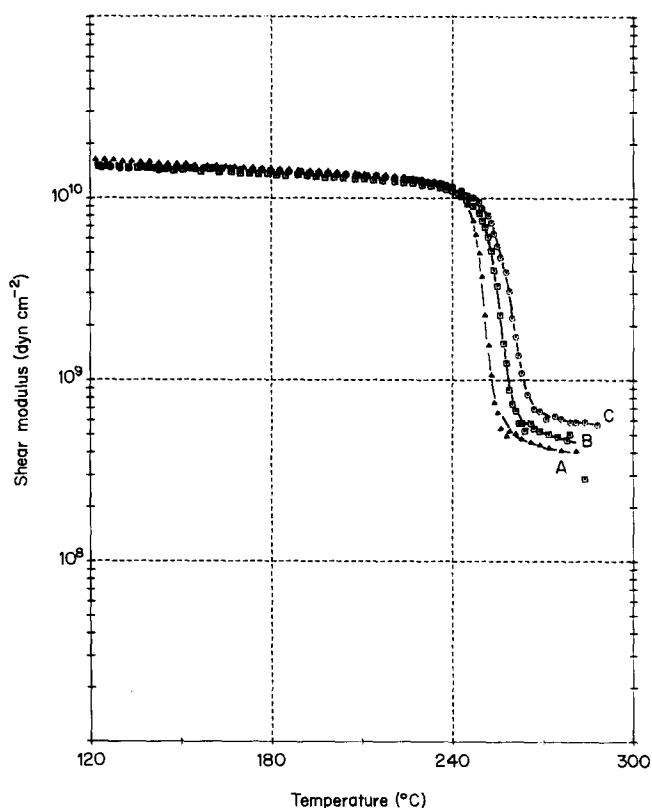


Figure 6 Change in shear modulus versus temperature curves on irradiation with various doses for PI-II (LARC-TPI®): A, unirradiated; irradiated with B, 30 MGy; C, 90 MGy

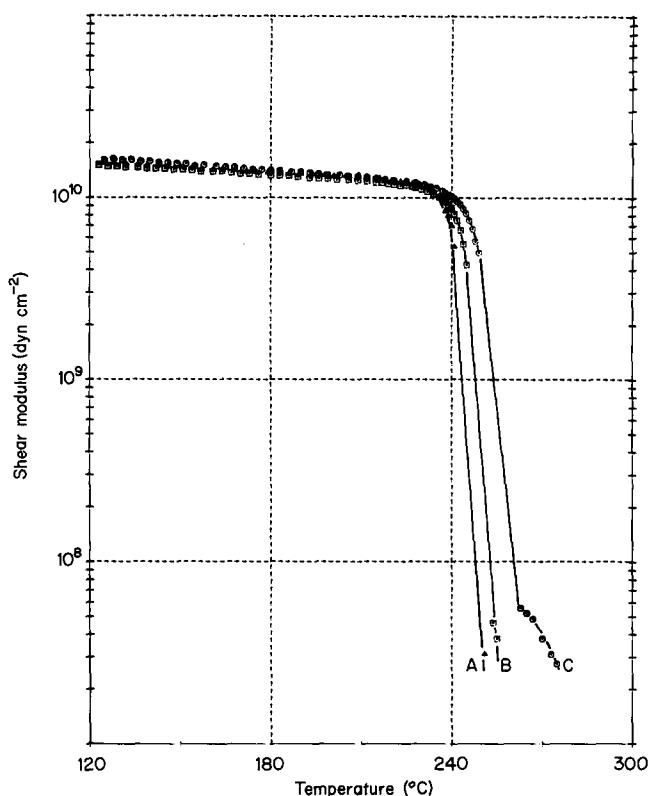


Figure 7 Change in shear modulus versus temperature curves on irradiation with various doses for PI-III (LARC-TPI 1500®): A, unirradiated; irradiated with B, 60 MGy; C, 120 MGy

indicating that this polymer has no three-dimensional structure, and LARC-TPI 1500® is modified to a thermoplastic polyimide.

