Radical yields in irradiated poly(ethylene terephthalate) fibres

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The formation of free radicals and their subsequent decay in irradiated polyethylene terephthalate monofilaments was studied by e.s.r. under a variety of conditions. A yield of 0.023 radicals per 100 eV was found, in agreement with the literature values. Reduced values were found in the presence of water, methylene chloride and chlorine. The decay followed a two-stage second order pattern presumably due to radicals in the crystalline and amorphous regions. At −196°C, *G* values of 0.7 of trapped electrons were found, rapidly decaying as the temperature was raised. At about −135°C the signal changed to the characteristic signal found at room temperature with a *G* value of 0.42. On adding methylene chloride to irradiated PET, comparatively rapid decay of the trapped radicals took place, the rate corresponding closely to the rate of sorption of the methylene chloride into the monofilaments. This indicated very rapid decay even from the crystalline regions, once the solvent is present. A number of other observations are presented and interpreted in relation to, for example, the radiation grafting yields in the presence of solvents.

INTRODUCTION

The reported yield of free radicals produced by the irradiation of polyethylene terephthalate (PET) is extraordinarily low[1], only about 0.025 radicals per 100 eV. An excellent discussion of the radiation chemistry of PET has been presented by Turner[2]. Nevertheless reasonable radiation grafting yields have been reported both by the mutual and pre-irradiation methods[3,4,5]. The present paper presents a number of experimental results using e.s.r. which were conducted in an attempt to rationalize this discrepancy and to clarify the reasons for the low radical yield in PET itself.

EXPERIMENTAL

PET monofilaments of 800 denier furnished by Monsanto had a number average molecular weight of 52 000. The sample was approximately 50% crystalline as determined by density and had a finish which was removed by washing in cold carbon tetrachloride. After washing, the samples were air-dried in the dark and vacuum extracted overnight. The fibre was cut into 1-inch pieces and a weighed amount was placed in 4 cm outside diameter Suprasil tubes, sealed under 10^{-5} mmHg and irradiated.

Irradiations were carried out in a Gammacell 220 Co^{60} source (Atomic Energy of Canada Ltd) at a dose rate of 0.41 Mrad/h. The dosimetry was performed using the modified Fricke dosimeter containing $CuSO_4$. Some irradiations were carried out at 77K in a Dewar flask. The dosimetry for this system was performed in the same flask filled with a mixture of 63.42% acetone and 36.58% water which was found to have the same linear absorption coefficient as liquid nitrogen. Precautions were taken that the samples be maintained at constant temperature during irradiation.

After annealing the paramagnetic centres in the quartz, the concentration of the free radicals in irradiated PET was determined using an X-band e.s.r. spectrometer with 100 kHZ field modulation produced by Japan Electron Optics Laboratory Co. (Model JES-ME1X).

The number of the free radicals in the sample was estimated by double integration of the first derivative spectrum and comparison with a reference sample. In order to achieve better accuracy, precautions were taken that the reference sample had the same volume and the same dielectric losses as PET sample and this was done by supporting DPPH on PET powder. A 10^{-5} M.DPPH solution in benzene was used, pouring a determined volume on a known amount of PET powder, evaporating in air in the dark, grinding it, and sealing a weighed amount in vacuum in an e.s.r. tube. A double mode cavity was used to record at the same time the signal of the sample and that of a marker. Then the sample was replaced by the DPPH reference sample and the signal recorded again. Comparisons between the area of the sample and that of the DPPH reference sample each normalized to the height of the marker were made. As a marker MnO uniformly dispersed in MgO was used.

The cavity could be cooled down at various temperatures between 77 and 273K and the temperature was controlled by means of a copper-constantan thermocouple. For measurements at low temperature, precautions were taken to avoid the saturation of the signal with power. A power of 0.2 mW was found satisfactory for this purpose.

