

# DSC Analysis of Electron-Beam Irradiated LARC-CPI

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## SYNOPSIS

This work illustrates the response of LARC-CPI (a crystallizable polyimide) to electron-beam radiation exposure under a nitrogen-purged atmosphere. The response of LARC-CPI was monitored exclusively by differential scanning calorimetry (DSC), although some limited X-ray scattering experiments were also employed. Three different types of LARC-CPI samples were irradiated: the "as-received" semicrystalline films, highly amorphous films that were quenched from the melt, and recrystallized films. Comparison of the DSC behavior of these specimens elucidated the effects of electron-beam irradiation on LARC-CPI as well as the influence of morphology (i.e., semicrystalline vs. amorphous states) on the radiation response of this polyimide. Results indicate that for the former two samples electron-beam radiation does not significantly alter the crystalline phase present during irradiation. However, upon subsequent heating and cooling, the level of crystallinity decreases in all samples exposed to high doses (in excess of 100 Mrad). In addition, the crystallization temperature increases substantially with increasing radiation dosage, while a slight increase in the glass transition temperature is also observed. These results suggest that cross-linking reactions may be occurring at sufficiently high doses, which would account for the observed melting and recrystallization behavior. However, due to the effects of thermal history on the crystallization behavior, there is some difficulty in definitively discerning all the specific effects of morphology on the radiation response of LARC-CPI.

## INTRODUCTION

LARC-CPI is a relatively new aromatic polyimide that has been developed by the NASA Langley Research Center. Although the majority of polyimides currently in use are amorphous polymers, LARC-CPI displays a crystalline superstructure. In general, it is well recognized that the presence of crystallinity in any polymer typically offers enhanced resistance to solvents (as compared to the amorphous analog) as well as an enhanced modulus, especially above the glass transition temperature. Hence, the crystallizability of high  $T_g$  polyimides would suggest considerable potential for their use as a structural matrix resin or adhesive with desirable properties and reasonable processing requirements. In fact, Hergenrother et al.<sup>1</sup> indicated that LARC-CPI may have utility for applications in aerospace vehicles.

This suggests that the response of LARC-CPI to ionizing radiation under an inert atmosphere is of practical interest. However, no previous work has been done to determine the effects of ionizing radiation on this relatively new LARC-CPI material, which is the subject of this report.

Radiation effects on polymers can be quantified by a number of techniques, since numerous changes in properties result from radiation exposure, usually due to changes in molecular weight. Some of these changes include modifications in mechanical properties (tensile strength, elongation, modulus), solubility, intrinsic viscosity, infrared absorption spectra, crystallinity, and thermal properties. The amount of pertinent information obtained by monitoring these changes will be dependent on the particular characteristics of the polymer in question. For example, monitoring mechanical property changes in semicrystalline polymers is somewhat limited since the effects of cross-linking and chain scission reactions may be masked due to the dominance of the crystalline phase on the mechanical

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properties. On the other hand, an amorphous elastomer lends itself more readily to this type of analysis since the mechanical properties would be very sensitive to changes in cross-link density and molecular weight. It should be noted, however, that radiation can significantly influence the mechanical properties of semicrystalline polymers, but a quantitative analysis based on these changes may be difficult since mechanical properties are influenced by the level of crystallinity present in the material.

Some limited irradiation studies of polyimides have been previously carried out by various investigators.<sup>2-4</sup> However, most of these studies focused on the changes in mechanical properties. This is not surprising, since polyimides are typically amorphous polymers, and as such, a thermal analysis, for example, may not be as productive. This present study, on the other hand, focuses on the thermal behavior and crystallinity changes of LARC-CPI induced by electron-beam radiation. Changes in these properties have been monitored using differential scanning calorimetry (DSC) and X-ray scattering. Because of the insolubility of LARC-CPI and the presence of crystallinity, analysis based on specific molecular changes was not employed.

Radiation effects on crystallinity and thermal properties have been presented in the literature for a variety of polymers. Kumar and Adams<sup>5</sup> reported on electron-beam-induced changes in unit-cell dimensions for a number of high-temperature semicrystalline polymers. Their results illustrated a strong correlation between the critical dose required for damage to unit-cell dimensions and the melt temperature of the polymer. In addition, numerous studies utilizing DSC have been made, particularly on polyethylene, polypropylene, and nylon.<sup>6-12</sup> A variety of effects have been observed. Birkinshaw et al.<sup>9</sup> showed that electron-beam radiation causes a reduction in the  $\alpha_1$  melting peak of nylon 66, while the  $\alpha_2$  peak remains unaffected. Some studies on polyethylene have shown that in certain dose ranges radiation does not reduce the level of crystallinity during exposure, but upon subsequent heating and cooling, a reduction in crystallinity was observed.<sup>10</sup>

This was attributed to the presence of cross-links, which hindered the ability of the chains to recrystallize. However, Bhajeta et al. reported that the initial level of crystallinity present in polyethylene can increase as a result of irradiation, likely due to chain scission of tie molecules between crystalline lamella with subsequent reorganization of the crystalline phase.<sup>11</sup> Other studies on polyethylene have shown a dependence of the extent of cross-linking on the amount of crystallinity present in the sample. It has been postulated that the level of crystallinity may also affect the relative extent of cross-linking and chain scission.<sup>12</sup> However, at least in the case of polyethylene, the influence of crystallinity on the extent of cross-linking is believed to be partially due to the increased concentration of unsaturated ends groups in the amorphous phase, which are excluded from the crystalline lamella.<sup>13</sup> This results in an increased cross-link density in the amorphous regions, due to the higher concentration of reactive end groups. Although these studies involve polymers that have very different structures than LARC-CPI, it does provide some basis for developing an understanding and discerning the radiation effects on LARC-CPI that will be presented here.

## EXPERIMENTAL

### Materials and Sample Preparation

The structure of the material studied in this work, LARC-CPI, is shown in Figure 1. It is a semicrystalline polyimide developed by the NASA Langley Research Center. Synthesis of this polymer has been described previously by Hergenrother et al.<sup>1,14</sup> This polymer was obtained in the form of thin, semicrystalline films with a thickness of ca. 3.5 mil (90  $\mu\text{m}$ ). The films were prepared from a solution of precursor polyamic acid in *N,N*-dimethyl acetamide that was centrifuged and cast onto a glass plate. The precursor polyamic acid in a 0.5% solution of *N,N*-dimethyl acetamide at 25°C has an inherent viscosity of 0.69 dL/g. This corresponds to a molecular

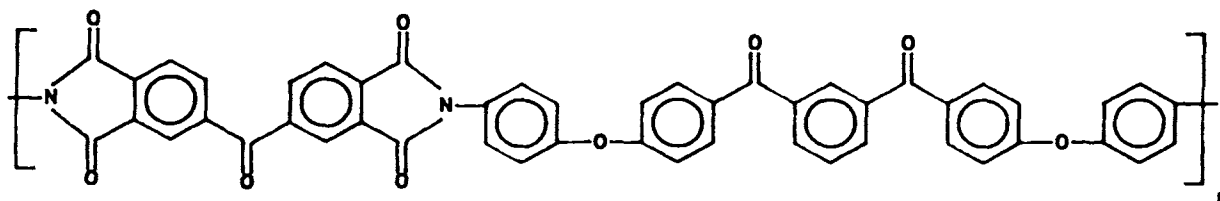


Figure 1 Molecular structure of LARC-CPI.

weight of 15,000–20,000 g/mol, based on measurements of similar materials with known molecular weight.<sup>1,14</sup> The films were converted to the polyimide by heating in air stepwise at 100, 200, and 300°C for 1 h.<sup>1</sup> These films were thermally treated several different ways prior to irradiation as follows: (1) as received, with no further treatment (denoted as CRY-LARC-CPI); (2) heated to 375°C (slightly above the melting point of ca. 365°C) and held for 10 min, followed by quenching in ice water (denoted as Q-LARC-CPI); and (3) heated to 375°C and held for 10 min, cooled to 300°C, and held for 45 min, followed by quenching in ice water (denoted as RECRY-LARC-CPI). Heating was performed by suspending samples in a test tube, which was then placed in a thermal chamber at 375°C for 10 min. Quenching was performed by quickly removing the test tube from the chamber and placing it in ice water. Some films were also *fast quenched* by removing the samples from the test tubes and placing them directly into ice water to eliminate heat transfer effects (denoted as FQ-LARC-CPI). This was done to determine the efficiency of the quenching procedure and whether the amount of residual crystallinity could be altered by the quenching procedure used, but these samples were not irradiated. Preparation of the Q-LARC-CPI and RECRY-LARC-CPI samples was done to allow comparison between amorphous and semicrystalline samples with similar thermal histories. In summary, four different types of LARC-CPI samples were prepared, but only three were actually irradiated (CRY-LARC-CPI, Q-LARC-CPI, and RECRY-LARC-CPI).

