

β - and γ -relaxations of low density polyethylene: Study by fluorescent probes

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Abstract

The temperatures of γ - and β -relaxation processes in low density polyethylene are studied by means of fluorescence spectroscopy. In this work, the fluorescent sensors employed, *p*-vinyliden derivatives of *N,N*-dialkylaminoaryl compounds, were adsorbed in polymer films, and their fluorescence analysed over the temperature range from -200 to 0 °C. In general, the fluorescence of the probes adsorbed in polyethylene decreases as temperature increases, as a consequence of the enhancement of the free volume fraction that favours the radiationless process of the lowest excited singlet state. Slope changes are observed in the temperature ranges -160 to -130 and -70 to -30 °C, attributed to the γ - and β -transitions, respectively. All fluorescent probes exhibit higher sensitivity at β - than at γ -relaxation. Since the former involves longer range segmental motion, and a greater decrease in rigidity of the probe surrounding allows the amino group rotation around the $N-C_{Ar}$ bond to happen in probes. The results correlated well with those obtained by means of dynamic mechanical analyses, which indicated the ability of these molecular rotors to sense the weak differences in chain mobility due to β - and γ -transitions of LDPE.

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1. Introduction

Although many investigations have been undertaken to characterize the thermal properties of linear and branched polyethylenes (PE), there is still no agreement respect to the structural factors and molecular motions involved in those processes. Polyethylene exhibits at least three relaxation processes below the melting temperature. In order of decreasing temperature, these are referred to as α -, β - and γ -transitions [1]. The α -relaxation is observed close to the melting point, in the temperature range of 300–350 K, and it is attributed to the motion of the chains associated with the crystalline phase [2]. It has been stated that structural factors, which reduce the level of crystallinity, decrease the intensity of this transition. The β -relaxation is usually detected in the range 230–280 K. It has been assigned by some authors, to diffusional motions of branched points in the interface between lamellae [3]. The interlamellar region increases with the degree of branching, and the β -relaxation

is clearly detected in branched polyethylenes, whereas it is not observed in some linear polyethylenes [4,5]. Other authors associate this relaxation to the glass transition, involving amorphous domains which are under strain by the crystalline phase [6]. Finally, γ -transition is observed at about 140 K, which would be originated from mobility of either chain ends or branches associated with the amorphous phase [7,8].

The secondary relaxations of polyethylenes have been characterized by means of different techniques, including mechanical and dielectric spectrometry, NMR, IR and Raman spectroscopies. In the last decade, several authors have studied secondary relaxations of homopolymers, copolymers and blends by means of luminescent probes, which were incorporated, free or covalently attached, to the polymer matrix [9–12]. The fluorescent guest is located in the amorphous and crystalline/amorphous interface regions, and its emission is sensitive to the relaxation processes related to these regions, since the emission of the molecular luminescent probe depends on both their intrinsic photophysical properties and their interactions with the surrounding polymer matrix [9,10].

The aim of this work is to study the relaxation processes of low density polyethylene, using the temperature dependence of

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the fluorescence emission of several fluorescent probes inserted in the system. Dynamic mechanical analysis (DMA) has been also used to determine the secondary relaxations of PE samples, in order to correlate the results with those obtained by the fluorescence technique. The fluorescent sensors employed, *p*-vinylidene derivatives of *N,N*-dialkylaminoaryl compounds, are fluorescent molecular rotors. These probes, upon electronic excitation, lead to the formation of an initial intramolecular charge transfer (ICT) state with partial electron transfer, generally followed by a twisting of the molecule to give a complete electron transfer in a twisted ICT state (TICT). Both excited states could be radiative or exhibit a non-radiative decay to ground state. Fluorescence quantum yields depend on the relationship between both processes (Eq. (1)):

$$\phi_F = \frac{k_F}{k_F + \sum k_{nr}} \quad (1)$$

where k_F is the rate constant for the emission process and $\sum k_{nr}$ is the sumatory of all first or pseudo first-order

non-radiative decays. Because twisting of some moieties of these molecules leads to a more relaxed states that deactivate through a non-radiative process, variations in rigidity of microenvironment will affect ϕ_F together with the maximum wavelength.

In previous work, the sensitivity of *N,N*-dialkylaminoaryl probes to changes of polarity and rigidity in their microenvironment has been demonstrated [13]. The fluorescent probes have been used to monitor the photopolymerisation reactions of mono- and di-functional acrylic and methacrylic monomers as well as the UV-curing process of adhesive systems [14]. An increase in fluorescence intensity was observed as photopolymerisation proceeded, directly related to the enhancement of the rigidity of the medium during polymerisation processes. The decrease in the non-radiative decay rate and consequently the increase in fluorescence quantum yield are observed. In this work, the ability of these molecular rotors to sense the weak differences in chain mobility due to β - and γ -transitions of LDPE is presented.

