Fluorescent Sensor as Physical Amplifier of Chemiluminescence: Application to the Study of Poly(ethylene terephthalate)

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ABSTRACT: Intramolecular charge-transfer fluorescent probes have been used as physical enhancers of chemiluminescence. PET exhibits low chemiluminescence emission; however, in the presence of Coumarin 337, the energy transfer from thermally generated excited carbonyl to ground-state probe molecule takes place, giving rise to the fluorescence emission from coumarin. Employing this method, the chemiluminescence emissions of several poly(ethylene terephthalate)s, initial and annealed at different temperatures, were studied. The observed emission has been proved to be sensitive to the morphology of polymer sample. The CL intensity increased in the temperature range 75−130 °C, and at higher temperature a decrease was detected. It was associated with exothermic recrystallization during heating, which would restrain the peroxyl radicals recombination, which originates the chemiluminescence emission. A lower chemiluminescence emission for annealed samples was observed. It was due to their enhanced crystallinity, which would affect both the mobility of hydroperoxides to recombine themselves and the energy transfer from excited donor to the acceptor fluorescent probe which occurs through a diffusion-controlled process. The CL results correlate with those obtained by means of other techniques also employed in this work: differential scanning calorimetry, dynamic mechanical analysis, and fluorescence spectroscopy. This result confirms that chemiluminescence emission studies can be used to sense temperature-dependent morphological changes, i.e., annealing processes, and to determine relaxation temperatures and exothermic recrystallization peaks. The use of fluorescent sensor to amplify the chemiluminescence emission allows to apply the innovative method, developed in this work, to all types of polymers, including those with low intensity emission.

Introduction

The years 1939−1941 brought important studies of polyesters[1] by Whinfield and Dickson and led to the development of poly(ethylene terephthalate), PET, as an example of the deliberated design of a polymer for a specific purpose, the production of fibers, with real understanding of what was required. Large scale production of this extremely important polymer began in 1955, and nowadays PET is the most important polyester in the polymer market. Its use is now widespread, both as a textile fiber and for packaging in the form of films or bottles. Films applications of PET have grown and expanded to high added value sectors; this is the case of the photographic films and recording supports due to its excellent mechanical properties.

Poly(ethylene terephthalate) is a widely used semicrystalline polymer. It can be quenched into the completely amorphous state, whereas thermal and thermomechanical treatments lead to partially crystallized samples with easily controlled degrees of crystallinity. The macroscopic properties of PET such as thermal, mechanical, optical, and permeation properties depend on its specific internal morphologies and microstructure arrangement. The crystallization behavior of thermoplastic polymers is strongly affected by process conditions. The degree of crystallization and the size of the resulting spherulites depend on both temperature and heating/cooling rate. The dependence of quiescent isothermal crystallization kinetics upon temperature has been widely studied.[2−4]

The chemiluminescence (CL) has become a useful technique for the study of polymer degradation,[5] oxidation mechanisms,[6] and kinetics[7,8] as well as stabilizer efficiency.[9,10] This fact is due to its offered advantages with respect to other well-established techniques.[11] It is well-known[12,13] that the chemiluminescence in polymers is due to the light emission that accompanies the thermal decomposition of the thermooxidative degradation products (hydroperoxides), which are formed during processing or in-service life of the material under ambient conditions.[6,14] This bimolecular reaction promotes ketone products to its lowest triplet state, and the radiative deactivation gives chemiluminescence emission in the visible region.

Several compounds, such us acridine orange, eosine, coumarin, and luminol, have been used as physical enhancers of luminescence for studying lipid peroxidation.[15,16] These sensitizers offer nonintrusive methods, amplifying the CL signal without altering the reaction kinetics. In polymers, the most likely photon-emitting reaction is the exothermic termination of two alkylperoxy radicals; this reaction produces alcohol, singlet oxygen, and excited carbonyl species. This thermogenerated carbonyl triplet state deactivates by phosphorescence emission (CL) to its ground state. The generation of peroxy radicals depends on the peroxide concentration, and the chemiluminescence can be related to the hydroperoxide content of the polymer.[17]

In this work, the chemiluminescence emission of several poly(ethylene terephthalate) samples (initial and annealed at different temperatures) has been studied.

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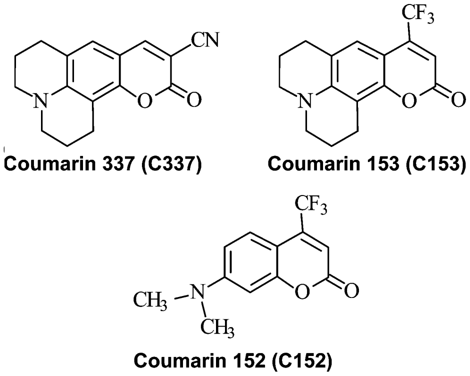

Coumarin 337 (C337) **Coumarin 153 (C153)**

Coumarin 152 (C152)

Figure 1. Structure of fluorescent probes.

Coumarin probes have been used as physical enhancer of chemiluminescence in PET since this polymer exhibited low emission intensity.[18] Also, the temperature dependence of the fluorescence intensity of probes adsorbed in PET has allowed to study the relaxation processes of poly(ethylene terephthalate)s with different crystallinity. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) measurements have been also used to determine the secondary relaxations of PET samples to correlate the results with those obtained by chemiluminescence and fluorescence methods.

Experimental Section

Materials and Sample Preparation. Commercial poly(ethylene terephthalate) sheets, 200 μm thickness, were kindly supplied by Selenis. The fluorescent probes Coumarin 152 (C152), Coumarin 153 (C153), and Coumarin 337 (C337) were supplied by Aldrich and used as received. The structures of probes used in this work are shown in Figure 1.

Slices of polymer sheet were cut and immersed in toluene probe solution (10^{-3} M) to allow the fluorescent probe to diffuse into the polymer matrix, as previously described.[19] Also, PET film was treated with toluene in the absence of probe, and this sample was taken as reference ($\text{PET}_{\text{initial}}$). The PET samples were annealed in an oven at different temperatures (105, 110, 115, and 120 °C) for a period of 15 min. From the corresponding UV absorption spectra of the PET films, a concentration of 2×10^{-4} M of the fluorescent probe adsorbed in the polymer matrix was determinated assuming that their molar absorption coefficients are the same as those previously measured in ethyl acetate solutions.

Thermal Analyses. *Calorimetric measurements* were performed on a Shimadzu DSC-50 and TA-50I thermal analyzer over the range 30−250 °C. All the measurements were made at a heating rate at 5 °C min^{-1}, and the instrument was calibrated with an indium standard ($T_m = 429$ K, $H_m = 25.75$ J g^{-1}).

The melting peak (T_m), the melting enthalpy (ΔH_m), the recrystallization peak (T_c), and the heat of recrystallization (ΔH_c) were obtained, and percentages of crystallinity were determined as it was described previously,[19] using the reference of 135 J g^{-1} for crystalline poly(ethylene terephthalate).[20]

Dynamic mechanical measurements were performed on a TA dynamic mechanical analyzer (DMA) working on the flexural bending mode at a constant frequency of 0.1 Hz. The experiments were carried out in the temperature range from −150 to 200 °C using a heating rate of 5 °C min^{-1}.

