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Characterization of static and dynamic properties of a low-density polyethylene. Evidence for translocation of fluorescent probes upon stretching and determination of relaxation processes at the mesoscopic level

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Fluorescence from anthracene guest molecules (AN) has been used to study secondary α, β and γ relaxation processes in unstretched and stretched low density polyethylene (LDPE) in the temperature range 15–400 K. The LDPE was characterized by several different techniques. It contains about 4 vinylidene, vinylene and vinyl type C=C bonds and about 320 CH_3 groups per 10 000 CH_2 units. The unstretched polymer is 31% crystalline and has a melting point, T_m, of 109°C. The 5× stretched polymer is 51% crystalline and $T_m = 110$°C. Although the degree of crystallinity of the films suffers a large change upon macroscopic stretching, the melting temperature (determined by d.s.c. and fluorescence spectroscopy) and the relaxation temperatures do not. However, plots of total fluorescence intensity or fluorescence intensity ratios at different wavelengths vs temperature indicate that dynamic processes involved with the excited singlet states of anthracene are dependent upon polymer stretching. These results, in combination with others obtained previously, suggest that stretching reduces the average amount of free volume at guest sites and induces a translocation of anthracene molecules toward sites at the crystalline–amorphous interfaces. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Secondary relaxation processes of polymers occur at different temperatures and with different activation energies that depend on the size and intermolecular interactions of the set of segmental motions involved[1,2]. Although studied extensively, the mechanisms of relaxation processes of polyethylene are not well understood. However, there is agreement that polyethylene experiences at least three relaxation processes, referred to as α, β and γ in order of decreasing temperature[2–6].

We have used the luminescence from a non-covalently attached probe molecule, anthracene (AN), to study two of the low temperature relaxation processes of low and high density polyethylenes[4] and their 50/50 blends[5]. The data monitor changes in the amorphous or interface regions of the polymer matrices since the probe molecules cannot be incorporated inside the crystallites of polyethylene[7]. The relaxation observed at 231 K was assigned to the β process, which involves motions of long segments of the polymer chains (as expected for the glass transition[2,8]), and the other, at 140 K, was assigned to the γ process involving motions of short chain segments.

Polyethylene films are commercially produced by blowing or casting procedures that influence the nature of their mechanical properties and relaxation processes[9]. As pointed out by Jang *et al.*[10], spherulites of crystalline domains are destroyed and crystalline lamellae of polyethylene are distorted during the yield process. Using dielectric loss data, Yang *et al.* concluded that stretching LDPE increases β- and γ-loss processes and decreases α-loss due to changes in the orientation of dipoles.

Also, we have shown that the number of chains that are oriented along the axis of draw increases during macroscopic stretching of LDPE films[11,12]. From e.s.r.[13], ^{2}H n.m.r.[14,15] and linear dichroism measurements[10,11,16–21] on dopant molecules and the polymer itself, there is strong evidence that film stretching aligns partially the chains of the amorphous region and allows dopant molecules residing nearby to experience a more ordered environment. During the stretching process, some dopant molecules near branching points may also be translocated to crystalline–amorphous interfacial

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regions[10,13,16]. Some of these changes are due to decreases in the average free volume at sites where the dopant molecules reside[11,12,22].

Here, we investigate the relaxation processes of both unstretched and stretched LDPE using the fluorescence of anthracene. On the basis of these data, we discuss the molecular mechanism of the α, β and γ relaxation processes of LDPE and their relationship to the translocation of the probe molecules toward crystalline–amorphous interfaces. Only the melting transition is first order; the others occur over fairly wide temperature ranges. We attribute abrupt changes in the photophysical properties of the anthracene molecules to the aforementioned relaxation processes. Their presence in the polyethylene sample being investigated is inferred from previous work[1,2] and/or has been detected by differential scanning calorimetry.

EXPERIMENTAL

Anthracene (Carlo Erba) was recrystallized from hot cyclohexane. Commercial, additive-free low density polyethylene (LDPE) blown film (NA203) was purchased from Poliolefinas, Brazil. According to the manufacturer, the as-received polymer has M_w and M_w/M_n equal to 510 000 and 10.4 respectively. Before being used, the films were soaked in chloroform for 25 h in order to remove impurities and were then dried under reduced pressure.