In PI-II, the glass transition shifts to higher temperature and the modulus above the glass transition temperature increases with dose. It is concluded that LARC-TPI is a crosslinkable polyimide by non-oxidative irradiation. LARC-TPI 1500 can also be considered to be a crosslinkable polymer by non-oxidative irradiation, as judged from the shift of the glass transition to higher temperature with dose. The fact that the shear modulus of the specimen irradiated with 120 MGy remains of the order of 10^7 dyn cm^{-2} (10^6 Pa) after the glass transition proves radiation-induced crosslinking has taken place.

The temperature dependence of mechanical loss for the unirradiated PI-II and PI-III is shown in Figure 8. The β relaxation peak temperature of PI-III is slightly lower than that of PI-II and the magnitude of the γ relaxation is also lower. However, the overall relaxation spectra are regarded to be the same for both polyimides. This indicates that their chemical structures are similar.

The γ' relaxation for the three polyimides is observed in the same temperature region. Similar relaxation is often observed in highly crosslinked epoxy resins and assigned to a local motion related to the crosslinking structure^{10,11}. The γ' relaxation for the three polyimides however, cannot be attributed to the same molecular process as in epoxy resins, because the γ' relaxation also appears in PI-III which does not have a crosslinked structure. The assignment for this relaxation is not known, but it is responsible for the imide structure.

Radiation effects on crystallization

Figure 9 shows the heating curves for PI-IV unirradiated and irradiated with 5 MGy. In the unirradiated

specimen there is an abrupt change in the heat flow; the exothermic and endothermic peaks are observed at 250, 360 and 390°C, respectively. The abrupt change in the heat flow results from the change in the specific heat during the glass transition. The exothermic peak is due to crystallization and the endothermic peak is related to the melting of crystallites. In the irradiated specimen, the change in the specific heat is observed but the exothermic and endothermic peaks are unclear. This means that crystallization does not occur under the scanning at this heating rate ($20^\circ\text{C min}^{-1}$), indicating that crystallization is inhibited by irradiation.

Figure 10 shows the isothermal crystallization curves at 320 and 330°C for the unirradiated PI-IV. The exothermic heat flow is due to crystallization. The time giving maximum exothermic heat corresponds to that for the maximum rate of crystallization (TMC). In the isothermal crystallization at 320°C, the exothermic heat becomes a maximum at 260 s and for crystallization at 330°C it becomes a maximum at 200 s. Figure 11 shows

