Photoluminescence Study of β Relaxation of Polyethylene Blends

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SYNOPSIS

Secondary β relaxation of polyethylene blends (50/50 HDPE/LDPE) were studied by photoluminescence of anthracene molecules dissolved in the polymer bulk. The temperature of the β relaxation has been determined as $T_\beta = -40°C$ by the dependence of the ratio of vibronic components of the fluorescence band on the temperature. The molecular mechanism of this relaxation has been discussed considering the possibility of the energy migration involving anthracene molecules in the singlet electronic excited and ground states. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The studies of high density polyethylene/low density polyethylene (HDPE/LDPE) blends are relevant from both the fundamental and technological point of view because the applications of these materials are strongly dependent on their morphology. The morphology is dependent on the chemical structure of the polyethylene, on the crystallization processes, and in the case of blends, on the composition and types of the polymers. In general this research field is related to the studies of morphology that try to establish the conditions of preparation of the blends involving co-crystallization or segregation between the phases.

Rault et al.[1,2] studied 50/50 HDPE/LDPE blends by small-angle X-ray scattering (SAXS) and described the scattering in terms of a paracrystalline model having a bimodal distribution of the crystalline phases. They concluded that the phase segregation, the morphology, and the crystalline index of each phase are controlled by the weight-average dimension of the coils in the melted state before the crystallization and that the entangled amorphous chains take an important role on the interlamellae crystallization. The entanglements in the melted phase are also important in the case of crystallization of branched and polydisperse polyethylene.

Other studies of crystallization of 50/50 HDPE/LDPE blends by SAXS suggested that the HDPE component in the blend dominates the process during the early stage and the kinetic process is hardly affected by the LDPE component. The LDPE would separate out to form an amorphous gap between the lamella stacking formed mainly by the HDPE component. These components are crystallized separately on an interlamellar scale and no co-crystallization was obtained. Segregation of the homopolymers is obtained in the case of 50/50 blend upon slow cooling, isothermal crystallization at two successive temperatures (110 and 100°C), and in rapidly cooled (110°C/min) preparation forms.[3,4]

From quite general phase diagrams Keller et al.[5,6] established some polymer properties of the polyethylene that could produce greater phase separation: higher branch content in polyethylene chains, higher molecular weight of linear polyethylene, and broader molecular mass grades of branched or linear polyethylenes.

Although there are many studies about the morphology of the polyethylene blends, there are only a few works about relaxation processes in these blends. Even for polyethylene the assignments for the α, β, and γ relaxations and the glass-transition temperature are controversial.[7-19]

In this work we present the studies for the determination of the temperature of the β relaxation

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for a 50/50 HDPE/LDPE blend in two different cooling rates (3 and 15°C/min) using fluorescence spectroscopy of anthracene dissolved in the bulk. The samples in this composition should be incompatible in the solid state because both polymers have a high molecular weight and they are polydisperse. These conditions were chosen in order to compare the β relaxation temperature with those obtained for the homopolymers.

EXPERIMENTAL

Anthracene (AN) (Carlo Erba) was used as received.

Commercial low density polyethylene (LDPE), $\bar{M}_w$ = 510,000 g/mol, polydispersity $\bar{M}_w/\bar{M}_n$ = 10.4; and high density polyethylene (HDPE), $\bar{M}_w$ = 740,000 g/mol, polydispersity $\bar{M}_w/\bar{M}_n$ = 12.2 were provided by Polialdem without additives. The molecular weights and polydispersities were determined by GPC using a Viskotek model 100 chromatograph. 1,2,4-Trichlorobenzene was used as diluent at temperature of T = 135°C.

The fluorescent molecules were incorporated in the polymers by swelling the polymer mass with a well-defined volume of $10^{-3}M$ anthracene solution in dichloroethane. After this process the solvent was evaporated at room temperature. The volume of the anthracene solution is defined in order to restrict the maximum concentration of anthracene incorporated in the polymer or polymer blends of about $10^{-5}M$ to prevent aggregation of these molecules.