### Radiation Exposure

Electron-beam radiation exposure of the LARC-CPI samples was carried out using an Energy Sciences CB150 Electrocurtain operating with a 175 kV accelerating voltage, a beam current of 4.7 mA, and a conveyor speed of 20 ft/min. Irradiation was performed under a nitrogen atmosphere that had an oxygen content of 250–300 ppm. Under these conditions, 15 Mrad dosages were deposited in a sample in a single pass, which takes about 2 s. Hence, the films were intermittently exposed to very high dose rates (ca. 7–10 Mrad/s). In addition, the film thickness (ca. 3.5 mils) is thin enough to ensure a reasonably uniform depth-dose profile. Samples were exposed to doses of 50, 100, 500, and 1000 Mrad by making multiple passes until the desired dose level was achieved. It should be noted here that although the radiation exposure was done under a purged nitrogen atmosphere, the samples were ex-

posed to air between each pass. Furthermore, several samples were irradiated under air to determine if the presence of oxygen during irradiation has any effect on the subsequent melting and recrystallization behavior for the processing condition employed in this study. Results illustrated that the DSC behavior was not affected, likely due to the high-dose rate employed that will minimize any oxidative degradation. Hence, the effects of oxygen during processing were not pursued and will not be considered hereafter.

### Thermal Analysis

Differential scanning calorimetry (DSC) was performed using a Seiko I differential scanning calorimeter. The samples were sealed in aluminum pans and scans were made from 80 to 390°C at a rate of 10°C/min under a nitrogen purge. After the first scan was completed, the samples were quickly removed from the chamber and quenched to room temperature. A second scan was then made under the same conditions as the initial scan. This procedure is necessary to evaluate the melting and recrystallization behavior of LARC-CPI regardless of the initial morphological state of the samples. Some samples were run several times to determine the reproducibility of the DSC scans, which was found to be very good. Temperature corresponding to the peak maximums (or minimums) and glass transitions varied by no more than 0.5°C and peak areas varied by less than 10%.

### X-ray Scattering

Both small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were carried out on the as-received films (CRY-LARC-CPI) irradiated to low and high doses (50 and 1000 Mrad). SAXS was performed using a Siemens Kratky camera equipped with a M. Braun position-sensitive detector from Innovative Technology Inc. to determine the angular intensity dependence. A Philips PW 1729 table-top X-ray generator was used operating at 40 kV and 20 mA. The radiation source was  $\text{CuK}_{\alpha}$ , with a wavelength of 1.54 Å. Lead stearate was used to calibrate the SAXS angular measurements. Lupolen® polyethylene was used for absolute intensity measurements. The sample to detector distance was 30.5 cm. Data were slit-smearred; a computer program developed by Vonk<sup>15</sup> was used to desmear the data.

WAXS was performed using a Siemens model I1 transmission X-ray diffractometer operating at 40

kV and 30 mA.  $\text{CuK}_\alpha$  was used as the radiation source, with graphite as the monochromator. The goniometer was calibrated with a silicon standard having a characteristic peak maxima at 3.14, 1.92, and 1.64 Å. Constant time measurements of 20–60 s (depending on sample thickness) were made at  $2\theta$  intervals of  $0.1^\circ$ . Samples were scanned through an angular range of  $10^\circ$ – $35^\circ$ . Thin films were stacked and mounted in a flat film holder that was rotated at a constant rate during scanning to eliminate any possible orientation effects resulting from the casting process. Data were smoothed using a Fourier transform smoothing program.

## RESULTS AND DISCUSSION

### DSC Behavior of Quenched LARC-CPI

Figure 2 depicts the initial and second DSC scans for the quenched LARC-CPI material (Q-LARC-CPI) prior to any radiation exposure. Inspection of the DSC scan for the nonirradiated material shows the following behavior: Upon heating, the material goes through the glass transition at ca.  $220^\circ\text{C}$ . Above

the glass transition, the molecular chains gain sufficient mobility such that crystallization takes place, which is apparent by the presence of an exothermic crystallization peak at  $306^\circ\text{C}$ . Following crystallization, the melting of the crystals occurs at about  $369^\circ\text{C}$ , as characterized by the endothermic peak. Note that there is a 2.6 mJ/mg difference between the integrated area under the melting and crystallizing peaks. This indicates that there may be a small amount of initial crystallinity in the quenched samples. To determine if this is a result of the quenching procedure, a more efficient quench was performed on the material (see Experimental section for details). The difference between the integrated areas under the melting and crystallization peaks was found to be 3.3 mJ/mg. This suggests that the quenching procedure utilized in this study is as efficient as possible. However, there may still be a small amount of crystallinity or partial order present in the quenched samples. This may be due to the relatively short time period that the polymer is held above the melt temperature (i.e., 10 min), which may be insufficient to completely disorder the crystalline phase. Longer melting times were not employed due to the possibility of thermal degradation

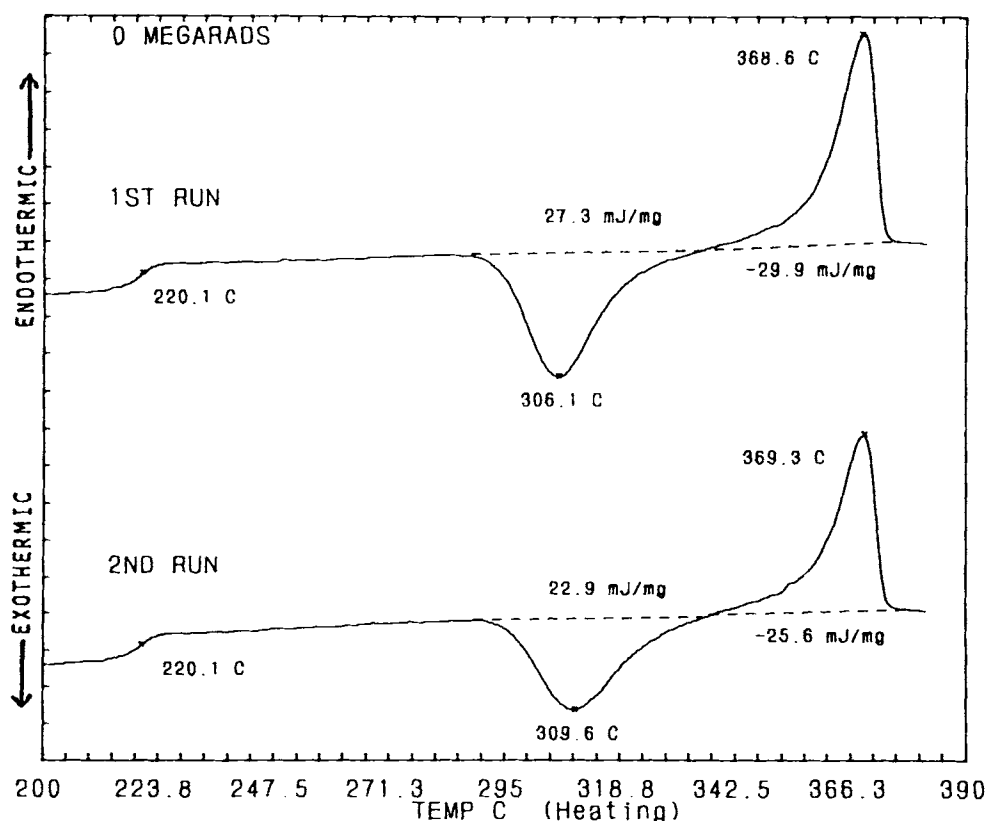


Figure 2 First- and second-run DSC scans for Q-LARC-CPI prior to irradiation.

occurring. In any case, the possibility that a small amount of crystallinity is present in the Q-LARC-CPI samples may explain some interesting behavior that will be subsequently discussed.

