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Excimer probing of phase transition in polypropylene

J. Mayer*, T. Szreder

Institute of Applied Radiation Chemistry, Technical University, Wróblewskiego 15, 93-590 Lodz, Poland

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Abstract

Luminescence from electron-irradiated polypropylene doped with naphthalene and pyrene was investigated in the temperature range 77–273 K. Excimer emission of the aromatic admixture was observed in the temperature range 240–260 K of the high temperature radiothermoluminescence peak where the glass transition was recorded. The mechanism of solute excimer formation is discussed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

It is commonly accepted that excimers can be generated in liquids by the association of excited and non-excited molecules. The excited solute molecules can be produced as a result of photoexcitation and by ion recombination in systems irradiated using ionizing radiation. Brocklehurst and Russell [1] have shown that solute excimers resulted also from the neutralization of dimer cations at low temperature. In the case of polymer systems doped with aromatic additives, excimer generation can be also observed [2–4] for high aromatics content. In order to get such information the spectral distribution of the radiothermoluminescence (RTL) of γ-irradiated doped polymers has to be investigated [3]. Usually, in polymers, RTL for samples γ-irradiated at 77 K occurs as a series of few peaks at certain temperatures depending on both, the chemical structure and polymers morphology. In the case of pure, oxygen-free polypropylene samples, RTL maxima were found at 91, 116, 211 and 234 K whereas for the polypropylene containing pyrene strong maxima were detected at ca. 91 K and poor resolved one in the 200–240 K [5]. The RTL peaks in the high temperature region can be attributed to the recombination of mobile molecular solute ions as it was proposed for polyethylene [3]. Solute excimer emission has been observed in high temperature RTL peak in the case of doped polyethylene [2].

The aim of this paper is to provide information concerning solute excimer formation in stationary irradiated polypropylene containing aromatic compounds, i.e. pyrene and naphthalene. It is worth to mention that contrary to the pyrene doped polyethylene no excimer emission was detected in doped polypropylene at room temperature using ns pulse radiolysis technique even if pyrene content in polymer system was close to ~0.02 mol dm^{-3} [6].

2. Experimental details

Isotactic polypropylene (PP), ~50% crystallinity, was produced by Great Lakes of Milan, Italy; samples were 60–70 μm thick films containing ca. 50 ppm irganox 1076. PP was purified by soaking for several weeks in *n*-hexane (puriss, Fluka) with repeated changes of the solvent in order to remove irganox type and other impurities. The solvent after extraction was monitored using UV–VIS absorption measurements. After 4 to 5 changes of the *n*-hexane the UV absorption responsible for irganox and another impurities was found to be constant and considerable low, however, the exact concentration of these compounds left in the polymer cannot be determined in this way. Pyrene (Py), analytical grade, UEB, Belgium after the crystalization from ethanol was additionally purified by sublimation whereas naphthalene (Nph), analytical grade, POCh, Poland was purified by sublimation too.

Acceptor molecules were introduced into PP by immersing the previously purified PP films in *n*-hexane solution containing a suitable aromatics for at least 1 week in order to establish an equilibrium concentration of the additive in PP. Afterward the polymer films were rinsed with methanol

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* Corresponding author.

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or ethanol to remove traces of acceptor molecules from the surface. The PP film was dried in the vacuum (10^{-4} Torr for ca. 20 h) in order to remove any traces of the solvent. For comparison, in the case of PP–Py system, the samples were prepared by extrusion from the melt or by casting the polymer-acceptor mixture on a film maker at ca. 450 K under the N_2 atmosphere.

The concentration of additives in PP was determined spectrophotometrically using a Hewlett–Packard HP 8452 A diode array spectrophotometer.

The emission spectra were recorded using the equipment described previously [3]. The essential feature was a novel data acquisition system. In the modified unit, the signal from the photomultiplier (9558 QB type, Thorn EMI), the temperature of the samples and the quartz monochromator (SPM-2, Zeiss-Jena) wavelength setting were simultaneously recorded by a computer (PC IBM AT 386 DX). The photomultiplier current was measured by an analog Keithley 409 picoammeter and through digital milivoltmeter (Merazet V-629) was fed to the computer. A constantan-copper thermocouple connected to the digital milivoltmeter (Merazet V-629) was used for temperature measurements. The time was measured by the computer internal clock.