Samples containing AN were prepared by immersing the polymer films for different periods of time (1 min, 15 min, 1 h) in 10^{-3} M AN in *n*-heptane. Then the films were washed with methanol in order to remove AN molecules at or near the LDPE surfaces. The samples were dried under vacuum for 24 h at room temperature. The concentrations of AN in the LDPE were determined by measuring the absorption spectra of the doped films, removing the AN by exhaustive extraction into *n*-heptane, and re-recording the absorption spectra of the extract solutions at known volumes. The relationships between optical densities were used to determine the true optical pathlength of the polymer. Using these values, the AN concentrations (wt/wt) in the doped films were calculated (see figure captions). The thickness of the unstretched film was found to be 140 μm from interference patterns in the infrared region[23,24].

Fluorescence measurements at various temperatures were recorded using an instrument described previously[25]. AN was excited at 350 ± 10 nm. Spectra and intensities were obtained by first cooling the films and then warming them progressively; onset temperatures of relaxation processes refer to the lower value. Fluorescence-derived transition temperatures are taken from the intersection points of slopes from graphs of the logarithm of intensity vs the inverse of temperature (see below). They, and transition data derived from differential scanning calorimetry, are estimated to be accurate to ±5 K. X-ray diffraction patterns were recorded on a Shimadzu XD-3A diffractometer, operating with CuKα radiation over the range $5° < 2\Theta < 50°$. Films were stretched to 500% of their original lengths using a universal traction machine, EMIC, at a rate of 5 mm min^{-1}.

Thermograms of stretched and unstretched samples were recorded using a Dupont 1090 differential scanning calorimeter and a TA 2000 Controller from 123 K (−150°C) to 423 K (150°C) at a heating rate of 10° min^{-1}. The instrument was calibrated with indium for temperature (m.p. 157.4°C). The heat of the endothermic peak for melting was used to calculate the percentage crystallinity (X_c) of each sample, assuming $\Delta H_m = 286$ J g^{-1} for completely crystalline polyethylene[26].

Films of cleaned and unstretched LDPE were also characterized chemically to ascertain their degree of unsaturation. Small pieces of LDPE film were placed in a solution of 40 g bromine (reagent, Fisher) in 200 g chloroform (Spectrar, Fisher) and left there for 2 h in dim red light. While maintaining the dim red light, the films were removed, washed with chloroform, and placed in 100 ml chloroform for 2 h. The chloroform was twice replaced with fresh aliquots. The brominated LDPE films were then air dried and stored in opaque bottles. Elemental analyses performed by Desert Analytics (Tucson, Arizona) showed: C 84.03%, H 14.84%, Br 0.43%.

The density of the LDPE at room temperature was found to be 0.917 g cm^{-3} by immersing a piece in methanol and adding water until it remained suspended in the mixed solvent. An aliquot of the solvent was transferred to a volumetric flask and the calculated density was taken to be that of the polyethylene[27].

RESULTS AND DISCUSSION

Characterization of LDPE

LDPE (NA-203) was characterized using several different techniques. U.v./v.i.s. absorption spectroscopy allowed the type and degree of unsaturation to be determined. The absorption maximum of an isolated C=C bond is near 185 nm[28], which is slightly below the lower limit for our spectrometer. However, the absorbance at 190 nm is sufficient to obtain the information needed. U.v. absorption spectra of brominated and unbrominated LDPE are very different. Before bromination, LDPE has essentially no absorbance above 215 nm when light scattering is taken into account. A broad, strong absorption around 190 nm is largely due to the presence of individual or isolated C=C bonds. After bromination, the absorbance increased nearly linearly from 0.3 at 285 nm to 1.2 at 205 nm (due primarily to absorption by C–Br bonds). Since some absorbance at 190 nm remains in the brominated LDPE, a fraction of isolated C=C bonds has not been brominated. Assuming that the absorbance decrease at 190 nm is due to C=C bonds that were brominated, a lower limit to their concentration can be calculated. We use as the C=C extinction coefficient at 190 nm the value for *trans*-4-methylpent-2-ene (9900 cm^{-1} M^{-1} [28]). Then the concentration of the C=C bonds accessible to the bromine reagent is at least 3.5 C=C bonds per 10 000 CH_2 units.