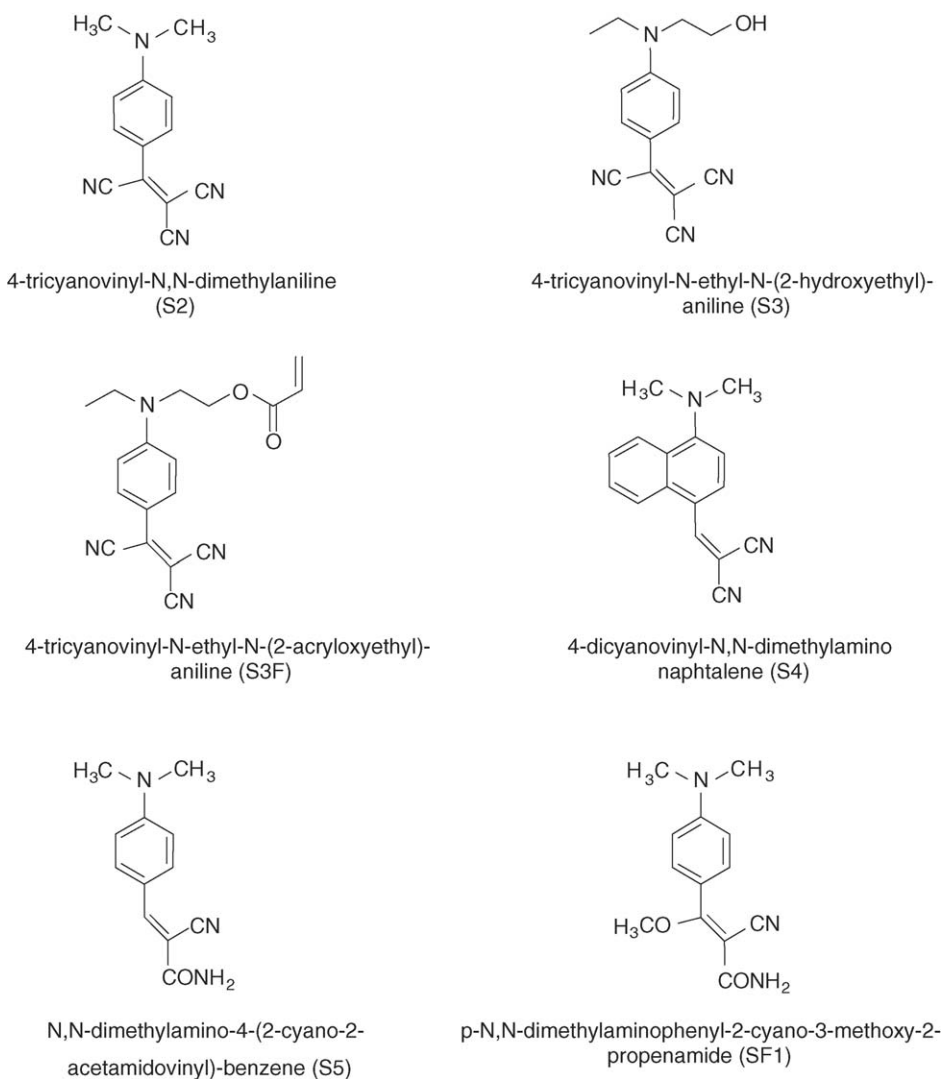


Fig. 1. Structure of fluorescent probes.

2. Experimental procedures

2.1. Materials and sample preparation

4-Tricyanovinyl-*N,N*-dimethylaniline (S2), 4-tricyanovinyl-*N*-ethyl-*N*-(2-hydroxyethyl)-aniline (S3), 4-dicyanovinyl-*N,N*-dimethylaminonaphthalene (S4), *p*-*N,N*-dimethylaminophenyl-2-cyano-3-methoxy-2-propenamide (SF1), *N,N*-dimethylamino-4-(2-cyano-2-acetamidovinyl)-benzene (S5) and 4-tricyanovinyl-*N*-ethyl-*N*-(2-acryloxyethyl)-aniline (S3F) were synthesised according to procedures already described [13,14]. The structures of probes are shown in Fig. 1.

Commercial low density polyethylene sheets were supplied by an European manufacturer. Slices of polymer sheet about 3.5 mm (width) \times 12.5 mm (length) \times 0.12 mm (thickness) were cut and immersed in an ethyl ether solution of the fluorescent probe (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 at room temperature for 1 week time period. The molar concentrations of probe in the polymer matrix were calculated from UV absorption spectra assuming that their molar absorption coefficients are the same as those previously measured in cyclohexane solutions. Under the mentioned conditions, concentrations in the range of $0.5\text{--}1.3 \times 10^{-4}$ M were measured for the adsorbed probes in the PE samples.