A polymer mixture of a 50/50 HDPE/LDPE (60 mg) containing anthracene is transferred to a 5-mm quartz tube (3 mm internal diameter), submitted to vacuum for several hours, and finally the tube was sealed. The sample in this sealed tube is heated until the melting of the polymer mass and maintained under this condition for about 30 min. After this time the sample was cooled at different rates: 3 or 15°C/min to room temperature.

Thermograms of the samples were obtained using a DuPont differential scanning calorimeter model 1090 over the range −150 to 150°C, with a heating rate of 10°C/min. The instrument was calibrated with an indium standard (T_m = 429.6 K and H_m = 25.75 J/g). The area of the melting endothermic peaks have been used to calculate the crystalline index X_c (DSC) for the samples crystallized by different cooling rates. In this case the reference data of ΔH_m = 288.7 J/g was considered for the crystalline polyethylene.[20]

X-ray diffraction scatterings were recorded from a Shimadzu diffractometer model XD-3A, operating with CuKα radiation over the range $5° < 2\Theta < 50°$, current 20 mA and 30 kV. Total crystalline indexes were calculated from the area under the reflections (110) (2θ = 21.7°) and (200) (2θ = 24.2°) and amorphous band.[21] These areas are obtained by deconvolution of the X-ray diffraction pattern.

Fluorescence spectra of each sample were recorded in different temperatures with a spectrofluorimeter as described elsewhere.[22]

RESULTS AND DISCUSSION

Characterization of Samples

The X-ray scattering patterns of the samples are composed of two crystalline peaks assigned to the reflections of indexes (110) and (200) and one band at 2θ = 20.5° assigned to the amorphous phase [Fig. 1(a–f)]. From these diffractograms it is evident that the relative intensity of the crystalline peaks and the amorphous band are different for each sample, although the positions of the peaks are the same. Therefore we could conclude that: the crystalline phase of the different types of PE has the same crystalline structure (orthorhombic); the anthracene molecules will not incorporate inside the crystals; and the crystallinity of each sample is different. The total crystalline index, X_c, calculated by the relationship between the area under the crystalline peaks and the total scattering area of the diffractogram are shown in Table I.[21] From these results we could conclude that the samples submitted to slow cooling exhibit: the highest crystalline index; the crystalline index for HDPE is higher than for LDPE; and the total crystalline index for the 50/50 HDPE/LDPE blend presents an intermediate value between those for the HDPE and LDPE.

DSC traces of these samples are shown in Figure 2. The homopolymers (HDPE and LDPE) submitted to different cooling rates give single endothermic peaks. However these peaks exhibit different characteristics:

1. both melting temperature and enthalpy of HDPE are higher than LDPE;
2. the width of the melting peak of HDPE is shapper than LDPE, although both samples present a high polydispersity;
3. the position of the peaks varies only slightly, but the melting enthalpies vary with the cooling rate.

From the data of melting enthalpies we have calculated the crystalline indexes. These values are