Quantitative *FT*i.r. spectroscopy in the region from 800 to 1000 cm^{-1} was used to determine the types and concentrations (C_M) of the various types of C=C bonds. Peaks at 888, 909, 965 and 1378 cm^{-1} are related to C–H bending vibrations of vinylidene (C=CH_2; $\epsilon = 8.2$), vinylene (CH=CH; $\epsilon = 9.3$), vinyl (CH=CH_2; $\epsilon = 7.5$) and methyl (CH_3; $\epsilon = 1.3$) groups, respectively[29]; the units of ϵ (absorptivity) are cm^2 g^{-1} as 1000 CH_2 groups per CH_3 or cm^2 g^{-1} as 1000 CH_2 groups per C=C bond. The C_M values collected in *Table 1* indicate that the LDPE has a total of about 4 C=C bonds per 10 000 CH_2 units. Since the experimental error in these experiments is

Table 1 Concentrations C_M of C=C bonds and methyl groups per 1000 CH_2 units in LDPE-NA-203 using *FT*i.r. measurements

C=C type	Vinylidene	Vinyl	*Trans*-vinylene	Total C=C[a]	CH_3
C_M	0.29	0.12	0.02	0.43	32

[a] The concentration of *cis*-vinylene is assumed to be negligible

rather large, it is difficult to state whether the 10–15% of C=C bonds calculated not to be accessible to the bromine reagent is accurate. Clearly, some unsaturated units are in locations that the swelling solvent $CHCl_3$ did not reach or where bromination was incomplete. Given the enormous excess of bromine and the forcing reaction conditions, we prefer the latter explanation and suggest that the inaccessible C=C bonds may be in the crystalline parts.

Peaks at 1474 and 1463 cm^{-1} are due to the scissor motions of the methylene groups, whereas peaks at 1368 and 1378 cm^{-1} are assigned to asymmetrical deformations and wagging vibrations of CH_3 and CH_2 groups, respectively[29]. The C_M of the methyl groups can be estimated using a procedure similar to the one above that also corrects for peak overlaps (*Table 1*). From the average molecular weight, perfectly linear NA-203 polyethylene would have 2 methyl groups per 36 000 CH_2 units. The concentration of methyl groups requires an average of ~ 110 branches per chain.

X-ray diffraction 'powder' patterns of the LDPE are composed of two crystalline peaks assigned to reflections of indices (110) and (200) and one broad reflection at 20.5° from the amorphous part. Consistent with the conclusions from the d.s.c. experiments, the X-ray data indicate that the polymer is only partially crystalline (*Figure 1*). Furthermore, the degree of crystallinity increases with film stretching, and there is an increase in the relative intensity of the peak assigned to the (200) plane, suggesting that the orientation of the macromolecular chains induced by drawing is parallel to this crystalline plane. Degrees of crystallinity (and melting points) from the two methods are collected in *Table 2*.

We find that introduction of AN molecules into LDPE by swelling with *n*-heptane does not change perceptibly the degree of crystallinity of the polymer. Thus AN molecules are not incorporated in crystalline domains. Consistent with the prior findings of others and ourselves[4–6,11,12,30], we conclude that the AN molecules reside only in the amorphous part and at the interface between the crystalline and amorphous domains of the matrix.

Fluorescence spectra of anthracene

Conflicting and contrary results concerning the influences of AN concentration and LDPE stretching on fluorescence intensities and spectra have appeared[31]; thus a re-examination is both pertinent and necessary. The electronic absorption spectrum of anthracene consists of a lowest energy ^1L_a transition with a set of vibronic bands with the 0,0 maximum at 350 nm. The polarization of this band is along the short axis of the molecule. The other vibronic bands are similarly polarized but are mixed somewhat with a forbidden ^1L_b transition whose polarization is along the long molecular axis.

