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Study of secondary relaxations of poly(ethylene terephthalate) by photoluminescence technique

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Abstract

The α and β relaxation processes in two types of poly(ethylene terephthalate) with different degrees of crystallinity were studied by means of three methods, differential scanning calorimetry, dynamic-mechanical analysis and fluorescence spectroscopy. Information provided is complementary in the mean that every method sense phenomena that may occur at different times and length scales. Several probes, Coumarin 152 (C152), Coumarin 153 (C153), Coumarin 337 (C337) and 4′-dimethylamino-4-nitrostilbene (DMANS), were adsorbed in polymer films, and their fluorescence analysed over the temperature range from − 150 to 150 °C. In general, a decrease in fluorescence intensity of probes as temperature increase was observed. This behaviour has been explained as a consequence of the enhancement of the free volume fraction that favoured the radiationless process of the lowest excited singlet state. Plots of fluorescence intensity versus temperature showed changes around the secondary relaxation temperatures. Therefore, good correlations between fluorescence and dynamic mechanical and calorimetric analysis were established. The obtained results indicated that the fluorescence from the probes incorporated to the material was dependent on the crystallinity of polymer. It would indicate that the fluorescence emission from those probes can be used to analyse annealing processes in semicrystalline polymers.

Keywords: Poly(ethylene terephthalate); Relaxation processes; Fluorescent probes

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1. Introduction

Fluorescent sensors have become a powerful tool to study different processes in polymers. This is due to several advantages of the fluorescence with respect to conventional techniques: high sensitivity and selectivity, very short time response ($<10^{-9}$ s), nondestructiveness, and processes that occur at different time scales may be studied *in real time* [1,2]. In general, probes are sensitive to changes of polarity, viscosity, and pH in their microenvironment. This characteristic allows the study of dynamic processes in polymers, such as: polymerization kinetics, swelling, secondary relaxations and thermal transitions, miscibility in polymer blends and phase separation, etc. Recently, fluorescent probes have been used to monitor the photooxidation of a polyurethane-acrylate adhesive [3]. The sensitivity of the fluorescence based method developed was found to be comparable to that of chemiluminescence (CL), which is considered a competitive analysis technique for the study of polymer degradation, due to its offered advantages with respect to many conventional techniques [4]. By fluorescence spectroscopy and CL, it is possible to asses the very first stage of photooxidation in polymer, well before any defects become visible.

Secondary relaxations of semicrystalline polymers have been characterized using various methods, including mechanical and dielectric spectrometry, NMR, IR and Raman spectroscopies. The use of luminescent probes to investigate motions of macromolecules has become important. In the last decade the study of secondary relaxations by using fluorescent probes for several polymers is reported in the literature, polystyrene, poly(*n*-alkyl methacrylate)s, poly(vinyl alcohol) hydrogel, polyethylene, polyethylene-poly(vinyl chloride) blends, etc. [1,2,5,6]. It is based on the strong temperature dependence of photophysical properties of probe in the polymeric material. The co-operative motions of macromolecular segments modify the photophysical processes of the fluorescent guests. Hence, the intensity of the emission of the molecular luminescent probe

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depend on both their intrinsic photophysical properties and interactions with the polymer matrix [1,2]. It has been observed a decrease in fluorescence intensity with the temperature increase. It was theorized that enhancement of the free volume of the medium leads to an increase in the nonradiative decay rate and consequently a decrease in fluorescence quantum yield.

Poly(ethylene terephthalate) (PET) has been used as a very useful model material to study relaxation processes in semicrystalline polymers [7–11]. It can be quenched into the completely amorphous state, whereas thermal and thermo-mechanical treatments lead to partially crystallized samples with easily controlled degrees of crystallinity. PET shows two well known relaxation processes, one designated as α and the other called β occurring at lower temperatures. The former is coincident with the well-established glass transition 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 is dramatically broaden and shifted to higher temperature in crystalline samples. At the molecular level, various interpretations have been proposed for the sub-glass local β relaxation [7,12–15]. That process is insensitive to morphology, and shows asymmetric profile. It has been attributed by Menegotto et al. [16], using thermally stimulated currents (TSC), to noncooperative motions of carbonyl groups (β_2) and cooperative mobility of phenyl rings (β_1).

The aim of this work is to study the relaxation processes of several poly(ethylene terephthalate)s with different crystallinity, using the temperature dependence of the fluorescence intensity of several probes. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) measurements have been also used to determine the secondary relaxations of PET samples, in order to correlate the results with those obtained by fluorescence technique.

2. Experimental procedures

2.1. Materials and sample preparation

Commercial poly(ethylene terephthalate) sheets with different crystalline content were supplied by Eastman–Kodak. 4′-dimethylamine-4-nitrostilbene (DMANS) was synthesised to be used as fluorescent probe as previously described [17]. Coumarin 152 (C152), Coumarin 153 (C153) and Coumarin 337 (C337) were supplied by Aldrich and used as received. The structures of probes used are shown in Fig. 1.

Slices of polymer sheet about 3.5 mm (wide) × 6 mm (length) and 0.2–0.4 mm (thick) were cut and immersed in a chloroform or toluene probe solution (10^{-3} M), for a period of 2 h in order to allow the probe to diffuse into the polymer matrix. The surface of the samples were washed with solvent to remove any remaining probe adhered on the surface, and finally, samples were dried by removing the solvent with an extensive vacuum treatment for a week time period. The molar concentrations of the fluorescent probe in the polymer matrix were calculated from the corresponding UV absorption spectra assuming that their molar absorption coefficients are the same as those previously measured in ethyl acetate solutions. Under the mentioned conditions, a concentration of 2×10^{-4} M was measured for the adsorbed probes in the PET samples.