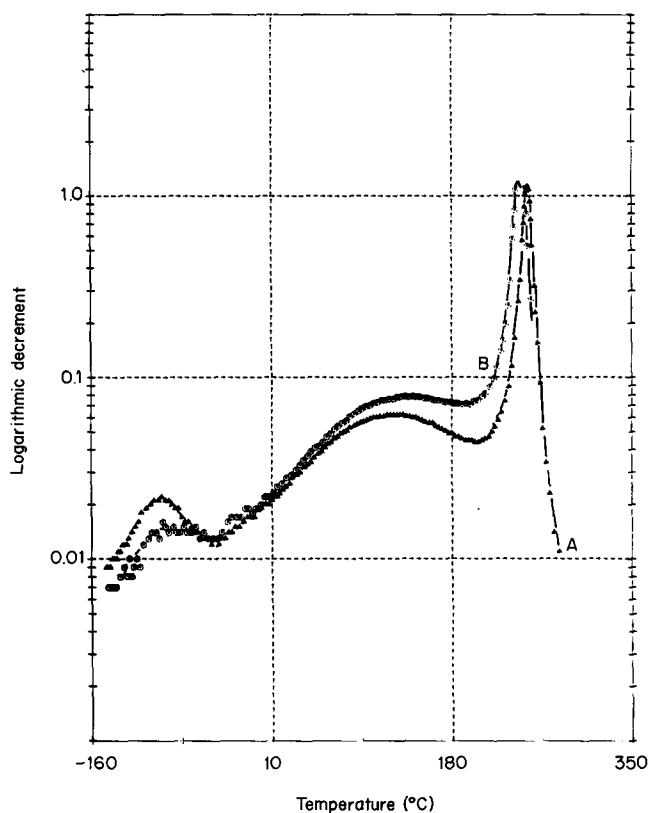


Figure 8 Comparison of relaxation spectra of PI-II (A) and PI-III (B)

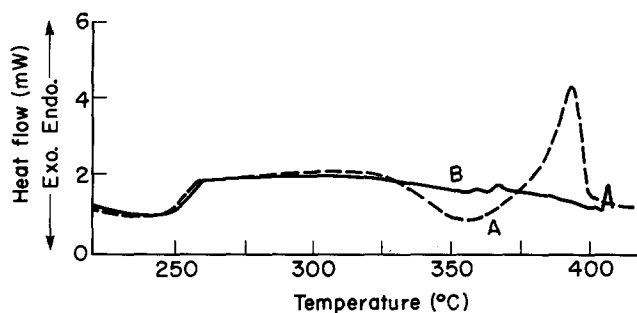


Figure 9 Differential scanning calorimetry heating curves of PI-IV (new-TPI): A, unirradiated; B, irradiated with 5 MGy

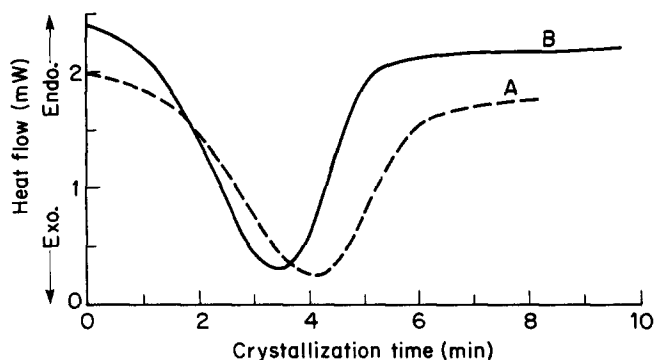


Figure 10 Isothermal crystallization curves of PI-IV crystallized at: A, 320°C; B, 330°C

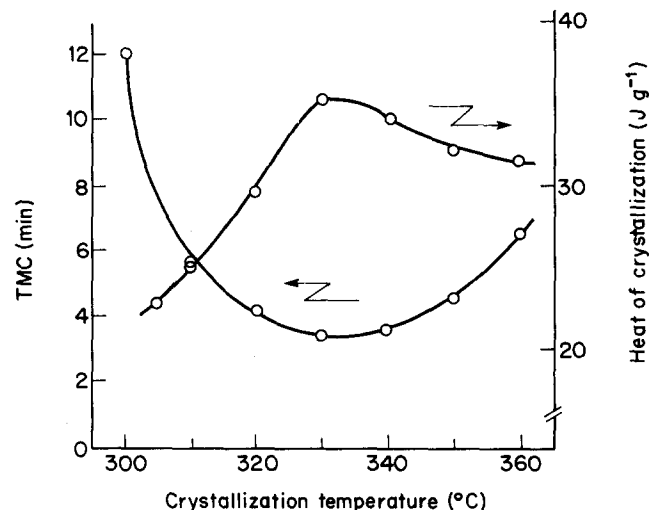


Figure 11 Time giving maximum rate of crystallization (TMC) and heat of crystallization as a function of crystallization temperature for unirradiated PI-IV

