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RTL Investigation on the Radiochemical Oxidation of Polyolefins

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Summary: High energy radiation causes deep modification of exposed polymers. In the irradiated polymers, the main macroscopic process is the formation of free radicals. The ''cooled'' electron distribution at the temperature of liquid nitrogen will develop the existence of various electron gaps with certain depths by smooth heating up to room temperature. In this paper, low density polyethylene, high density polyethylene and polypropylene were subjected to the action of gamma rays for causing structural modifications. The glow curves of quantum emission were recorded by slow heating from 106 to 286 K. The characteristic shoulders were obtained, which were ascribed to various electron traps consisting of unsaturation or carbonyl groups. For depicting the influence of molecular structures, the influence of CH_3 number/100 carbon atoms on the intensity of radiothermoluminescence (RTL) signal was studied on three types of LDPEs. A sharp decrease of maximum RTL intensity at advanced branching was pointed out. A mechanism of RTL emission is based on the present measurements.

Keywords: radiothermoluminescence (RTL); radiation; polyolefins

Introduction

High energy radiation induces structural modifications in the exposed polymers due to the consumption of transferred energy on material macromolecules. On macroscopic scale, it can be observed the appearance of oxygenated functions due to the reactions of free radicals with molecular oxygen.[1] On microscopic scale, the electrons that are ejected from molecules by ionization are thermalized. At this state of energy they are trapped by various moieties of molecules (branched chains, methylene groups, double bonds or parts of molecules containing heteroatoms).[2] The thermally stimulated release of charge carriers accompanied by their recombination will expel quanta at characteristic temperatures. The gap depth (the energy required for liberation of charge carrier) will depend on the type of the site, where it was scavenged.

Several recent papers[3–5] have reported the radiothermoluminescence (RTL) investigations on polymers, emphasizing the involvement of particular structure of material in the facility or difficulty in the emission of thermally stimulated photons.

General mechanism for RTL emission is presented in Figure 1.

At low temperatures, below glass transition temperature, the backbone moieties are moving around fix positions. The expel of thermally stimulated radiation as a consequence of the recombination of charge carriers (reaction 7) is tightly correlated to the molecular motions which allow the trapped charges to become free.

The present paper describes the application of radiothermoluminescence emission to the study of some polyolefins, whose special behavior under the action of high

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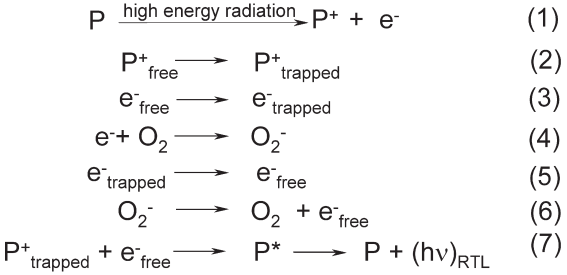

$$P \xrightarrow{\text{high energy radiation}} P^+ + e^- \quad (1)$$
$$P^+_{free} \longrightarrow P^+_{trapped} \quad (2)$$
$$e^-_{free} \longrightarrow e^-_{trapped} \quad (3)$$
$$e^- + O_2 \longrightarrow O_2^- \quad (4)$$
$$e^-_{trapped} \longrightarrow e^-_{free} \quad (5)$$
$$O_2^- \longrightarrow O_2 + e^-_{free} \quad (6)$$
$$P^+_{trapped} + e^-_{free} \longrightarrow P^* \longrightarrow P + (h\nu)_{RTL} \quad (7)$$

Figure 1.
RTL emission mechanism reported for polyolefins.

energy radiation validates the structural modifications.

Experimental

This study is applied on five sorts of polyolefins, whose characteristics in the pristine state are listed in Table 1.

For the correlation of thermal degradation with radiochemical processing of studied materials, two different ageing procedures were applied. Thermal degradation was performed at 80, 95 and 104 °C in an air-circulation oven. Other kind of modified samples was obtained by exposure to γ-radiation of polyolefin sheets in air, at room temperature in a ^{137}Cs irradiator (GAMMATOR – USA) at a dose rate of 0.46 kGy/h.

The recording of RTL signals was done using a cryostat coupled with a photomultiplier EMI-9558 QA and a recorder ORION-EMG. The increase in temperature was measured with a thermocouple iron/constantan at a heating rate of 90 °C/min.