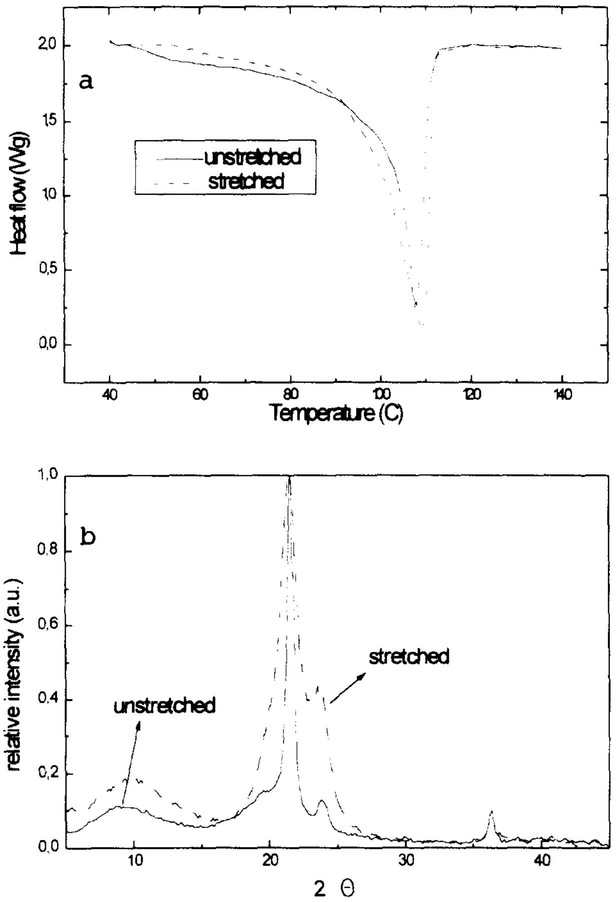

Figure 1 D.s.c. traces showing the region of melting (a) and X-ray diffraction profiles (b) for unstretched and 500% stretched LDPE samples

Table 2 Approximate temperatures of relaxation processes (K), apparent activation energy (E_a (kcal)) of fluorescence intensity changes in the temperature regions between relaxation onsets, and degrees of crystallinity (X_c) of unstretched (u) and stretched (s) LDPE

LDPE	T_γ(K)	E_a	T_β(K)	E_a	T_α(K)	E_a	T_m(K)	X_c(%)
u	150	0.10	230	0.15	340	2.5	380	31
s	150	0.10	240	0.15	340	3.0	380	51

Fluorescence spectra of different concentrations of anthracene in unstretched and stretched LDPE excited by 350 ± 10 nm radiation at various temperatures are shown in *Figure 2*. The spectra of the lowest concentration are similar to those from 10^{-5} M AN in *n*-heptane. Their appearance is strongly dependent on concentration and, at least in the range examined, independent of the stretching degree. At the lowest concentrations (*Figures 2a* and *2b*), the 0,0 emission band is the most intense. Its relative intensity decreases progressively with increasing AN concentration (*Figures 2c–f*). This behaviour is the classic signature of radiative ('trivial') energy transfer[32] in which emitted radiation is reabsorbed by a ground state AN molecule before it escapes the confines of the LDPE. The efficiency of trivial energy transfer is dependent upon the overlap between the AN emission spectrum and the AN absorption spectrum, the molar extinction coefficients in the region of overlap, and the local concentration of AN; in essence, the ability to absorb the fluorescence is governed by Beer's law.

