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## BISPHENOL-A POLYSULFONE AS A TEMPERATURE PROBE FOR THE ELECTRON-BEAM IRRADIATION OF POLYMERS

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### ABSTRACT

A procedure is described for determining the temperature of polymers during electron beam irradiation at high dose rates by measurement of the soluble fractions of samples after various doses of radiation. The soluble fraction data are analyzed to derive values of the crosslinking yield,  $G(X)$ , at different times, which are compared with the  $G(X)$  values obtained for irradiation at various temperatures at lower dose rates, e.g., with  $\gamma$ -radiation, when the temperature is controlled and remains constant. The technique is demonstrated for bisphenol-A polysulfone, which is suggested as a standard reference that can be used to provide an estimation of the temperature rise in other polymers with similar dimensions during electron beam irradiation at high dose rates. Low dose-rate electron beam irradiation (3 Mrad/h) has been shown to give the same  $G$  values as  $^{60}\text{Co}$   $\gamma$ -irradiation (0.1 MGy/h) under the experimental conditions.

### INTRODUCTION

Electron-beam irradiation provides much higher dose rates (up to 300 MGy/h) than are available from  $\gamma$ -irradiation (typically 0.001–0.01 MGy/h), thus reducing the irradiation times required to deliver the doses necessary for industrial processes. Electron-beam machines producing these high dose rates are used for acceler-

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$G(X)$  for PSF has been shown by Brown and O'Donnell [5, 6] to be strongly temperature-dependent in the range 30–220°C from measurements of the soluble fraction after  $\gamma$ -irradiation at low dose rates when radiation heating was insignificant.

PSF is particularly suitable as a temperature probe since it has a high  $T_g$  of 190°C. It can be readily molded to the same shape and dimensions as the polymer sample under investigation. Also, the soluble fractions can be conveniently measured by gel permeation chromatography [7, 8].

## EXPERIMENTAL

### Polymer Sample Preparation

Bis-A polysulfone was obtained from Union Carbide (Udel P-1700) and compression molded under nitrogen into 0.55 mm and 1.85 mm thick sheets after drying the pellets at 150°C for 24 h in a vacuum oven. The sheets were cut into 5 mm  $\times$  15 mm specimens and stored in a desiccator. Each sample was placed on a water-cooled aluminum platform in an aluminum irradiation cell mounted onto the flight tube of a Van de Graaff electron beam accelerator and evacuated with continuous pumping at  $< 1$  Pa.

### Irradiation

The Van de Graaff accelerator produced 0.7 MeV electrons with a pulse width of 0.3  $\mu$ s at a repetition rate of 1.1 kHz. The electron beam was found to diverge from the end of the flight tube with a solid angle of 45°, giving dose rates in the sample from 3 to 36 MGy/h depending on the distance from the accelerator window. The dose rate was determined using dosimeter films supplied by Far West Technology (FWT). The films were calibrated using  $^{60}\text{Co}$   $\gamma$ -radiation, since it had been shown that  $^{60}\text{Co}$   $\gamma$ -rays and 1.0 MeV electrons produce the same changes in optical density (OD) of the films [9]. The spatial distribution of the electron beam was determined by 1) measuring the OD of the FWT dosimeter films at various positions and 2) using Faraday cups of various diameters. The soluble fraction measurements were made on the central region of the samples, which was shown to receive a uniform dose.

The dependence of the soluble fraction on dose at different temperatures was determined at low dose rates with  $^{60}\text{Co}$   $\gamma$ -radiation. The temperature was controlled by placing the polymer samples in an aluminum block fitted with a cartridge heater and a thermostat, which maintained the temperature within  $\pm 1^\circ\text{C}$ . The dose rate in the  $\gamma$ -radiation experiments was determined using standard Fricke dosimetry [10] at ambient temperature in the aluminum block.

After irradiation, the samples were heated to 130°C for 15 h, which has been shown to remove most of the trapped radicals. This procedure ensured that chemical changes resulting from irradiation were complete and did not vary due to different postirradiation treatment. The soluble fractions of the irradiated polymers were measured using the GPC technique [8].