2.2. Spectroscopic measurements

UV spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer. Steady state fluorescence measurements at various temperatures were recorded using a Perkin–Elmer LS50-B luminescence spectrophotometer coupled to a cryostat DN1704 Oxford Instruments designed for optical spectroscopy. The sample temperature can be continuously varied from −200 to 200 °C using the temperature controller ITC-4 Oxford instruments. The heating rate was always maintained at 5 °C min^{-1} and the scan rate selected to record one spectrum every minute. Under these conditions, all the measurements in the polymer films were carried out under nitrogen atmosphere.

2.3. 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 10 °C min^{-1} and the instrument was calibrated with an indium standard ($T_m = 429$ K, $H_m = 25.75$ J g^{-1}). The crystalline index of poly(ethylene terephthalate) samples, X_C, was determined as follow:

$$X_C = \Delta H_m / \Delta H_{m0}$$

where $\Delta H_m = \Delta H_f - \Delta H_C$; ΔH_f is the heat of melting and ΔH_C is the heat of recrystallization. The absolute value of the heat of fusion of the crystalline poly(ethylene terephthalate) is $\Delta H_{m0} = 135$ J g^{-1} [18].

Dynamic mechanical measurements were performed on a TA Dynamic-Mechanical Analyser (d.m.a.) 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}. The samples were prepared as films with dimensions 10 × 5 × 0.5 mm^3.

Thermogravimetry (TGA) measurements were performed in a Perkin–Elmer thermobalance, model TGA 7. The experiments were carried out in a nitrogen atmosphere, using 4 mg of sample and heated at a rate of 10 °C per minute.

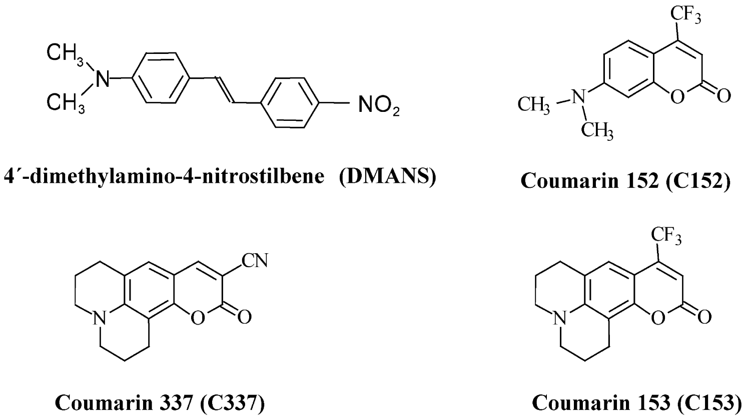

Fig. 1. Structure of fluorescent probes.

3. Results and discussion

3.1. Differential scanning calorimetric analyses

Firstly, DSC heating scanning of poly(ethylene terephthalate) samples from Eastman, were undertaken to determine the degree of crystallinity in the polymer film. The thermograms with PET_I and PET_{II} are shown in Fig. 2(a) and (b), respectively, and the corresponding data are included in Table 1. Also, in Table 1 all the DSC results obtained in different conditions are summarised.

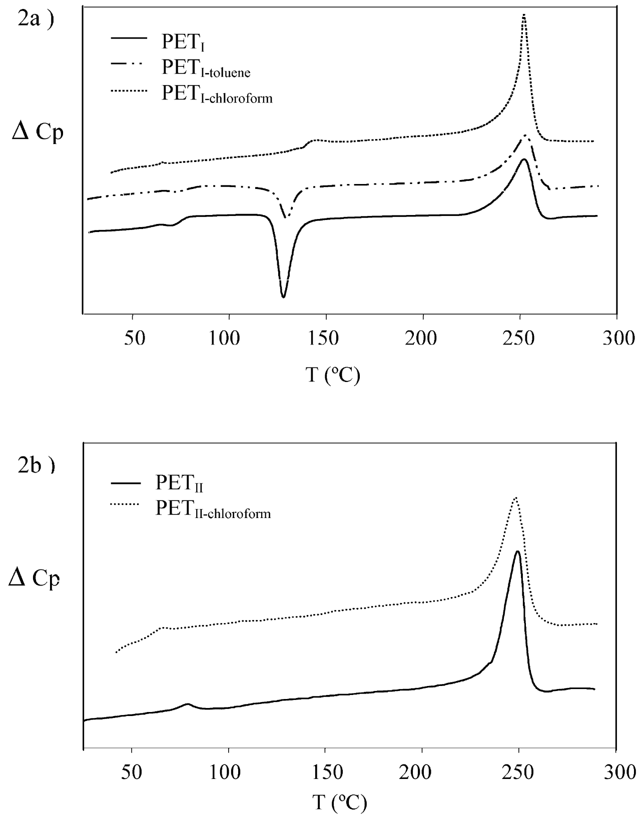

Fig. 2. DSC heating thermograms of: (a) PET_I initial (PET_I), treated in toluene ($PET_{I\text{-toluene}}$), treated in chloroform ($PET_{I\text{-chloroform}}$); (b) PET_{II} initial (PET_{II}), treated in chloroform ($PET_{II\text{-chloroform}}$).