Comparison of the initial and second DSC scans of Q-LARC-CPI unveils differences in the crystallization behavior upon successive heating cycles (see Fig. 2). In particular, the amount of crystallization occurring during heating decreases by ca. 4.4 mJ/mg. This also produces a decrease in the size of the melting peak of the same magnitude, although the difference between the melting and crystallization peaks in the second scan remains relatively unchanged. In addition, the crystallization peak is about 4°C higher in the second scan compared to the first scan. Since the DSC behavior is the criteria used for evaluating the radiation response of LARC-CPI, it is important to realize how this behavior is affected by thermal cycling; otherwise, the influence of thermal history may be confused with the changes induced by irradiation that would result in an incorrect analysis.

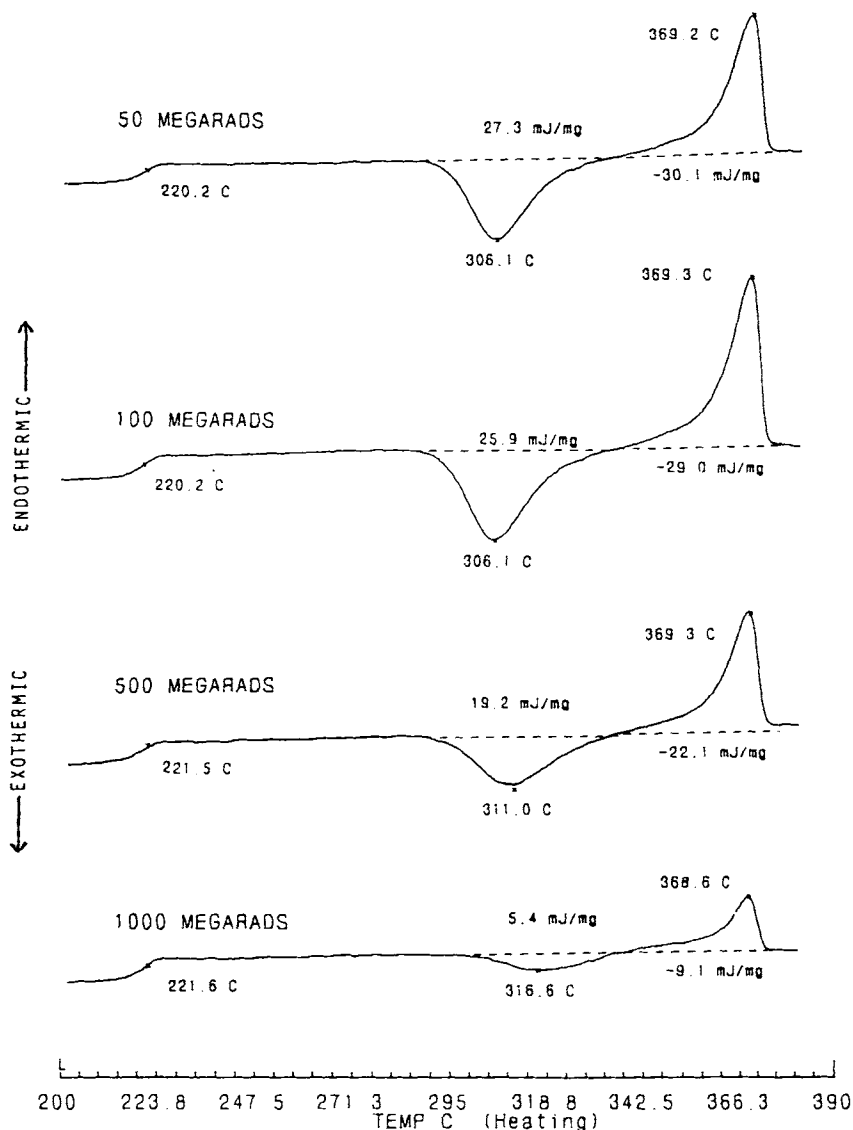
Figure 3(a) and (b) illustrate the first- and second-run DSC thermal behavior (respectively) of the Q-LARC-CPI samples irradiated with doses of 50, 100, 500, and 1000 Mrad. Comparison of these DSC scans with the unirradiated material shows no observable radiation effects on the initial scan up to a dose of 100 Mrad. It should be realized that this is a considerable dose, especially when compared to a dose of 2.5 Mrad, which is typically used for radiation sterilization. Inspection of the second-run DSC scan on these materials shows a slight decrease (about 2.7 mJ/mg) in the extent of crystallization for the sample exposed to 100 Mrad, as compared to the second scan of the unirradiated sample and, hence, is not very significant. However, above 100 Mrad, the effects of electron-beam radiation exposure on the thermal behavior become evident in both runs of the DSC analysis.

Inspection of Figure 3(a) and (b) reveals the effect of radiation dose on the total heat evolved during crystallization upon heating. As the dosage is increased to 500 and 1000 Mrad, there is a steady decrease in the amount of crystallization occurring during thermal cycling. The difference in the amount of crystallization between the first and second runs for each dose remains relatively constant (about 5 mJ/mg); hence, this is not likely to be a result of the radiation exposure. However, the *total amount* of crystallization occurring does decrease with increasing dose, indicating that radiation exposure is hindering the crystallization process. This claim is further supported by the behavior of the peak crys-

tallization temperature,  $T_c$ , with respect to the radiation dose. As illustrated in Figure 4, the peak crystallization temperature significantly increases at dosages above 100 Mrad. This indicates that either more thermal energy is required to initiate crystallization or the crystallization kinetics is slowed as a result of irradiation. Both of these possibilities suggest that the crystallization process is being suppressed to a certain extent and kinetically decreased. The crystallization peak temperature increases further during the second-run DSC scan, but this increase is fairly constant regardless of dose, indicating that this is not a result of electron-beam exposure. These observations of decreasing heat of crystallization and increasing crystallization temperature with increasing dose is likely the result of cross-linking processes that would restrict chain mobility. However, this is a speculation since neither a swelling nor an extraction analysis is feasible on this polyimide since it is insoluble in virtually all solvents.

The melting behavior of Q-LARC-CPI appears to be influenced only by the corresponding crystallization behavior with no direct effect from the electron beam [see Fig. 3(a) and (b)]. The total heat absorbed during the melting process does decrease with increasing radiation exposure, but this is simply due to the lower extent of crystallization occurring during heating. In addition, the melting temperature remains unaffected by the radiation dose or the heating cycle (i.e., the initial or second-run DSC scan). This suggests that only the extent of crystallization is affected by irradiation, while the crystalline phase that develops upon subsequent heating remains unaltered.