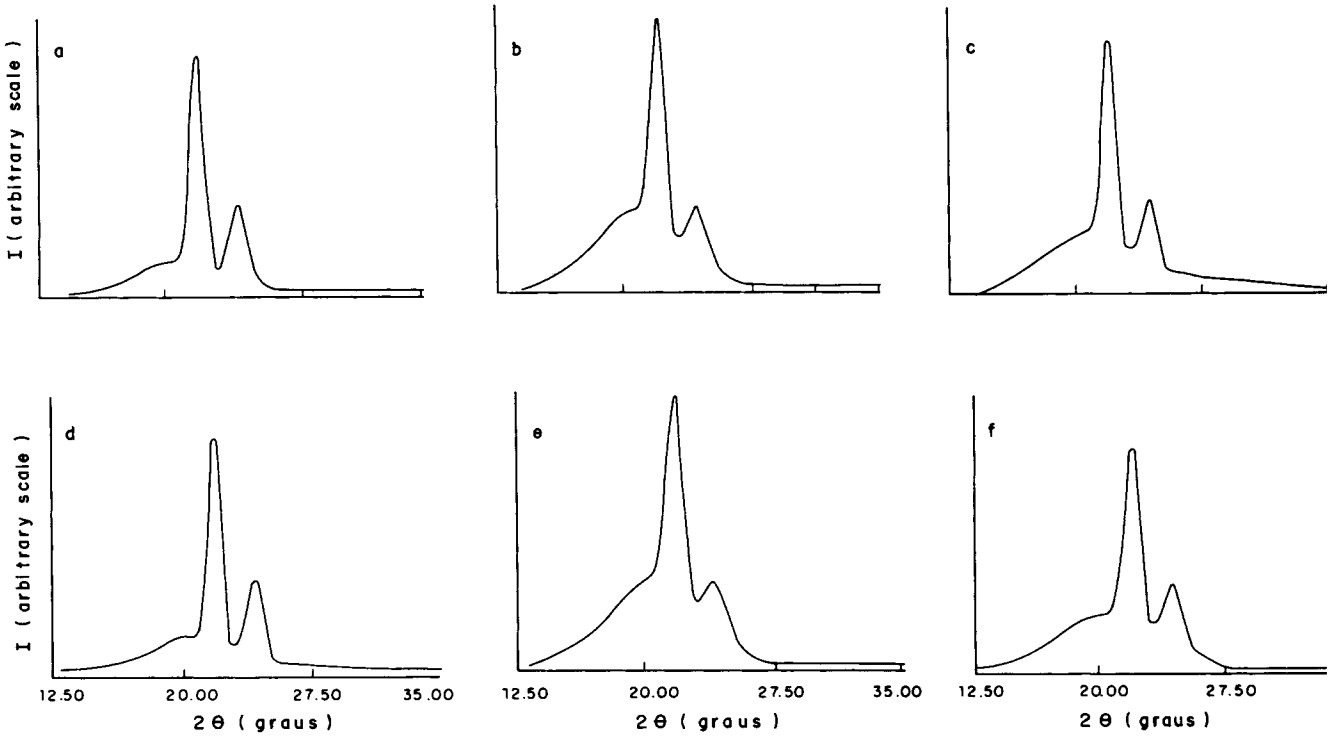

Figure 1 X-ray patterns for samples prepared using cooling rate of: 3°C/min (a) HDPE, (b) LDPE, and (c) 50/50 HDPE/LDPE; and 15°C/min (d) HDPE, (e) LDPE, and (f) 50/50 HDPE/LDPE.

comparable to those obtained from the X-ray scattering (Table I).

We obtained the DSC traces for 50/50 HDPE/LDPE blend prepared by different cooling rates. In this case we observe two peaks. The first one, at the lower temperature (104°C) may be assigned to the LDPE and it appears at lower temperature than the correspondent homopolymer (melting temperature T_m = 108°C) for the same cooling rate. The second peak, at the higher temperature (134°C) may be assigned to the HDPE and the temperature is lower than the correspondent homopolymer (melting temperature T_m = 139°C). The relative intensity of these peaks is proportional to the melting enthalpy and does not correspond to a 50/50 mass proportion, that is, the heat flow involved in each peak is lower than for each homopolymer prepared at the same cooling rate. From the enthalpy involved with each

Table I Crystalline Indexes for Two Cooling Rates

Samples	Cooling Rate (°C/min)	ΔH (J/g)	X_c (X-ray)	X_c (DSC)	T_m (°C)
HDPE	3	219.0	0.80	0.76	139.1
	15	209.3	0.69	0.72	138.4
LDPE	3	120.5	0.56	0.42	108.5
	15	113.1	0.41	0.39	107.3
50/50 HDPE/LDPE	3	19.5	0.59[a]	0.13	104.4
		88.6		0.62	133.9
	15	12.1	0.58[a]	0.08	104.9
		74.6		0.52	134.9

X_c (X-ray), values obtained from X-ray diffraction pattens; X_c (DSC), values obtained from DSC traces using ΔH_m = 288 J/g for crystalline polyethylene (indium as a standard T_m = 156.39°C and ΔH_f = 25.75 J/g).

[a] Total crystalline index.