The evaluation of received dose, Fricke dosimeter was selected applying a radiation yield for oxidation of divalent iron, $G(Fe^{3+}) = 15.5$ and a correction according to the equation:

$$\text{Dose (polyolefins)} = 1.028 \times \text{(Fricke dose)}$$

The number of CH_3/100 C was determine from IR spectra (Specord M75 Zeiss, Germany) at 1378 cm^{-1}.[6] The crystallinity level was obtained according Hendus-Schnell method[7] by dividing absorbance at 1894 cm^{-1} to the absorbance at 1300 cm^{-1}. The concentration of unsaturated moieties was calculated at 964 cm^{-1} (*trans*-vinylene unit), 910 cm^{-1} (end vinyl unit) and 885 cm^{-1} (vinylidene units) for polyethylene, and 1642 cm^{-1} (vinylidene units) for polypropylene[6].

IR spectroscopic determination of carbonyl accumulation was carried out at 1715 cm^{-1}.

All molar coefficients of absorbance used for our IR evaluation of concentrations were reported by Dole.[8]

Results and Discussion

The glow curves present characteristic shape related to the irradiated substrate In Figure 2 the radiothermoluminescence

Table 1.
Some characteristics of studied olefins

Characteristics	Polymer				
	LDPE 1	LDPE 2	LDPE 3	HDPE	PP
Density ($g \cdot cm^{-3}$)	0.919	0.913	0.912	0.952	0.934
Number of CH_3 for 100 C	2.71	2.45	3.15	0.96	21.36
Crystallinity (%)	45.70	48.73	45.45	66.11	76.15
Thickness (μm)	57	267	201	32	48

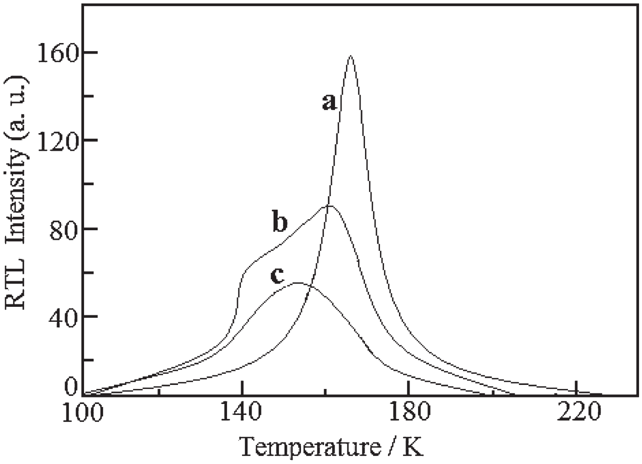

Figure 2.
RTL curves for (a) LDPE 1 (I/10), (b) HDPE (I/1) and (c) PP (I/1).

intensity dependency on recombination temperature for two sorts of polyethylene and one kind of polypropylene are presented. These materials were irradiated at liquid nitrogen temperature at a dose of 400 Gy. The low density polyethylene specimen exhibits two peaks at 145 and 173 K, while high density polyethylene shows the glow peaks at 131 and 158 K. Polypropylene has one peak placed at 143 K. These maxima can be ascribed to various categories of phenomena. The peaks situated at low temperatures appeared due to the relaxation of macromolecular chains, when the scavenged charges are easy released. In the cases of LDPE and HDPE, these maxima are determined by γ transitions caused by the rotation of the 4 four methylene groups from the main backbone and for PP, maximum is appeared after the transition δ resulting from the rotation of methyl moieties around the ax, which is perpendicular on the chain. Similar results were reported[9] by the application of dielectric spectroscopy on irradiated polyethylene at various doses. The correlation between electrical properties and RTL emission can be done considering the molecular relaxation on the same range of temperature.

Regarding the nature of electron traps, which are involved in RTL emission, the majority of authors have agreed that on the low temperature range, the unsaturated sites play the role of traps. Boustard and Charlesby[10] stated that the defects created by unsaturation on main chain are due to the difference in the lengths of simple and double bonds. However, the data listed in Table 2 would not sustain this explanation. For the measurements performed under the same conditions, PP free of double bonds provides higher RTL intensity, but LDPE with higher content of unsaturation shows lower value of emission intensity than polypropylene.

In addition, for the same kind of polyolefin, LDPE1 presenting an unsaturation level of three times higher than similar value for LDPE 2, but the intensity ratio is favorable to the last material.

Table 2.
Some features for RTL measurements

Characteristics	Polymer				
	LDPE 1	LDPE 2	LDPE 3	HDPE	PP
Maximum RTL emission intensity at low temperature (a. u.)	97300	184400	56300	300000	139400
Total unsaturation $(\mathrm{mol} \cdot \mathrm{g}^{-1}) \cdot 10^4$	0.56	0.16	—	0.653	0

It is easier to explain the RTL emission at low temperature by the release of trapped electrons in physical caves that are formed by the irregular arrangement of macromolecular chains in a certain zone of polymer phase. In this case, the differences between the maximum intensities of LDPE and HDPE would be correlated to the rotation of methyl groups. Figure 3 illustrates the effect of methyl groups on the decreasing RTL signal.