An interesting point to note is that the small difference between the heat of crystallization and the heat of melting during the initial-run DSC scan (as previously discussed) remains relatively unchanged with respect to radiation dose [see Figs. 3(a) and (b)]. This suggests that there is indeed a small amount of crystallinity present during radiation exposure, and it does not seem to be affected by irradiation. In fact, for the 1000 Mrad-exposed sample, the difference between the heat of crystallization and the heat of melting (3.5 mJ/mg) corresponds exactly to the total amount of melting occurring during the second-run DSC scan. This suggests that only the chain segments that were originally present in the crystal lattice are able to recrystallize after exposure to 1000 Mrad of electron-beam radiation and one DSC heating cycle. Hence, the entire initial amorphous phase may have been sufficiently chemically altered such that crystallization is no longer possible, while the initial crystalline phase remains



**Figure 3** (a) First- and (b) second-run DSC scans for the Q-LARC-CPI irradiated with doses of 50, 100, 500, and 1000 Mrad.

relatively unchanged. This is likely the result of cross-linking reactions selectively occurring in the amorphous phase, which would restrict the mobility of the polymer chains and explain this observed behavior. Cross-linking would also explain why recrystallization of the small fraction of initial crystalline phase occurs. The presence of cross-links in the surrounding amorphous regions would restrict the mobility of the lattice chains and therefore be able to undergo reordering quite readily. However, this would not necessarily hold true at higher levels of crystallinity since there may not be sufficient cross-links in close proximity to all the lattice chains to restrict mobility and promote reordering. This

point should be kept in mind during the subsequent discussion of the irradiation effects on the semi-crystalline "as-received" LARC-CPI.

One other effect that can be observed from Figures 3(a) and (b) is the effect of radiation on the glass transition temperature of the LARC-CPI. As shown in Figure 5, the glass transition temperature begins to increase very slightly at doses above 100 Mrad. At a dose of 1000 Mrad, there is a 2°C increase in the glass transition temperature. Although the glass transition temperature is generally insensitive to changes in molecular weight of high molecular weight polymers, the initial molecular weight of the LARC-CPI is low enough such that molecular

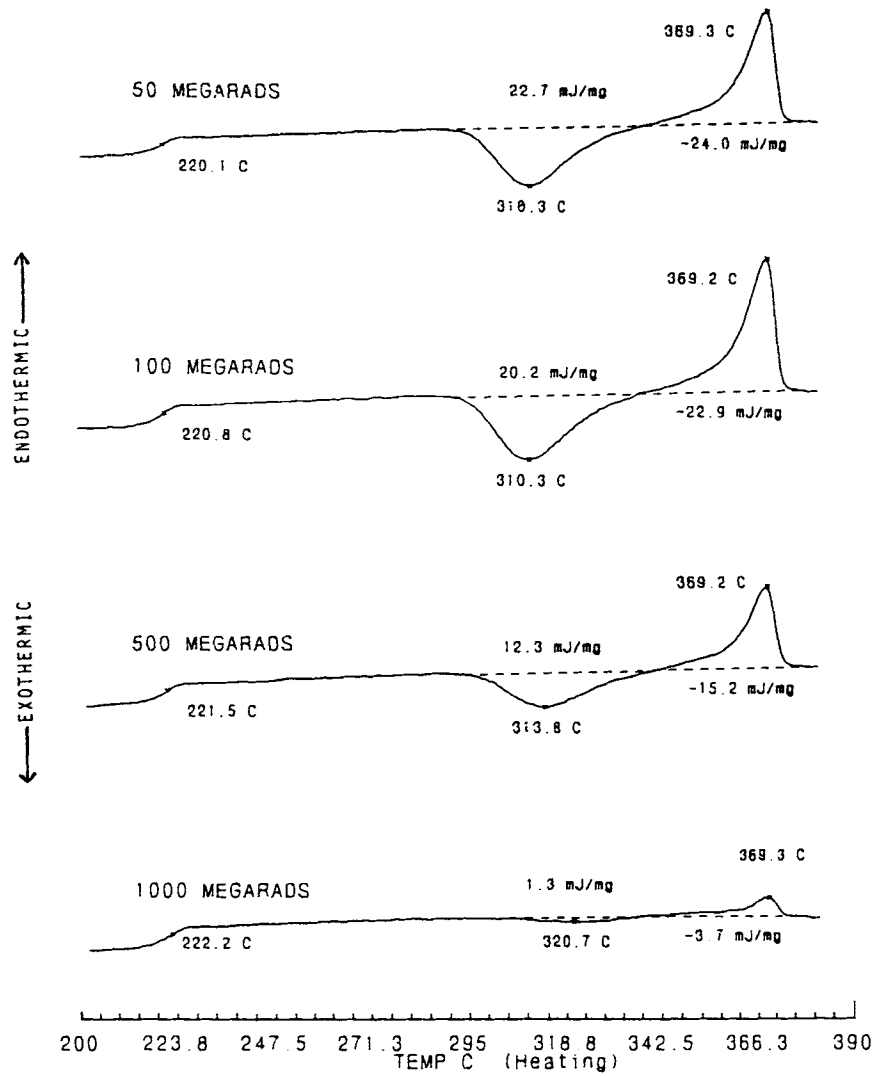


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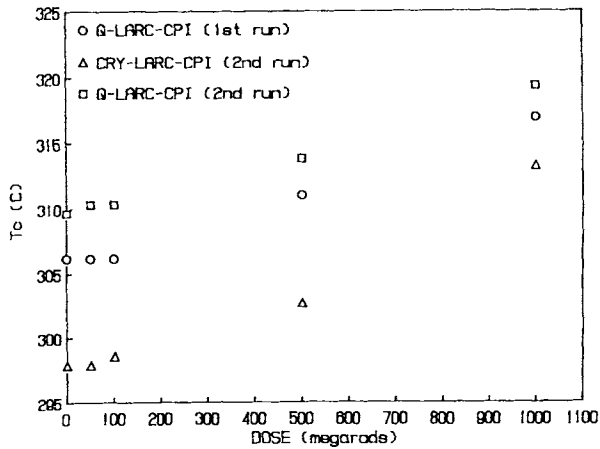


Figure 4 Effect of radiation dose on the crystallization temperature ( $T_c$ ) of Q-LARC-CPI and CRY-LARC-CPI as determined by the first-run DSC scan.