Chemiluminescence. Chemiluminescence spectra of film samples were obtained using an earlier described CL400 ChemiLUME apparatus from Atlas Electric Devices Co.[21] The film samples (4 mm diameter) were held in aluminum pans, and two different types of tests were performed. Dynamic tests: material samples are heated to 150 °C with a heating rate (5 °C/min) under constant flow (50 mL/min) of gas, nitrogen or oxygen. Isothermal tests: samples of material are heated with pretest ramp (1 °C/min) to the test temperature (150 °C) under constant flow (50 mL/min) of dry gas, nitrogen or oxygen.

In the case of chemiluminescence measurements of fluorescent probes powders, 5 mg of each product was placed in the aluminum pan covering its surface as a powder layer.

Spectroscopic Measurements. UV spectra were recorded by means of a Perkin-Elmer LS-35 spectrophotometer.

Fluorescence spectra, in a temperature range from 30 to 275 °C, were recorded by using a Perkin-Elmer LS50-B luminescence spectrophotometer coupled to a differential scanning calorimeter (Shimadzu model DSC-50). The optical assembly of the spectrofluorimeter to the photocalorimeter has been successfully acomplished using a Y-connection of optical fiber boundle. In this way, the samples were located in the holder of the photocalorimeter. They were then front-face excited through the optical fiber with light provided by the fluorimeter. Fluorescence is collected with the optical fiber, having the other extreme in the fluorimeter chamber positioned at 90° respect to the UV excitation beam. Heat flow data vs time were simultaneously recorded during heating.

The heating rate was always mantained at 5 °C min^{-1}, and the scan rate was selected to record two fluorescence spectra every minute. Under these conditions, all the measurements in the polymer films were carried out under a nitrogen atmosphere.

Results and Discussion

Table 1. DSC Analysis of Poly(ethylene terephthalate) Films[a]

	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J g^{-1})	% X_c
$\text{PET}_{\text{initial}}$	72	126	252	27	20
$\text{PET}_{\text{anneal 105°C}}$	73	124	251	35	26
$\text{PET}_{\text{anneal 110°C}}$	74	123	251	37.8	28
$\text{PET}_{\text{anneal 115°C}}$	75	122	251	40.5	30
$\text{PET}_{\text{anneal 120°C}}$			251	43.8	32

[a] At scan rate 5 °C min^{-1}.

Thermal Analysis of PET Films Annealed at Different Temperatures. *Differential Scanning Calorimetric Analyses.* DSC heating scanning of $\text{PET}_{\text{initial}}$ and PET after annealing at various temperatures ($\text{PET}_{\text{anneal 105°C}}$, $\text{PET}_{\text{anneal 110°C}}$, $\text{PET}_{\text{anneal 115°C}}$, $\text{PET}_{\text{anneal 120°C}}$) was undertaken to determine the degree of crystallinity in the polymer films (Figure 2). From the thermographs, different parameters have been determined under heating scan mode: glass transition temperature (T_α), exothermic recrystallization peak (T_c), melting peak (T_m), melting enthalpy (ΔH_m), and degree of crystallinity (% X_c). All the calculated data are summarized in Table 1.

The first feature from these data is the observation that the glass transition temperature increases slightly with annealing temperature. In addition, the exothermic peak corresponding to the crystallization of amorphous regions is decreasing with annealing temperature, and the peak widths (ΔT_c) are broader than that of the initial sample (Figure 2). This earlier recrystallization observed for the annealed poly(ethylene terephthalate) is in agreement with the results obtained by other authors.[22] It has been interpreted as result of the enhancement of segmental mobility due to the annealing above glass transition temperature, which reduces the free energy barrier for nuclei formation and accelerates the rate of recrystallization.

DSC heating scanning of poly(ethylene terephthalate) with adsorbed fluorescent probes (PET_{C152}, PET_{C153}, PET_{C337}) was undertaken to check any effect of the probe on the thermal properties and crystallinity degree of annealed PET. A similar behavior was found for all

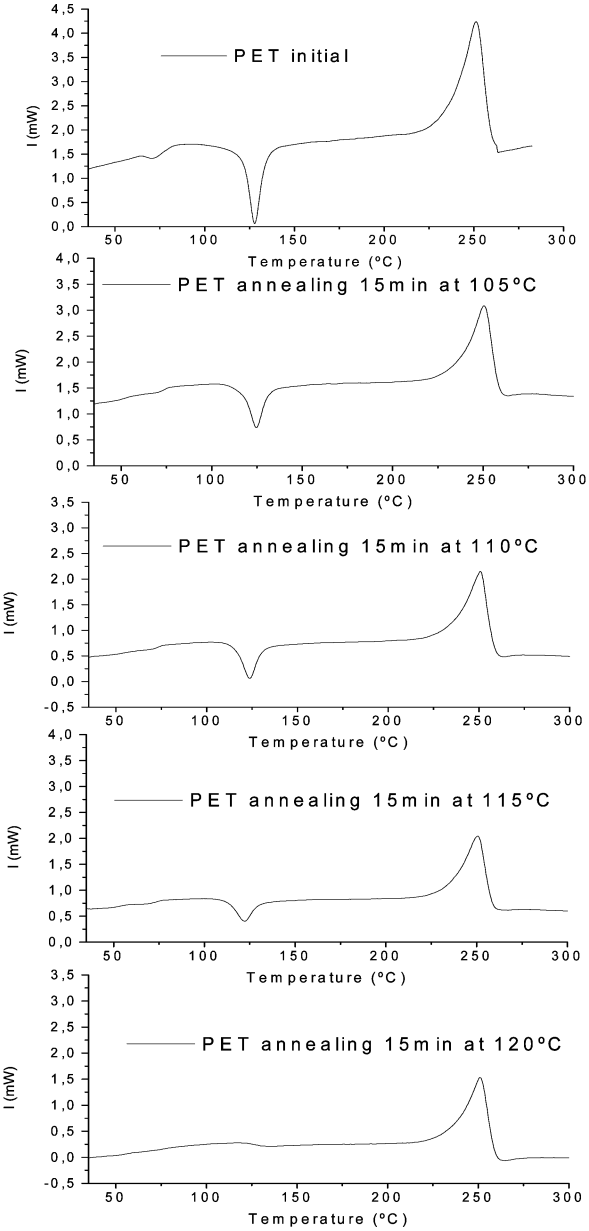

Figure 2. DSC heating thermograms of $PET_{initial}$ and after annealing for 15 min at different temperatures (105, 110, 115, and 120 °C).

the samples to that obtained for the reference $PET_{initial}$, which would indicates that polymer crystallinity is not influenced by the presence of coumarin probes, at least at the concentrations used in this work.

Dynamic Mechanical Analyses. All the poly(ethylene terephthalate) samples mentioned before were studied by dynamic mechanical analysis. In general, the dynamic mechanical properties are highly influenced by changes on the degree of crystallinity. PET showed two relaxation processes, referred to as α and β, in order of decreasing temperature. The results corresponding to the α- and β-transition temperatures, the loss moduli maxima (E''_{max}), and its peak width parameter are summarized in Table 2.