It is the great probability that the emissive transition would be happened in the crystalline phase, where the ordering degree is higher than in amorphous phase.

The higher RTL emission intensity of polypropylene would be the consequence of great number of methyl units, which can be rotated around the main chain. The δ transition was reported by other papers[11,12].

The maxima placed on the higher temperature range (158 K for HDPE and 173 K for LDPE) are due to the presence of oxygen. The electrons that became free by the ionization can be scavenged by molecular oxygen preexisting in polymer matrix, because oxygen acts as efficient trap. The release of electrons is occurred either thermal activation, or by the migration of O_2^- entities, followed by a reaction with a free radical (Figure 1). The lack of this kind of peak in polypropylene proves that molecular oxygen does not penetrate crystallites (crystallinity of pristine polypropylene was 96.54%). In the amorphous region, which is easier to be rearranged, the majority of recombination acts take place.

In Figures 4 (a, b and c) the glow curves of pristine and irradiated polyolefins are presented.

It may be specified that oxygen does not capture any positive charge because of its strong electronegative potential.

For γ-exposed polyolefin samples, the RTL intensity decrease sharply after irradiation at low doses (50 kGy). This dose does not exceed the gel dose. It means that the problem of movement hindering is not real one, because polyethylene does not start to crosslink. It may be assumed that the oxidative degradation must be responsible for this decrease in emission intensity. The main oxidation product that can be involved in radiothermoluminescence emission is carbonyl-containing molecules. Figure 5 demonstrated the severe decrease in RTL intensity at higher temperature.

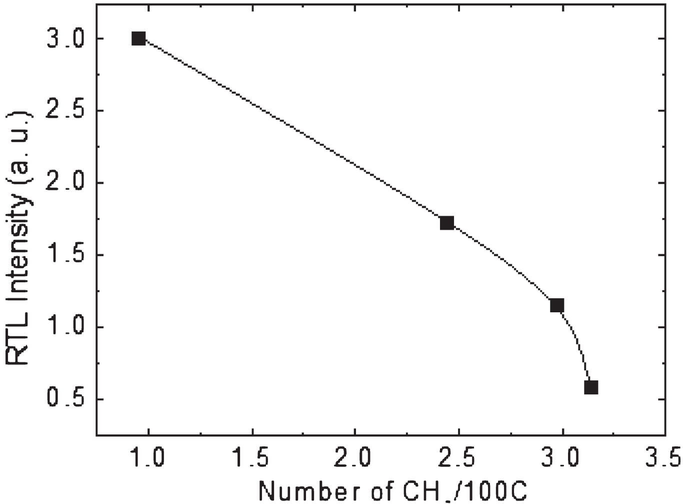

Figure 3.
The influence of methyl group concentration on the maximum intensity of RTL emission for polyethylene at low temperatures.