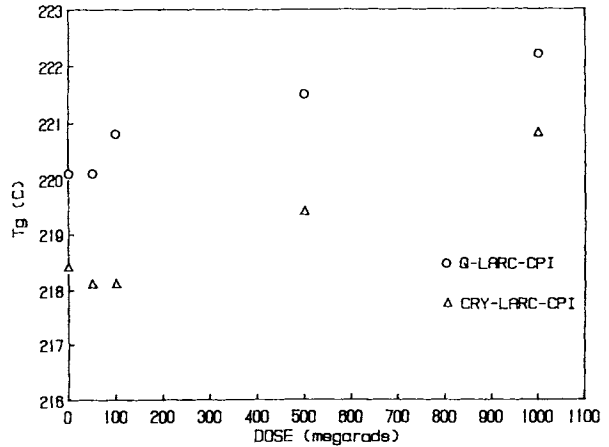


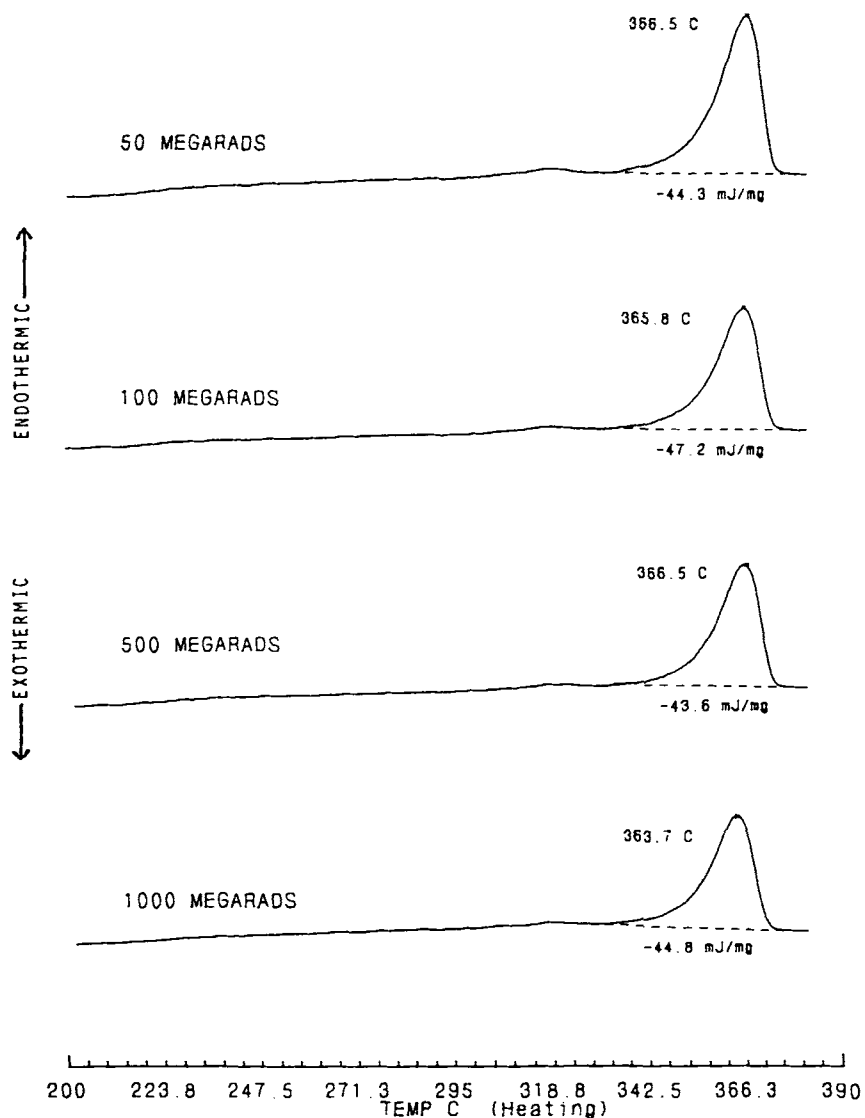
Figure 5 Effect of radiation dose on the glass transition temperature ( $T_g$ ) of Q-LARC-CPI and CRY-LARC-CPI as determined by the first-run DSC scan.

weight changes may well influence the glass transition. Although no quantitative analysis has been made to determine the absolute molecular weight of this polymer, it is believed that the molecular weight is in the range of 15,000–20,000 g/mol. This molecular weight range is based on viscosity measurements of the soluble polyamic acid precursor made by NASA, which were compared with viscosity measurements of similar materials of known molecular weight.<sup>1,14</sup> This slight (but reproducible) increase in the glass transition at high doses suggests that the molecular weight is increasing, likely due to cross-linking reactions. This would certainly explain the changes occurring in the thermal behavior of the

LARC-CPI. As discussed, the extent of crystallization taking place during heating decreases with increasing dose while the crystallization temperature increases. Both of these observations could be attributed to a decrease in chain mobility as a result of branching or cross-linking, with a corresponding increase in molecular weight.

#### DSC Behavior of "As-Received" Semicrystalline LARC-CPI

Irradiation of the "as-received" semicrystalline LARC-CPI material (CRY-LARC-CPI) was performed to determine if the presence of a crystalline



**Figure 6** (a) First- and (b) second-run DSC scans for the CRY-LARC-CPI irradiated to the doses indicated.



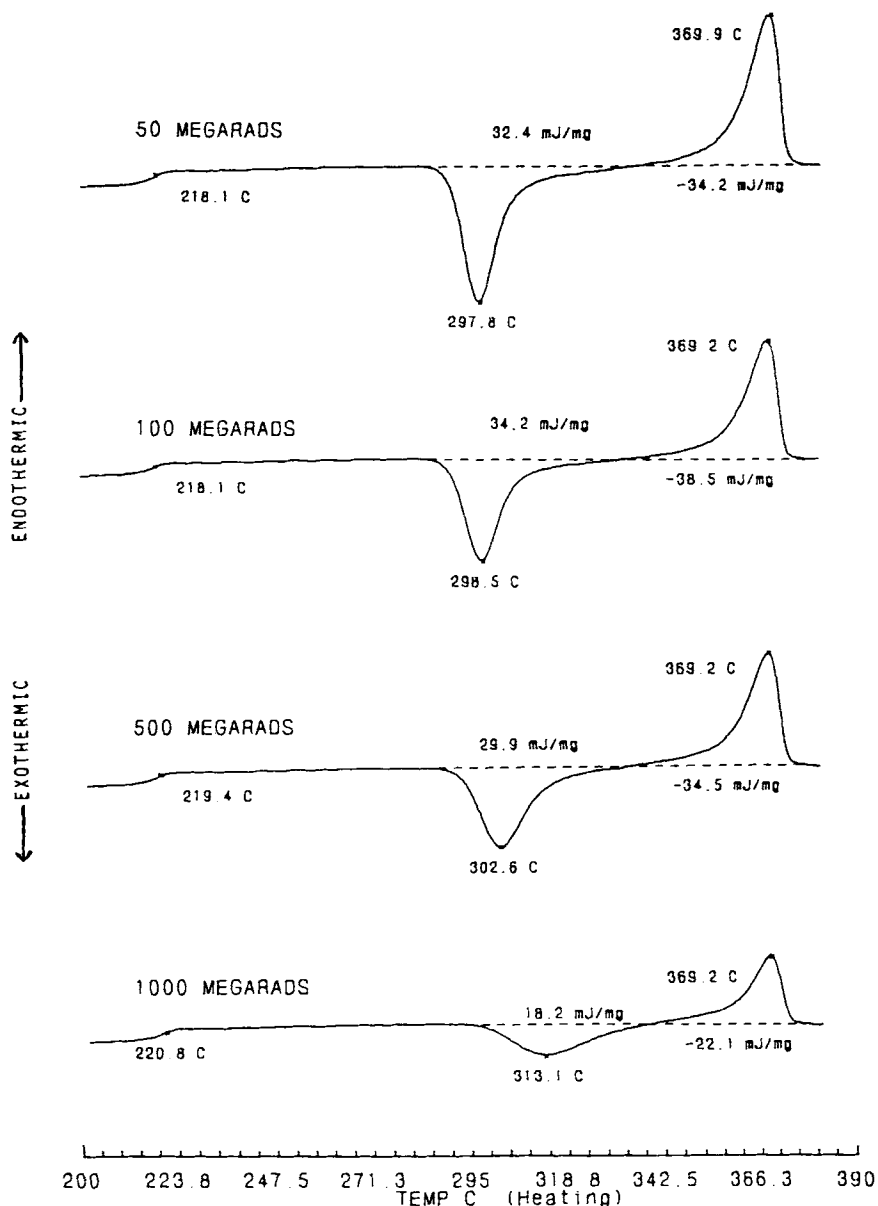


Figure 6 (continued from the previous page)

phase affects the radiation response of this polymer. To this point, discussion has predominately focused on amorphous LARC-CPI (Q-LARC-CPI) that may have had a very small amount of crystallinity present (as previously described). In contrast, CRY-LARC-CPI has a crystalline content of ca. 30%, as reported by Hergenrother and Havens.<sup>14</sup> Figure 6(a) shows the initial run DSC scan of CRY-LARC-CPI at the various dosages indicated. Notice that the heat of fusion during this initial run remains relatively unaffected by the dose level. This further supports the claim made that there is no direct major alteration of the crystalline phase present during the ra-

diation exposure. However, as illustrated in Figure 6(b), the ability of the polymer chains to recrystallize after melting is strongly affected by the dose level. Figure 6(b) shows the second-run DSC scans for the CRY-LARC-CPI samples. Up to 100 Mrad, there is no significant change in the extent of crystallization during heating. In fact, at a 500 Mrad dose, the heat of crystallization decreases by only about 4 mJ/mg. However, the heat of crystallization becomes significantly reduced at a dose of 1000 Mrad. At this dose, the heat of crystallization decreases from about 33 mJ/mg (0 Mrad) to about 19 mJ/mg (1000 Mrad). However, this is a signifi-

cantly higher extent of crystallization than was present in the predominately amorphous sample (Q-LARC-CPI) irradiated with a 1000 Mrad dose, as previously discussed (see Fig. 3). It should be realized, however, that this difference is partly due to the additional thermal cycle that the amorphous samples were subject to prior to irradiation. The effect of this additional thermal cycle can be qualitatively eliminated by comparing the *relative* decreases in extent of crystallization occurring in both the Q-LARC-CPI and CRY-LARC-CPI samples. For the initial DSC scan of the Q-LARC-CPI sample, a 1000 Mrad dose results in a 70% decrease in the heat absorbed upon melting, while a 43% decrease occurs in the CRY-LARC-CPI sample. This strongly indicates that some radiation protection is afforded to this material by increasing the crystallinity content. This is believed to be due to the increased probability of free-radical recombination in the crystal lattice relative to the amorphous regions. The crystal lattice imposes a certain degree of order and reduced mobility to the molecular chains, which can promote the recombination of a free-radical pair produced by the electron beam. In the amorphous

phase, there is more free volume and no order, and, hence, a free-radical pair may be more prone to "lose each other" and react with other chains promoting cross-linking reactions instead of recombining.<sup>16,17</sup>