From the data obtained with the original PET_I material, different parameters have been determined in heating scan: glass transition temperature (T_α), exothermic recrystallization peak (T_C) and endothermic peak (T_m). However, in the case of PET_{II} material the exothermic peak was not observed under the same conditions. This fact is in accordance with the clear difference of crystallinity of both samples, PET_{II} (33%) and PET_I (5%). PET_I can recrystallize easily in contrast with PET_{II} sample due to its much higher crystallinity.

In order to study the influence of solvent in the morphology of the polymer, DSC of PET_I films treated with toluene ($PET_{I\text{-toluene}}$) were undertaken. The first feature from this data is the observation that the exothermic peak, shown in Fig. 2, corresponding to the crystallization of amorphous regions is reduced on $PET_{I\text{-toluene}}$, compared with the original PET_I, and a higher value of crystallinity, 22% X_c, was determined. Our data are in agreement with those obtained by other authors [19–21]. PET is known to crystallize when brought in contact with liquids and solvents, and the phenomenon called as solvent induced crystallisation (SINC). This fact provides a method for the

Table 1
DSC analysis of poly(ethylene terephthalate) films at scan rate 10 °C min^{-1}

	T_α (°C)	T_c (°C)	T_m (°C)	ΔH_m (J g^{-1})	$\%X_c$
PET_I	75	125	252	27.7	5
$PET_{I\text{-toluene}}$	77	126	251	43.6	22
$PET_{I\text{-tolC152}}$	72	126	251	38.9	20
$PET_{I\text{-tolC153}}$	73	127	250	38.5	18
$PET_{I\text{-tolC337}}$	72	127	251	39.0	20
$PET_{I\text{-tolDMANS}}$	74	126	250	44.5	22
$PET_{I\text{-chloroform}}$	63	–	253	37.7	34
$PET_{I\text{-chlC152}}$	58	–	251	37.8	35
$PET_{I\text{-chlC153}}$	60	–	250	37.4	35
PET_{II}	72	–	249	41.7	30
$PET_{II\text{-chloroform}}$	58	–	247	45.6	34
$PET_{II\text{-chlC152}}$	57	–	246	51.1	35
$PET_{II\text{-chlC153}}$	58	–	245	54.8	35
$PET_{II\text{-chlC337}}$	55	–	245	48.5	36
$PET_{II\text{-chlDMANS}}$	58	–	245	44.9	34

morphological modification of semicrystalline polymers at temperatures well bellow the glass transition temperature. The process involves diffusion of solvent in the polymer and interruption of the intersegmental forces due to solvent–polymer interaction, and the degree of crystallinity is dependent on the polarity, solvent type, and the solubility parameter of the solvent [22,23]. A model for diffusion with induced PET crystallization to describe sorption kinetics of solvents has been described by Durning et al [24].

Also, measurements of films treated with a probe solution in toluene, $PET_{I\text{-tolC152}}$, $PET_{I\text{-tolC153}}$, $PET_{I\text{-tolC337}}$, $PET_{I\text{-tolDMANS}}$, were undertaken to check any effect of the probe on the thermal properties and crystallinity degree of poly(ethylene terephthalate). A similar behaviour was found for the samples to that obtained for $PET_{I\text{-toluene}}$, which would indicate that polymer changes are not influenced by the presence of probes, at least at the concentrations used in these experiments. Furthermore, incorporation of different probes to the polymer host induced crystallisation always until the same level, between 18 and 22%, as shown in Table 1, and these values compared well with $PET_{I\text{-toluene}}$.

A more dramatic SINC effect is observed when poly(ethylene terephthalate) samples with low initial crystallinity are immersed in a polar solvent such as chloroform, ($PET_{I\text{-chloroform}}$, $PET_{I\text{-chlC152}}$, $PET_{I\text{-chlC153}}$). From the data on Table 1, all the PET_I chloroform treated samples exhibit higher degrees of crystallinity compared to $PET_{I\text{-toluene}}$ and PET_I. The crystallinity values enhance with chloroform treatment from 5% X_c to 34–35% X_c. As expected when the crystallinity is high, nonexothermic peak is observed. In general, the glass transition temperature decreases with solvent treatment. Our results are in accordance with the fact that in semi-crystalline polymer the crystallization behaviour is changed by diffusion of solvent. It has been reported that glass transition temperature of such polymers depresses with the diffusion of solvent where the polymer is immersed [25].

When high crystallinity samples, PET_{II}, are treated with chloroform, the crystallinity increases slightly in comparison to initial sample, from 30% X_c to 34–36% X_c. Again, as it was observed in PET_I, with solvent treatment the glass transition temperature is reduced from 72 to 55–58 °C.

The thermogravimetric analysis of all poly(ethylene terephthalate) films were undertaken to determine the presence of solvent in the polymer. The thermograms for PET_{II} and $PET_{II\text{-chloroform}}$ are showed in Fig. 3. At temperatures below 100 °C, no loss of weight fraction was observed. It would indicate that the content of solvent in the polymer films is at level of traces, which would act as plasticizer depressing the glass transition temperature. At temperatures above 150 °C, sample treated in chloroform, $PET_{II\text{-chloroform}}$, exhibited higher loss of weight fraction than the original sample PET_{II}. This behaviour could be attributed to the before mentioned solvent induced crystallization of amorphous domains. It would result in the formation of small domains with a very low degree of perfection, and partial melting of the defective crystals at temperatures below 250 °C. The results would be on agreement with those obtained by DSC, Fig. 2, where two exothermic peaks are observed for $PET_{II\text{-chloroform}}$. The presence of multiple melting peaks in PET has been attributed by other author to the presence of two types of crystalline morphology [26], and recently, the same effect in PEN (poly(ethylene 2,6-naphtalate)) has been reported [25].