## RESULTS AND DISCUSSION

Irradiation of a 1.85-mm thick sheet at 36 MGy/h converted the sample into a foam after 3 MGy due to the combined effect of an increase in temperature beyond the glass transition ( $T_g = 190^\circ\text{C}$ ) and the evolution of volatile radiation products, comprising mainly sulfur dioxide.  $G(\text{total gas}) = 0.65$  has been reported previously [5] for  $\gamma$ -irradiation at  $240^\circ\text{C}$ ; this would cause a 10-fold expansion of the polymer after 3 MGy, which was approximately the effect observed.  $G(\text{total gas}) = 0.04$  at  $30^\circ\text{C}$  [5], and increases with increasing temperature. However, if the temperature does not exceed  $T_g$ , the evolved gases would cause a build-up of internal stresses. The foaming of PSF observed at 36 MGy/h, under the experimental conditions employed, demonstrates that high dose rates can cause very large increases in the temperature of a polymer sample and produce marked changes in its material properties.

The soluble fractions ( $s$ ) of irradiated polymers after different doses ( $D$ ) can be analyzed by the Charlesby-Pinner plot [11] of  $s + s^{1/2}$  versus  $1/D$  to give  $G(X)$  and  $G(S)$ , according to Eq. (1). This analysis assumes random crosslinking by the H-linking mechanism. However, for PSF, there is evidence that the predominant mechanism of crosslinking (for  $\gamma$ -irradiation at low dose rates at 30 and  $150^\circ\text{C}$ ) involves the formation of Y-links, and that Eq. (2) is applicable [8] when a plot of  $1 + 3s^{1/2}$  versus  $1/D$  should be linear.

Charlesby-Pinner equation:

$$s + s^{1/2} = \frac{G(S)}{2G(X)} + \frac{4.82 \times 10^9}{G(X)M_n(0)D} \quad (1)$$

Y-linking equation:

$$1 + 3s^{1/2} = \frac{2G(S)}{G(X)} + \frac{1.93 \times 10^7}{G(X)M_n(0)D} \quad (2)$$

where  $s$  is the soluble fraction,  $D$  is the dose in Gy,  $M_n(0)$  is the initial number-average molecular weight, and  $G(S)$  and  $G(X)$  are, respectively, the number of scission and crosslinking events occurring per 16 aJ (100 eV) of energy absorbed.

The variation in the soluble fraction for a 0.55-mm sheet irradiated with 0.7 MeV electrons from the Van de Graaff accelerator at 3 MGy/h showed a linear relationship between  $1 + 3s^{1/2}$  and  $1/D$  in accordance with Eq. (2), which was identical with  $^{60}\text{Co}$   $\gamma$ -irradiation at  $30^\circ\text{C}$ . This result indicates that 1)  $G$  values for scission and crosslinking in PSF are the same for electron beam and  $^{60}\text{Co}$   $\gamma$ -radiation, 2) there is no effect of dose rate on  $G(S)$  and  $G(X)$  between 0.01 and 3 MGy/h for these experimental conditions, and 3) there is no significant temperature rise at 3 MGy/h under the experimental conditions.

The effects of electron-beam irradiation at high dose rates and for different sample thickness are shown in Fig. 1, where the soluble fractions are plotted according to Eq. (2) and compared with the linear relationships obtained at 30 and  $150^\circ\text{C}$  from experiments at low dose rates. All three plots show curvature, indicating systematic deviations, increasing with dose, from the results for irradiation at a