2.2. Spectroscopic measurements

UV spectra were recorded by means of a Perkin-Elmer LS-35 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 20°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

Differential scanning calorimetry (DSC) was undertaken using a Shimadzu DSC-50 and TA-50I thermal analyzer over the range $30\text{--}140^\circ\text{C}$. All the measurements were made at a heating rate of 5°C min^{-1} . The instrument was calibrated with an indium standard ($T_m = 429\text{ K}$, $H_m = 25.75\text{ J g}^{-1}$). In order to determine the crystalline index X_c of each polymer sample, the area of the melting endothermic peak was measured and related to a reference of $H_m = 293\text{ J g}^{-1}$ for crystalline polyethylene [15].

Dynamic mechanical measurements were performed on a TA Dynamic Mechanical Analyser (DMA) working on the flexural-

bending mode at a frequency of 0.1 Hz. The experiments were carried out in the temperature range from -150 to 50°C using a heating rate of 5°C min^{-1} . The samples were prepared as films with dimensions of $10\text{ mm} \times 5\text{ mm} \times 0.5\text{ mm}$.

3. Results and discussion

3.1. Characterization of polyethylene samples

The original low density polyethylene was characterized by DSC, to determine the degree of crystallinity and melting point in the polymer film. The polyethylene exhibited a crystalline degree of $X_c = 14\%$ and a melting point of 110°C . Also, measurements of films treated with ethyl ether solution of the fluorescent probes (PE_{S2}, PE_{S3}, PE_{S3F}, PE_{S4}, PE_{S5} and PE_{SF1}), were undertaken to check any effect of the solvent or probe on the thermal properties and crystallinity degree of polyethylene. The same thermal behaviour was found for all samples to that obtained for the original polyethylene film. This indicates that polymer properties were not influenced by neither the solvent treatment nor the presence of probes, at least at the times and concentrations used in these experiments.

Dynamic mechanical analysis of all the polyethylene samples was undertaken. The curves of loss moduli (E'') dependence on temperature of untreated PE (PE₀), treated with solvent (PE_{ether}) and treated with a solution of the fluorescent probe S4 in ether (PE_{etherS4}) are showed in Fig. 2. Similar plots were found for the rest of PE-probe samples.

The original untreated sample, PE₀, showed two relaxations referred to as β and γ , respectively, in order of decreasing temperature. β -Relaxation was observed around -20°C and γ -relaxation was detected at -120°C . After treatment in ethyl ether or probe solution, slight changes on the dynamic mechanical properties were detected. The temperature peak corresponding to the transitions remained nearly constant, whereas the intensity of the peaks increased as a consequence of solvent occlusion.

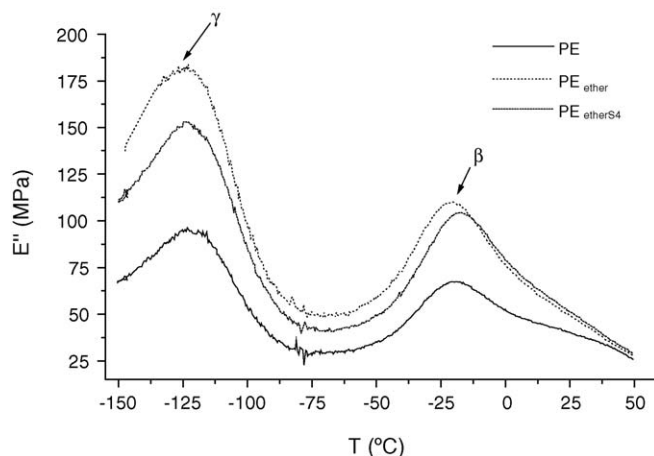


Fig. 2. Temperature dependence of the loss moduli (E'') for the γ - and β -relaxations of PE samples.

3.2. Relaxation processes by fluorescence analysis

In this work, the twisted intramolecular charge transfer fluorescent probes (TICT), 4-tricyanovinyl-*N,N*-dimethylaniline (S2), 4-tricyanovinyl-*N*-ethyl-*N*-(2-hydroxyethyl)-aniline (S3), 4-dicyanovinyl-*N,N*-dimethylaminonaphthalene (S4), *p*-*N,N*-dimethylaminophenyl-2-cyano-3-methoxy-2-propenamide (SF1), *N,N*-dimethylamino-4-(2-cyano-2-acetamidovinyl)-benzene (S5) and 4-tricyanovinyl-*N*-ethyl-*N*-(2-acryloxyethyl)-aniline (S3F) were selected to study the relaxation processes in low density polyethylene films. These probes contain both an electron donor (D) and acceptor (A) groups which, 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 state (TICT), in which the π -system of donor is perpendicular to the π -system acceptor. In general, the sensitivity of the probe to the rigidity of the polymer matrix is expected to be highly dependent on Van der Waals volume of the rotating molecular fragments [16].

Firstly, the absorption and fluorescence properties of the probes in cyclohexane solution and adsorbed in poly(ethylene) films were measured. Cyclohexane was selected as control solvent since it provides similar polarity and structural parameter than PE. The data are summarised in Table 1.