3.2. Dynamic mechanical analyses

All the poly(ethylene terephthalate) samples commented before were studied by dynamic mechanical analysis. In general, changes on the degree of crystallinity have a great effect on the dynamic mechanical properties. The results corresponding to the α- and β-transition temperatures, the loss moduli maxima (E''_{max}) and its width peak parameter are summarised in Table 2. The original untreated samples, PET_I and PET_{II}, show two relaxations referred to as α and β, respectively, in order of decreasing temperature.

α *transition*—PET_I sample exhibits a peak at 70 °C assigned to its α relaxation, Fig. 4. After treatment in toluene, the temperature corresponding to the α transition remain constant. Otherwise, the intensity of the peak decreases in all the samples after the solvent treatment from 400 to 180 MPa, Table 2. Also, the signal becomes broader. In order to quantify this effect, it has been calculated the width of E'' peak at the intensity of $E''_{max}(\alpha)/2$. The width increases from a value of 4.5 for the original sample PET_I to a value of 12 after the solvent treatment. Similar behaviour was found for PET_I sample treated in chloroform, $PET_{I\text{-chlC152}}$ and $PET_{I\text{-chlC153}}$. Although higher broadening of the peak was observed for both samples, which increase to a width value of 28. This effect observed on the materials is directly related with the enhancement of the crystallinity induced by solvent, and it is in good agreement with results obtained by DSC.

A much higher α transition temperature was found for initial PET_{II}, which exhibits a peak at 105 °C, Fig. 5. This behaviour can be attributed to the effect of crystal size on the amorphous regions; at high crystallinity, the crystallites are generally fewer and larger, and allow more freedom to the segments in the amorphous regions. Again the SINC by chloroform is accomplished with a decreasing of E''_{max} intensity, Table 2. With this analysis, the α relaxation can be related with the glass transition temperature of the system. The values obtained are slightly different to T_g reported by DSC, which is a general finding in polymers [27]. It has been attributed to different ranges of frequency for the two experimental techniques.

β *transition*—Its dynamics is insensitive to the degree of crystallinity as it was found for PET_I and PET_{II}, which exhibited a peak around −65 °C. It has been reported that β relaxation is entirely due to the amorphous phase. The β

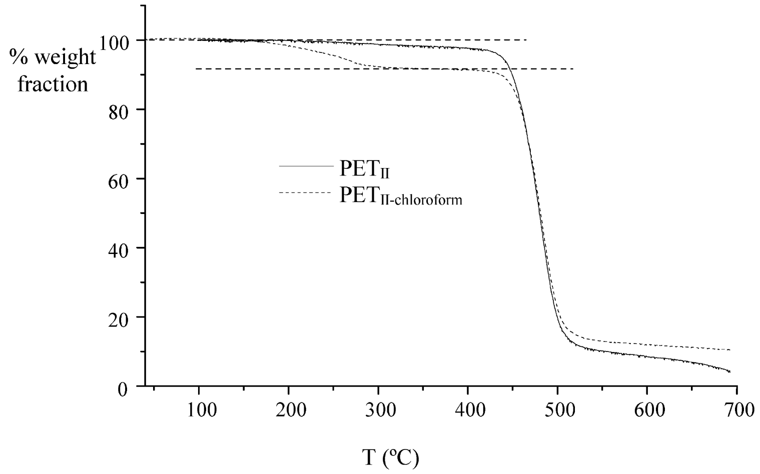

Fig. 3. TGA curves of PET$_{II}$ initial and treated in chloroform (PET$_{II-chloroform}$).

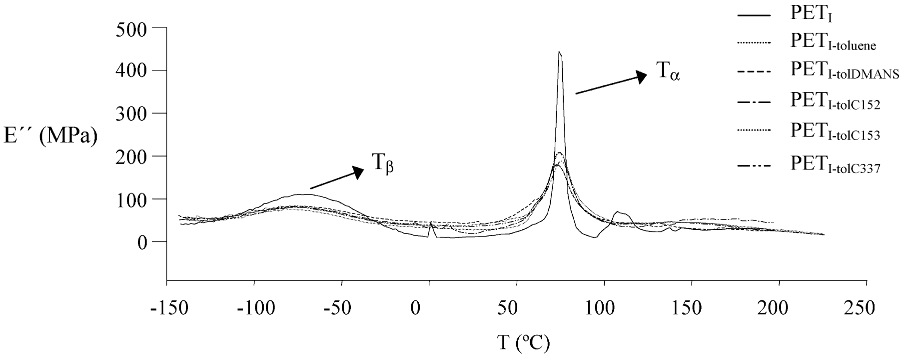

Fig. 4. Temperature dependence of the loss moduli (E'') for the α and β relaxations of PET$_{I}$ samples.

process is attributed to torsional vibrations of the main-chain correlated over a length corresponding to one monomer [11,14,15]. Here, two different behaviours have been observed depending on the nature of the solvent used in the sample treatment. With toluene, in general, no shift is observed for β transition temperature of PET$_{I-toluene}$ in comparison with the untreated sample, as showing in Fig. 4. However in the case of chloroform, it was found a double peak referred to β2 and β1 transitions in PET$_{I-chloroform}$, Table 2. This fact could be associated to the influence of the chloroform occluded in the amorphous phase on the molecular motions of short range segment, which involves carbonyl groups (β_2) and phenyl rings (β_1). Similar effect has been also observed for the samples of high crystallinity when are treated in chloroform, PET$_{II-chloroform}$, as showed in Fig. 5.

