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Radioluminescence of γ-irradiated polypropylene at low temperatures

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Abstract

The radiothermoluminescence glow curves of polypropylene samples, γ-irradiated at 77 K, were recorded in the temperature range 77–270 K at a low heating rate. For oxygen-free polypropylene, thermoluminescence maxima were found at 90, 116, 211 and 234 K. Dose dependences of the isothermal luminescence at 77 K and the radiothermoluminescence peaks were observed. The influence of soaking in hydrocarbon solvent, oxygen and pyrene on the radioluminescence of polypropylene was examined. Preliminary results on the spectral distribution of polypropylene radioluminescence are presented. The ionic processes responsible for the isothermal luminescence and radiothermoluminescence peaks are discussed.

Keywords: Polypropylene; Radioluminescence; Radiothermoluminescence; Ionic processes; Isothermal luminescence; Low temperature radiolysis

1. Introduction

Since 1960, the radioluminescence of γ-irradiated polyethylene has been investigated in considerable detail [1–3], but the closely related polymer, polypropylene, has received little attention [4]. A few Russian papers have dealt with this problem [5,6]. In general, the interpretation of the scarce data on polypropylene radioluminescence has been based on the assumption that the isotactic polypropylene can be treated as a regularly methyl-substituted polyethylene. Boustead and George [4], as early as 1972, indicated that the polyethylene interpretation should be applied only with extreme caution.

Our interest in the radioluminescence of hydrocarbon-related polymers (polyethylene, etc.) started towards the end of the 1980s [3,7–11] when a long-term research programme in this field was introduced in our laboratory. These polymers are very important materials due to their application in the nuclear industry (insulating materials, etc.) and radiation technologies (sterilization, etc.).

This paper reports some novel features associated with the radioluminescence mechanism of polypropylene ("pure" and in the presence of additives, i.e. oxygen, aromatics etc.) irradiated at 77 K. Using specially designed radiothermoluminescence equipment with a low heating rate, the dose dependence of the glow peaks for polypropylene was investigated for the first time for doses up to 100 kGy and new information on the transitions in hydrocarbon-related polymers was found.

2. Experimental details

Commercial isotactic polypropylene (PP) (Malen-P F-601, Poland) (isotacticity index, 95%; melt flow index, 5.5–8.5 g (10 min)$^{-1}$; density, 0.9024 g cm^{-3}; granules) was used. The amount of additives (calcium stearate, Irganox B-215) did not exceed 0.2%. Low-density polyethylene (PE) (commercial, additive free, PE II-020/FO, Poland, granules) was used [3]. The following solvents were applied: cyclohexane (ACS reagent; Aldrich) and *n*-hexane (puriss; Fluka). Pyrene (Py) (analytical grade; POCh, Poland) was recrystallized twice from ethanol. In order to remove the additives, PP and PE granules were soaked in alkane solvents. The solvent was changed every week for 6 months. The absorption spectra of the hydrocarbon extracts were recorded on a diode array spectrophotometer (Hewlett-Packard HP 8452A). The absorption of the extracts at 276 nm, typical of hindered phenolic antioxidants [12] decreased with extraction time. Traces of absorption at 276 nm were still observed for extraction periods longer than 6 weeks.

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Py was introduced into amorphous regions of PP by soaking the granules (purified as described above) for 6 months in *n*-hexane solutions of Py. Afterwards, the samples were washed in pure solvent to remove traces of Py from the surface.

The samples were degassed for 20 h using a typical vacuum line (approximately 10^{-4} Torr). In order to determine the effect of oxygen, the samples, after deaeration, were exposed to air for 24 h.

Irradiation with γ-rays from a ^{60}Co source was carried out in the dark under liquid nitrogen at a dose rate of approximately 1.7 Gy s^{-1}.