In general, both the shape and the absorption wavelength maxima showed no strong differences when measured in solution and in polymer media, however, their fluorescence properties were strongly dependent on the rigidity of the medium. A bathochromic shift of the wavelength emission maxima was observed from cyclohexane solution to poly(ethylene) film (Table 1). In previous work, this has been 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 than in fluid media and it is observed at longer fluorescence maximum wavelength.

In addition, S2 and S3 probes, which do not show measurable fluorescence in fluid cyclohexane, displayed good emission spectra in PE films. The results obtained would indicate that the fluorescence emission from those extrinsic probes could be useful to study polymer relaxations.

In polymer systems, it is assumed that at very low temperatures the translational and rotational motions are totally frozen

and thus, the radiative deactivation of the fluorescent probe from its singlet excited state is the favoured pathway. Polymer relaxations involve a variety of motions of shorter and longer macromolecular segments, and an enhancement of the free volume fraction of the medium takes place. As a consequence, an increase in the non-radiative decay rate of the singlet excited state of the probe, due to the internal rotation of certain molecular fragments of probes should occur, and therefore, a decrease in fluorescence quantum yield should be observed. The polymer relaxation temperature may be defined by the change of the slope in linear or Arrhenius plot of the fluorescence intensity (I_F) versus temperature.

Fluorescence spectra of the probe-doped low density poly(ethylene) films were recorded at a temperature range from -200 to 0°C , and the intensity of fluorescence (I_F) was measured at the maximum of the emission band. The excitation wavelength was selected at the maximum absorption band of each probe. In Fig. 3, the fluorescence spectra for S2, S4 and SF1 at several temperatures are showed as an example. The fluorescence of the probes adsorbed in PE decreases as temperature increases, and except to SF1, no shift neither shape change on the maximum emission wavelength is observed (Fig. 3), so the response of the probes towards changes in the rigidity could be directly quantified measuring the intensity of the fluorescent band at the maximum wavelength. The particular behaviour of SF1 will be discussed later.

The type curves, fluorescence intensity and first derivative of I_F versus temperature, for all probes, except SF1 are showed in Fig. 4. The plots exhibit some pronounced peaks at temperatures that can be correlated with the onset of γ - and β -relaxation processes of the polymer samples. In general, a very weak slope change of fluorescence intensity was observed in the temperature range -130 to -160°C , which is the interval where the γ -transition takes place. A more pronounced slope change was observed in the temperature range -30 to -70°C , assigned to the β -transition. It was found that the relaxations of polyethylene determined by using fluorescent probes correlate well, with those obtained by means of dynamic mechanical analyses. The data of γ - and β -transitions determined by means of fluorescence are compiled in Table 2.

The sensitivity of the probes, S , could be described as: $S = \Delta I_F = I_F - I_{F0}$, and gives information about the suitability of a probe for sensing a particular process. In this case, I_{F0} and I_F have been taken as the initial and final values of the maximum of fluorescence intensity in the temperature range of the transition.

Table 1

Spectroscopic properties of fluorescent probes in cyclohexane solution and adsorbed in poly(ethylene) films at room temperature

Probe	Cyclohexane		Poly(ethylene)	
	Absorbance λ_{max} (nm)	Fluorescence λ_{max} (nm)	Absorbance λ_{max} (nm)	Fluorescence λ_{max} (nm)
S2	482	–	490	507, 545(s)
S3	488	–	519	601
S4	428	512	436	488, 520
S5	386	440	390	459
SF1	–	390, 460(s)	325	419, 465
S3F	483	520	498	505

Table 2

Transition temperatures observed for fluorescent probes adsorbed in polyethylene films

Probe	T_γ ($^\circ\text{C}$)	T_β ($^\circ\text{C}$)	V (\AA^3)
S2	-160	-54	213
S3	–	-48	234
S4	-165	–	240
S5	-140	-58	207
S3F	-150	-65	302
SF1	-160	-50	231