The $PET_{initial}$ sample exhibits a peak at 72 °C assigned to its α-relaxation, which is coincident with the well-established glass transition temperature for poly(ethylene terephthalate), and hence, it has been associated with long-range segmental motion in the amorphous regions. The α-relaxation is quite sensitive to the presence of the crystalline fraction, and after the annealing process, the temperature corresponding to the α-transition increases slightly (Table 2). Otherwise, the intensity of the peak decreases in all the annealed samples from 185 to 88 MPa, depending on the temperature of treatment. The signal becomes broader, and the width of the peaks determined at the height, $E''_{max}(\alpha)/2^{1/2}$, increases from a value of 11 for the $PET_{initial}$ to a value of 21 after annealing at the highest temperature. This effect observed on the materials is directly related with the enhancement of the crystallinity induced by annealing, and it is in accordance with results obtained by DSC.

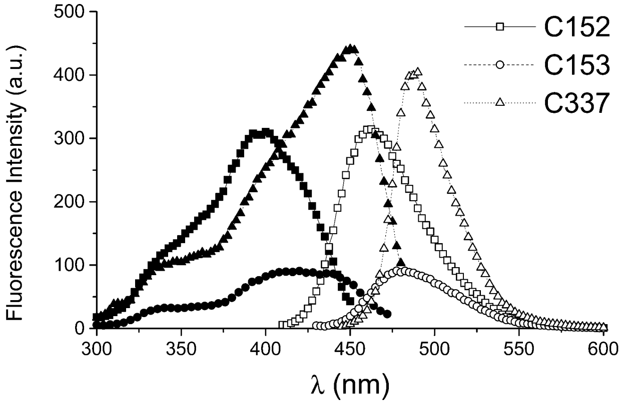

Figure 3. Emission (open symbols) and excitation (solid symbols) fluorescence spectra of C337, C153, and C152 adsorbed in in poly(ethylene terephthalate) films.

Table 2. Dynamic Mechanical Analysis of Poly(ethylene terephthalate) Films at Scan Rate 5 °C min^{-1} and Frequency 0.1 Hz

	β (°C)	α (°C)	$E''_{max}(\alpha)$ (MPa)	width of E'' peak at $E''_{max}(\alpha)/2^{1/2}$
$PET_{initial}$	−70	72	185	11
$PET_{anneal\ 105°C}$	−68	73	179	12.5
$PET_{anneal\ 110°C}$	−70	75	162	13.3
$PET_{anneal\ 115°C}$	−70	76	122	15.7
$PET_{anneal\ 120°C}$	−69	79	88	20.9

A second peak at −70 °C, assigned to the β-transition, was observed for $PET_{initial}$. In general, no shift is observed for β-transition temperature of annealed PET in comparison with $PET_{initial}$. This peak is entirely due to the amorphous phase relaxation and, as is expected, shows no sensitivity to the degree of crystallinity.

Fluorescence Behavior of Coumarin Derivatives Adsorbed in PET Films. In this work, the temperature dependence of the fluorescence emission of Coumarin 152, Coumarin 153, and Coumarin 337 adsorbed in poly(ethylene terephthalate) was studied with the aim of relating fluorescence changes with the observed thermal transitions. These fluorescent probes, containing both an electron donor (D) and acceptor (A) groups, are intramolecular charge-transfer fluorescent probes (ICT). In previous work,[19] this type of fluorescent dye molecules have been proved to be strongly sensitive to the morphology of polymer samples. Since their fluorescence properties are dependent on their microenvironment, the fluorescence emission from those extrinsic probes could be used as a valuable method to analyze annealing processes in semicrystalline polymers.

The excitation and emission fluorescence spectra for initial samples, PET_{C337}, PET_{C153}, and PET_{C152}, at room temperature are shown in Figure 3. The maximum emission wavelengths of the fluorescent probes adsorbed

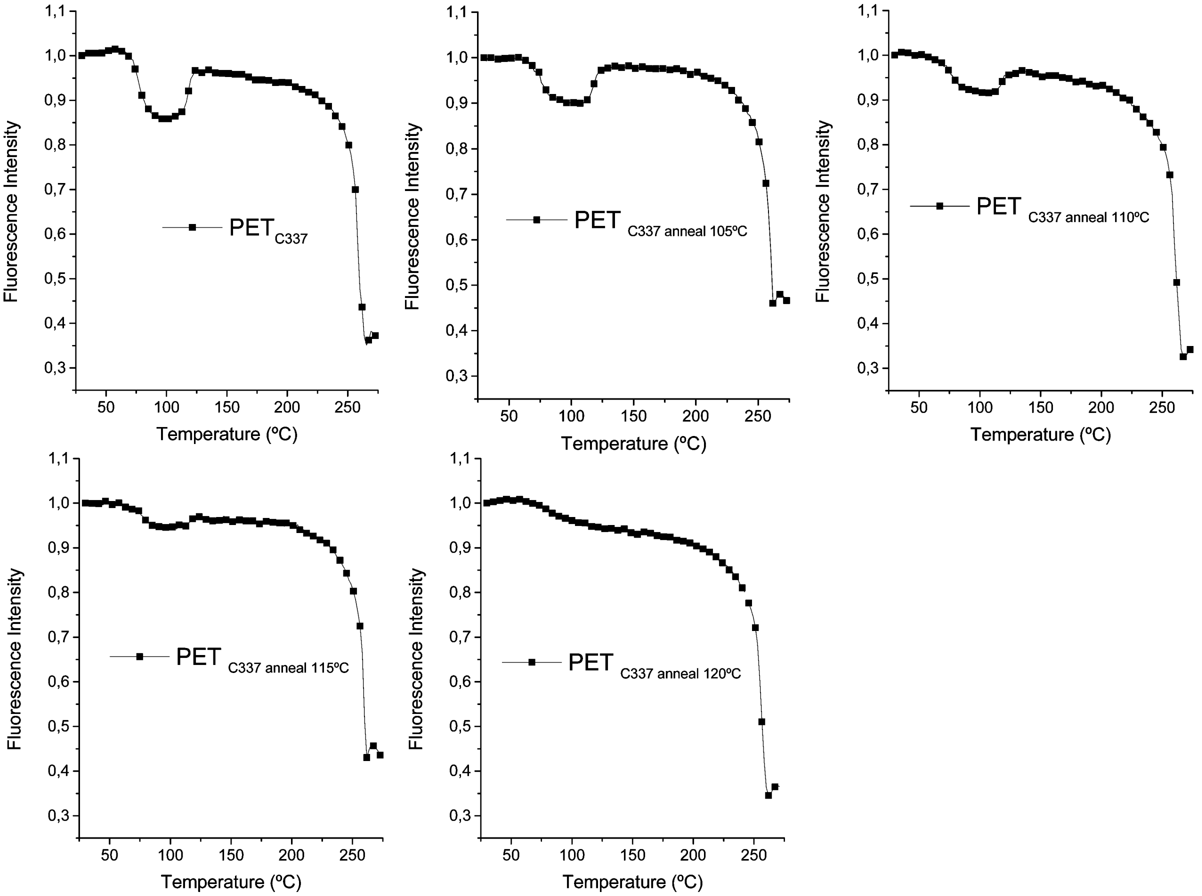

Figure 4. Fluorescence intensity vs temperature for C337 adsorbed in PET.

in poly(ethylene terephthalate) were determined to be $\lambda_{max}(C337) = 490$ nm, $\lambda_{max}(C153) = 482$ nm, and $\lambda_{max}(C152) = 462$ nm. Poly(ethylene terephthalate) exhibits two peaks of fluorescence centered at 330 and 370 nm,[23] assigned to the phenylene moiety in the crystalline and amorphous regions, respectively. Hence, these observed emissions would confirm that the emission bands of fluorescent probes adsorbed in PET are not affected by the intrinsic fluorescence of the polymer.