The emission spectra were recorded using the equipment described previously [3]. Measurements of the radiothermoluminescence (RTL) were performed using the modified apparatus described previously by Kroh and Wypych [13]. The essential feature was a novel data acquisition system. In the modified system, the signal from the photomultiplier, the temperature of the sample and the time from the beginning of the measurement were simultaneously recorded by a computer (PC IBM AT 386SX). The photomultiplier current was measured by a Keithley 185 autoranging picoammeter with a GPIB interface. A constantan–copper thermocouple connected to a digital millivoltmeter (Meratronik, Poland) on line with an 8255 interface was used for temperature measurements. The time was measured by the computer internal clock. The average heating rate varied between 0.9 and 1.0 K min^{-1}.

3. Results and discussion

3.1. Isothermal luminescence (ITL) of PP at 77 K

The ITL of γ-irradiated PP at 77 K can be observed at liquid nitrogen temperature for a long period of time, up to several hours. The intensity of the ITL for solvent-treated PP is higher than that for untreated PP.

In agreement with Płonka's model [14] of the time-dependent rate constant, the intensity of ITL (I_t) can be represented by the following expression

$$I_t = a t^{(\alpha-1)} \exp\left(-\frac{B}{\alpha} t^{\alpha}\right) \tag{1}$$

where a, B and $0 < \alpha \leqslant 1$ are constants. The numerical values of B and α allow the determination of the distribution of the reaction constants. The lower the value of α, the wider the distribution function f(k); B corresponds to the time- independent, classical rate constant. The ITL decay, as represented by Płonka's approach, is shown in Fig. 1. The α values were calculated to be around 0.52 for solvent-treated PP irradiated at 77 K with doses of 3.35 kGy and 15.9 kGy; however B values were found to be 0.068 $min^{-\alpha}$ and 0.0075 $min^{-\alpha}$ for the above mentioned doses respectively. The influence of different irradiation times at 77 K can explain the observed dose effect on the B values. The α value of 0.52 is higher than $\alpha = 0.3$ found for trapped electron (e_t^-) decay at 77 K in irradiated PP observed by the electron paramagnetic resonance (EPR) method [15]; α values in this range suggest that thermally assisted charge tunnelling may contribute to ITL in PP as was proposed previously for PE [3].

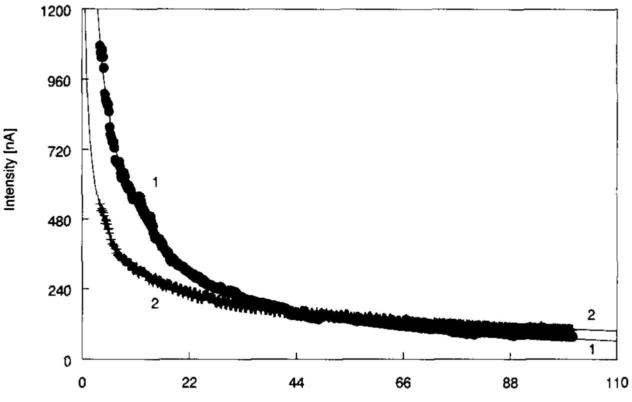

Fig. 1. The ITL decay at 77 K for solvent-extracted, oxygen-free PP as represented by Eq. (1): 1, 3.35 kGy, $\alpha = 0.49$, $B = 0.068$ $min^{-\alpha}$; 2, 15.9 kGy, $\alpha = 0.55$, $B = 0.0075$ $min^{-\alpha}$.