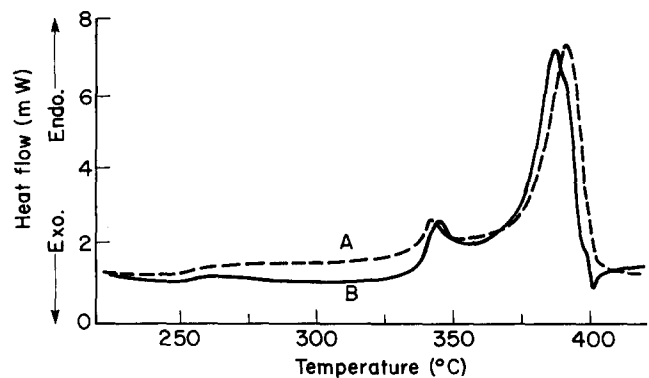


Figure 12 Differential scanning calorimetry heating curves of PI-IV after isothermal crystallization at 330°C: A, unirradiated; B, irradiated with 5 MGy

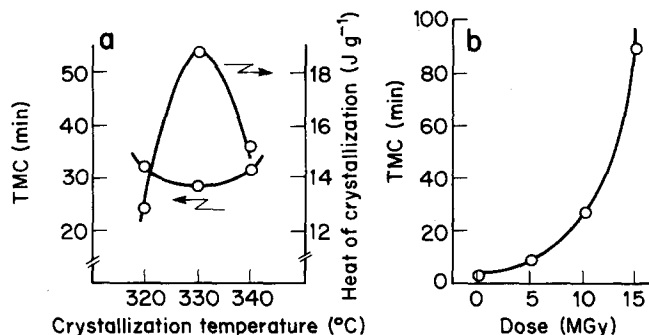


Figure 13 Change in crystallization behaviour on irradiation. (a) Time giving maximum rate of crystallization (TMC) and heat of crystallization as a function of crystallization temperature for the specimen irradiated with 5 MGy. (b) Change in TMC with dose

the TMC and the heat of crystallization as a function of crystallization temperature for the unirradiated specimen. The TMC becomes a minimum and the heat of crystallization becomes a maximum at a crystallization temperature of 330°C, indicating that the rate of crystallization is fastest at 330°C.

Figure 12 shows the heating curves after isothermal crystallization at 330°C for the specimens unirradiated and irradiated with 5 MGy. The same endothermic peaks are observed in both specimens. This shows that crystallization even occurs in the irradiated specimen by isothermal crystallization. A small peak appears near the crystallization temperature, indicating that two kinds of crystallites are produced by isothermal crystallization.

Figure 13a shows the TMC and the heat of crystallization of the specimen irradiated with 10 MGy against the isothermal crystallization temperature. It can be seen that the rate of crystallization is fastest at 330°C even in the irradiated specimen. However, the TMC increases to 28 min (i.e. the rate of crystallization is lowered) and the maximum heat of crystallization decreases to 60% of that in the unirradiated specimen. Figure 13b shows the TMC for the isothermal crystallization at 330°C as a function of dose. The rate of crystallization is lowered exponentially with dose, and crystallization was not observed in the specimen irradiated with > 20 MGy within the time of observation.

These results from thermal analysis clearly show that crystallization is inhibited by irradiation. The inhibition of crystallization is brought about by crosslinking induced by non-oxidative irradiation.

CONCLUSIONS

The effects of high dose rate electron irradiation on the tensile properties, molecular motion and crystallization behaviour of four aromatic polyimides were studied. The following conclusions are drawn: the tensile properties are scarcely affected by irradiation up to 100 MGy; the modulus of UPILEX-BOARD® and LARC-TPI® is constant above the glass transition temperature, which means that these polymers have a network structure; LARC-TPI 1500® is modified to an entirely thermoplastic polyimide; all four polyimides are crosslinked by non-oxidative irradiation.

Finally it is noted that these polyimides are suitable polymers for use in radiation fields, and LARC-TPI 1500® and new-TPI® have possibilities for use as matrix resins in thermal- and radiation-resistant fibre reinforced plastics.

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Irradiation effects on polyimides: T. Sasuga

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