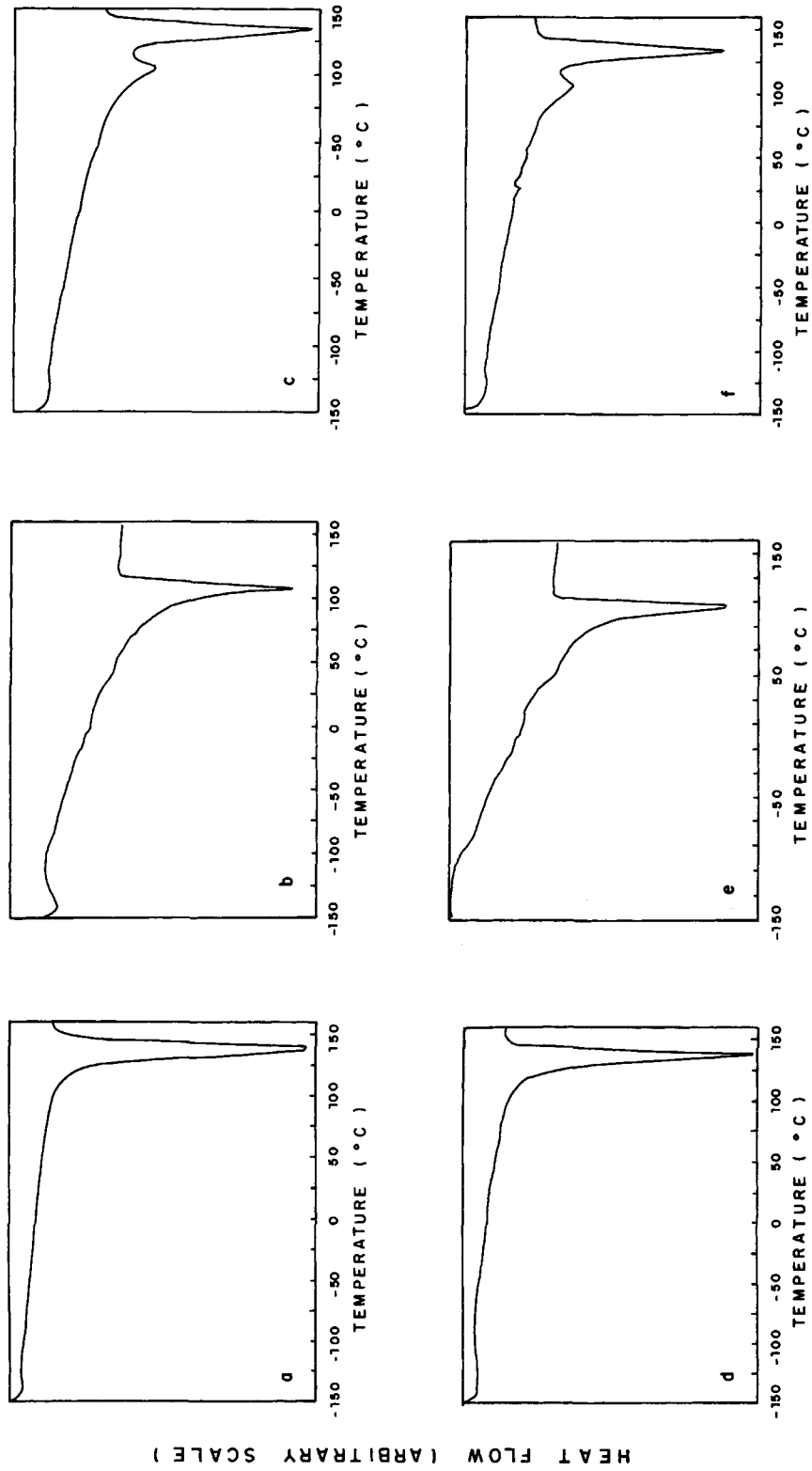

Figure 2 DSC traces obtained from heating the quenched samples at 10°C/min for cooling rates of 3°C/min (a) HDPE (6.340 mg), (b) LDPE (6.780 mg), and (c) 50/50 HDPE/LDPE (8.720 mg); and 15°C/min (d) HDPE (6.340 mg), (e) LDPE (6.780 mg), and (f) 50/50 HDPE/LDPE (9.170 mg).

melting process we have calculated the crystalline index for HDPE and LDPE in the blends. These results indicated that the crystalline index of each homopolymer in the blend is lower than in the isolated form of the homopolymer and that the crystallinity of the phase containing LDPE is very low (Table I). It is noteworthy that although the crystalline index determined by X-ray diffraction does not consider the different components of the phases, the crystalline indexes determined by DSC for each blend separately consider peaks of both crystalline phases.