#### DSC Behavior of Recrystallized LARC-CPI

Although it is likely that the presence of crystallinity in LARC-CPI provides some radiation protection, this is difficult to precisely quantify due to the effects of the additional thermal cycle imposed on the amorphous samples, as previously mentioned. Recall that Figures 4 and 5 illustrated that the crystallization temperature and glass transition temperature (respectively) are dependent on the thermal history of the sample. This is evidenced by the values obtained for these characteristic temperatures on the unirradiated amorphous and semicrystalline samples. Figures 4 and 5 also showed that the crystallization and glass transition temperatures are slightly higher for the irradiated amorphous material than for the irradiated crystalline material, which suggests that more chain restriction is present in the amorphous samples. However, the values for

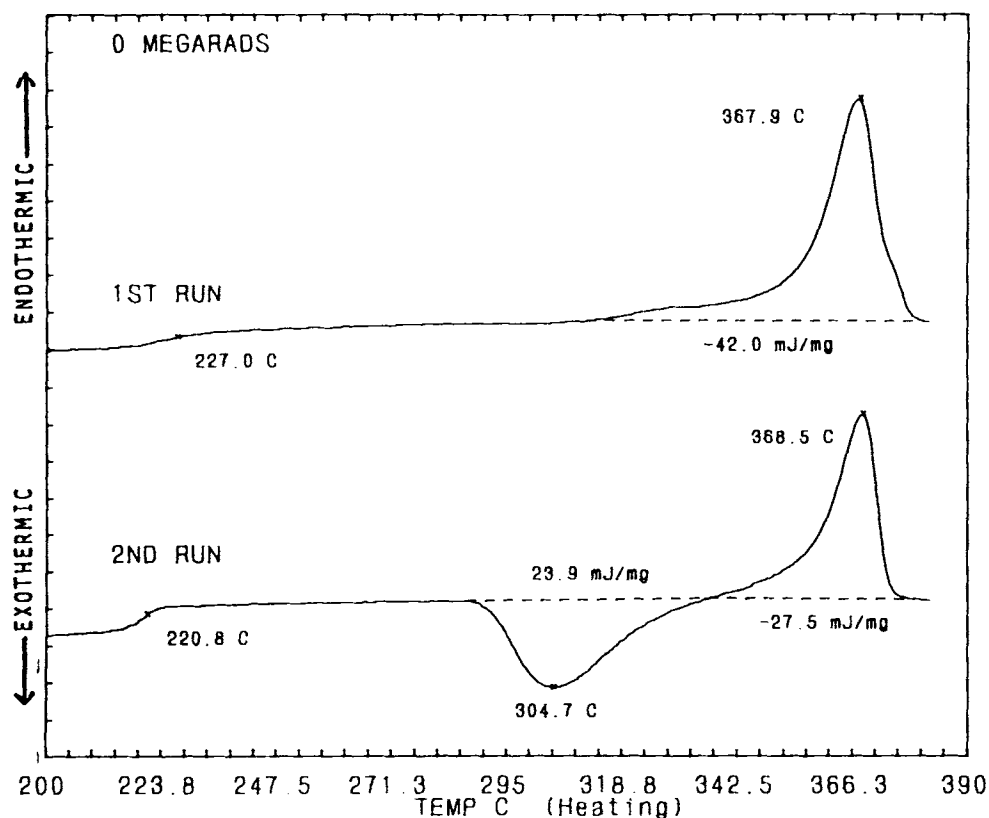
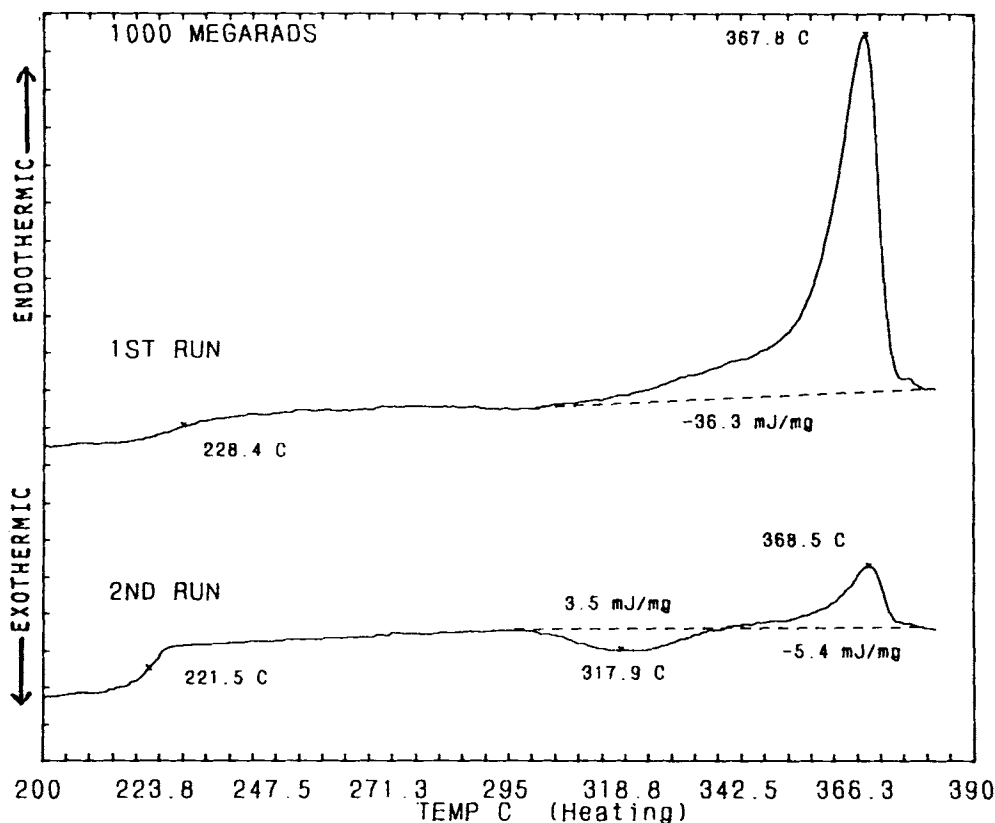


Figure 7 First- and second-run DSC scans for the RECRY-LARC-CPI prior to irradiation.

these parameters are also higher for the unirradiated samples. Hence, these differences may be the result of thermal treatment rather than morphological influences on the radiation response of this polymer. To resolve this uncertainty, a third LARC-CPI sample was prepared (RECRY-LARC-CPI). This sample was treated identically as the amorphous samples, except that it was allowed to recrystallize during cooling rather than quenched directly to the amorphous state (see Experimental section). This should eliminate some of the differences imposed by the different thermal histories of the amorphous and crystalline materials (discussed to this point) as well as some of the ambiguity in the above comparison. Figure 7 shows the first- and second-run DSC scans for the RECRY-LARC-CPI. Comparison of the second-run DSC scan for this sample with the second-run scan of the Q-LARC-CPI (see Fig. 2) shows good agreement, the only significant difference being the crystallization temperature—The amorphous LARC-CPI (Q-LARC-CPI) has a crystallization temperature that is 5°C higher than the recrystallized sample (RECRY-LARC-CPI).