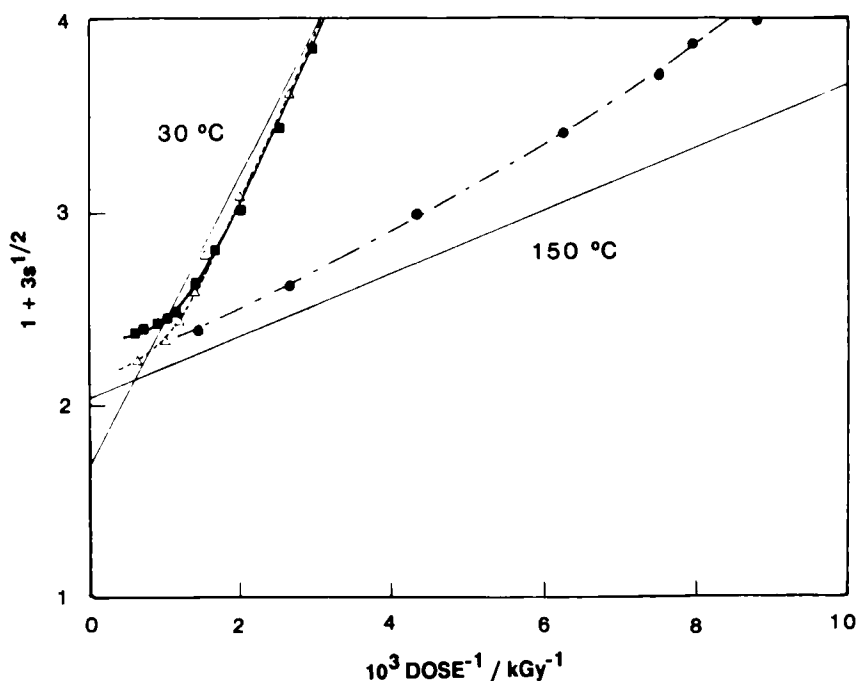


FIG. 1. Soluble fraction data plotted according to Eq. (2) for electron beam irradiation of bis-A PSF at an ambient temperature of 30°C in vacuum at 18 MGy/h: (■) 0.55 mm sheet, (△) 1.85 mm sheet, (●) outer layer of a 2 × 1.85 mm laminate. The full lines represent the results obtained for irradiation at 30 and 150°C with  $\gamma$ -rays or an electron beam at low dose rates when the temperature of the polymer sample did not increase significantly with irradiation time.

constant temperature of 30°C, achieved at low dose rates. These deviations can reasonably be attributed to increasing temperature of the sample during irradiation. This is consistent with the melting of the polymer observed in thick samples after high doses under these conditions. The solid lines in Fig. 1 correspond to  $\gamma$ -irradiation at low dose rates at 30 and 150°C [5, 6], when there is no increase in temperature during irradiation.

The value of  $G(X)$  for any irradiation time or dose can be obtained from the slope of the plot in Fig. 1 according to

$$G(X) = \frac{1.93 \times 10^7}{\text{slope} \times M_n(0)} \quad (3)$$

A plot of  $G(X)$  versus temperature for  $\gamma$ -irradiation at 0.01 MGy/h is shown in Fig. 2. It can be seen that  $G(X)$  increases rapidly over the temperature range 30–110°C and then more slowly. At  $T_g$  there is a discontinuity in  $G(X)$ , which increases from 0.64 at 150°C to 1.34 at 220°C. The relationship in Fig. 2 provides a calibration curve to determine the sample temperature during electron beam irradiation at high dose rates. The variations in sample temperature with irradiation time can

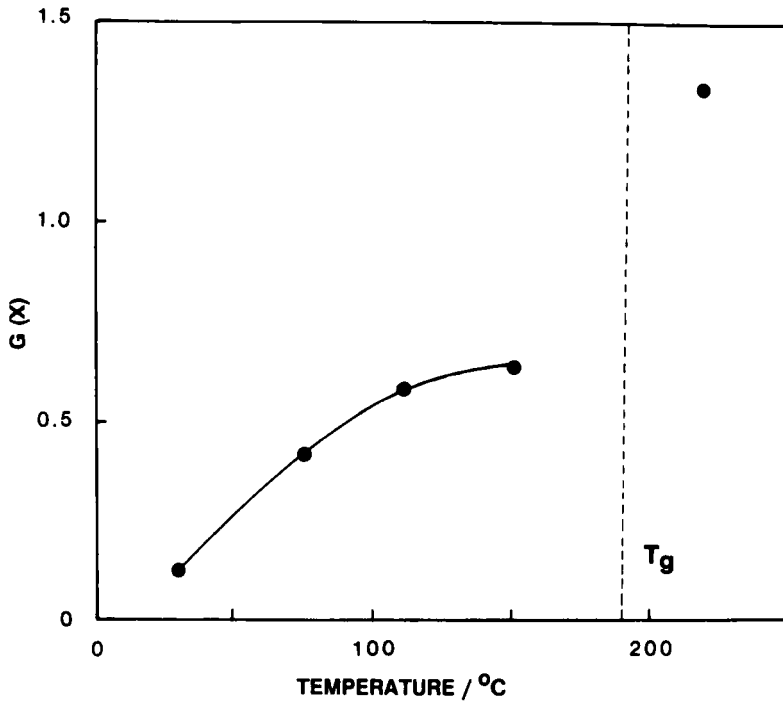


FIG. 2. The dependence of  $G(X)$  on temperature for  $\gamma$ -irradiation of PSF at 0.01 MGy/h in vacuum, determined from soluble fractions using Eq. (3).