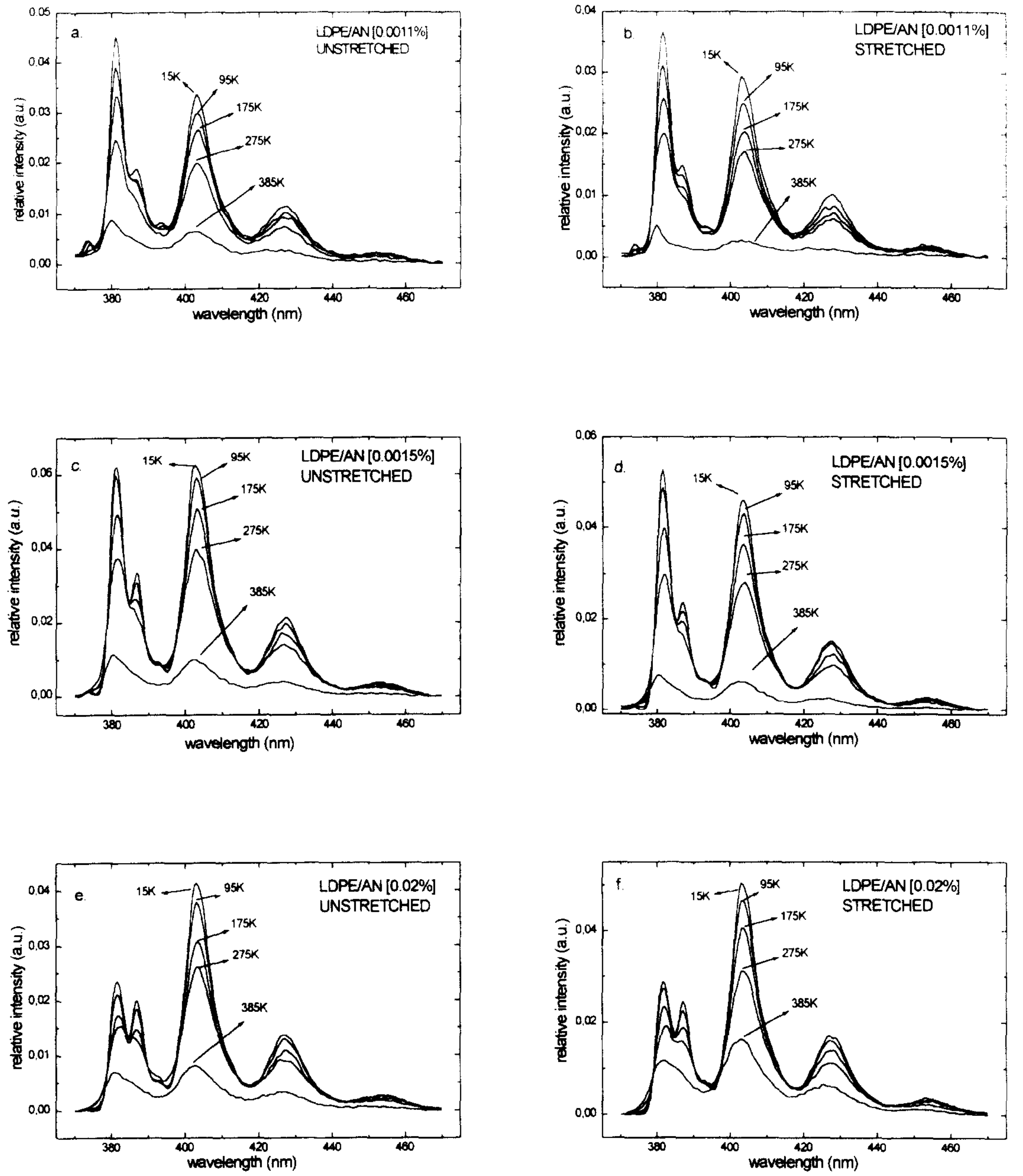

Figure 2 Fluorescence spectra of 0.0011% (a) and (b), 0.0015% (c) and (d), and 0.02% (e) and (f) AN in LDPE. Unstretched samples (left) and 500% stretched samples (right). Temperatures T (K) are 20, 95, 185, 275 and 385, in order of decreasing intensity

Under steady-state conditions and in the absence of added quenchers, the fluorescence quantum yield of AN, q_{FM}, is given by equation (1):

$$q_{FM} = k_{FM}/\{k_{FM} + k_{IM} + k_{ST} + k_{DM}[AN]\} \quad (1)$$

The rate constants are for fluorescence emission (k_{FM}), radiationless internal conversion (k_{IM}), intersystem crossing (k_{ST}) and quenching by collisional and Förster mechanisms (k_{DM})[32,33]. In fact, since the donor and acceptor molecules in the Förster energy transfer here are the same, the process $^1AN + AN \rightarrow AN + {}^1AN$ does *not* lead to a diminution of fluorescence intensity, I_F. By contrast, radiative energy transfer between molecules of the same structure leads to a bizarre situation: at ^1AN emissive wavelengths where AN can absorb, $I_F(\lambda)$ is decreased; at emissive wavelengths where AN does not absorb, $I_F(\lambda)$ suffers an increase. However, the total integrated fluorescence intensity is decreased by trivial energy transfer since $q_{FM} < 1$.

When k_{DM} [AN] $\ll k_{FM} + k_{IM} + k_{ST}$, it may be neglected. This condition is most easily achieved at low AN concentrations. However, when k_{DM} is dominated by collisional (diffusion-related) processes, lower temperatures can usually be used to decrease k_{DM}. In anisotropic media such as LDPE, temperature changes may change the 'local concentration' of guest molecules, leading to aggregation or dispersion in the amorphous or interfacial sites. Thus, expressions like equation (1) must be applied to media such as LDPE with caution. Under static conditions, even when k_{DM} [AN] is not negligible, changes in the fluorescence intensity, I_F, can be related to an 'activation energy', E_a, by an Arrhenius-like expression (equation (2)) if the sum of the unimolecular rate constants can be related to a single E_a value. This condition can be achieved if one rate constant is much larger than the others:

$$\ln\,[(I_F^0/I_F) - 1] = A - E_a/RT \qquad (2)$$

In equation (2), I_F^0 is the fluorescence intensity at low temperature where it becomes (nearly) temperature independent. In this work, we take I_F^0 to be the intensity at 15 K, the lowest temperature employed. The E_a values reported in *Table 2* may be only approximations since the I_F^0 values have not been shown definitively to be in the temperature-independent regime (*Figures 3 and 5*; see below). Calculations employ the total integrated fluorescence intensity at each temperature rather than the intensity at one wavelength.