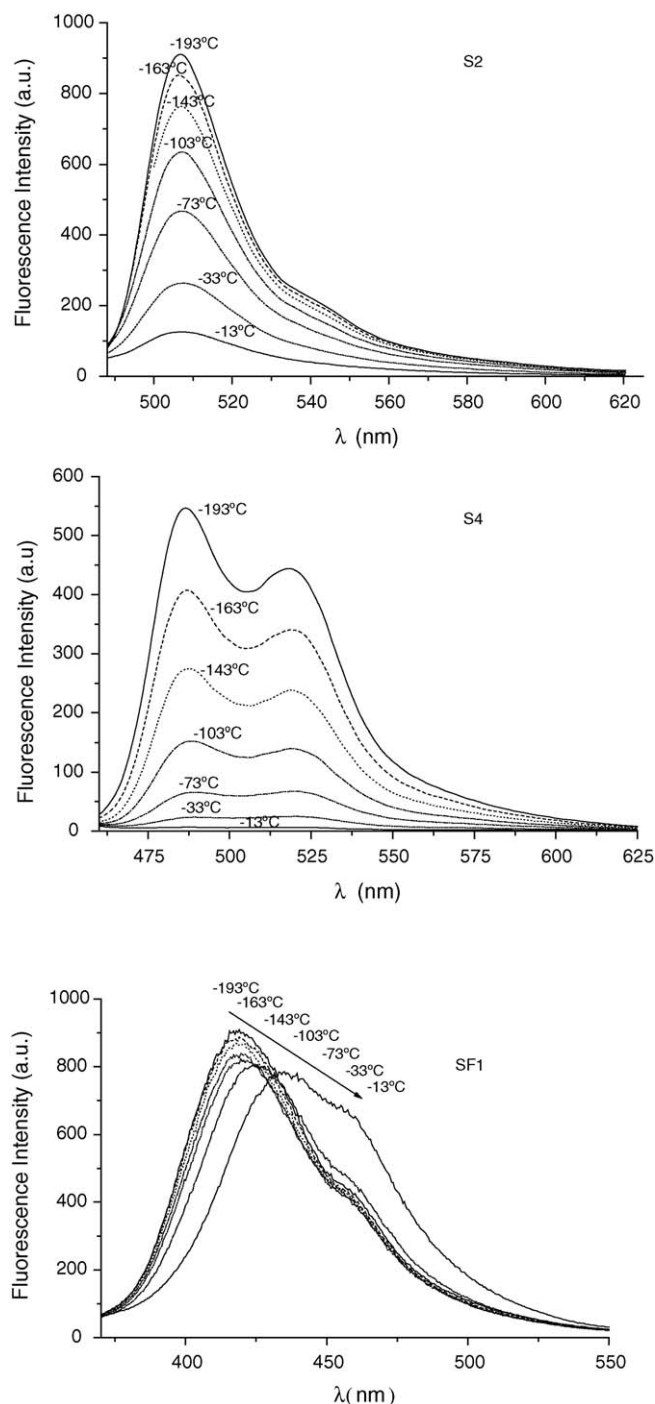


Fig. 3. Fluorescence spectra of S2, S4 and SF1 adsorbed in polyethylene film at several temperatures.

The sensitivity of the probes to changes in their microenvironment at γ (S_γ)- and β (S_β)-relaxations are compiled in Table 3, also the calculated molecular volumes are included.

All fluorescent probes, except S4, exhibited higher sensitivity at β - than at γ -relaxation. This can be explained in terms of the enhancement of the free volume of the medium with temperature. β -Transition involves motions of longer segments (as expected for the glass transition) than γ -relaxation, and a greater decreasing rigidity of the probe microenvironment

Table 3

Sensitivity of the probes S2, S3, S4, S5 and S3F to γ - and β -relaxations, and calculated molecular volumes

Probe	V (\AA^3) ^a	S_γ	S_β
S2	213.4	89	151
S3	252.7	9	95
S4	243.2	117	49
S5	207.0	145	208
S3F	302.3	33	185

^a Molecular volumes calculated by AM1 semi-empirical method.

allows the rotation of the amino group around the aromatic ring in probes. This group movement leads to an increase of the non-radiative decay rate of singlet state probe (k_{nr}) and consequently a decrease in fluorescence quantum yield. In previous work, these probes have been used as fluorescent sensors to monitor photopolymerisation reaction of some mono- and di-functional acrylate monomers and photocurable acrylic adhesives. It was seen that the fluorescence intensity for these probes was proportional to the polymerisation degree and the rates of polymerisation were obtained for each probe/monomer system [14]. Similar trend was observed for plots of first derivative (I_F) versus temperature, and higher sensitivity was observed around β -transition temperatures.

The first feature from these data is the observation that the rigidity dependence of probe behaviour, at very low temperatures, is highly influenced by their structure. S4 together with S5 exhibited the highest sensitivity to rigidity changes at γ -transition. In previous work, the excellent behaviour of S5 as fluorescent sensor to rigidity changes has been detected monitoring the curing reaction of photocurable systems, and it has been associated to the presence of $-\text{CO}-\text{NH}-$ group in the structure of the probe [17].

The tricyanovinyl derivatives S2, S3 and S3F are less sensitive towards rigidity on their microenvironment, and lower decrease of fluorescence intensity was observed. Apparently, the rotation around $\text{N}-\text{C}_{\text{Ar}}$ bond is not sterically dependent on the different substitution and similar sensitivity values were obtained for these probes. Several effects should be reflected on the probe behaviour in polymer system. Size and shape are playing an important role in probe reorientation dynamics. It has been seen that these factors affect the translational diffusion coefficient, as long as the probe is sufficiently bulky to exhibit coupling of its dynamics to the polymer relaxation [18]. The time correlation between macromolecular motion and photophysical process should be considered. The best fluorescence response is related to a slowest structural relaxation compared to the fluorescence rate decay. In previous work, fluorescent probes have been proved to be able to sense temperature-dependent morphological changes, i.e. induced by SINC. Since their fluorescence properties are strongly influenced by the crystalline index of the polymeric matrix where they were adsorbed [10].