Table 2
Dynamic-mechanical analysis of poly(ethylene terephthalate) films at scan rate 5 °C min^{-1}. Frequency 0.1 Hz

	β (°C)	α (°C)	$E''_{max}(\alpha)$ (MPa)	Width of E'' peak at $E''_{max}(\alpha)/2$
PET$_{I}$	−68	70	400	4.5
PET$_{I-toluene}$	−70	72	180	12
PET$_{I-tolC152}$	−70	70	185	11
PET$_{I-tolC153}$	−70	72	209	10
PET$_{I-tolC337}$	−70	72	187	11.5
PET$_{I-tolDMANS}$	−70	70	182	12.5
PET$_{I-chlC152}$	−87; −30	68	137	27
PET$_{I-chlC153}$	−85; −30	70	139	28.5
PET$_{II}$	−65	105	600	32
PET$_{II-chloroform}$	−75; −14	70	95	38
PET$_{II-chlC152}$	−75; −25	65	112	44
PET$_{II-chlC153}$	−75; −15	70	115	44
PET$_{II-chlC337}$	−80; −18	70	130	36
PET$_{II-chlDMANS}$	−80; −18	55	120	44

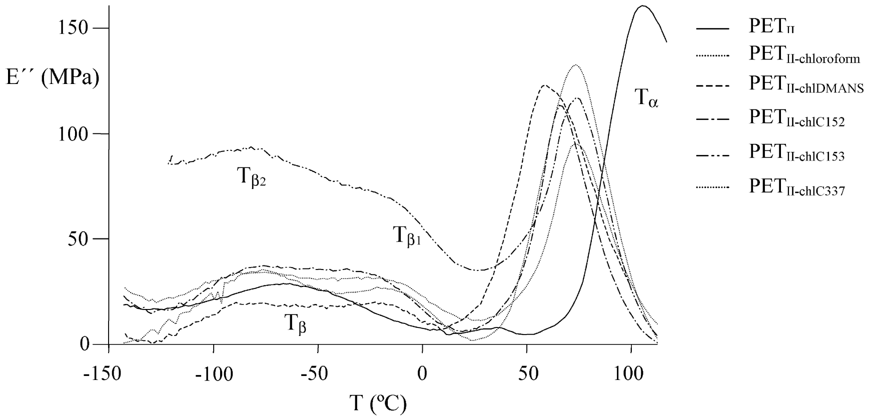

Fig. 5. Temperature dependence of the loss moduli (E'') for the α and β relaxations of PET_{II} samples.

3.3. Relaxation processes by fluorescence analyses

In this work, the intramolecular charge transfer fluorescent probes (ICT), Coumarin 152 (C152), Coumarin 153 (C153), Coumarin 337 (C337), and the 4′-dimethylamine-4-nitrostilbene (DMANS) were selected to study the relaxation processes in PET_I and PET_{II}. These probes containing both an electron donor (D) and acceptor (A) groups, upon electronic excitation, lead to the formation of an ICT state with partial electron transfer. In special cases it is followed by a twisting of the molecule leading a twisted ICT (TICT) state, in which the π-system of donor (D) is perpendicular to the π-system acceptor (A). The internal rotation of certain molecular fragments of TICT probes has a significant influence on their fluorescence emission and it is highly dependent on the rigidity of the polymer matrix [28–30]. In previous papers, these types of flexible fluorescent dye molecules have been proved to be sensitive to both the local viscosity (rigidity) and polarity of the surrounding. Variations in Van der Waals volume of the rotating part, by introduction of voluminous groups or by extension of aromatic system have been used to enhance the fluorescence response for monitoring polymerisation reactions [17, 31–33].

Firstly, the absorption and fluorescence properties of the probes adsorbed in poly(ethylene terephthalate) films were measured and the data summarised in Table 3. The absorption wavelength maxima are not influenced by the morphology of poly(ethylene terephthalate) samples, and the probes exhibit similar properties in both polymer media, PET_I and PET_{II}. However, their fluorescence properties are strongly dependent on the crystalline index. With all the used probes, bathocromic shift of the wavelength emision maxima is observed as the crystallinity enhanced, from $PET_{I\text{-probe}}$ ($X_c = 20\%$) to $PET_{II\text{-probe}}$ ($X_c = 35\%$), Table 3. A plausible explanation could be related to the fact that the dielectric coupling between the excited state and the polymer reduces the energy of the lowest excited state. Hence, the emission takes place from a more relaxed state and is observed at longer wavelength fluorescence maxima. Due to the requirement of orientation motions for dielectric coupling during the excited lifetime, it seems feasible that coupling will be less favoured with higher SINC increase in PET_I (from 5% X_c in PET_I to 20% X_c in $PET_{I\text{-probe}}$), and as a result emission shift to shorter wavelengths. It seems that a good correlation between fluorescence and crystallinity could be established, so that the fluorescence emission from those extrinsic probes can be used as a valuable method to analyse annealing processes and thermal properties in semicrystalline polymers.