Figure 8 shows the DSC scans for the RECRY-

LARC-CPI exposed to a 1000 Mrad dose. Comparison of the first-run scans in Figures 7 and 8 shows that irradiation results in a decrease in the original level of crystallinity present in this sample. For the 1000 Mrad dose, there is almost a 6 mJ/mg decrease in the heat of melting, which was not observed in the CRY-LARC-CPI samples. Notice the presence of a "shoulder" on the melting endotherm of the RECRY-LARC-CPI (see Fig. 7), which seems to be altered by the electron beam (see Fig. 8). The crystals corresponding to this shoulder have a lower melting point and, hence, are less stable than are the predominant crystals present. It has been shown in other high-temperature polymers that the minimum dose required for damage to the crystal unit cell correlates well with the melting temperature.<sup>5</sup> This may explain why this shoulder is altered and the crystallinity decreases as a result of electron-beam exposure. Hence, recrystallizing the LARC-CPI films may alter the fine structure of the crystalline phase such that it has less resistance to electron-beam radiation than the crystalline phase present in the as-received (CRY-LARC-CPI) samples. In fact, differences in the long spacing of the



**Figure 8** First- and second-run DSC scans for the RECRY-LARC-CPI exposed to 1000 Mrad of electron-beam radiation.

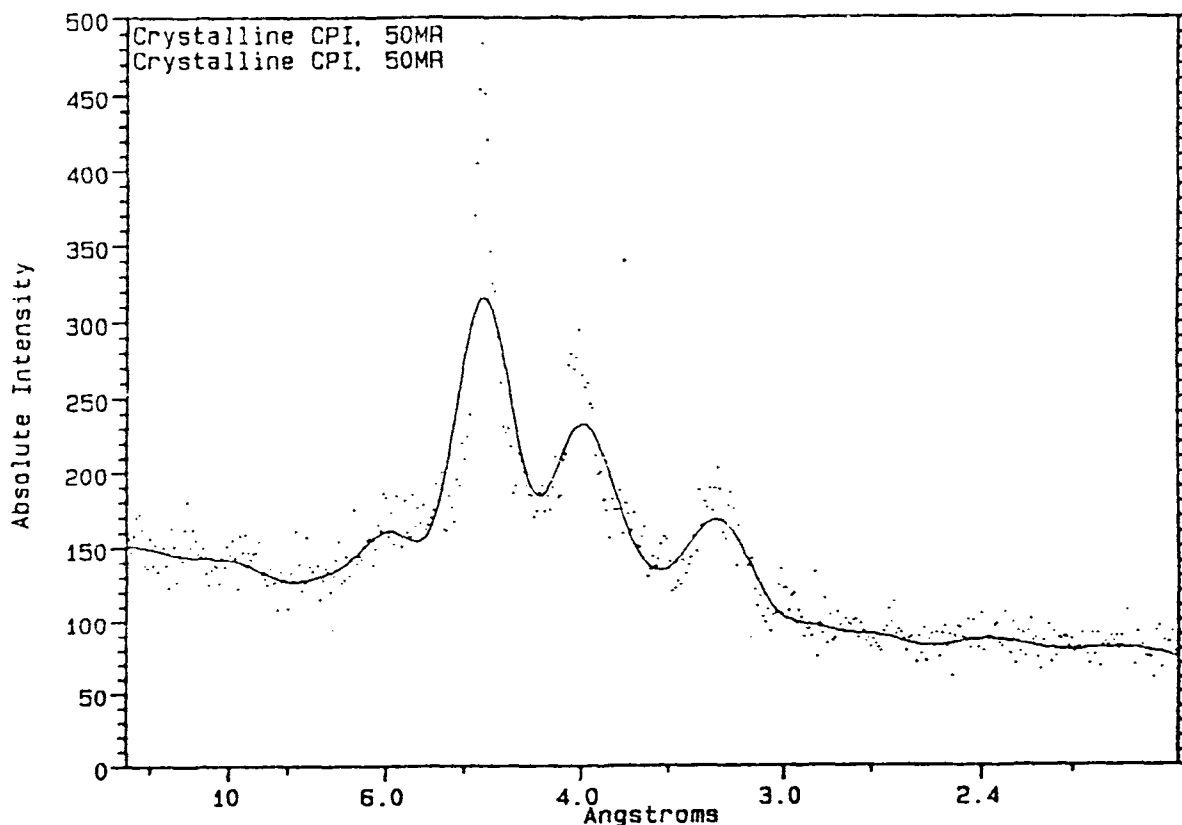
crystalline lamella (as determined by SAXS) have been detected between the as-received (CRY-LARC-CPI) and recrystallized (RECRY-LARC-CPI) films.<sup>18</sup> In addition, changes in the crystalline superstructure resulting from recrystallization of the "as-received" LARC-CPI films has also been observed from SEM and STEM analyses as reported by Muellerleile et al.<sup>19</sup>

Comparison of the second-run DSC scans for the irradiated and unirradiated RECRY-LARC-CPI shows similar behavior to the other LARC-CPI samples (see Figs. 7 and 8). For instance, there is an increase in the glass transition and crystallization temperatures, and a decrease in the extent of crystallization (during the second run) as a result of electron-beam exposure, while there appears to be no effect on the melting behavior.

Comparison of the second-run DSC scan for the irradiated RECRY-LARC-CPI (Fig. 8) with the second-run DSC scan for the Q-LARC-CPI [Fig. 3(b)] irradiated to the same dose level (i.e., 1000 Mrad) shows the differences in the radiation re-

sponse arising from a variation in the sample morphology (i.e., mainly amorphous vs. semicrystalline states). However, both of these samples have been thermally cycled to 375°C prior to irradiation, so this comparison may give a better indication of the influence of morphology on the radiation response of LARC-CPI than does the comparison of Q-LARC-CPI and CRY-LARC-CPI (CRY-LARC-CPI was not heated prior to irradiation). The recrystallized sample (RECRY-LARC-CPI) has a higher extent of crystallization upon heating (3.5 mJ/mg) than does the quenched (Q-LARC-CPI) sample (1.3 mJ/mg). In addition, the glass transition and crystallization temperatures are slightly lower for the recrystallized sample. This suggests that some radiation resistance is indeed afforded by the presence of a crystalline phase during irradiation. However, this effect is not large and is certainly much less than would be indicated by a comparison of the thermal behavior of the Q-LARC-CPI and CRY-LARC-CPI samples.

It should be stressed that the radiation dosages



**Figure 9** WAXS profiles of CRY-LARC-CPI that has been irradiated to (a) 50 and (b) 100 Mrad. Shown are both the data points and results from the smoothing program (solid line).