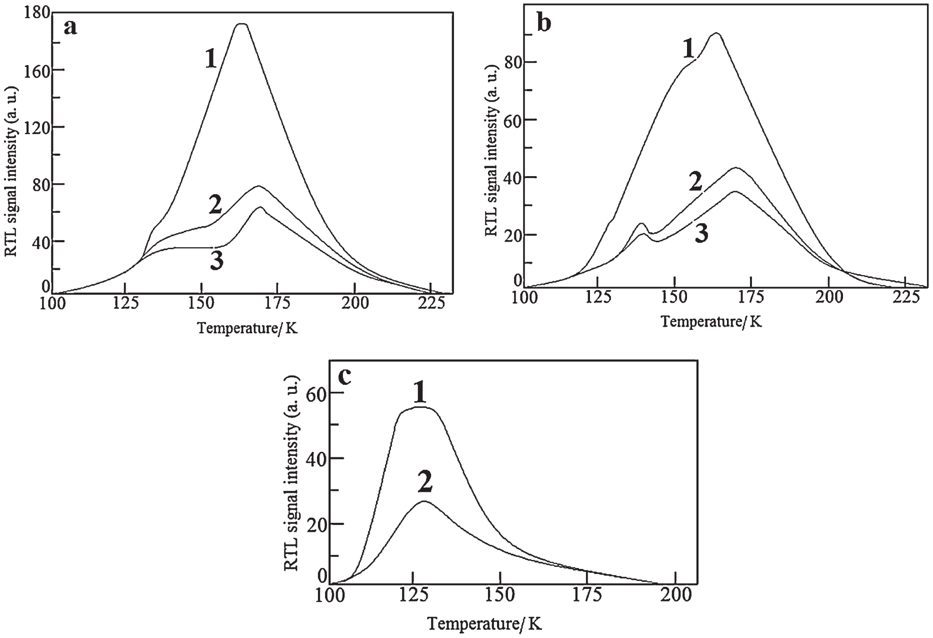

Figure 4.
RTL curves for irradiated samples of various polyolefins (a) LDPE 1: (1) unirradiated (I/5), (2) irradiated at 50 kGy (I/2.5) and (3) irradiated at 250 kGy (I/1). (b) HDPE: (1) unirradiated (I/10), (2) irradiated at 50 kGy (I/4) and (3) irradiated at 250 kGy (I/1). (c) PP: (1) unirradiated (I/10) and (2) 100 kGy (I/1).

The synergistic effect of heat and high energy radiation is presented in Figure 5. It can be remarked the prominent decrease in the second peak intensity, which can be recorded at higher temperature. The recombination occurs faster due to the higher received energy even on the first stage of degradation.

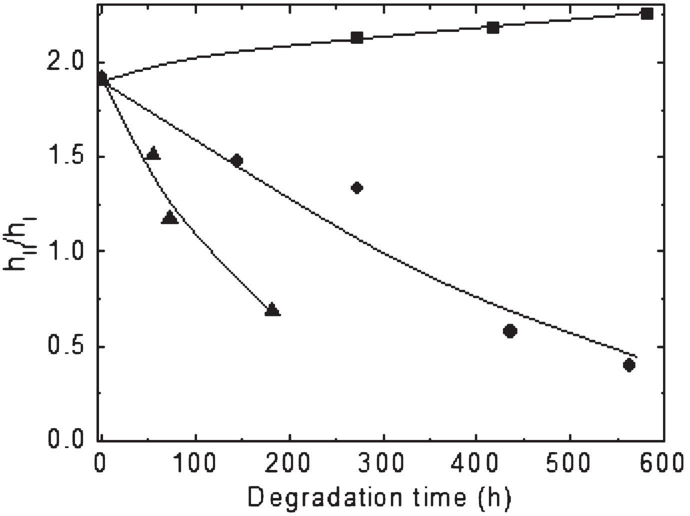

Figure 5.
The modification of maximum height ratio for LDPE at various degradation temperatures. (■) 80 °C; (●) 95 °C; (▲) 104 °C.

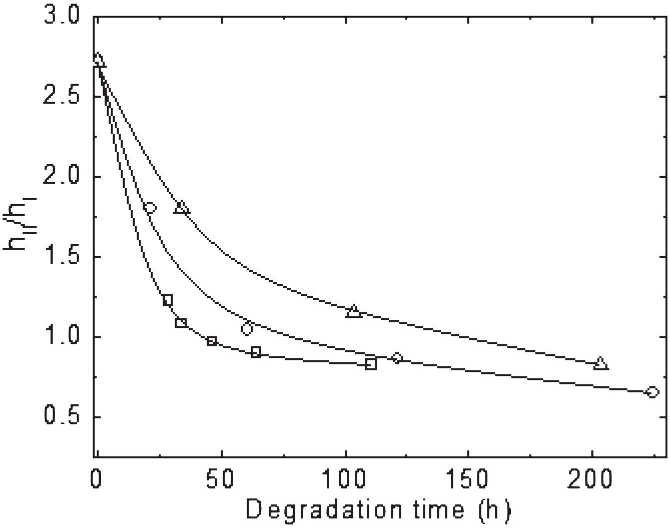

Figure 6.
The modification of maximum height ratio for LDPE at the simultaneous action of heat and high energy radiation. (△) thermal oxidation at 104 °C; (○) radiochemical oxidation (460 kGy/h); (□) simultaneous action.

It is well known that thermal oxidation[13,14] and exposure to ionizing radiation[15,16] generate large amounts of carbonyl compounds. Various carbonyl structures, easy established by IR spectroscopy on the region 1685–1785 cm^{-1} contribute to the trapping of charges and, afterwards, to the RTL emission by their release and recombination.

Conclusion

The radiation thermoluminescence study on polyolefins has revealed the structural modifications occurred during irradiation. This method is able to differentiate the radiochemical behaviour of similar compounds by the recording of the emission at various temperatures. The different trap depths describe the capture strength of radiolysis products that are formed during exposure, especially oxygenated moieties and unsaturated structures.

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