The relationship between the temperature and fluorescence of probes has been described by several authors, in homopolymers [1,2,34,35] copolymers [36] and blends [6, 37]. The excited singlet state of probe promoted by absorption of a photon, can be deactivated by radiative process (fluorescence k_r), and nonradiative pathway, dependent (k_{nr}^T) or independent (k_{nr}) of temperature. The

Table 3
Spectroscopic properties of fluorescence probes adsorbed in PET_I and PET_{II} films

Probe	PET_I		PET_{II}	
	Absorbance λ_{max}	Fluorescence λ_{max}	Absorbance λ_{max}	Fluorescence λ_{max}
C152	398	458	398	464
C153	423	481	420	490
C337	446	482	447	491
4-DMANS	455	551	460	575

λ in nm.

fluorescence quantum yield, ϕ_F, is described by:

$$\phi_F = \frac{K_r}{K_r + K_{nr} + K_{nr}^T} \tag{1}$$

At very low temperatures, the radiative deactivation is the favoured pathway because of the nonradiative processes dependent on the temperature (k_{nr}^T) become zero, absolute fluorescence quantum yield, ϕ_{F0}, is defined, and the following equation is obtained:

$$\frac{I_{F0}}{I_F} = \frac{\phi_{F0}}{\phi_F} = 1 + \frac{K_{nr}^T}{K_r + K_{nr}} \tag{2}$$

where I_F is the intensity of fluorescence, and I_{F0} is the intensity of fluorescence at very low temperature. Since k_{nr}^T can be expressed by an Arrhenius plot, the dependence of intensity of fluorescence with temperature is expressed by the following equation:

$$\ln\left(\frac{I_{F0}}{I_F} - 1\right) = -\frac{E_a}{RT} + k \tag{3}$$

When polymer relaxation takes place, the free volume of the medium enhances. It leads to an increase in the nonradiative decay rate of singlet state probe, i.e. due to the internal rotation of certain molecular fragments of probes, and consequently, a decrease in fluorescence quantum yield is observed. The onset temperature ascribed to a specific polymer relaxation processes is defined by the change of the slope in linear or Arrhenius plot of I_F versus temperature.

Fluorescence spectra of the probe-doped PET films were recorded at temperature range from −150 to 150 °C, and the intensity of fluorescence (I_F) measured at the maximum emission wavelength for a fixed excitation at the maximum absorption of each probe. The fluorescence intensity of the probes versus temperature are showed in Figs. 6 and 7, for PET_I and PET_{II}, respectively. The data are compiled in Table 4.

In general, the fluorescence of the probes adsorbed in PET_I decreases as temperature increases, Fig. 6. An abrupt slope change is observed with all the studied probes in the temperature range −50 to −25 °C, attributed to the β transition. And a more pronounced slope change is observed in the temperature range 50–75 °C, assigned to the α transition, which involves motions of long segments (as expected for the glass transition). The first feature from this data is the observation that the probe sensitivity is highly influenced by their structure. In previous work, the changes of fluorescence emission of DMANS at different temperatures in hexane was studied [17] and compared with those of different D–π–A diarylethylene and diarylbutadiene derivatives. It was found that the onset of the probe mobility occurred at a temperature/viscosity that depended on the size of the fluorescent probe.

Table 4
Transition Temperatures for C152, C153, C337 and DMANS adsorbed in PET_I and PET_{II}

Probe	PET_I		PET_{II}	
	β (°C)	α (°C)	β (°C)	α (°C)
C152	−48	57	−83; −33	57
C153	−48	62	−83; −23	57
C337	−43	62	−83; −23	57
DMANS	−43	67	−85; −28	67

Coumarin 152 exhibit higher decrease of fluorescence intensity than Coumarin 153 and Coumarin 337. This can be explained in terms of the enhancement of the free volume of the medium with temperature. β transition involves motions of short segment chain, hence it allows the amino group rotation around the aromatic ring to happen in Coumarin 152. This group movement leads to an increase of the nonradiative decay rate (k_{nr}) and consequently a decrease in fluorescence quantum yield. Hence, this probe structure is more sensitive to rigidity changes than C153 and C337, where the amino group rotation is sterically hindered. Sensitivity of C152 is also greater than that of DMANS, which has also a free dimethyl amino group. Size effect could contribute to a more efficient deactivation process due to the smaller molar volume of C152 (205 Å^3) compared to that of DMANS (258 Å^3).

A similar trend has been observed for probes adsorbed in the high crystallinity sample, PET_{II}, Fig. 7. Their fluorescence decreases as temperature increases, and slope changes are observed around α and β relaxation temperatures. All fluorescent probes exhibit higher sensitivity at α than at β relaxation. The former involves long-range segmental motion in the amorphous regions. It results in larger free volume variations than those involved in the β relaxation, and a greater decreasing rigidity of the probe surrounding.

The curve of fluorescence intensity of probes versus temperature exhibit two peaks around −85 and −28 °C referred to β2 and β1 transitions. The results correlate well, under experimental uncertainty, with those obtained by means of dynamic mechanical analyses, where the loss moduli (E'') versus temperature showed a double peak. However, β relaxation temperature of PET_I determined by fluorescence is higher than those obtained from d.m.a. Moreover, fluorescence data show significant differences between PET_I and PET_{II}, which are not so clear in d.m.a. As solvent treatment causes changes of the crystallinity which are more pronounced in PET_I that in PET_{II} it could be expected translocations of the fluorescent probes due to the decrease of the free volume fraction. Therefore, they may diffuse and sense different domains in the same material depending on morphological changes.