The fluorescence properties of the probes adsorbed in poly(ethylene terephthalate) films were measured at temperatures ranging from 35 to 275 °C, and the intensity of fluorescence (I_F) was measured at the maximum emission wavelength. In Figure 4, the normalized fluorescence intensity of the Coumarin 337 vs temperature is shown for the different annealed samples. Also, the corresponding data for the three fluorescent probes employed in this work are compiled in Table 3.

It was observed that the fluorescence of the probes adsorbed in PET films decreases as temperature increases (Figure 4). First, for PET_{C337} profiles at different annealing temperatures, an abrupt slope change is observed with this probe C337 in the temperature range 60−90 °C. This drop in the fluorescence signal is attributed to the α transition, which involves motions of long segments (as expected for the glass transition). The relationship between the transition temperature and fluorescence of probes in polymers has been described by several authors.[24−26] When polymer relaxation takes place, the free volume of the medium enhances. As far as an environmental sensitive fluorescent probe is used, the fractional free volume changes may cause a modification of the relaxation mode of fluorescent probe. For example, in the ICT studied probes, the nonradiative decay process of singlet excited-state probe is the favored pathway, and consequently, a decrease in fluorescence quantum yield is observed. Table 3 shows the glass transition temperatures determined from the midpoint on the decay fluorescence curves with temperature.

Table 3. Transition Temperatures for Annealed PET Samples, Measured by Fluorescence Profiles of the Coumarin Probes C337, C153, and C152 Adsorbed in the Films

sample	T_g (°C)	ΔI_{f-T_g}	$slope_{maxT_g} \times 10^3$	T_c (°C)	ΔI_{f-T_c}
PET_{C337}	76	0.16	7.7	117	0.11
$PET_{C337\ anneal\ 105°C}$	76	0.10	4.8	117	0.08
$PET_{C337\ anneal\ 110°C}$	76	0.09	3.4	117	0.05
$PET_{C337\ anneal\ 115°C}$	77	0.07	2.6	116	0.02
$PET_{C337\ anneal\ 120°C}$	78	0.04	1.7		
PET_{C153}	78	0.09	3.7	121	0.05
$PET_{C153\ anneal\ 105°C}$	79	0.06	3.1	115	0.04
$PET_{C153\ anneal\ 110°C}$	78	0.13	2.7	115	0.03
$PET_{C153\ anneal\ 115°C}$	81	0.09	2.1	114	0.01
$PET_{C153\ anneal\ 120°C}$					
PET_{C152}	77	0.09	5.2	119	0.12
$PET_{C152\ anneal\ 105°C}$	76	0.07	2.6	116	0.09
$PET_{C152\ anneal\ 110°C}$	79	0.05	1.2	115	0.03
$PET_{C152\ anneal\ 115°C}$	81	0.03	0.8	114	0.02
$PET_{C152\ anneal\ 120°C}$					

Second, an increase of fluorescence intensity was observed around 100 °C for all the samples except for PET_{C337} annealed at 120 °C, where no crystallization was observed. It would be associated with exothermic recrystallization during heating and the corresponding decrease of the matrix volume, which restrain the nonradiative relaxation pathway. Also, if it may be

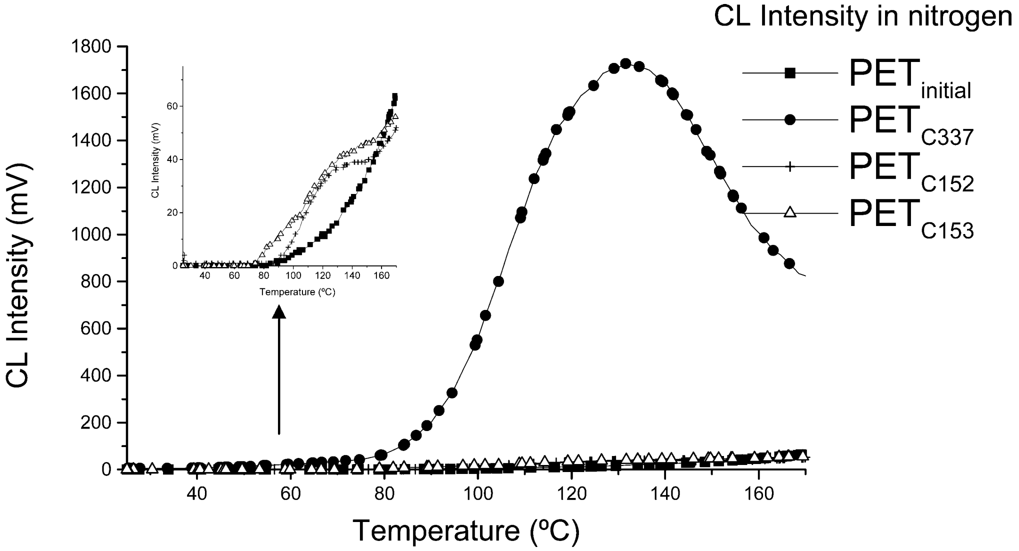

Figure 5. Chemiluminescence temperature-ramping curves obtained for PET$_{initial}$, PET$_{C337}$, PET$_{C152}$, and PET$_{C153}$, under nitrogen.

considered the main factor affecting the fluorescence behavior of coumarins in PET films; other considerations, i.e., changes of the light scattering associated with the recrystallization during heating, would not be rejected.

The temperature ascribed to α-relaxation processes (T_g) is obtained as the inflection point of first linear decreasing zone of the plot of I_F vs temperature. The same criterion was considered for recrystallization peak (T_c) but in the fluorescence increasing range. The sensitivity of fluorescent probes to glass transition and crystallization process is reflected as the difference between the maxima and minima intensities in the decreasing and increasing zones, ΔI_{f-T_g} and ΔI_{f-T_c}, respectively. For glass transition the slope$_{\max T_g}$ as a parameter of sensitivity has also been determined.

Similar behavior was observed for PET$_{C153}$ and PET$_{C152}$ vs temperature, and T_g and T_c were determined (Table 3). However, the probe sensitivity was seen to be highly influenced by their structure. Coumarin 337 exhibited higher sensitivity than Coumarin 153 and Coumarin 152 for both glass transition and crystallization processes, as is expressed by ΔI_{f-T_g} and ΔI_{f-T_c}.