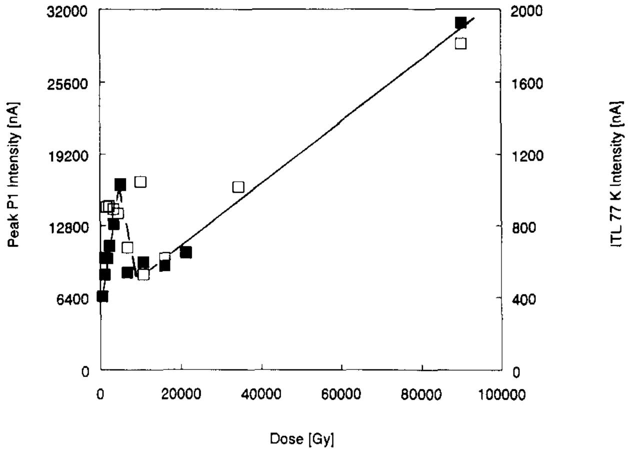

Fig. 2. Dose dependence of ITL at 77 K (□) and peak P1 intensity (■) for solvent-extracted, oxygen-free PP.

The dose dependence of the ITL intensity measured 180 s after the end of irradiation (Fig. 2) is very similar to that found by Mayer et al. [7] for high-density PE. The ITL intensity increases with dose at low doses, passes through a maximum at about 5 kGy and then decreases. In the high dose range, from 22 kGy to 110 kGy, the ITL intensity again increases with dose. It is worth mentioning that the concentration of e_t^- in PP [15] and PE [16], γ-irradiated at 77 K, passes through a maximum in a similar dose range (about 4.8 kGy for PP [15]). At the same time, for PP irradiated with 110 kGy, no EPR signal corresponding to e_t^- is detected [15].

3.2. Radiothermoluminescence (RTL) of PP

For oxygen-free, solvent-untreated PP, γ-irradiated at 77 K, the RTL peaks appear at about 90–91 K (P1), 116 K (P2) and in the temperature range 250–260 K; however, the latter emission is rather weak. The RTL curve for solvent- treated, deoxygenated PP, γ-irradiated at 77 K, consists of four peaks: P1 at 91 K, P2 at 116 K, P3 at 211 K and P4 at 234 K (Fig. 3). Peaks P1 and P2 in the RTL curve of PP were observed by Boustead and Charlesby [1], but the resolution of their glow curves was very poor and only traces of the P1 maximum were detected. The high temperature peaks (P3 and P4) have not been observed previously [1,4], probably due to the very low luminescence intensity in this temperature range. Poorly resolved low temperature RTL peaks have been detected for PE previously [1]. The RTL curve for solvent-treated PE, γ-irradiated at 77 K, obtained using our equipment is also shown in Fig. 3.

The RTL intensity of solvent-treated, oxygen-free PP is much stronger than for untreated PP. The hydrocarbon solvent extracted the hindered phenolic antioxidants present in commercial PP. These compounds are poor emitters with very low quantum yields of fluorescence and phosphorescence (approximately 10^{-3} in non-polar solvents) [12], and may quench matrix luminescence.

3.3. The influence of additives on RTL peaks

The RTL intensity in the low and high temperature ranges for PP granules soaked in *n*-hexane containing Py increases substantially compared with the undoped matrix. In the presence of Py, the resolution of the RTL peaks in the low and high temperature ranges is rather poor (Fig. 4). The intensity of the high temperature peak of PP increases with Py concentration in the range 10^{-3}–10^{-2} mol dm^{-3} in *n*-hexane solution used for soaking, whereas the P1 peak intensity decreases (Fig. 4).

In the presence of oxygen, peak P2 at 116 K and an additional maximum at about 151 K are detected for the PP sample containing Py. The latter emission