For SF1 probe, a strong dependence in the emission band with the temperature was observed. The intensity of fluorescence of SF1 adsorbed in polyethylene film, exhibited a similar trend to the others probe, and the emission decreased as the temperature increased. However, SF1 experimented variations in the

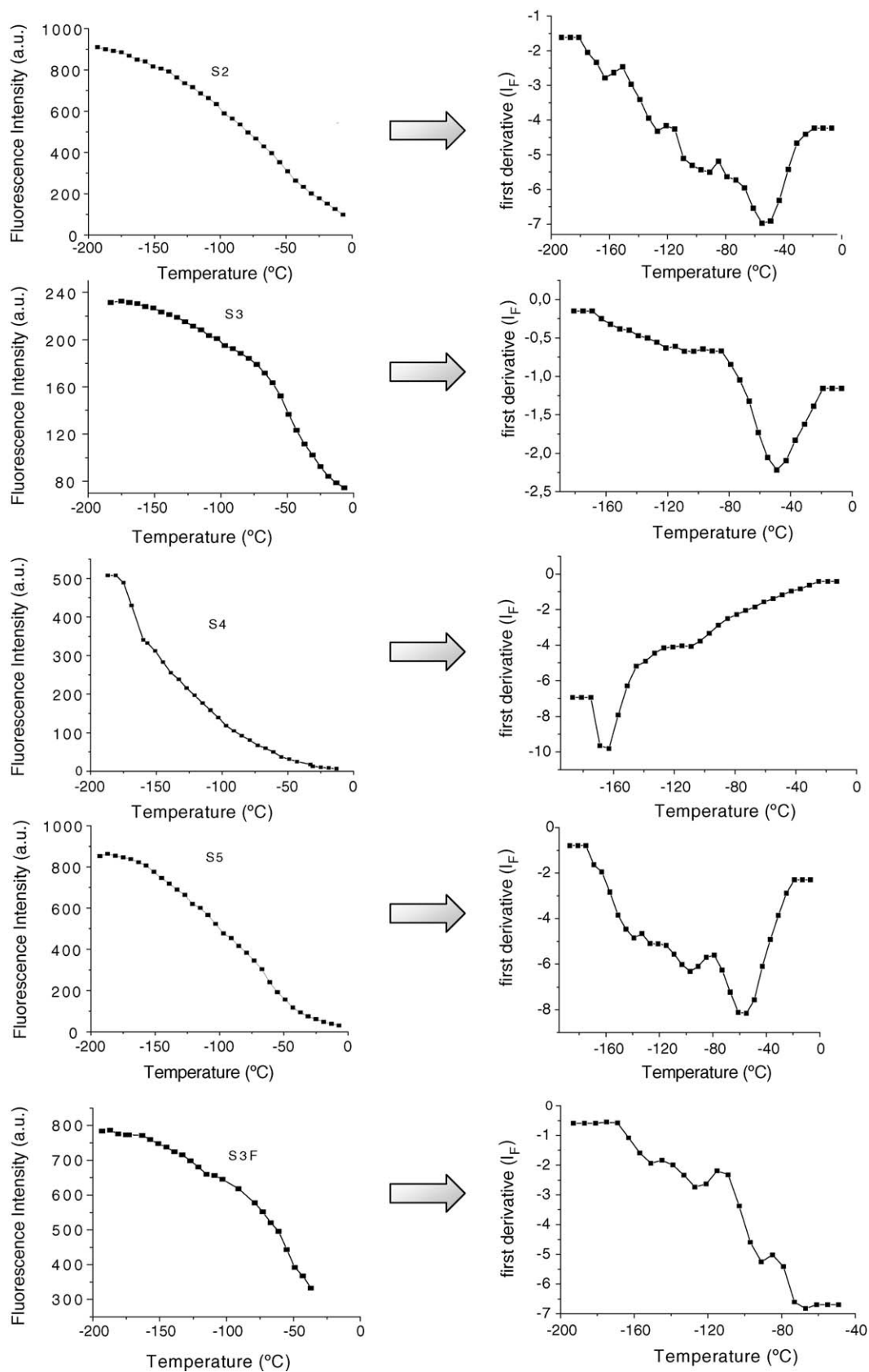


Fig. 4. Variation of fluorescence intensity and first derivative of I_F with temperature of probes S2, S3, S4, S5 and S3F adsorbed in polyethylene film.