The thermal behavior of annealed poly(ethylene terephthalate) was studied by means of fluorescent probes. Figure 4 shows the fluorescence vs temperature of C337 adsorbed in PET annealed at different temperatures. In general, the glass transition temperature increases slightly with annealing temperature (Table 3). Otherwise, the sensitivity to the glass transition peak, ΔI_{f-T_g}, decreases in all the annealed samples from 0.16 to 0.04, depending on the temperature of treatment, and the signal becomes broader, as is expressed by the decrease of slope$_{\max T_g}$ from a value of 7.7 for PET$_{C337}$ to a value of 1.7 after annealing at 120 °C. This behavior corresponds to the reduced mobile amorphous fraction, where the fluorescent probe is localized. PET is a very well-known three-domain model, containing crystalline (all-trans), constrained noncrystalline (trans-rich), and amorphous (gauche-rich) phases. During annealing above glass transition, the isothermal crystallization takes place and includes three phenomena: (1) reorganization of amorphous regions, (2) crystallization of amorphous chain segments, and (3) reorganization of crystalline regions. Annealing above glass transition favors the segmental mobility of PET; thus, a nucleating effect occurs as a consequence of the reduction of the free energy barrier for nuclei formation, and the recrystallization rate is accelerated. As a result of annealing, a conformation conversion is observed; the gauche and amorphous trans contents decrease linearly as the crystalline trans content increases, and a clear relationship between the fraction of the trans conformation and the crystallinity may be established.[27] The results obtained are in good agreement with results obtained by DSC and dynamic mechanical analysis, where the intensity of the peak decreased with annealing, revealing the usefulness of fluorescence method to study crystallization processes in poly(ethylene terephthalate).

Chemiluminescence of Poly(ethylene terephthalate) under Nitrogen. First, the chemiluminescence under nitrogen of fluorescent probes employed in bulk was examined in order to determine their possible emission which could affect the poly(ethylene terephthalate) chemiluminescence measurement. Under this condition, all the samples exhibited very low intensity of emission, and it may be considered negligible in PET samples, since the probe content is relatively low.

The chemiluminescence temperature-ramping tests under nitrogen of PET$_{initial}$ and treated with a probe solution in toluene, PET$_{C152}$, PET$_{C153}$, and PET$_{C337}$, were undertaken. The chemiluminescence profiles are shown in Figure 5.

For all samples, under nitrogen no chemiluminescence emission was detected at temperatures below 75 °C, where the α transition of poly(ethylene terephthalate) takes place. This transition involves motions of long segments which favors the mobility of the hydroperoxides and their bimolecular termination reaction, which is responsible for chemiluminescence emission in polymers, through the deactivation of the generated carbonyl moieties in the excited state. Even though chemiluminescence intensity is increasing, PET$_{initial}$ showed weak emission in the whole range of temperature. Since in the absence of oxygen the species responsible for the chemiluminescence correspond to the initial concentration of peroxy radicals, which is proportional to the hydroperoxide content generated during the processing of the material.[28] It would indicate that no significant amounts of chemiluminescence species were induced by oxidation during film processing.

Table 4. Fluorescence Wavelength Maxima, Energy of Singlet Excited State, and Relative Quantum Yields of Fluorescence Emission for C337, C153, and C152 Adsorbed in PET

probe	λ_{max} (nm)	E_S (kJ mol^{-1})	$\phi_{F\ relative}$
C337	486	258	0.78
C153	483	270	0.50
C152	463	281	1

The same trend was observed for PET$_{C152}$ and PET$_{C153}$, and very low emission intensity was detected over the temperature range. However, amplified chemiluminescence emission intensity was found for PET$_{C337}$ as compared to those obtained for the other samples. It is proposed that in the presence of fluorescent probes the energy transfer from excited carbonyl (donor molecule) to an originally unexcited acceptor molecule can take place. Because the energy of excitation of the acceptor comes from the excited donor, the donor is radiationlessly deactivated to its ground electronic state. The acceptor molecule, which has become excited at the expense of the donor, may return to its ground state, and fluorescence emission from acceptor is detected (Scheme 1). A requirement for energy transfer is the overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor. Therefore, the probability of energy transfer increases with the degree of overlap.

Scheme 1

$$\mathrm{POO^{\bullet} + POO^{\bullet} \rightarrow POH + {}^{1}O_2 + P\,{}^{3}(C{=}O)^{*} \rightarrow PCO} + h\nu_{\mathrm{PET}} \quad (1)$$

$$\mathrm{P\,{}^{3}(C{=}O)^{*} + coumarin \rightarrow P(C{=}O) + coumarin^{*} \rightarrow coumarin} + h\nu_{\mathrm{coumarin}} \quad (2)$$

From the fluorescence spectra of coumarins (Figure 3), the energy of singlet excited state (E_S) may be calculated as the energy at 10% of fluorescence intensity maxima (λ_{max}). Also, the relative quantum yields of emission fluorescence for coumarins adsorbed in PET were determined. The data obtained are summarized in Table 4. Coumarin C337 exhibited the lowest energy of singlet excited state. Then, the energy transfer from excited triplet state of carbonyl to the singlet state may be more favorable for C337, which would act as the most effective physical enhancer of the chemiluminescence emission.

For PET$_{C337}$, the chemiluminescence intensity increased with temperature in the range 75−130 °C (Figure 5). At higher temperatures, a decrease in the emission was detected. It could be due to exothermic recrystallization during heating and the corresponding decrease of the free volume fraction, which would restrain the peroxyl recombination, which originates excited carbonyl moieties and the energy transfer to the fluorescent probe. The recrystallization is a very fast and complex process, and a description of poly(ethylene terephthalate) recrystallization is still controversially discussed even though it has been studied by different authors.[29] However, from these data, a new approach is envisaged to analyze in depth this process by using a very sensitive analytical technique such as chemiluminescence.

The Arrhenius type curves, ln(I_{CL}) vs 1/T, are plotted in Figure 6. For all PET samples, the Arrhenius plots exhibit pronounced slope changes in the chemiluminescence emission with temperature, and different zones are distinguished.

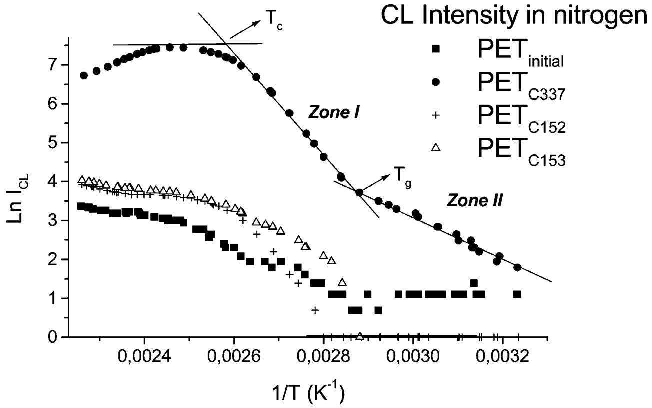

Figure 6. Arrhenius plots of chemiluminescence intensity vs 1/T for PET$_{initial}$, PET$_{C337}$, PET$_{C152}$, and PET$_{C153}$, under nitrogen.