As pointed out by Keller et al.[5,6] a double or multipeaked endotherm might be expected to appear on subsequent heating in DSC if segregation occurred. The resulting phase-segregated system can be regarded as a composite consisting of dominant lamellae of the HDPE component and the matrix of the branched material.[4] Therefore the results obtained in this work for 50/50 blends suggests that they exhibit phase segregation of HDPE and LDPE crystalline domains. Song et al.[4] indicated that the crystallization of a 50/50 HDPE/LDPE blend is a two-step process. The first one, at higher temperatures, involves the crystallization of HDPE. After this the LDPE will crystallize into lamellae between the already formed HDPE lamellae. Moreover, the crystallization of polymers are strongly dependent on the entanglements in the melt as pointed out by Rault et al.[2,23] In this case there are two important parameters controlling the crystallization process: the distance between entanglements and the dimensions of the coils in the melt state. The kinetics of crystallization is controlled by the relationship between the mean growth time, t_G, and the time of propagation of the tension along the chain, t_t. If t_t is greater than the mean growth time t_G, the crystallization is limited by the distortion of the amorphous phase. Using the model proposed by Rault et al.[2,23] we are suggesting that the crystallization of the LDPE in the 50/50 HDPE/LDPE blends studied in our work is strongly inhibited by the previous crystallization of the HDPE. This crystallization limits the distortion of the amorphous phase leaving the LDPE component to maintain the entanglements. Consequently it does not acquire the appropriated conformation to crystallize.[7]

From these results we could consider that the 50/50 HDPE/LDPE is composed of at least three well-defined phases: two crystalline phases (HDPE and LDPE) and one amorphous phase formed by the macromolecules of LDPE and HDPE. The crystalline phase is preferentially formed by HDPE and the amorphous phase contains the greatest proportion of LDPE.

Aromatic condensed hydrocarbon molecules (like anthracene) dissolved in semicrystalline polymers may be preferentially located in two different sites: the amorphous phase and on the surfaces of the crystallites.[24-27] These propositions are based on the Peterlin general model for the morphology of polyethylene.[28] Using the results for the morphology of the blends prepared in our work and the most probable distribution of the anthracene molecules in semicrystalline polymers, we could suggest that the fluorescent probe (anthracene) may be localized in three different types of sites: amorphous phase, interface regions of HDPE and LDPE.

β Relaxation Process

In order to study the β relaxation processes in PE blends we measured the dependence of fluorescence intensity of anthracene on the temperature as reported elsewhere.[22,29,30] In these cases the fluorescence intensity is plotted as a ratio of the intensities of the vibronic bands at $\bar{\nu}_I$ = 25,900 cm^{-1} (I_I) and $\bar{\nu}_{II}$ = 24,870 cm^{-1} (I_{II}). If the energy transfer process involving migration energy from the excited singlet electronic state occurred, this ratio would be modified.[31] As is well known, the efficiency of the migration energy is strongly dependent on the distance between the acceptor and donor molecules.[29-32] If the distance of separation is about the Foster radium (3–5 Å) the singlet energy migration process is very effective and there is a relative decrease of the intensity of the $\bar{\nu}_I$ band compared with $\bar{\nu}_{II}$. In Figure 3 the fluorescence spectra of anthracene dissolved in 50/50 w/w HDPE/LDPE blends at different temperatures are shown. The relative intensity of the vibronic band at 25,900 cm^{-1} (384 nm) is higher than that at 24,870 cm^{-1} (400 nm) and there is a broadening of the former as the temperature increases. These results are consistent with the singlet energy migration process and with the increase of the mobility of the polymer segments for temperatures higher than for the relaxation process.