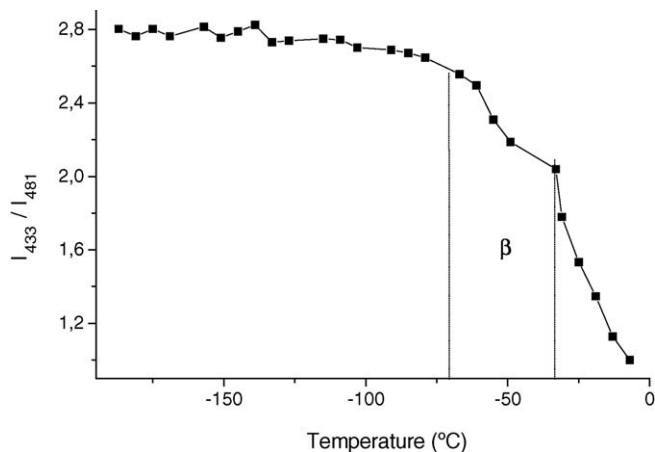


Fig. 5. Plot of fluorescence intensity ratio of probe SF1 adsorbed in polyethylene film vs. temperature.

position of the band, and bathochromic shift of the fluorescence peak was observed as the temperature increased. For this type of ICT probes, the method based on the fluorescence intensity ratio ($I_{\lambda_1}/I_{\lambda_2}$) at two fixed wavelengths [19], was used to study fluorescence changes. Where λ_1 is wavelength at the half-height on the shorter wavelength side on the band and λ_2 is wavelength close to the emission maximum to avoid the influence of photo-products. The fluorescence intensity ratio (I_1/I_2) for SF1 versus temperature is shown in Fig. 5. It was observed a reduced fluorescent guest sensitivity at low temperatures and γ -relaxation was not detected. However, this probe structure exhibited the highest sensitivity to the β -relaxation processes.

Similar trend was observed by using the maximum emission wavelength of SF1 with temperature (Fig. 6). At low temperature, the emission maxima of the probe remains constant at 419 nm. As temperature increases, the emission maximum shifted to longer wavelengths and a slope change can be observed around the β -relaxation temperature. It could be expected due to the increase of the free volume fraction near to the glass transition, where larger molecular motions are involved. The results would confirm that the wavelength shift of the fluorescence sensor can be useful to examining processes where viscosity and mechanical properties change abruptly, as relaxation processes,

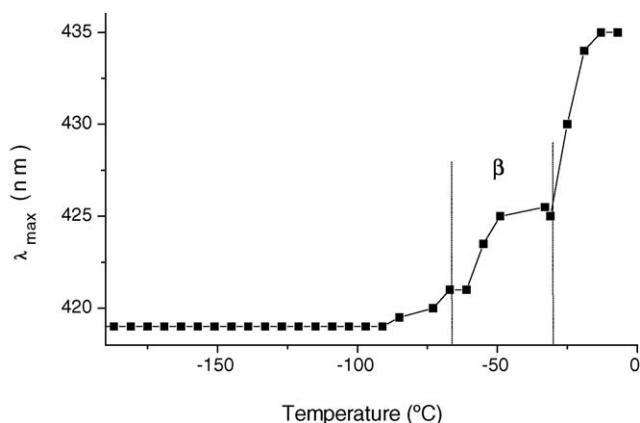


Fig. 6. Variation of maximum wavelength with temperature for probe SF1 adsorbed in polyethylene film.

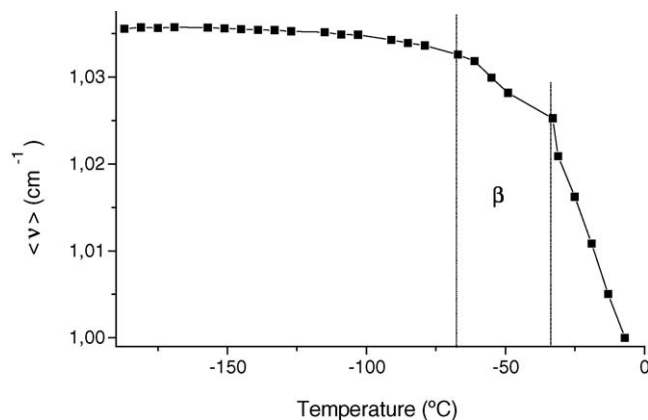


Fig. 7. First moment of fluorescence vs. temperature for probe SF1 adsorbed in polyethylene film.

or polymerisation reactions, as it was described in previous work [20].

The variation of the first moment of the fluorescence has been proposed by other authors [21] to monitor both free radical and step-growth polymerisation, since the value of the fluorescence intensity at the maximum depends on experimental factors such as incident intensity, probe concentration, etc. The first moment of the fluorescence, $\langle \nu \rangle$, is defined as the weighted average wave number in the following equation:

$$\langle \nu \rangle = \frac{\sum I_F(\nu)\nu}{\sum I_F(\nu)}$$

In this work, the first moment of the fluorescence band has been determined at different temperature, and the results are showed in Fig. 7. The plot followed the same behaviour as described previously when using the fluorescence intensity ratio and maximum wavelength. The $\langle \nu \rangle$ value remained nearly constant at low temperatures, and an abrupt slope change can be appreciated around -70°C . These results would indicate that the first moment of fluorescence is also a good parameter to study relaxation processes in polymers.