As mentioned, the bimolecular quenching term in equation (1) can suffer apparent modifications due to enhanced or diminished radiative energy transfer when temperature changes lead, respectively, to diminished or enhanced AN proximity. The influence of this process will be characterized by decreases in the relative fluorescence intensity only at those wavelengths where the AN absorption spectrum and the ^{1}AN fluorescence spectrum overlap. Due to its Beer's law-like nature at these wavelengths, the efficiency of trivial energy transfer has a $1/r^2$ dependence (where r is the separation between a molecule of AN and an AN excited singlet). Another process that depends upon spectral overlap between AN absorption and fluorescence is dipole–dipole (Förster) energy transfer. However, it differs from radiative energy transfer in that the shape of the donor emission spectrum is independent of its overlap with the acceptor absorption spectrum and the efficiency depends upon $1/r^6$[32].

In viscous or rigid media such as LDPE, where diffusion is much slower than the rate of fluorescence ($\sim 2 \times 10^8\,\mathrm{s}^{-1}$ for AN in hydrocarbon solvents[33]), the efficiency of this quenching process, Ω_{EF}, is given by equation (3):

$$\Omega_{ef} = R_0^6/(R_0^6 + r^6) \qquad (3)$$

$R_0 = 8.8 \times 10^{-25} Jn^{-4}K^2\phi_0$ is the critical donor–acceptor separation where the energy transfer and the sum of the unimolecular decay processes in equation (1) have the same probability, J is the normalized overlap between the absorption spectrum of the acceptor and the fluorescence spectrum of the donor (AN and ^{1}AN, respectively, in this work), n is the refractive index of the medium, ϕ_0 is the quantum yield of the donor in absence of the quencher (taken as the value at low AN concentrations here), and K is an orientation factor for the angle between the transition dipole moments of donor and acceptor molecules ($K^2 = 2/3$ for an isotropic distribution)[32]. The total contribution to J is from the 0, 0 bands for absorption (350 nm) and emission (382 nm) in AN; J is small but non-zero due to the small Stokes shift. Nevertheless, Förster energy transfer should have very little effect on q_{FM} or I_F in this case, for the reasons cited above.

As pointed out earlier[34], the fluorescence spectrum of AN is composed of a set of vibronic bands whose relative intensities depend on the nature and efficiency of the energy transfer processes. In quantitative terms, the efficiency of radiative energy transfer, ϕ_{FM}, is expressed by equation (4)[32,33]:

$$\phi_{FM} = [q_{FM}(1 - \underline{a})]/(1 - \underline{a}q_{FM}) \qquad (4)$$

The parameter $\underline{a}$ (equation (5)) defines the self-absorption dependence on the molar extinction coefficient at frequency ν, $\epsilon(\nu)$, the fluorescence intensity, $F(\nu)$, the concentration of AN and the thickness d of the sample[33]:

$$\underline{a} = [2.313[\mathrm{AN}]\,d/q_{FM}] \int_0^\infty F(\nu)\epsilon(\nu)\,\mathrm{d}\nu \qquad (5)$$

In fluid solutions, this type of process is not important when the donor and acceptor are both condensed aromatic hydrocarbons since the overlap factor J is small, making R_0 small. This, and the short singlet lifetime of AN, require that its concentration be very large for Ω_{ef} not to be negligible.

At the bulk concentrations of AN in LDPE calculated here, neither trivial nor Förster processes should be important. However, the data in *Figure 2* indicate that the trivial transfer mechanism is operative. Several factors can explain this result. First, it must be remembered that only the non-crystalline parts of the LDPE matrix can accommodate AN molecules. This means that the true 'bulk' concentration in unstretched and stretched films are about 1.4 and 2.0 times, respectively, the values that assume that the total volume of the LDPE is accessible to guest molecules. Second, there are reasons to believe that guest molecules such as AN aggregate at specific site types[35]. Even if two AN molecules are not overlapping or occupy the same host site, their proximity has the effect of making the stochastic values of r smaller. Thus, we believe that contact, radiative and Förster processes occur even at the apparently low AN concentrations employed due to aggregation promoted by specific host sites. Furthermore, aggregation probably increases when LDPE films are stretched, owing to translocation of some guest molecules from amorphous to interfacial sites. Static contact quenching from pairs of AN molecules occupying the same site may also be occurring[35], but the very low quantum efficiency for their excimer emission has precluded our detecting it directly. Indirectly, such quenching diminishes the overall intensity of AN emission at all wavelengths.