This luminescence unit was equipped with home-made cryostat which enabled detection of emission spectra at 77 K and RTL spectral distribution at desired temperature from liquid nitrogen up to room temperature.

During the RTL detection the average heating rate varied from ~3 K min^{-1} in the low temperature range (80–140 K) to ~1.5 K min^{-1} in the high temperature range (200–260 K).

The irradiations were carried out in darkness, under the surface of liquid nitrogen. As a radiation source a linear accelerator (ELU-6, USSR made) was used. Each polymer sample obtained 8 ×4 μs pulses. Total dose was kept in the range 4–6 kGy.

3. Results and discussion

The spectral distribution of isothermal luminescence (ITL) for irradiated PP at 77 K containing Py (1.9×10^{-2} mol dm^{-3}) measured at the same temperature is shown in Fig. 1. The spectrum of emission can be attributed to the well known monomer fluorescence of Py (λ_{max}~400 nm). The phosphorescence of the solute (550–700 nm) was found to be negligible. The methods of sample preparation (PP soaking in Py solution or extrusion from the polymer-acceptor melt) have no influence on spectral distribution of light emitted. Using these two methods of Py sample preparation it was possible to get similar Py content in polymer system, but the Py molecules distributions in matrix were different. In polymer samples prepared by 'soaking method' the Py molecules should be distributed in non-random way in amorphous regions of PP only whereas the 'melt method' produces PP containing Py molecules distributed homogeneously. The method of sample preparation should probably influence the intensity of emission but in less degree the spectral distribution. The decay of ITL at 77 K measured at λ~390 nm is shown in Fig. 1 (insert). The solid line approximating the experimental ITL decay was calculated according to the Plonka's model of time-dependent rate constant [3,5,7] applied to solute ion recombination reaction (4) shown later in the text. Plonka's [7] model of time-dependent rate constant of the form

$$k(t) = \beta t^{(\alpha-1)}$$

where β and $0<\alpha\leq1$, are constants, can satisfactorily describe the decay of ITL. In agreement with this approach, the intensity of ITL can be given by

$$I_{\mathrm{t}} = at^{(\alpha-1)} \exp\left(-\frac{\beta}{\alpha}t^{\alpha}\right)$$

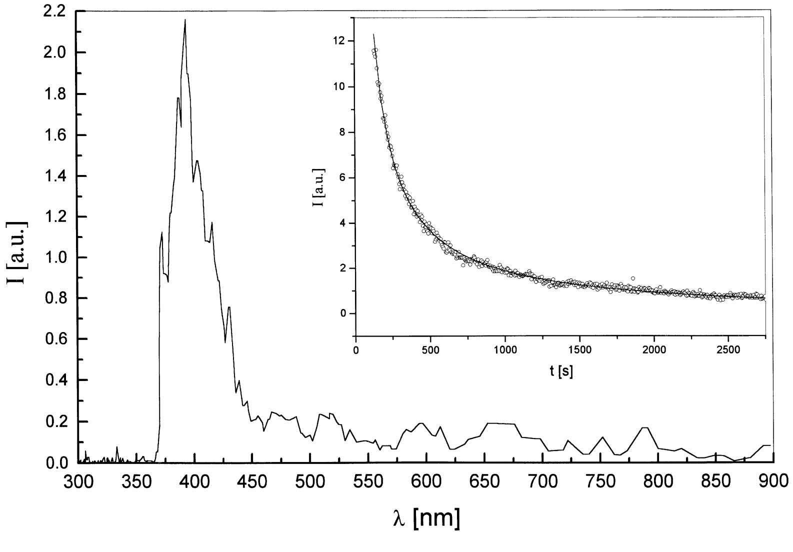

Fig. 1. The spectral distribution of ITL at 77 K for deaerated PP–Py sample ([Py]=1.9×10^{-2} mol dm^{-3} by soaking method). Dose: 4.6 kGy. Insert: the ITL decay at 390 nm, dose 3.8 kGy, solid line calculated according to the equation: $I_{\mathrm{t}}=at^{(\alpha-1)}\exp(-\beta t^{\alpha}/\alpha)$ where a, β and $0<\alpha\leq1$ are constants [7].

where a denotes a constant proportional to the concentration of charge pairs at time. The lower value of α, the wider the distribution function of rate constants $f(k)$; for $\alpha=1$, one gets a monoexponential decay, and β corresponds to the time-independent, classical rate constant. The solid line representing the ITL decay curve in Fig. 1 (insert) corresponds to the α value equal to 0.29 suggesting the tunnelling mechanism for electron transfer.