The relative intensity I_I/I_{II} for the LDPE, HDPE, and 50/50 w/w HDPE/LDPE blends prepared by the two different cooling rates (15 and 3°C/min) are shown in Figure 4. These curves are composed of two segments of different slopes, with an inflection at −40°C. The first segment (from −170 to −40°C) of the curves indicated an increase of the singlet energy migration process involving the anthracene–donor molecule in the electronic excited state and the anthracene–acceptor molecule in the electronic ground state. The efficiency of this process may be explained by the shortest distance between the molecules involved with the energy transfer process. As

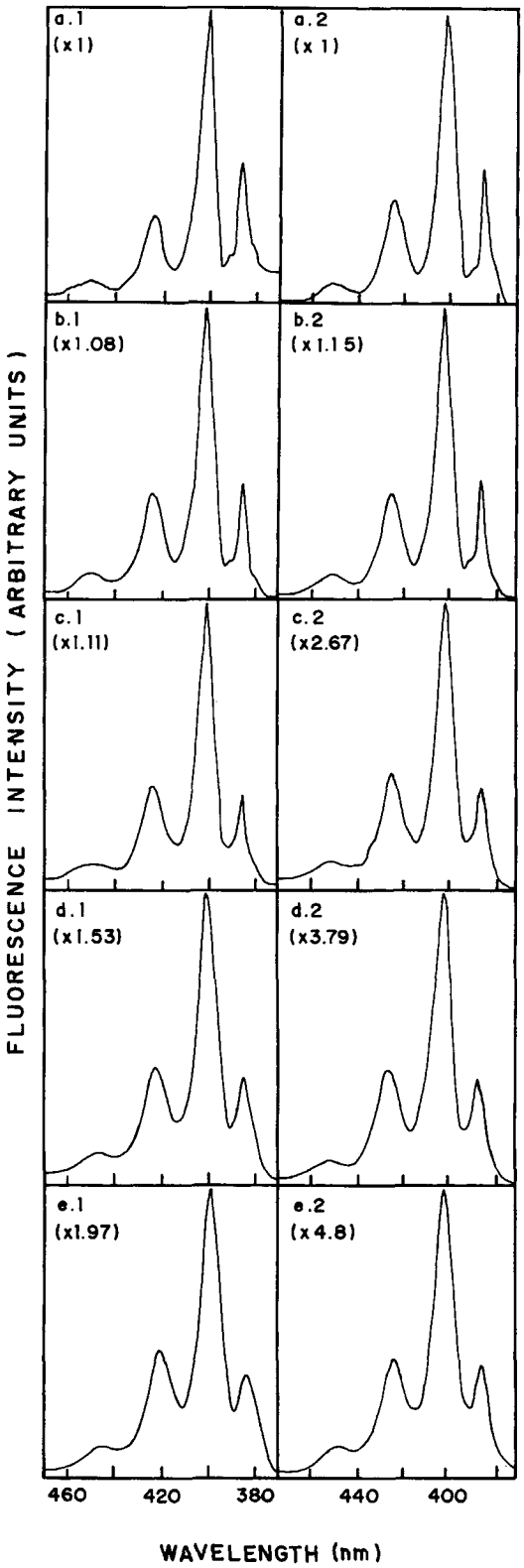

Figure 3 Fluorescence spectra of anthracene dissolved in 50/50 w/w HDPE/LDPE blends, at different temperatures: (a) −190°C, (b) −150°C, (c) −60°C, (d) −20°C, and (e) 20°C. Cooling rates: 1. 15°C/min (left side) and 2. 3°C/min (right side) (multiplication factor).

soon as the polymer matrix displays a relaxation process (T = −40°C), a sufficient free volume will be generated, and the distance between the anthracene molecules will increase. As a consequence of the increase of the distance between the anthracene molecules, the efficiency of the energy migration process will decrease and the relative values I_I/I_{II} stop to decrease. This effect is observed for all samples prepared by the two cooling rates. We have also noted that after the relaxation processes of the polymer take place, the relative intensity of the vibronic bands I_I/I_{II} increase with the temperature. This effect may be explained by the thermal expansion process of the matrix with the temperature. However, the explanation for this result is not simple because there is a very complex coupling of effects between the more flexible polymer matrix and the fluorescent probe that cannot be discriminated by the photostationary technique used in this work. Considering that the anthracene molecules are situated in both the amorphous and interface domains of the polymer bulk, we may assign the relaxation processes of these polyethylene blends to these regions, as obtained for the homopolymers.[30]