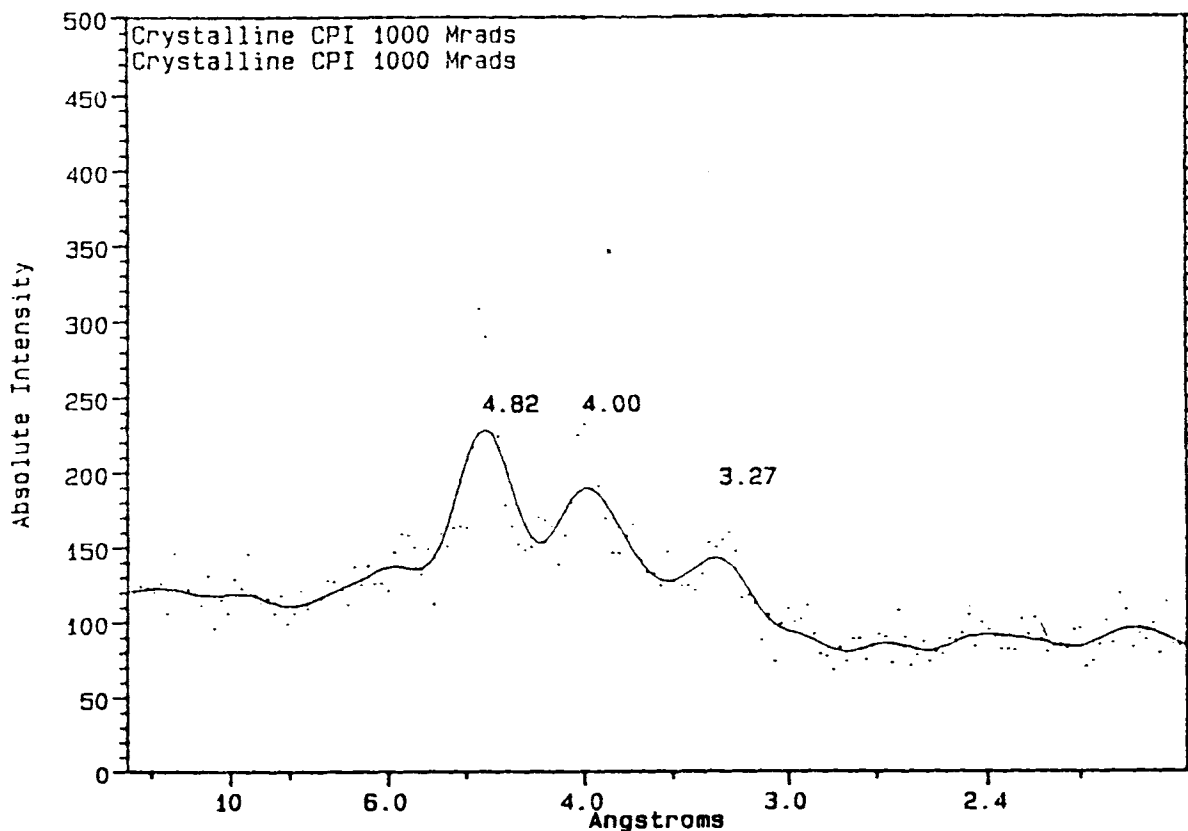


Figure 9 (continued from the previous page)

necessary to alter the DSC behavior of LARC-CPI are quite high. Consider, for example, that the typical dose used for radiation sterilization is 2.5 Mrad, while a dose exceeding 100 Mrad is necessary to effect any change in the DSC behavior of LARC-CPI. Furthermore, doses approaching 1000 Mrad are necessary to strongly influence the extent of crystallization that occurs during the subsequent DSC analysis. However, even at this extremely high dose there are no observable changes in the creasability of the films, color, or other qualitative properties. In addition, the presence of oxygen during irradiation to a dose of 1000 megarads had no effect on the DSC behavior of this polyimide when compared to samples irradiated under nitrogen. This should not be surprising considering that a quite high dose rate was employed, thus limiting the possibility of oxidative degradation occurring.

#### X-ray Scattering Analysis

As a supplement to the DSC analysis, both SAXS and WAXS experiments were carried out on the as-received films (CRY-LARC-CPI) irradiated to 50

and 1000 Mrad to determine if any differences in the scattering profiles were arising from radiation exposure. It was found that radiation exposure produces no changes in the SAXS profile of LARC-CPI (data not shown). This suggests that irradiation to high doses does not alter the long-range crystalline order present in the films. However, differences do exist in the WAXS profiles of these two samples (see Fig. 9), indicating that there are radiation-induced changes in the short-range crystalline order (i.e., on the order of unit-cell dimensions). The decrease in the scattering intensity at 1000 Mrad suggests that the crystalline content has decreased, possibly due to radiation-induced defects and distortions in the unit cells of the crystal lattice resulting from cross-linking reactions and gas evolution. In fact, the crystalline content of these two samples was determined from the WAXS profiles, following the procedure of Herman and Weidinger.<sup>20</sup> The crystalline content of the 50 and 1000 Mrad CRY-LARC-CPI was determined to be 38 and 30% ( $\pm 2\%$ ), respectively, with the former corresponding well with the value given by Hergenrother and Havens<sup>14</sup> for a similarly prepared material. This

corresponds to a ca. 21% reduction in the crystalline content of CRY-LARC-CPI after exposure to 1000 Mrad. This compares with a 35% decrease in the heat absorbed during melting in the *second-run* DSC scan of the same samples [see Fig. 6(b)]. These numbers are reasonable, since one would expect a decrease in crystalline content after melting and recrystallizing a sample that has undergone prior cross-linking. Because of the hindered mobility of the chain segments in close proximity to the cross-links, crystallization would be suppressed in these regions, which may have not been initially distorted or contributing to the reduced scattering intensity.

It is interesting to note that there is no corresponding decrease in the heat absorbed during melting of the 1000 Mrad CRY-LARC-CPI during the *first-run* DSC scan [see Fig. 6(a)]. This discrepancy may suggest that crystalline phase is not being destroyed (i.e., transformed into amorphous regions) such that the internal energy (and corresponding thermal behavior) is being altered, but sufficiently distorted to reduce the X-ray scattering intensity. The presence of defects or distortions in the crystalline phase after irradiation is supported by DSC because there is a 3°C decrease in the melting peak temperature [see Fig. 6(a)] after exposure to 1000 Mrad, which is indicative of a decrease in the stability of the crystalline phase. However, there is no longer a melting-point depression after melting and recrystallizing the CRY-LARC-CPI exposed to 1000 Mrad [see Fig. 6(b)]. This seems reasonable, since it is likely that any radiation-induced defects in the crystal lattice would be excluded during recrystallization and, hence, no depression in the melting point would occur. However, it should also be noted that the second-run melting endotherm of the 1000 Mrad CRY-LARC-CPI [see Fig. 6(b)] is skewed somewhat to lower temperatures and the crystallization exotherm is skewed toward higher temperatures. This also indicates that radiation exposure reduces the stability of the crystalline phase as well as hindering the crystallization kinetics. Hence, even though the defects are excluded during recrystallization, they manifest a reduction in crystal stability and crystallization kinetics.

## CONCLUSIONS

This study has illustrated how electron-beam radiation affects the DSC behavior of LARC-CPI. Although the DSC behavior of this polymer is sensitive to its thermal history, which has indeed complicated

the analysis of morphological influences on the radiation response, several features of the radiation-induced changes in LARC-CPI have been elucidated. In particular, it has been shown that high doses of electron-beam radiation are necessary to produce changes in the DSC behavior. In fact, doses up to 100 Mrad have negligible effects in this respect. Above this dose level, the heat of crystallization for a quenched, amorphous specimen decreases with increasing dose, while the temperature of crystallization as well as the glass transition temperature increases. This suggests that the polymer chains are being restricted as a result of irradiation, which has been speculated to be due to cross-linking. This has been shown to be true regardless of the crystallinity content during exposure. However, the effects of the presence of a crystalline phase on the extent of these radiation-induced changes is somewhat obscured by the dependence of the thermal behavior on the thermal history.

An attempt was made to eliminate thermal history influences on the DSC behavior by recrystallizing LARC-CPI prior to irradiation so that the amorphous and crystalline samples had similar thermal histories. The results indicate that the presence of crystals in the polymer may lessen the effects of irradiation, although there is not a large difference in the resulting DSC behavior. There are only slight differences in the transition temperatures, but the heat of crystallization in the recrystallized sample is more than twice that of the quenched sample. Finally, it has been shown that the thermal history may also influence whether or not irradiation alters the crystalline phase. In particular, the results have indicated that recrystallized LARC-CPI may have a somewhat lower resistance to electron-beam irradiation. It has been proposed that this may be due to thermally induced changes in the character of the crystals, which reduces the radiation resistance of the polymer.

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