The spectral distribution of ITL was taken ca. 1080 s after the irradiation hence the distortion of the ITL spectrum due to changes of the ITL intensity with time should be rather insignificant. The scanning time for wavelength range 350–450 nm never exceeded ca. 16 s.

The spectral distribution of ITL for PP containing Nph (1.5×10^{-2} mol dm^{-3}) exhibited two emission bands which were assumed to represent the fluorescence (300–360 nm) and phosphorescence (460–600 nm) of the solute. Similar results to those described above were found for polyethylene doped with Nph [3].

The spectral distribution of RTL was unchanged in the temperature range up to ca. 200 K in the case of PP–Py samples prepared from the melt. At higher temperatures, in particular in the range 240–260 K, an additional band centred at ~480 nm was observed (Fig. 2). The intensity of the new band depended on the Py concentration and increased for higher Py content (Fig. 2, insert). The emission band with λ_{max}~480 nm can be attributed to the excimer emission of Py [8].

Similar experimental results concerning the Py excimer formation were previously found for polyethylene–Py system [2]. In the latter case apart from Py fluorescence emission (monomer and excimer ones) the Py phosphorescence band was observed in the temperature range 190–210 K.

It is worth to mention that for the PP–Py samples prepared by 'soaking method' the Py excimer band was also detected at lower temperatures than 200 K (but>160 K) although the emission intensity was rather weak there comparing with 240–260 K temperature range.

The influence of temperature on the spectral distribution of RTL for PP-Nph (1.5×10^{-2} mol dm^{-3}) system is shown in Fig. 3. Starting from ~192 K, in the spectral distribution of RTL, one can find an additional emission band centred at 395–400 nm. The traces of this band can be just found at 192–194 K together with Nph monomer fluorescence (300–360 nm) and phosphorescence (460–600 nm). The band under consideration can be attributed to the Nph excimer emission [8]. It is interesting that at the highest temperature, i.e. ~254 K only Nph excimer emission was observed (see Fig. 3, insert).

Excimer excited states are usually formed in liquids by the association of excited and non-excited molecules. In systems irradiated by ionizing radiation (γ or accelerated electrons), the excited solute molecules can be generated by ion recombination followed by excimer formation [9].

Aromatic solute excimer emission corresponding to the high temperature RTL peak for γ-irradiated polyethylene containing Nph and Py was found to be produced as a result of solute dimer cation neutralization [2,9] as it had been proposed before by Brocklehurst and co-workers [1,10] for hydrocarbon matrices doped with aromatics.

In order to identify the mechanism of aromatic solute excimer formation in doped PP the 'annealing method' [11] introduced in our laboratory was applied. Fig. 4 shows the influence of annealing at ca. 250 K on the spectral distribution of ITL measured at 77 K from PP containing Py ([Py]~1.2×10^{-2} mol dm^{-3}). It is seen that for an-