Phillips et al.[33-36] reported dielectric relaxation studies of aromatic molecules in different types of polyethylene and concluded that: the β and γ relaxation processes are clearly associated with an amorphous phase that is oriented by stretching the matrix and they are most likely to the interfibrillar amorphous material; the γ process involves short-range motions of the chains and takes place over a distance equal to or greater than 2.5 Å but less than 4.3 Å; the β process permits motions of the aromatic molecules that a significant component of spinning about their longest axis might be present; and this process is associated with the glass-transition process as proposed by Boyer.[8] Those results suggest that the magnitudes of the motions of the polymer during the relaxation process and the dielectric molecules are on a similar scale.

Similar results were obtained for the deactivation processes of luminescent molecules, suggesting that the γ relaxation of polyethylene may be determined using the quenching processes of phosphorescent molecules (like benzophenone) by molecular oxygen; and in this case the quenching process involves a change of the diffusion rate of small molecules. The diffusion of small molecules may be induced by motion of short segments of the polymer chains. The temperature of the γ relaxation in this case is T_γ = −130°C[22,30,37] and this value is similar to that determined by other techniques.[9-15]

We also noted that there was not a significant change of the slope of the curves for relative inten-

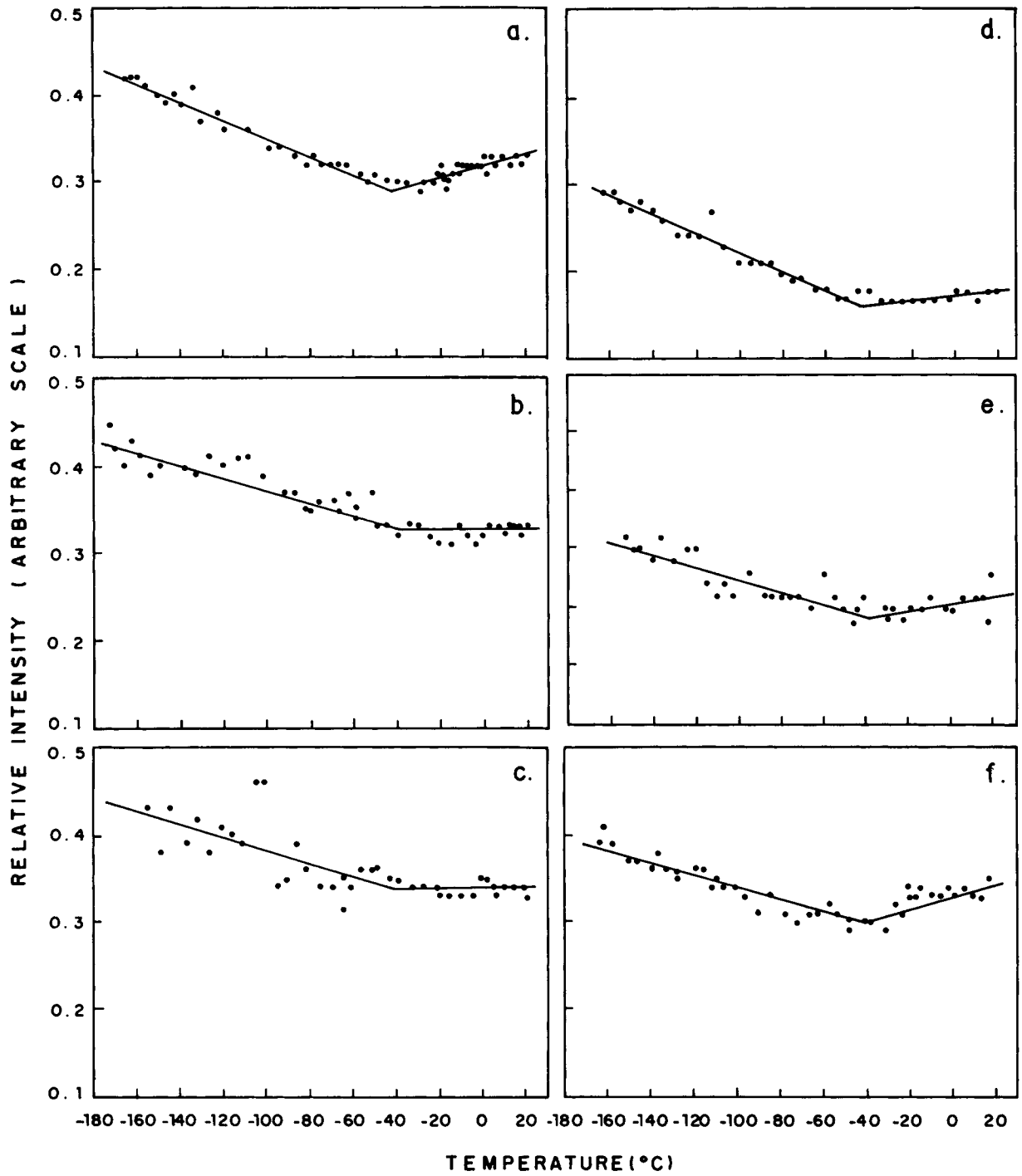

Figure 4 Relative intensity of the vibronic bands $\bar{\nu}_I = 25{,}900\ \mathrm{cm}^{-1}$ and $\bar{\nu}_{II} = 24{,}870\ \mathrm{cm}^{-1}$ of anthracene in: (a) and (d) LDPE; (b) and (e) HDPE; (c) and (f) 50/50 w/w HDPE/LDPE. Cooling rates of 15°C/min (left side) and 3°C/min (right side).

sity I_I/I_{II} versus temperature for anthracene molecules dissolved in the homopolymers or in the blends at $T_\gamma = -130°C$ as shown in Figure 4, that suggests that there is no modification in the efficiency of the singlet migration energy process in this case unless the relaxation process of the polymer involves the longest segments of the macromolecules. These results are also similar to those reported for dielectric and dynamic mechanical behavior of polyethylene.[27,33-36] The relaxation process involving