4. Conclusions

The γ - and β -relaxation processes in low density polyethylene have been studied by using *p*-vinyliden derivatives of *N,N*-dialkylaminoaryl compounds, as fluorescent molecular rotors. These probes have been proved to be sensitive to the changes of free volume fraction in polymer samples and their fluorescence properties are strongly dependent on the rigidity of their microenvironment. In general, the fluorescence of the probes adsorbed in polyethylene, decreases as temperature increases. Slope changes are observed in the temperature ranges -160 to -130 and -70 to -30°C , attributed to the γ - and β -transitions, respectively. The results correlated well with those obtained by means of dynamic mechanical analyses. The curves of temperature dependence of the loss moduli (E'') exhibited two relaxations in the temperature ranges corresponding to the mentioned γ - and β -transitions.

In general, fluorescent probes exhibit higher sensitivity at β - than at γ -relaxation. The former involves longer range segmental motion, and a greater decreasing rigidity of the probe surrounding allows the amino group rotation around the N–C_{Ar} bonds to happen in probes. It has been observed that the probe behaviour is highly influenced by their structure. Both SF1 and S5 containing –CO–NH– group in their structure exhibited an excellent behaviour as fluorescent sensor towards relaxation processes, as it has been previously detected on the curing reaction of photocurable systems. Apparently, non-radiative decay of the probes is not only dependent on the molecular volume of the probes. It would indicate that factors such as the time correlation between macromolecular motion and photophysical process should be considered on the probe behaviour in polymer system.

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References

- [1] D.E. Kline, S.A. Sauer, A.E. Woodward, *J. Polym. Sci.* 22 (1956) 445.
- [2] Y. Ohta, H. Yasuda, *J. Polym. Sci. Part B: Polym. Phys.* 32 (1994) 2241.
- [3] M. Glotin, R. Domszy, L. Mandelkern, *J. Polym. Sci. B: Polym. Phys. Ed.* 21 (1983) 285.
- [4] E. Suljovrujic, *Polymer* 43 (2002) 5969.
- [5] R. Popli, M. Glotin, L. Mandelkern, *J. Polym. Sci. B: Polym. Phys. Ed.* 22 (1984) 407.
- [6] R.F. Boyer, *J. Polym. Sci. Polym. Symp.* 50 (1975) 189.
- [7] P. Audren, D. Ronarch, *J. Appl. Phys.* 60 (1986) 946.
- [8] C. Stehling, L. Mandelkern, *Macromolecules* 3 (1970) 242.
- [9] M. Christoff, T.D. Atvars, *Macromolecules* 32 (1999) 6093–6101.
- [10] M.R. Vigil, J. Bravo, T.D. Atvars, *J. Baselga, Macromolecules* 30 (1997) 4871–4876.
- [11] T. Corrales, C. Peinado, P. Bosch, F. Catalina, *Polymer* 45 (2004) 1545.
- [12] S.M. Martins-Franchetti, T.D.Z. Atvars, *J. Appl. Polym. Sci.* 50 (1993) 1591.
- [13] P. Bosch, A. Fernández-Arizpe, J.L. Mateo, A.E. Lozano, P. Noheda, *J. Photochem. Photobiol. A: Chem.* 133 (2000) 51.
- [14] P. Bosch, A. Fernández-Arizpe, J.L. Mateo, F. Catalina, C. Peinado, *J. Photochem. Photobiol. A: Chem.* 153 (2002) 135.
- [15] J.W. Teh, H.P. Blom, A. Rudin, *Polymer* 35 (8) (1994) 1680.
- [16] M.A. Winnik (Ed.), *Photophysical and Photochemical Tools in Polymer Science: Conformation, Dynamics and Morphology*, NATO ASI Series, 1985.
- [17] P. Bosch, A. Fernández-Arizpe, J.L. Mateo, *Macromol. Chem. Phys.* 202 (2001) 9.
- [18] D.B. May, D.D. Deppe, K.E. Hamilton, A. Dhinokwala, J.M. Torkelson, *J. Non-Cryst. Solids* 235 (1998) 48.
- [19] R. Popielarz, S. Hu, D.C. Neckers, *J. Photochem. Photobiol. A: Chem.* 110 (1997) 79.
- [20] P. Bosch, A. Fernández-Arizpe, F. Catalina, J.L. Mateo, C. Peinado, *Macromol. Chem. Phys.* 203 (2002) 334.
- [21] F. Mikes, J. González-Benito, J. Baselga, *J. Polym. Sci. Phys. B40* (2001) 405.