In some experiments the fibre was irradiated after soaking in deionized water, gently wiping and then sealing in e.s.r. tubes at 10^{-5} mmHg after three freeze-thaw cycles. Some PET samples were irradiated in a Cl_2 atmosphere. These samples were prepared in the following manner. PET was

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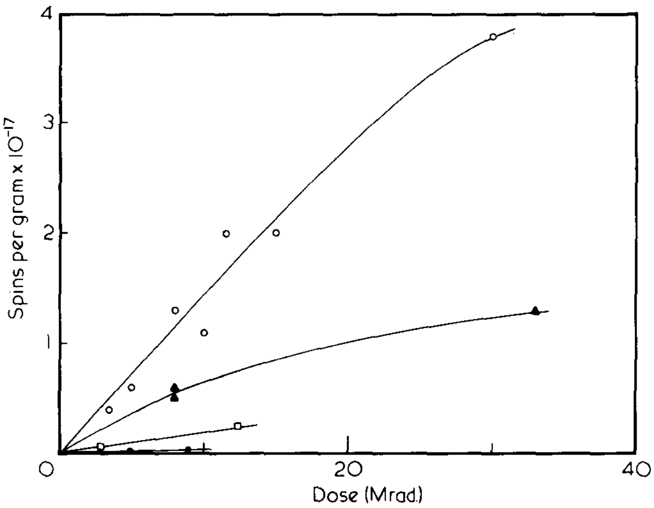

Figure 1 The build up of free radicals with dose at 25°C; dose rate 0.41 Mrad per hour. ○, PET; ▲, PET saturated with water; □, PET plus chloride; ●, PET saturated with methylene chloride

degassed overnight in a separated part of the vacuum line. Cl$_2$ was condensed from a bomb to a liquid nitrogen trap in the vacuum line. After the air was removed from Cl$_2$ by several freeze-thaw cycles, contact of the PET with gaseous Cl$_2$ was allowed. PET was again separated by turning a stopcock but this time it was in a Cl$_2$ atmosphere. Cl$_2$ was condensed by plunging the end of the tube in liquid nitrogen so that the tube could be sealed. The final chlorine pressure in the tube containing PET was about 1 atmosphere.

The swelling of PET fibre in CH$_2$Cl$_2$ was followed by weighing the fibre after various times of contact.

RESULTS

The accumulation of free radicals with dose is presented in *Figure 1*. From the linear portion of the curve a free radical yield, 0.023 radicals per 100 eV, was calculated. This is in agreement with the value of 0.025 ± 0.005 determined by Campbell *et al.*[1].

The decay of the free radicals produced in PET irradiated at three different doses was followed and the results are presented in *Figure 2*. The curves can be regarded as having two regions each representing a second order decay. The rate constants for the first portion were calculated and are presented in *Table 1*. As can be seen, the rate constants are decreasing as the total dose increases.

Figure 1 includes the effect of some added substances on the free radicals production in irradiated PET. The results show that H$_2$O reduces the concentration of free radicals; the effect is bigger for Cl$_2$, and CH$_2$Cl$_2$ almost totally suppresses the formation of free radicals. In this latter case, more precautions were taken to eliminate the errors: after the irradiation, the sample was vacuum extracted to remove completely the CH$_2$Cl$_2$ which introduces dielectric losses in the magnetic field. After a dose of 9 Mrad, only 1% of the radicals produced in PET were present in PET–CH$_2$Cl$_2$ swollen. To verify this result a different approach was followed. Degassed PET samples were irradiated at a dose of 9 Mrad and methylene chloride then distilled under vacuum into the tube. At various times the methylene chloride was removed from a sample and the radical concentration measured. The radical concentration is plotted in *Figure 3* as a direct function of the time of contact with the methylene chloride and also as a first-order plot. The time scale of these experiments is much shorter than the normal rate of decay of radicals in PET so negligible error was introduced by the procedures used.

The rate of sorption of methylene chloride into the PET monofilaments was measured separately and the results are shown in *Figure 4*. The sorption is linear with time. The small decrease in the amount sorbed after attaining 'equilibrium' can be attributed to a small amount of additional crystallization.

Samples were also irradiated at liquid nitrogen temperatures, the fibre turned purple-violet and the signal recorded at −196°C was a strong singlet. *Figure 5* shows the increase in the concentration of trapped species at −196°C with the time of irradiation. A G value for the trapped species of 0.67 was obtained; these results are in good agreement with the value already reported[6] of 0.70. As the sample was allowed to warm up, the intensity of the signal decreased and around −135°C the signal appeared *identical* to that recorded following irradiation at room temperature; i.e., a poor resolved signal having a width of approximately 200 G's. The spectrum is shown in *Figure 6*. *Figure 7* shows the