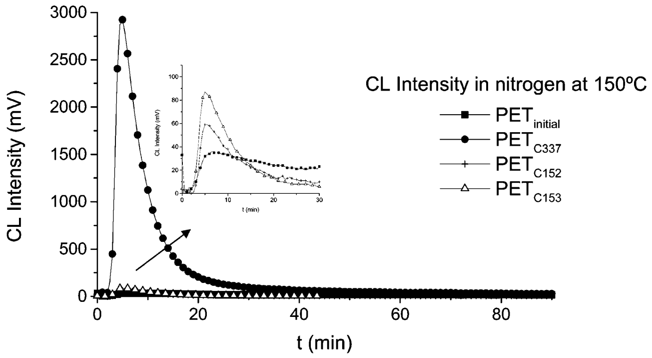

Figure 7. Chemiluminescence curves vs time at 150 °C under nitrogen of PET$_{initial}$, PET$_{C337}$, PET$_{C152}$, and PET$_{C153}$.

Table 5. Thermal Transitions and Activation Energies Determined by Chemiluminescence under Nitrogen

sample	$E_{act\ I}$ (kJ mol^{-1})	$E_{act\ II}$ (kJ mol^{-1})	T_g (°C)	T_c (°C)
PET$_{initial}$	100		74	113
PET$_{C152}$	118		77	116
PET$_{C153}$	113		78	115
PET$_{C337}$	116	42	75	113

A slope change was observed around 75 °C, assigned to the α transition of poly(ethylene terephthalate), as has been mentioned above. Also, another slope change is observed around 113 °C, attributed to the exothermic recrystallization peak (T_c). The activation energy above (temperature range I) and below (temperature range II) glass transition temperature were calculated, and the data are summarized in Table 5 with the T_g and T_c values.

The activation energy values corresponding to lower temperatures ($E_{act\ II}$) are lower than those obtained above glass transition ($E_{act\ I}$), where recrystallization during heating takes place. In fact, the former is only clearly detected in PET$_{C337}$ due to the enhanced emission previously mentioned. At temperature range above T_c, the chemiluminescence emission is decreasing. This phenomenon could be associated with the more restricted mobility of hydroperoxide in the polymer after the crystallization process during heating.

The isothermal chemiluminescence analysis under nitrogen at 150 °C was undertaken for all PET films. The obtained results are plotted in Figure 7. As expected, the intensity of chemiluminescence and the area

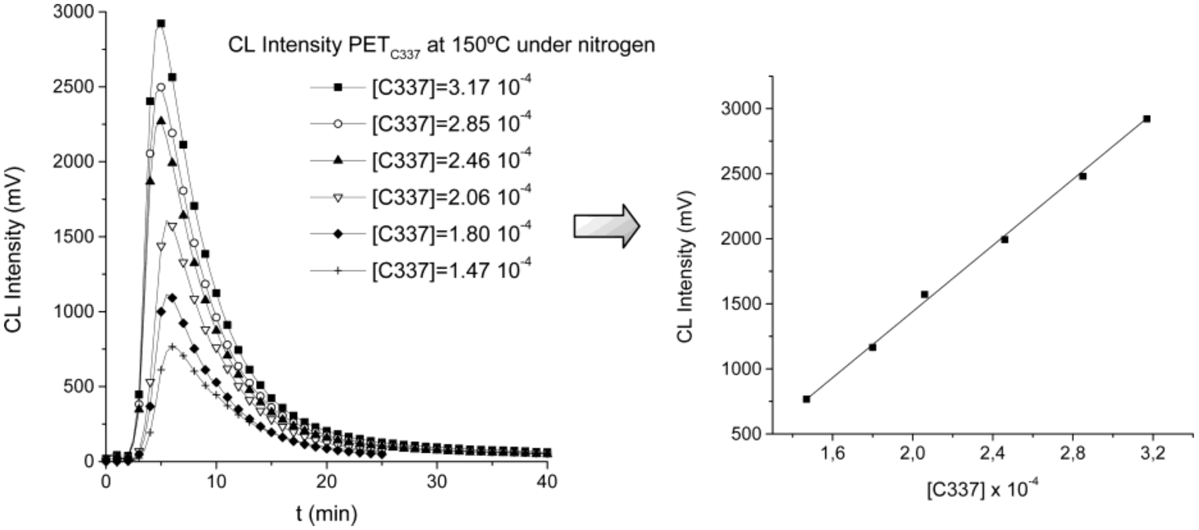

Figure 8. Chemiluminescence emission at 150 °C under nitrogen of PET$_{C337}$ with different C337 content.

of the emission curve for PET$_{initial}$ were very low. An slight increase of CL emission was detected for those films containing the fluorescent probes (PET$_{C152}$ and PET$_{C153}$) when compared with the reference sample. However, a greater enhancement (more than 30-fold) of CL intensity was observed for PET$_{C337}$. It would confirm the role of C337 as effective physical enhancer of chemiluminescence to study mechanism and kinetics of oxidation processes in polymers which give very weak light intensity emission upon oxidation.

The sensitization of fluorescence of an acceptor molecule is considered a concentration-dependent process. The chemiluminescence emission of PET$_{C337}$ has been studied at different concentrations of fluorescent probe. The chemiluminescence profiles and the CL emission intensity vs C337 concentration are shown in Figure 8. The enhancement of chemiluminescence with the coumarin content was observed in the range of concentrations studied. This result would indicate that energy transfer is a diffusion-controlled process. The requirement for donor and acceptor to diffuse near or have actual physical contact with each other suggests that rigidity of the medium would influence greatly the energy-transfer process from excited carbonyl moieties to coumarin fluorescent probes. Then, the chemiluminescence emission decrease at temperatures above 130 °C (Figure 5) would be related with the decrease of energy-transfer process during heating. Since that is a diffusion-controlled process, this fact may be explained in terms of the more restricted mobility of hydroperoxides and coumarin to diffuse near each other, in the polymer after the crystallization process during heating.

Chemiluminescence of Annealed Poly(ethylene terephthalate) under Nitrogen. The nonisothermal chemiluminescence tests under nitrogen of PET$_{C337}$, PET$_{C152}$, and PET$_{C153}$ after annealing at various temperatures were undertaken to determine the influence of degree of crystallinity in the bimolecular decomposition of hydroperoxides. The chemiluminescence profiles for all mentioned PET samples are shown in Figure 9.

The PET annealed samples followed a similar trend to their corresponding nonannealed PET samples, and very low intensity was detected for PET$_{C153}$ and PET$_{C152}$ in the whole range of temperatures studied. In general, it was observed a lower chemiluminescence emission for annealed samples respect to the initial sample. It may be due to the increasing crystallinity of annealed poly(ethylene terephthalate) samples, which would restrict the mobility of hydroperoxides to recombine themselves (eq 1 in Scheme 1).