the longest segments of the PE chain is the β relaxation and it is observed at the temperature range from -40 to $10°C$.[16-18,27,33-36,38] Although there are controversies about the molecular mechanisms for this relaxation process the results obtained using fluorescent[22,30] and dielectric probes[34-36] are in agreement and both indicate that the β relaxation involves motions of long segments of the polymer chains that allow diffusion processes of the probes through the matrix. In this sense the dimensions of these segments should be of the same order as the long axis of the molecular probes, that is, at least seven methylene units of the macromolecules.

Although the morphology of the blends used in our work are different as indicated by the crystalline index, we ascertained that the temperature of the β relaxation is independent of the cooling rate and it is the same as that observed for the homopolymers.[31] This result might be explained by the size of the groups involved in the relaxation process being very short compared with the total size of the macromolecule chain. Moreover the polyethylenes used in our work are both of high molecular weight and both of them present a high polydispersity.

CONCLUSIONS

From the data obtained in this work we could conclude that:

1. fluorescent molecules (like anthracene) are very useful in following some relaxation processes of polymers;
2. those processes must involve motions of segments of the macromolecules of the same dimension of the aromatic molecules;
3. the fluorescent probes appear to be located in domains determined by the polymer structure like amorphous or interfacial regions;
4. the concentration of anthracene used in this work is sufficiently low to prevent its crystallization;
5. the β relaxation process of polyethylene may be determined by the energy migration from the electronic excited singlet state of anthracene–donor molecules to the ground state anthracene–acceptor molecules and the cooperative motion of the polymer modifies the efficiency of this photophysical process;
6. these motions are independent of the crystallinity and thermal history used in the preparation of these samples;
7. the β relaxation may be observed in the homopolymers and in the 50/50 HDPE/LDPE blends that present phase segregation, at the same temperature.

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