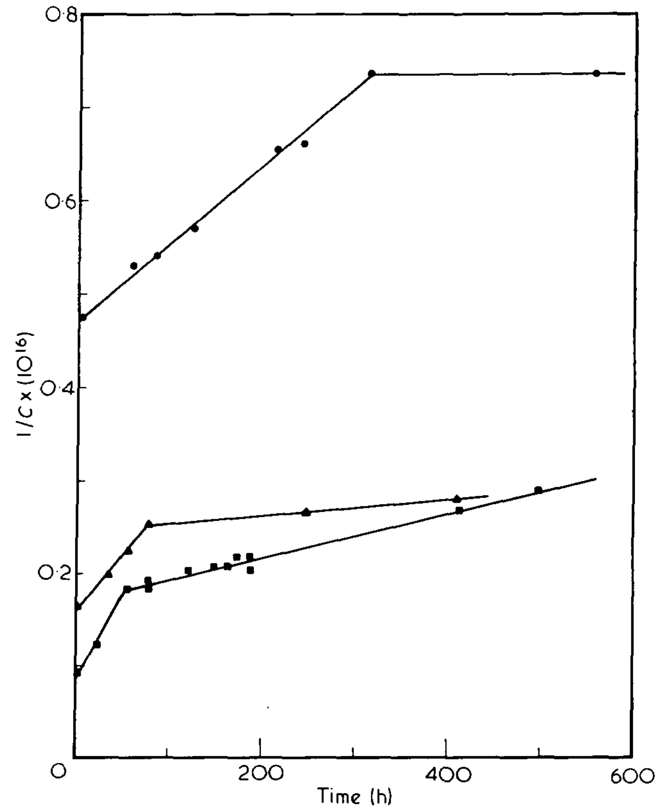

Figure 2 Decay of radicals in PET at 25°C. ●, dose 15.0 Mrads; ▲, dose 7.5 Mrads; ■, dose 3.5 Mrads

Table 1 Second order rate constants for the initial disappearance of free radicals in PET irradiated in vacuum at room temperature

Dose (Mrads)	k (radical^{-1} g h^{-1})
3.5	1.8 x 10^{-19}
7.5	1.1 x 10^{-19}
15	8.3 x 10^{-21}

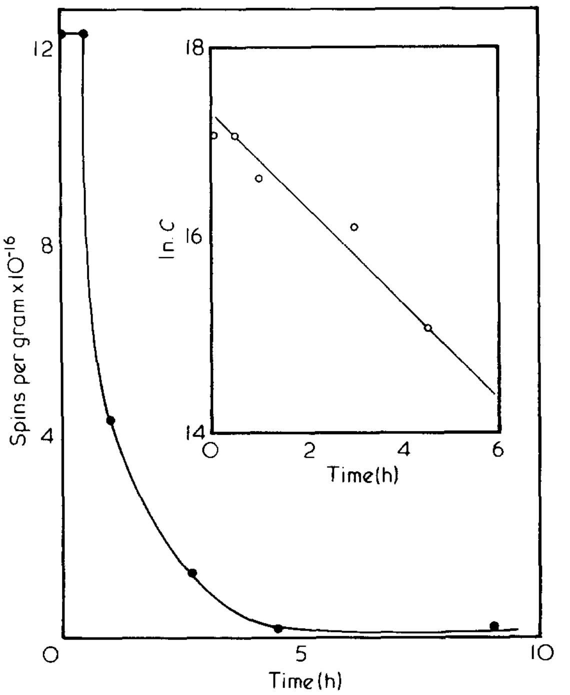

Figure 3 Decay of radicals in PET at 25°C on addkng methylene chloride. Inset in same data as a first-order plot