The SINC in PET_{II} seems to reduce fluorescent guest sensitivity with the exception of DMANS. Two factors should be considered: (i) size effect, already mentioned in PET_I and (ii) the time correlation between macromolecular motion and photophysical process. Thus, DMANS has bigger volume than C152, and size effect should be

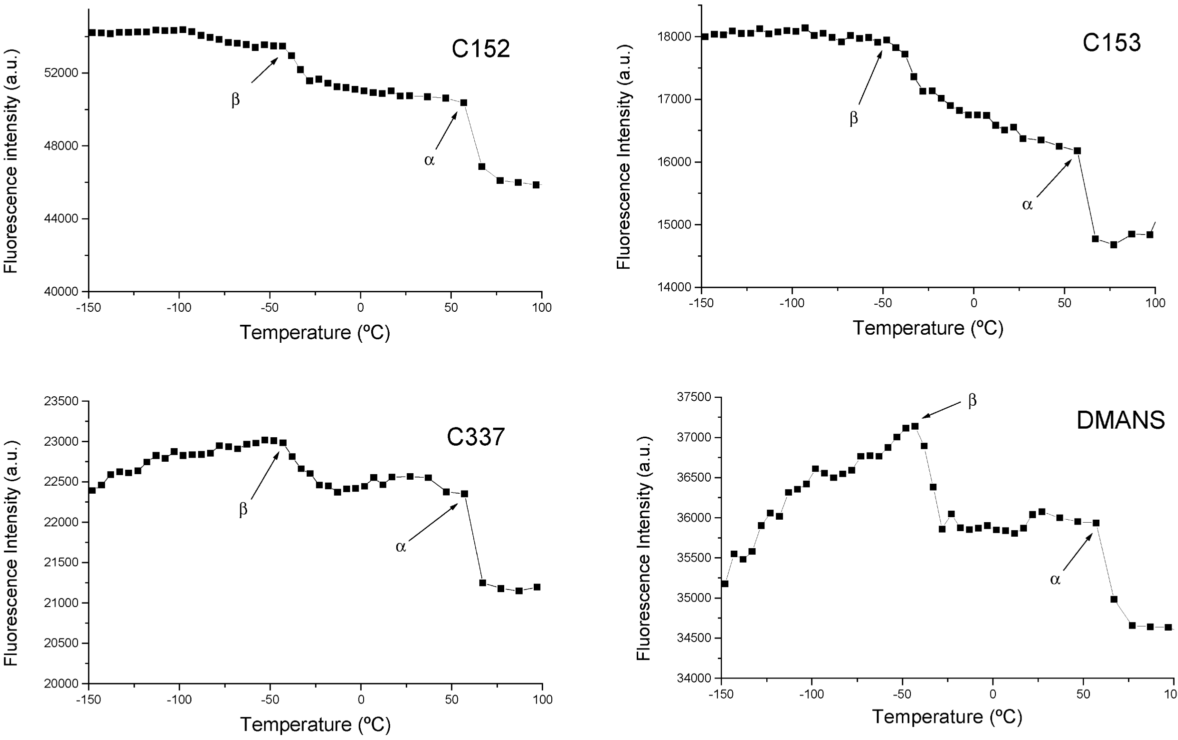

Fig. 6. Fluorescence intensity versus temperature for C152, C153, C337, and DMANS adsorbed in PET_I.