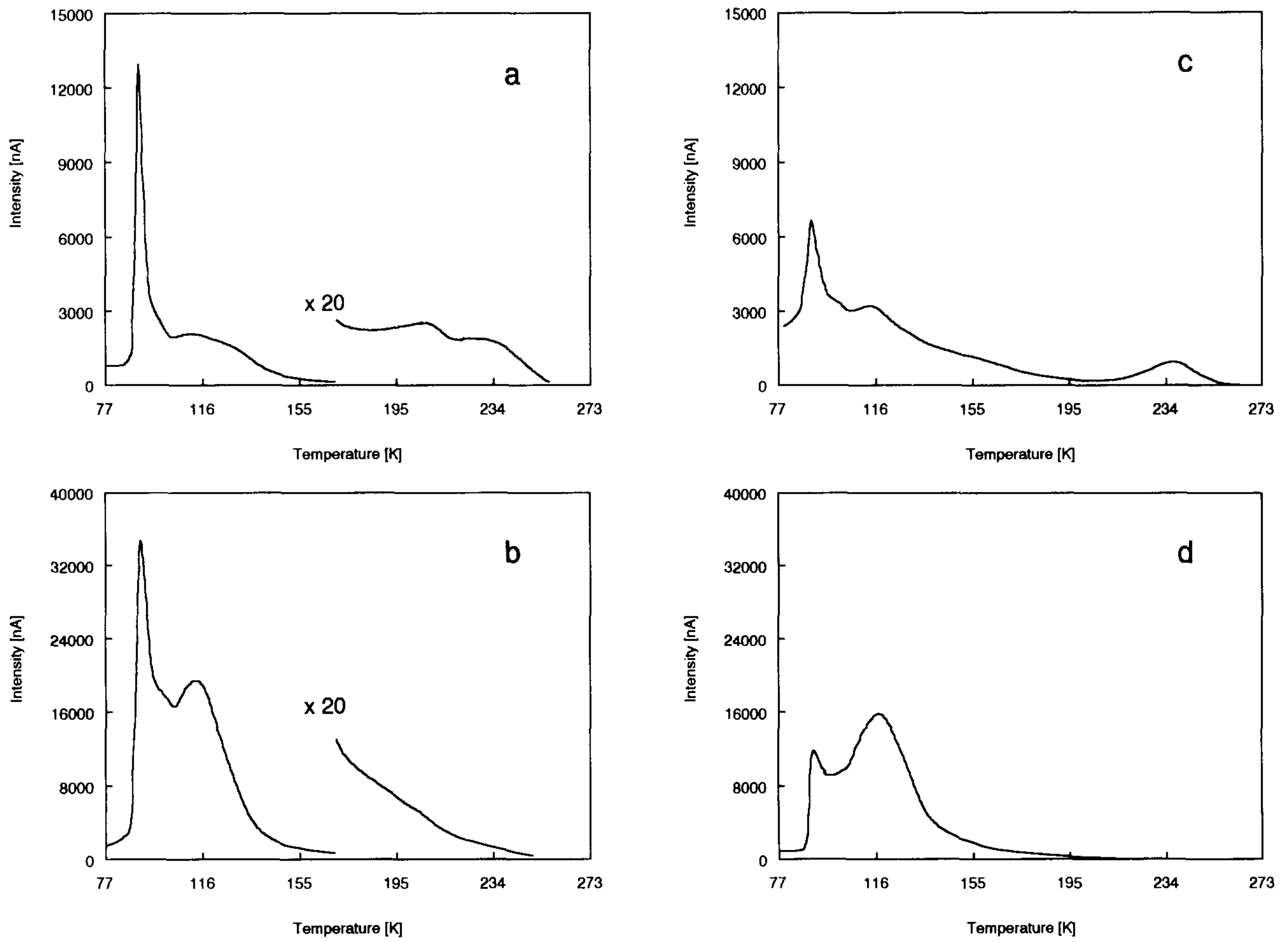

Fig. 3. Thermoluminescence glow curves of solvent-extracted, oxygen-free polymers: (a) PP, 3.35 kGy; (b) PP, 90.1 kGy; (c) PE, 3.0 kGy; (d) PE, 102 kGy.