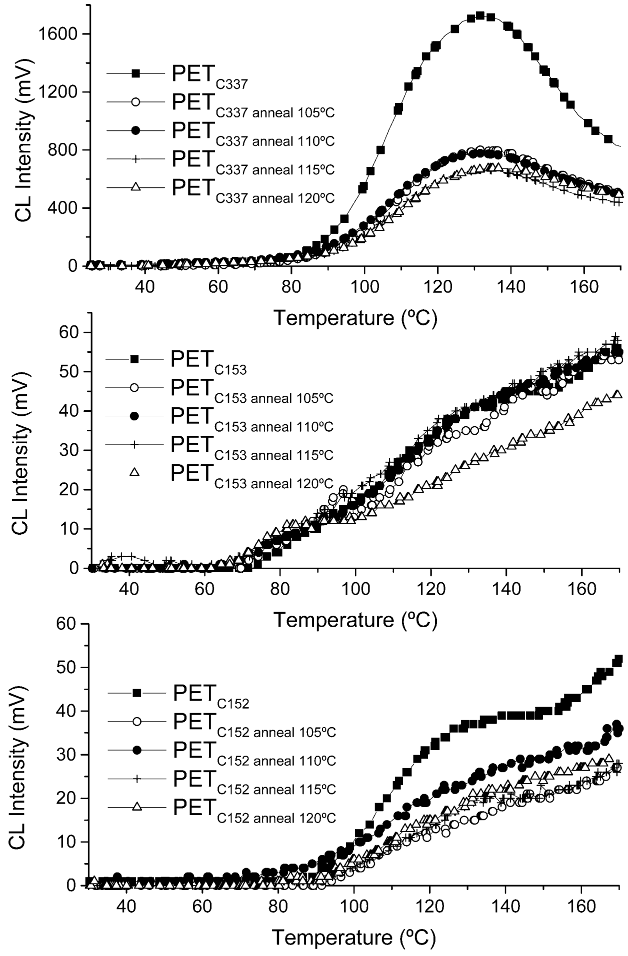

Figure 9. Chemiluminescence temperature-ramping curves obtained under nitrogen for PET$_{C337}$, PET$_{C152}$, and PET$_{C153}$ and after annealing at different temperatures.

Annealed PET$_{C337}$ showed enhanced chemiluminescence emission with respect to equivalent PET$_{C153}$ and PET$_{C152}$ samples, as was observed for samples before annealing. In general, no significant emission below α transition was detected for PET$_{C337-anneal}$

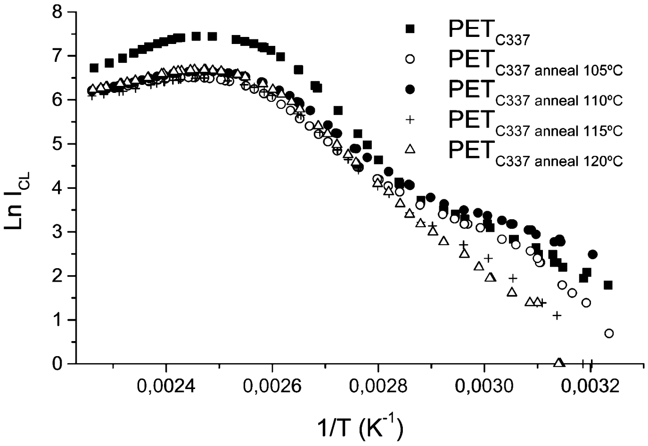

Figure 10. Arrhenius plots of chemiluminescence intensity vs 1/*T* for PET$_{C337}$ and after annealing at different temperatures, under nitrogen.

(Figure 9). The chemiluminescence intensity increased with temperature in the range 75−130 °C, and the increase of chemiluminescence intensity was interrupted at temperature higher than the exothermic recrystallization peak, as was previously described for PET$_{C337}$. PET$_{C337-anneal}$ at different temperatures exhibited lower chemiluminescence emission than PET$_{C337}$. In this case, several factors may affect the chemiluminescence emission. The increasing crystallinity of annealed poly(ethylene terephthalate) samples may be considered, which would restrict the mobility of hydroperoxides to react due to the higher rigidity of the medium. Furthermore, since the energy transfer from the triplet excited state of carbonyl to the singlet state of coumarin is considered a diffusion-controlled process, it would be highly affected by the degree of order in the medium.

Moreover, the translocation of fluorescent probe upon isothermal treatment of poly(ethylene terephthalate) should be taken in account to affect both the sensitivity of the probe and the energy-transfer process. During the annealing process, a net translocation of C337 molecules from amorphous to interfacial regions would take place, which would be influenced by the molar volume of the probe. The chain orientation and mobility in the interfacial region are intermediate between those of crystalline and amorphous regions. Then, the sensitivity of the probe to the changes of the microenvironment may decrease because of its reduced mobility, as was observed for annealed PET$_{C337}$ samples by means of fluorescence spectroscopy. The sensitivity to the glass transition peak, ΔI_{f-T_g}, and to the exothermic crystallization peak, ΔI_{f-T_c}, was seen to decrease in all the annealed samples with respect to the untreated samples.

The translocation of probe may also influence the probability of the energy transfer from the donor to the fluorescent probe, which would be less favored since the ability of the Coumarin 337 to undergo diffusional motion in poly(ethylene terephthalate) matrix may be more restricted.

The Arrhenius plots of all mentioned samples are represented in Figure 10, and the T_g, T_c, and activation energies ($E_{act\ I}$ and $E_{act\ II}$) are summarized in Table 6.

In general, the glass transition temperature increases slightly with annealing temperature as well as the E_{actII} associated with the bimolecular decomposition of hydroperoxide below T_g, increases. This phenomenon may be associated with the higher crystallinity after annealing process, as was observed by differential scanning calorimetry. Although, lower values of activation energies above glass transition (E_{actI}) were found for annealed samples than that for the initial, since the recrystallization of amorphous regions during heating is reduced with annealing temperature increase.

The chemiluminescence emission for annealed PET$_{C337}$ samples was measured under nitrogen at 150 °C. The obtained results are plotted in Figure 11, and the chemiluminescence parameters CL decay rate, I_{CL-max}, and $A_{CL-peak}$ are shown in Table 7. The parameter CL decay rate was calculated from the slope of the reciprocal of the square root of the chemiluminescence intensity