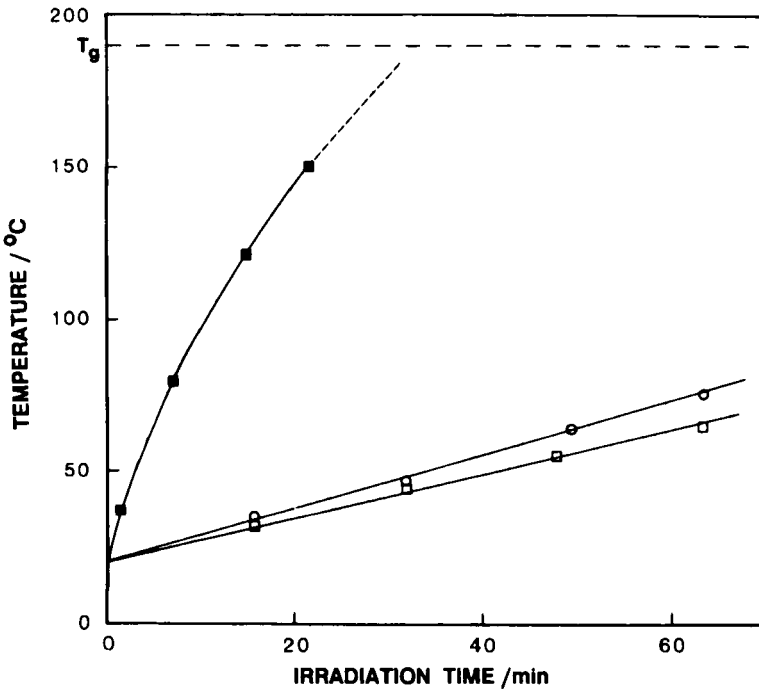


FIG. 3. Temperature of PSF samples during electron irradiation at 18 MGy/h in vacuum; (■) 3.7 mm laminate (outer layer), (○) 1.85 mm sheet, (□) 0.55 mm sheet.

therefore be determined by using the values of  $G(X)$  obtained from the slopes of the plots in Fig. 1, and are shown in Fig. 3 for different sample thicknesses at a dose rate of 18 MGy/h.

The temperature of the 0.55-mm sheet increased to 70°C after 70 min (20 MGy), whereas the outer 1.85 mm layer of the 3.7-mm laminate increased to 150°C after 25 min and exceeded the  $T_g$  of 190°C after 35 min, as observed by foaming of the sample. The effect of sample thickness indicates the importance of the efficiency of heat transfer through the polymer to the cooled metal mounting plate. The temperature of the sample continued to rise over a long period of irradiation and did not reach a steady-state value.

When the experimental data of Davis et al. [12] for electron beam irradiation of PSF were treated by the above procedure, a curved plot of  $1 + 3s^{1/2}$  versus  $1/D$  was obtained, indicating that the temperature probably increased during irradiation in their experiments. The maximum temperature was calculated to be up to 150°C, which would explain the differences between the  $G$  values which they reported and other results [5] for  $\gamma$ -irradiation.

## CONCLUSIONS

Determination of  $G(X)$  by measurement of soluble fractions using GPC is a convenient method for deducing the increase in temperature of PSF during electron-beam irradiation at high dose rates.

The determination of  $G(S)$  and  $G(X)$  by using this technique can be used to evaluate the temperature rise in any polymer sample with a particular geometry under specific irradiation conditions.

PSF can be used as a standard polymer for this method if specimens are prepared with the same size and shape as the sample under investigation. The procedure is adaptable to accelerated testing of polymer materials, including carbon fiber composites, and work is currently in progress to assess whether  $G(S)$  and  $G(X)$  for PSF are affected by the presence of carbon fiber. It is possible that the spatial uniformity of large test samples could be examined by using this technique.

Electron-beam irradiation at dose rates less than 3 MGy/h caused no significant temperature rise in 0.55 mm sheet mounted on a water-cooled aluminum plate, as the  $G(S)$  and  $G(X)$  values were similar to the values obtained previously for  $\gamma$ -irradiation.

Irradiation at more than 18 MGy/h caused the sample temperature to increase with irradiation time, and it was possible to exceed  $T_g = 190^\circ\text{C}$ .

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