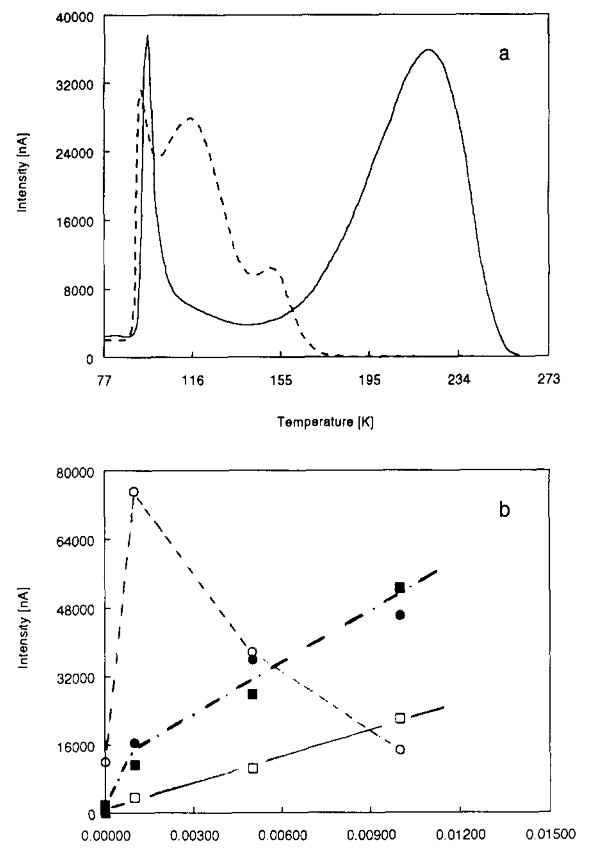

Fig. 4. (a) RTL glow curves of PP (γ-irradiated at 77 K) containing Py ([Py] in n-hexane solution, 5×10^{-3} mol dm^{-3}): deaerated sample (full line); in the presence of oxygen (broken line). Dose, 3.35 kGy. (b) Influence of Py concentration in n-hexane solution (used for soaking) on RTL peak intensity: ○, P1; ●, high temperature peak (220 K); ■, P2 in the presence of oxygen; □, "oxygen peak". Dose, 3.35 kGy.

represents the well-known oxygen peak [9]. The intensities of these two RTL peaks (P2 and the oxygen peak) increase with Py concentration in n-hexane solution (Fig. 4). The high temperature peak in the temperature range 200–240 K is quenched totally in the presence of oxygen regardless of the method of PP sample preparation. For solvent-treated PP granules and commercial PP, the low temperature part of the glow curve remains almost unchanged in the presence of oxygen. No "oxygen peak" at 151 K is observed in these samples.

3.4. The dose dependence of the RTL intensity

The intensities of the RTL peaks were measured in terms of the peak height, a valid measurement since the temperature bandwidths of those peaks which could be isolated were found to be almost independent of dose. Fig. 5 shows the dose dependence of peaks P2 and P3 + P4 for oxygen-free, solvent- treated PP. The dose dependence of peak P1 is very similar to that observed for the ITL of PP (Fig. 2), whereas the intensity of the P2 maximum increases linearly with dose up to 25 kGy and seems to saturate at higher doses (Fig. 5).

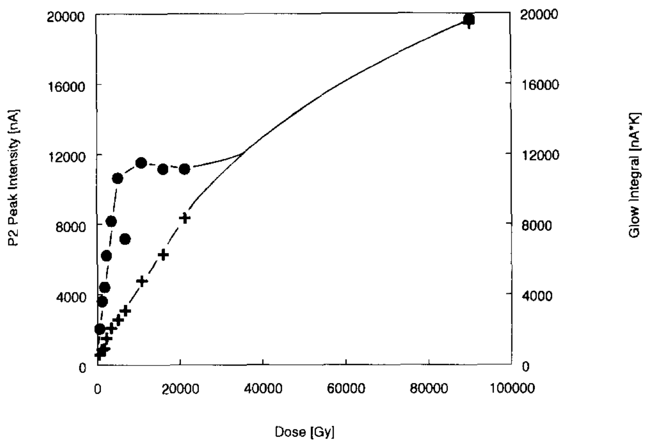

Fig. 5. Dose dependence of P2 peak intensity (+) and glow integral in the range 170–250 K (●) for solvent-treated, oxygen-free PP.