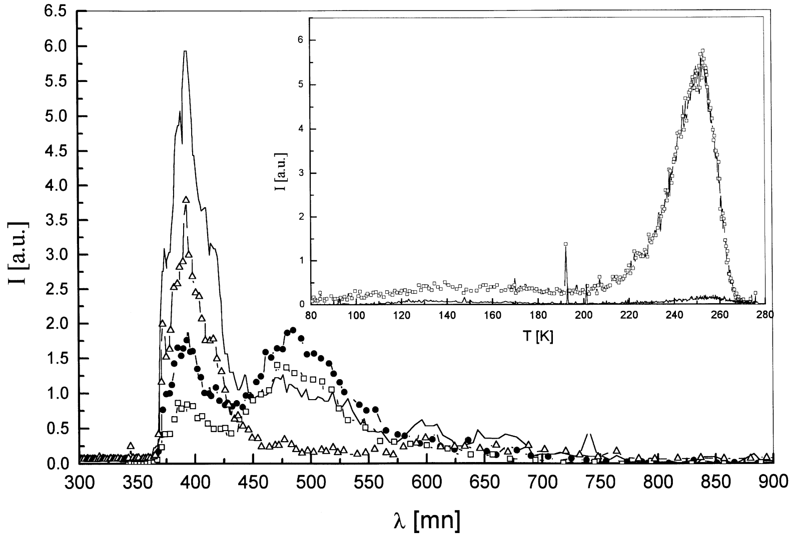

Fig. 2. The spectral distribution of luminescence from deaerated PP–Py ([Py]=1×10^{-2} mol dm^{-3} from the melt). Dose: 3.90 kGy; (Δ) 155.3–158 K; (—) 241.5–242.4 K; (●) 256.5–257.1 K; (□) 259.2–259.8 K. Insert: Influence of temperature on the intensity of luminescence at 480 nm; upper curve, –□–□–[Py]=1×10^{-2} mol dm^{-3}; bottom curve, [Py]=1.4×10^{-3} mol dm^{-3} (Soaking method).

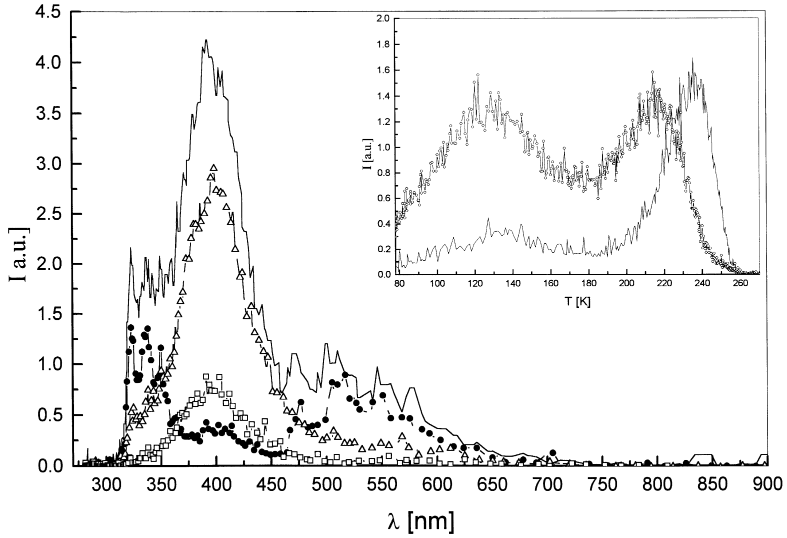

Fig. 3. The spectral distribution of luminescence from deaerated PP–Nph ([Nph]=1.5×10^{-2} mol dm^{-3} by soaking method). Dose: 3.8 kGy; (●) 191.8–194.2 K; (—) 235.2–236.7 K; (△) 244.2–246.2 K; (□) 253.2–254 K. Insert: influence of temperature on the intensities of luminescence at 324 nm (○) and 395 nm (—).

nealed sample the intensity of monomer fluorescence band (360–410 nm) decreases comparing with unannealed PP system. Warming of PP–Py matrix up to 260 K lead to total disappearance of ITL detected after recooling to 77 K.

As opposed to polyethylene–Nph system [2] in the case of PP matrix no Py excimer emission band was observed at 77 K for annealed samples. The storage temperatures in the range 250–260 K were within the glass transition region for PP polymer [12,13]. In such softened system the constraint imposed by the surroundings ought to be less than that in a rigid matrix at 77 K, allowing formation of the molecule-cation configuration sufficient to generate solute dimer cation (reaction 6). The formation of aggregated ion radicals of Nph and Py in alkane glasses induced by γ-irradiation and by subsequent warming was proved by Kira et al. [14].

Taking our results into account (Fig. 4) the neutralization of solute dimer cation (reaction 7) as a possible source of excimer formation has to be rejected in the case of PP system.