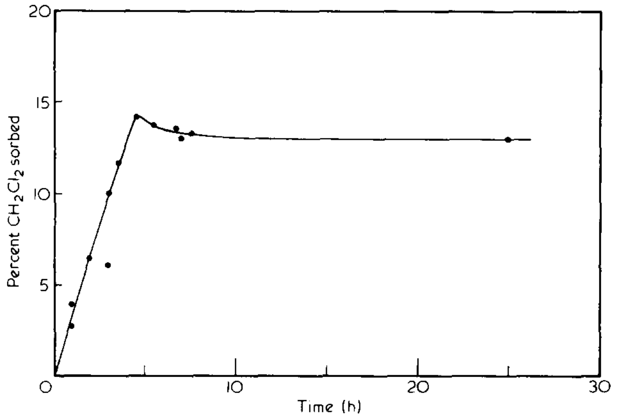

Figure 4 Sorption of liquid methylene chloride into PET at 25°C

decay of the signal intensity with the temperature for PET and for PET CH_2Cl_2 swollen both irradiated at −196°C. Although at −135°C the signal is that characteristic for free radicals, the presence of some trapped ions and electrons in low concentration can be presumed. Accordingly, in order to record the decay of free radicals only in PET at low temperatures, an annealing period of 5 minutes at −30°C was used during which the trapped electrons and ions were presumed to have disappeared completely. After annealing, the temperature was lowered to the desired value and the decay of the radicals recorded (*Figure 8*) for PET swollen in CH_2Cl_2 and irradiated in liquid nitrogen. The radicals were found to decay in the same way as in PET at room temperature (*Figure 2*) and the calculated second order rate constants for the first region are listed in *Table 2*. It should be mentioned that at this temperature, the radicals in unswollen PET do not decay at all within the same time scale.

DISCUSSION

The free radicals in PET are produced and disappear following types of curves which are common to many polymers. The curve has the same shape irrespective to the dose, temperature or nature of polymer, hence has to be interpreted in the view of these facts.

Radicals in PET are produced with the same G value in the amorphous and crystalline samples as Campbell and coworkers have shown[1,2]. At higher doses somewhat more radicals have accumulated in the crystalline samples which demonstrates that radicals in the crystalline regions disap-

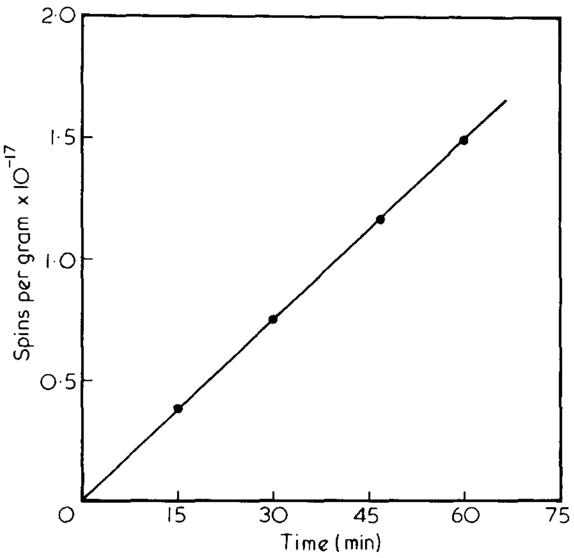

Figure 5 Build up of trapped electrons at −196°C in PET

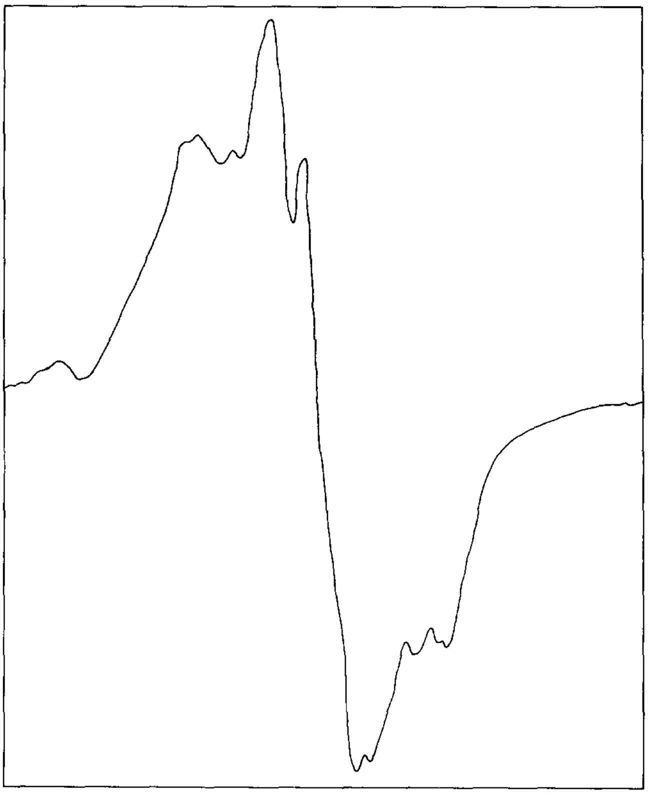

Figure 6 Spectrum of irradiated PET at −130°C and room temperature Mod. width 50G, width 200G