Due to the low intensity of the high temperature RTL peaks P3 and P4, only the integral luminescence intensity in the temperature range 170–250 K could be measured; hence, in Fig. 5, this dose dependence is shown. Some similarity between the P2 and P3 + P4 dose dependences is reasonable, since the integral luminescence intensity in the temperature range 170–250 K represents the P2 tail emission with traces of P3 + P4 peaks which are probably responsible for the observed low dose effect.

Similar dose dependences for the ITL and corresponding RTL peaks (P1 and P2) were also found for solvent-treated, low- density PE. Well-defined maxima were observed at a dose of 4.5 kGy. The high temperature RTL peak for γ-irradiated PE disappeared at a dose of 102 kGy (Fig. 3). It is probable that the P3 + P4 peaks for PP should also disappear at high doses, but the "tail effect" (Fig. 5) covers up the genuine dose dependence. Our dose dependence results for PE are similar to those obtained by Boustead [17].

3.5. Spectral distribution of PP radioluminescence — preliminary results

The spectral distribution of luminescence from PP, γ-irradiated at 77 K, taken at 77 K and in the temperature ranges in which the main RTL peaks were detected, is shown in Fig. 6. The radioluminescence spectra in the temperature range 77–110 K for untreated and solvent-extracted PP are very similar. The spectral distribution of ITL at 77 K from PP, following γ-irradiation at liquid nitrogen temperature, is characterized by two distinct maxima at 430 nm and 290–300 nm. The maximum of the emission band measured at about 110 K is shifted towards 460 nm compared with ITL. In the high temperature range, the RTL emission

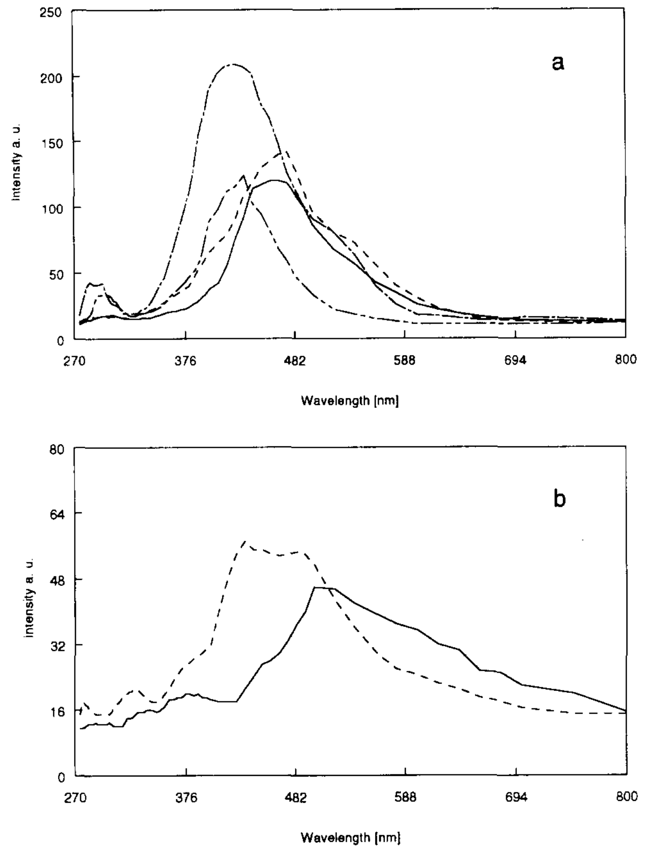

Fig. 6. Spectral distributions of luminescence from oxygen-free PP, γ-irradiated at 77 K, taken at different temperatures. Dose, 6.0 kGy. (a) ITL at 77 K: —-—, PP as received, sensitivity level ×0.1; — - - —, solvent-treated PP, sensitivity level ×0.3; 110 K: ——, PP as received; – – –, solvent-treated PP (in both cases sensitivity level ×0.3). (b) 264 K: ——, PP as received; 220 K: – – –, solvent-treated PP (in both cases sensitivity level ×0.1).