The aromatic solute excimer emission detected for PP–aromatic solute systems in the high temperature RTL peak (240–260 K) can be attributed to the neutralization reaction of molecular ions, i.e. solute anions and solute cations (reaction 5). Presumably, electron transfer takes place at sufficiently short distances so that excimer configuration can be created. In the glass transition temperature range the

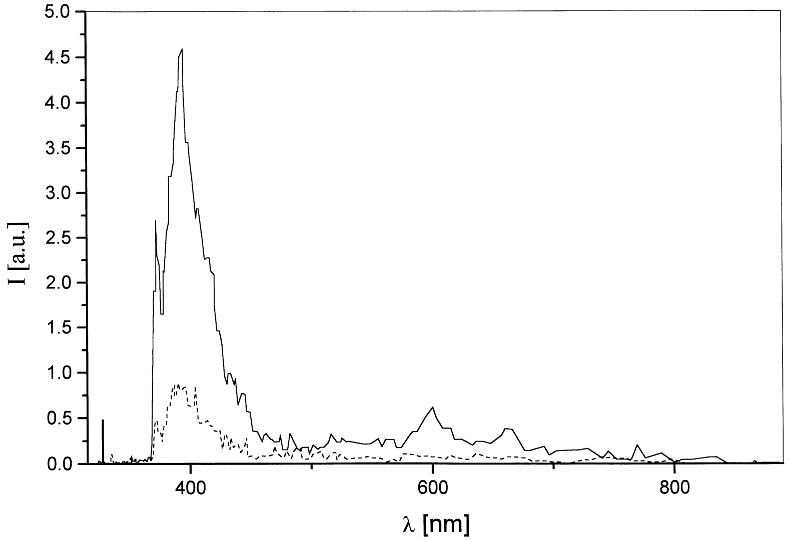

Fig. 4. ITL spectra from the PP matrix containing Py (1.2×10^{-2} mol dm^{-3}) measured at 77 K, dose 2.1 kGy; (—) no annealing, 3 min after the end of electron irradiation, (- - -) annealing by heating of the sample up to 250 K (during 11 min) and recooling down to 77 K.

softening of the matrix facilitates the formation of excimer structure.This part of discussion can be summarized by the following reactions

$$\mathrm{PP} \rightsquigarrow e^- + h^+ \qquad (1)$$

$$e^- + S \rightarrow S^{\bullet -} \qquad (2)$$

$$h^+ + S \rightarrow S^{\bullet +} \qquad (3)$$

$$S^{\bullet -} + S^{\bullet +} \rightarrow S^* + S$$

(ITL at 77 K by tunneling and after recooling from 250–260 K) (4)

$$S^{\bullet -} + S^{\bullet +} \rightarrow S^* + S \rightarrow S_2^*$$

(excimer emission during RTL peak, 240 –260 K) (5)

$$S^{\bullet +} + S \rightarrow {S_2}^{\bullet +}$$

(probably during the annealing in the range 250–260 K) (6)

$$S^{\bullet -} + S_2^{\bullet +} \not\rightarrow S_2^* + S$$

no excimer emission at 77 K after recooling from 250–260 K (7)

where e^- and h^+ denote electrons and positive holes, respectively, $S^{\bullet -}$ and $S^{\bullet +}$ the solute ions, ${S_2}^{\bullet +}$ the solute dimer cations whereas S^* and S_2^* denote solute monomer and excimer excited states, respectively. Having in mind the solute concentration used in our experiments ($\sim 10^{-2}$ mol dm^{-3}) all primary charges formed in reaction (1) should be scavenged by aromatic solutes (reactions (2) and (3)) [6].

The results shown in Figs. 2 and 3 (inserts) can be treated as a proof that solute excimer emission observed during the heating of the irradiated polymer-aromatic solute samples can be used as a probe for detection of glass transitions in such systems.In the case of preoxidized PP doped with Py we did not observed any solute emission after exposure to irradiation at conditions described in this paper. It is probably due to energy transfer from excited Py molecules to oxidized regions of PP chain [15].

4. Summary

Excimer of the aromatic admixtures (pyrene, naphthalene) was found to be generated in the temperature range 240–260 K where the glass transition was observed in polypropylene. Monomer fluorescence of the aromatics was observed in the temperature from 77 up to 260 K. Fluorescence (monomer and excimer) of aromatic additives was produced as a result of ionic recombination. At the lowest temperature, i.e. 77 K the tunnelling mechanism of electron transfer seems to be responsible for delayed luminescence whereas at higher temperatures diffusion assisted ion recombination should be taken into account.

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