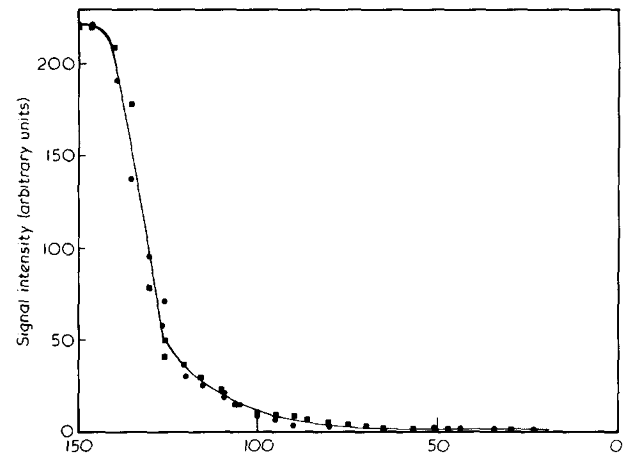

Figure 7 Decay of trapped electrons and other species in PET after irradiating at −196°C and allowing to warm up. ●, PET; ■, PET saturated with methylene chloride

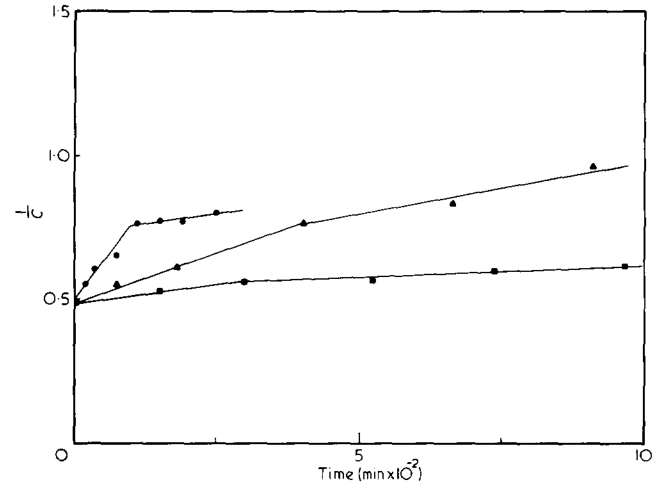

Figure 8 Decay of trapped species in irradiated methylene chloride saturated PET at ●, −30°C, ▲, −50°C, and ■, −130°C. Dose 5.3 Mrads at −196°C

pear at lower rates. As a consequence, at higher doses, the free radicals contained in the fibre will be more and more located in the crystalline regions, so the contribution of these radicals to the first portion of the decay curve will be higher at higher doses. Accordingly, a decrease of the rate constants for this first portion of the curve with the dose has to be expected. These expectations are confirmed by the results reported in *Table 1*.

The decay kinetics of the radicals produced in the PET have been treated quantitatively using the Q-function and equations developed by Dole *et al.*[6]. Excellent agreement with theory was found. These results have been reported elsewhere[7].

The use of a swelling agent such as methylene chloride should, in principle, enable us to destroy the radicals in the amorphous phase while preserving the radicals in the crystalline phase. On irradiating the fibre after swelling to equilibrium in CH_2Cl_2, a very low concentration of free radicals was recorded; 1% of the radicals present in unswollen PET irradiated with the same dose. This result appears hard to explain since the polymer is 50% crystalline and the radicals are formed with the same G in the amorphous and crystalline phase. Our result can, however, be explained if we admit that free radicals from crystalline regions migrate into the amorphous regions within the time of measurement and terminate there. The migration is present whenever a gradient of free radical concentration appears, as for example in the case of quick consumption of free radicals in the amorphous regions plasticized by CH_2Cl_2. As the concentration gradient decreases the rate of migration decreases and a stationary low concentration of free radicals in the crystalline regions remains (1% in our case).

The disappearance of free radicals swelling in CH_2Cl_2 (*Figure 3*) is first order, this may be due to the fact that the diffusion is the rate determinant step. An alternative explanation for the first order decay is the reaction of radicals with CH_2Cl_2, but this does not appear to be the case since in the grafting experiments where CH_2Cl_2 is the swelling agent G (grafted branches) is larger than G (radicals).

The migration of radicals from crystalline regions is present probably at low temperatures in the system PET + CH_2Cl_2 (*Figure 8*) and at room temperature in PET but at a lower rate for the disappearance of the radicals in the amorphous regions.

Another experimental fact supporting the hypothesis of free radical migration is that G(grafted branches) > G(radicals) in spite of the fact that the radicals in the crystalline region are supposedly unreactive. This can be explained only by admitting free radical migration from the crystalline to the amorphous regions.