spectra are more complex with two luminescence bands peaking at 500 nm and 380 nm for untreated PP. For solvent-treated PP, a wide emission band is found at 430–480 nm (Fig. 6). Generally, the resolution of the spectra examined is rather poor because of the weak intensity of PP radioluminescence.

3.6. The mechanism of PP radioluminescence

The experimental results presented in this paper may be explained by assuming that, in PP under the influence of γ-rays, trapped electrons (e_t^-) and positive holes can be generated. The yield of e_t^- in PP irradiated at 77 K was found to be rather low, i.e. 0.17–0.35 [15,16]. The positive holes may be trapped either by impurities present in PP, e.g. acceptor molecules A introduced into the matrix (e.g. Py), or by radiolysis products P formed as a result of polymer irradiation. These scavengers can react with e_t^-

$$\text{A or P} + e_t^- \longrightarrow \text{A}^{\bullet -} \text{ or } \text{P}^{\bullet -} \qquad (2)$$

$$\text{A or P} + \oplus \longrightarrow \text{A}^{\bullet +} \text{ or } \text{P}^{\bullet +} \qquad (3)$$

The radioluminescence of γ-irradiated PP at low temperature can be produced via charge recombination

$$e_t^- + \text{A}^{\bullet +} \text{ or } \text{P}^{\bullet +} \longrightarrow \text{A}^* \text{ or } \text{P}^* \qquad (4)$$

$$\text{A}^{\bullet -} \text{ or } \text{P}^{\bullet -} + \text{A}^{\bullet +} \text{ or } \text{P}^{\bullet +} \longrightarrow \text{A}^* \text{ or } \text{P}^* \qquad (5)$$

where A^* and P^* denote the additive and radiolysis product excited states.

The above reaction scheme is commonly accepted for PE [2,3]. Alkyl radicals are the dominant species formed during irradiation in both the crystalline and amorphous domains of PP [18]. Different chemistry can result from energy deposition in the two regions, since oxygen, antioxidants and acceptor impurities are excluded from the crystalline phase. Alkyl radicals have a high electron affinity and low ionization potential and thus it is probable that they will trap both positive holes and e_t^- [19]. Main chain unsaturation (vinyl/vinylene) may also be responsible for charge trapping [1,20] as suggested for PE. Radiation-produced charges may be trapped by α,β-unsaturated carbonyl groups of the enone type, which have been proposed to be responsible for PP emission excited by UV light [21]. The reactions responsible for ITL at 77 K and for individual RTL peaks are discussed below.

The tunnelling recombination of charges at 77 K (reactions (4) and (5)) leads to ITL emission. At low doses, e_t^- reaction is responsible for ITL, whereas in the high dose range, anion–cation recombination may explain the observed ITL dose dependence (Fig. 2). In the high dose range, e_t^- should be scavenged by radiolysis products, i.e. radicals producing the carboanion R^- [19].

The ITL decay is not measurably dose dependent in terms of the α value. This suggests that each recombination event occurs as an isolated event between geminate, or correlated, charge pairs characterized by a similar distribution of inter-ion distances. An α value of the order of 0.5 suggests that thermal activation may contribute to tunnelling charge recombination [14].

The P1 dose dependence is very similar to that found for ITL (Fig. 2); hence it may be explained by the same reactions, i.e. reactions (4) and (5) for low and high doses respectively. However, the distances between ions undergoing recombination by tunnelling must be larger than for ITL.

The low temperature peaks for PE were found to be influenced by the time the samples were held at 77 K before warming [22]. We might say that the first RTL peak represents accelerated ITL.