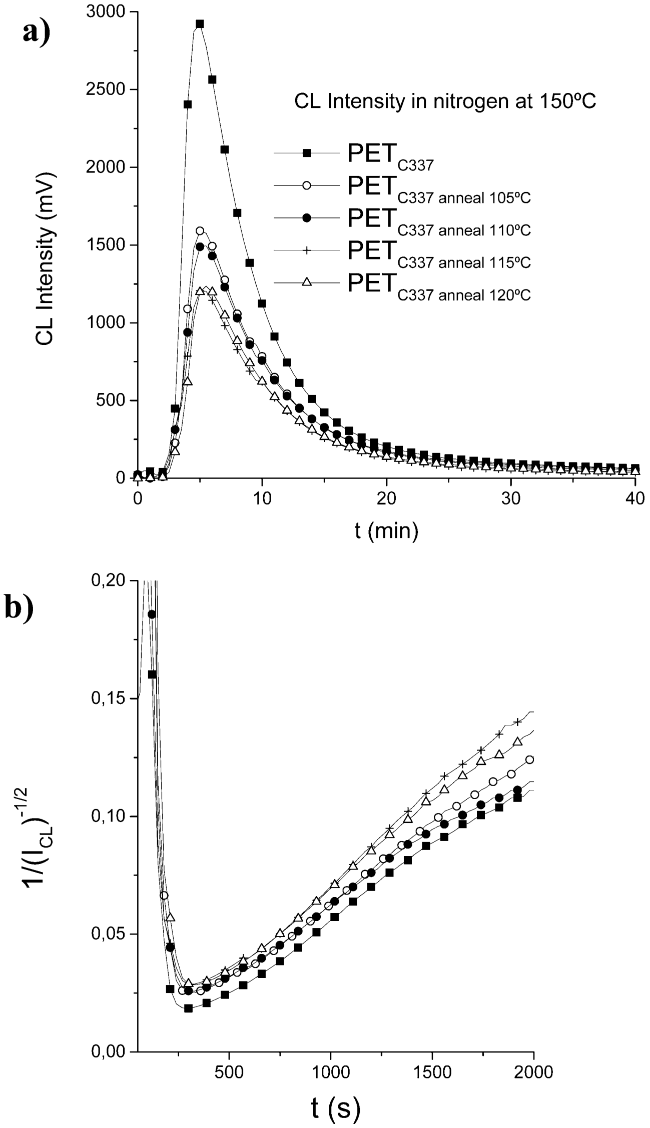

Figure 11. (a) Chemiluminescence curves vs time. (b) Plot of the reciprocal of square root of chemiluminescence intensity vs time, obtained at 150 °C under nitrogen for PET$_{C337}$, and after annealing at different temperatures.

Table 6. Thermal Transition and Activation Energies Determined by Chemiluminescence under Nitrogen

sample	$E_{act\ I}$ (kJ mol^{-1})	$E_{act\ II}$ (kJ mol^{-1})	T_g (°C)	T_c (°C)
PET$_{C337}$	116	42	75	113
PET$_{C337\ anneal\ 105°C}$	90	43	75	113
PET$_{C337\ anneal\ 110°C}$	92	55	76	113
PET$_{C337\ anneal\ 115°C}$	81	65	78	112
PET$_{C337\ anneal\ 120°C}$	78	73		112

Table 7. Chemiluminescence under Nitrogen at 150 °C of PET Films and Crystallinity Determined by DSC

sample	$I_{\mathrm{CL-max}}$ (mV) $\times 10^{-2}$	$A_{\mathrm{CL-peak}}$ (mV) $\times 10^{-3}$	CL decay rate $\times 10^{4}$ ($\mathrm{mV^{-1/2}\ s^{-1}}$)	% X_c
$\mathrm{PET_{C337}}$	29	2.1	0.62	20
$\mathrm{PET_{C337\ anneal\ 105°C}}$	16	1.4	0.68	26
$\mathrm{PET_{C337\ anneal\ 110°C}}$	15	1.3	0.71	28
$\mathrm{PET_{C337\ anneal\ 115°C}}$	13	1.1	0.79	30
$\mathrm{PET_{C337\ anneal\ 120°C}}$	12	1.0	0.83	32

vs time, as published by Kihara and Hosoda[30] (eq 3). This slope is defined as $\sqrt{k_b/f}$, where k_b is the bimolecular constant rate of the hydroperoxides decomposition.

$$\frac{1}{\sqrt{I_{\mathrm{CL}}}} = t\sqrt{\frac{k_b}{f}} + \frac{1}{([\mathrm{POO}^{\bullet}]_0\sqrt{fk_b})} \qquad (3)$$

A good correlation was seen between the chemiluminescence parameters. Lower values of the intensity of chemiluminescence in the peak top ($I_{\mathrm{CL-max}}$) and integrated area of CL signal ($A_{\mathrm{CL-peak}}$) with increasing the annealing temperature were found, as was observed in the nonisothermal chemiluminescence analysis. Moreover, the values of CL decay rate enhanced for the annealed samples, which corresponded with their higher crystallinity detected by differential scanning calorimetry. This fact may be associated with the higher oxidation level in the annealed samples, which allows a rapid decrease of the chemiluminescence emission due to the recombination of hydroperoxides in the amorphous region.

In this paper it is demonstrated the clear correlation between morphology and chemiluminescence emission properties which will allow, in the near future, to extend the application of this advantageous technique, as for example, the study of the influence of processing conditions in the physical properties of polymeric materials.

Conclusions

In this work, ICT (intramolecular charge transfer) fluorescent probes have been used as a physical enhancer of chemiluminescence in poly(ethylene terephthalate). PET exhibits low chemiluminescence emission; however, in the presence of an adequate fluorescent probe such as Coumarin C337, the energy transfer from excited carbonyl (donor molecule) to an originally unexcited acceptor molecule can take place, and amplified fluorescence emission from acceptor is detected. Coumarin 337 has been shown to be the most efficient enhancer due to its photophysical characteristics.

The chemiluminescence emission has been proved to be sensitive to the morphology of polymer samples, showing a strong dependence on the crystallinity. Therefore, chemiluminescence have been used to study the relaxation processes in semicrystalline polymers. The CL intensity increased with temperature in the range 75−130 °C. At higher temperatures, a decrease in the emission was detected. It has been associated with exothermic recrystallization during heating and the corresponding decreasing of the free volume fraction, which would restrain the peroxyl recombination, which originates the chemiluminescence emission. The Arrhenius plots of CL exhibit pronounced slope changes in the chemiluminescence emission with temperature, which correspond to the α transition (glass transition) and the exothermic recrystallization peak (T_c) of poly(ethylene terephthalate).

In general, it was observed a lower chemiluminescence emission for annealed samples with respect to the initial sample. It may be due to the enhanced crystallinity of annealed poly(ethylene terephthalate) samples, which would restrict the mobility of hydroperoxides to recombine themselves. Furthermore, since the energy transfer from excited oxidized species to the singlet state of coumarin is considered a diffusion-controlled process, it would be highly affected by the degree of order in the medium.

The CL results clearly correlate with the T_g and T_c temperatures in the initial and annealed films, determined by means of differential scanning calorimetry and dynamic mechanical analysis. Also, the results correlate with those obtained by means of fluorescence spectroscopy. In general, the fluorescence of the probes adsorbed in PET decreases as temperature increases. A slope change is observed in the temperature range 60−90 °C, attributed to the α transition, which involves motions of long segments (as expected for the glass transition), and the free volume of the medium enhances. Second, an increase of fluorescence intensity was observed around 100 °C. It has been associated with exothermic recrystallization during heating and the corresponding decrease of the matrix volume, which would restrain the nonradiative relaxation pathway.

Thus, it could be concluded that chemiluminescence method is a useful technique for the study of polymer degradation. Also, it is able to sense temperature-dependent morphological changes, i.e., annealing processes, and to determine relaxation temperatures and exothermic recrystallization peaks. The use of a fluorescent sensor to amplify the chemiluminescence emission allows to apply the innovative method, developed in this work, to all types of polymers including those with low intensity emission.

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