We do not have any particular knowledge about the nature of free radical migration but Dole's *et al.*[8] hypothesis of hydrogen atom hopping provides a reasonable picture of the process.

The methylene dichloride does not help in the production of trapped paramagnetic species when it swells PET,

Table 2 Second order rate constants for the decay of radicals produced in PET swollen in CH_2Cl_2 and irradiated at −196°C

T(°C)	k (radical^{-1} g h^{-1})
−30	11.1×10^{-19}
−50	2.70×10^{-19}
−90	8.1×10^{-20}
−120	7.4×10^{-20}

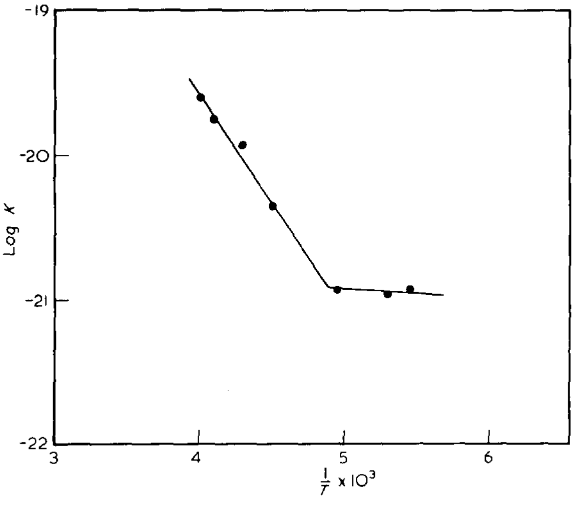

Figure 9 Decay rates of trapped species as a function of temperature details as for *Figure 7*

nor does it interfere in the process of transformation of these species into free radicals as can be judged from *Figure 7*. Its only role appears to be a plasticizing action making the rapid decay of the radicals possible even at very low temperatures (*Figure 7*) where the radicals in irradiated PET disappear extremely slowly. The calculated rate constants for the quicker second order decay were plotted against the temperature according to an Arrhenius plot and a T_g value of −65°C was found for the system PET–CH_2Cl_2 swollen (*Figure 8*). The plasticizing effect of a number of non-aqueous solvents on PET has been reported. Measuring the dynamic shrinkage of polyester yarn in these solvents T_g values were determined as being very low[9]. There is no value for PET–CH_2Cl_2, but similar substances like CH_2Br_2 and $CHCl_3$ lower the T_g to −81 and −95°C, respectively, in a 30% crystalline polyester yarn. Our PET was 50% crystalline since T_g increases with the degree of crystallinity, our value of −65°C seems reasonable.

The decay of trapped radicals at room temperature on the addition of methylene chloride is first order, at variance with the second order plots. However, this process is a complex function of diffusion and termination and would be difficult to interpret unequivocally.

The irradiation of PET at −196°C produced trapped species with a G (free radical) value of 0.67 compared with a G (free radical) value of 0.023 at room temperature. The signal recorded at −196°C is a strong singlet with g equal to that of the free electron, it can be photobleached and it saturates easily with power. It can be therefore attributed to trapped electrons. No excited triplet state has been reported at this temperature. A most important observation is that at −135°C the signal changes to that found at room temperature although some overlapping with the low temperature species presumably still exists. The G(trapped species) at −135°C is 0.42. Most of the radicals produced recombine before they can be detected by e.s.r. at room temperature. This is presumably due to some polymer chain mobility even at very low temperatures. A secondary transition has been detected for example at −100°C[10]. The low yield of hydrogen, $G(H_2) \sim 0.016$, is consistent with this explanation. Somewhat similar observations, including a change in the rate of decay at about −100°C, have been reported by Hamma and Okamoto[11]. The change in rate however is based on only one point, if this is ignored the curve is similar to *Figure 7* of this paper. When samples are irradiated in the presence of CH_2Cl_2 plus a reactive monomer such as styrene some of the radicals can presumably initiate polymerization before they can terminate leading to reasonable grafting yields. In the case of preirradiation grafting there is a smaller but still substantial yield. With both grafting methods there is probably chain transfer of the growing chain to the PET molecules leading to more grafted side chains. In this way the low yields of radicals measured by e.s.r. can be rationalized with the reasonable yields of graft copolymer. The grafting results are discussed in detail in another paper.

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