In the presence of Py, the total light output of the glow curve is increased because $\text{Py}^{\bullet +}$ replaces matrix cations. As a result of charge recombination (reactions (4) and (5)), Py^* is generated. The quantum yield of Py^* fluorescence is quite high, i.e. 0.72–0.91 in the temperature range 293–77 K in non-polar solvents [23].

The influence of Py concentration (reaction (2)) on the P1 peak intensity (Fig. 4) supports the contribution of e_t^- to the P1 luminescence.

The P2 dose dependence (Fig. 5) suggests that the luminescence at 116 K is associated with the recombination of ions formed from radiolysis products. The radical anion R^- is probably involved in this ion recombination because the free radical concentration increases progressively with dose at low temperature [18,19]. Main chain unsaturation may be responsible for positive hole trapping because it increases with irradiation dose for PE [19]. Charge recombination probably takes place along the polymer chain because the matrix in this temperature range is still quite rigid. Long distance tunnelling transfer cannot be excluded in this case. Peak P2 is particularly strong for the PP–Py system in the presence of O_2 (Fig. 4). In this case, peroxy radical anions $RO_2^{\cdot -}$ are probably formed which recombine with $Py^{\cdot +}$ to generate Py*. The suppression of P2 emission for the oxygen-free PP–Py system is probably due to the lower energy of recombination released in the latter system than in the former. Energy problems associated with ion recombination have been discussed for the PE–O_2 system [9].

The "oxygen peak" at 151 K is only detected when Py molecules are introduced into PP (Fig. 4). The intensity of the "oxygen peak" increases linearly with Py concentration in *n*-hexane solution used for soaking. The emission at 151 K is due to reaction (6)

$$O_2^{\cdot -} + Py^{\cdot +} \longrightarrow Py^* + O_2 \qquad (6)$$

as found previously for PE [9].

The high temperature peaks (P3 and P4) seem to be due to the recombination of mobile molecular acceptor ions (impurities introduced into the matrix), as proposed for PE [2,3,10]. The emission in this range is quenched by O_2, and its intensity increases with Py concentration. The high temperature peaks decrease with dose due to the competition with radiation-produced charge acceptors (Figs. 3 and 4). The latter effect is observed in particular for PE (Fig. 3).

The identification of luminescence centres in irradiated PP is still a matter of discussion. In the case of PP doped with Py, the observed radioluminescence can be associated with the corresponding fluorescence and phosphorescence bands of the solute, as was observed with doped PE [3,7].

The origin of the luminescence from solvent-treated PP is only speculative at present. The spectrum observed for solvent-treated PP, γ-irradiated at 77 K, resembles the spectral distribution of the photoemission from extracted PP [24,25]. Photoexcitation experiments indicate that the main fluorescent species in PP are foreign impurities originating from the ambient atmosphere and the contribution of phosphorescent species, such as carbonyl groups, incorporated in the polymer is small [25]. On the other hand, Allen [21] has concluded that the extractable fluorescent species in PP are a complex mixture of α,β-unsaturated carbonyl groups with a possible naphthalene component. The regeneration of fluorescence in the polymer after extraction may be due to an oxidation process which achieves rapid equilibrium [21].

Following our mechanism, the excited states of radicals or other radiolysis products formed during the γ-irradiation of PP at 77 K may be responsible for low temperature radioluminescence. Certainly, this problem needs further investigation.

Finally, we wish to emphasize that the P1 and P2 RTL peaks observed for both PP and PE at 90 K and 116 K respectively represent transitions not observed previously by other methods [21]. The migration of Renker-type defects in crystalline PE has been suggested to occur at about 123 ± 5 K [19]. The limited relaxation data obtained so far for PP do not permit a substantiated assignment to be made of the different transitions to specific structural formations.

In conclusion, the radioluminescence phenomena in γ-irradiated PP seem to be similar to those observed for PE.

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