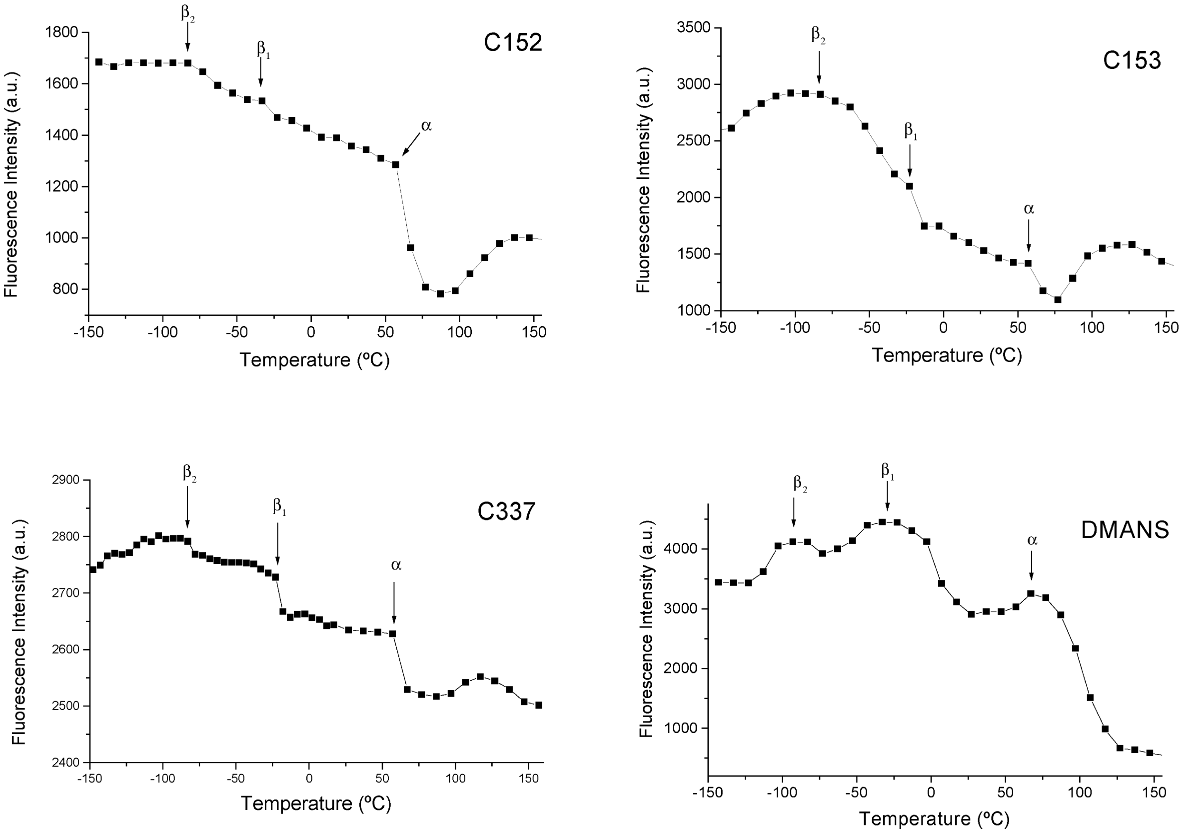

Fig. 7. Fluorescence intensity versus temperature for C152, C153, and DMANS adsorbed in PET_{II}.

excluded. So that, the best fluorescence response should be related to a slowest structural relaxation compared to the fluorescence rate decay, which depends on the microenvironment where the probe is located. Again, this behaviour points out to a heterogeneous distribution of the probe between the amorphous face or in the interface. This effect is more pronounced near to the glass transition where larger molecular motions are involved.

An increase of fluorescence intensity was observed at 100 °C for C152, C153 and C337. It could be due to exothermic recrystallization during heating and the corresponding decreasing of the matrix volume, which restrain the nonradiative relaxation pathway. Therefore, the fluorescence technique could be considered appropriate to study the crystallization processes in polymers.

For C152 and C153 in PET_{II} the fluorescence is decreasing in the whole range of temperature, and the Arrhenius type curves, $\mathrm{Ln}[(I_{F0}/I_F) - 1]$ versus $1/T$, can be represented, Fig. 8. The Arrhenius plots exhibit some pronounced slope changes at temperatures that can be correlated with the onset of α and β relaxation processes of polymer sample.

Moreover, fluorescence affords a means to examining free volume fraction changes near to the glass transition where viscosity and mechanical properties change abruptly. Some authors have established a relationship between fluorescence and mechanical properties during the progress of the curing of an acrylic polyurethane based polymer [38]. An additional advantage of fluorescence method is envisaged in order to gain further insight into the explanation of the relationship between secondary relaxations and mechanical properties.

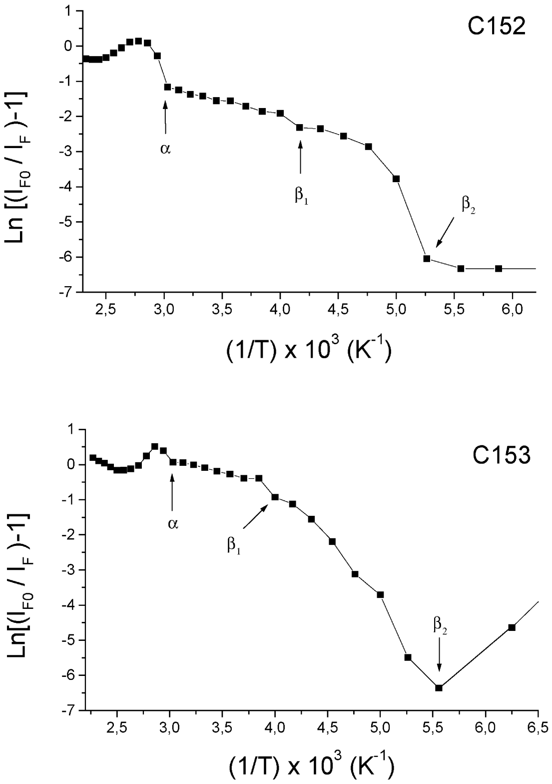

Fig. 8. Arrhenius plots of fluorescence intensity versus $1/T$ for C152 and C153 adsorbed in PET_{II}.

4. Conclusions

In this work, several ICT fluorescent probes has been used to study the α and β relaxation processes in poly(ethylene terephthalate) with different degrees of crystallinity. The fluorescent probes have been proved to be sensitive to the morphology of polymer samples, and their fluorescence properties are strongly dependent on the crystalline index. In general, the fluorescence of the probes adsorbed in PET decreases as temperature increases. Slope changes are observed in the temperature ranges −50 to −25 °C, and 50 to 75 °C, attributed to the β and α transition, respectively. All fluorescent probes exhibit higher sensitivity at α than at β relaxation. The former involves long-range segmental motion in the amorphous regions. It results in larger free volume variations than those involved in the β relaxation, and a greater decreasing rigidity of the probe surrounding.

It has been observed by DSC that PET samples after treatment with chloroform or toluene probe solutions crystallize, due to diffusion of solvent in the polymer and interruption of the intersegmental forces due to solvent polymer interaction. This phenomenon is called as solvent induced crystallisation (SINC). Also, by dynamic mechanical analyses, it has been observed that the peak corresponding to α relaxation becomes broader and its intensity decreases, as result of the higher degree of crystallinity in the samples treated with solvent. For samples treated with chloroform, it was observed a double peak of the loss moduli (E'') referred to β2 and β1 transitions, The results correlate with those obtained by means of fluorescence. The curve of fluorescence intensity of probes versus temperature exhibit two peaks around −85 and −28 °C referred to β2 and β1 transitions.

Differences on β relaxation temperature measured by DMA and fluorescence are due to the microheterogeneous distribution of probes in polymer. Thus, it could be conclude that fluorescence method is able to sense temperature-dependent morphological changes, i.e. induced by SINC, providing additional information.

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