Regardless, the high microviscosity of LDPE and the short excited lifetimes of AN singlets require that all energy transfer, regardless of its mechanism, should be virtually static: if the diffusion coefficient of AN in LDPE at the highest temperature employed is $\sim 10^{-8}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, each molecule will move about 4–5 Å (or about one molecular diameter) during its $\sim$ 5 ns lifetime. Below the glass transition temperature of the host, T_g, mobility should be reduced to the extent that there is almost no translational motion of excited AN molecules. As a result, significant intensity changes in fluorescence below T_g should not be ascribable to translocation of molecules or to changes in the efficiency of energy transfer.

In an attempt to distinguish qualitatively the contributions to changes in unimolecular deactivation of ^{1}AN and in the various types of energy transfer, we have plotted the temperature dependence of the total fluorescence intensity (I_F), and the ratios I_I/I_{II} and I_I/I_{III} (representing the intensity ratios from the first and second emissive bands at 382 and 402 nm and the first and third bands at 382 and 424 nm, respectively). The I_F vs T plot addresses all aspects of excited state deactivation, while the I_I/I_{II} and I_I/I_{III} vs T plots probe the role of trivial energy transfer.

As discussed previously, I_F in LDPE is expected to (and does) decrease progressively as temperature is increased, owing to enhanced radiationless deactivation processes. The molecular rate constants are also influenced to some extent by changes in cooperative processes with the polymer chains[36] and in medium electronic properties[37] (e.g., changes in medium dielectric and index of refraction) that accompany changes in temperature.

Relaxation processes in unstretched films

Plots of the dependence of the fluorescence intensity and the ratios of vibronic band intensities on temperature at three different AN concentrations are shown in *Figures 3* and *4*. Slope changes in intensity are more apparent when the data are plotted in an Arrhenius fashion (see below); temperatures of relaxation processes are taken from such plots, from d.s.c. thermograms, and from the literature[1,2].

In the 15–150 K temperature range, the decrease of fluorescence intensity at higher temperatures is noted more clearly in the lowest concentration sample. Since these temperatures are below T_g, the matrix is very rigid and diffusion is essentially nil. Therefore, the most important contribution to *changes* in fluorescence intensity should be (intramolecular) internal conversion.

Near 150 K, there is a small but perceptible slope change. The onset of γ-relaxation processes has been reported in the temperature range 110–160 K. These processes involve motions of short segments of polymer chains, involving 3–4 methylene groups, located either in amorphous domains or in the crystalline–amorphous interfacial regions[3–6]. The free volume generated by the γ-relaxation processes is smaller than that necessary for diffusion or even rotation of AN molecules. Consequently, as expected, γ-relaxation seems to affect only the unimolecular deactivation rate constants in equation (1) (and only to a small degree).

The 150–230 K temperature range includes the onset of β-relaxation process and involves the mobility of the chain branches located in the amorphous region of polyethylene[4]. For different types of polyethylene and for a 50/50 low-density/high-density polyethylene blend, using photoluminescence techniques, we have demonstrated that β-relaxation involves motions of segments of polymer chains whose dimensions are at least as long as an AN molecule. Thus, the free volume generated by the chain motions should permit AN diffusion and cause temperature-dependent changes in the *bimolecular* term of equation (1). These changes should have the largest influence on the fluorescence intensity of the most concentrated LDPE films. The data in *Figure 3* indicate that the three samples, differing by more than a factor of 15 in AN concentration, do not respond very differently to temperature changes. This indicates either that bimolecular processes remain unimportant or, less likely, that they are affected about equally within the AN concentrations explored.

α-Relaxation of polyethylene has been ascribed to at least three processes in the temperature range 304–363 K; each is thought to be associated with the crystalline phase of the polymer, and involves a form of diffusion of chains below the melting point[3]. Ohta *et al.* related the α_1-relaxation process to an intercrystallite (grain boundary) relaxation phenomenon and α_2-relaxation to an intracrystallite (single chain) phenomenon; the specific origin of α_3-relaxation is unclear[3].

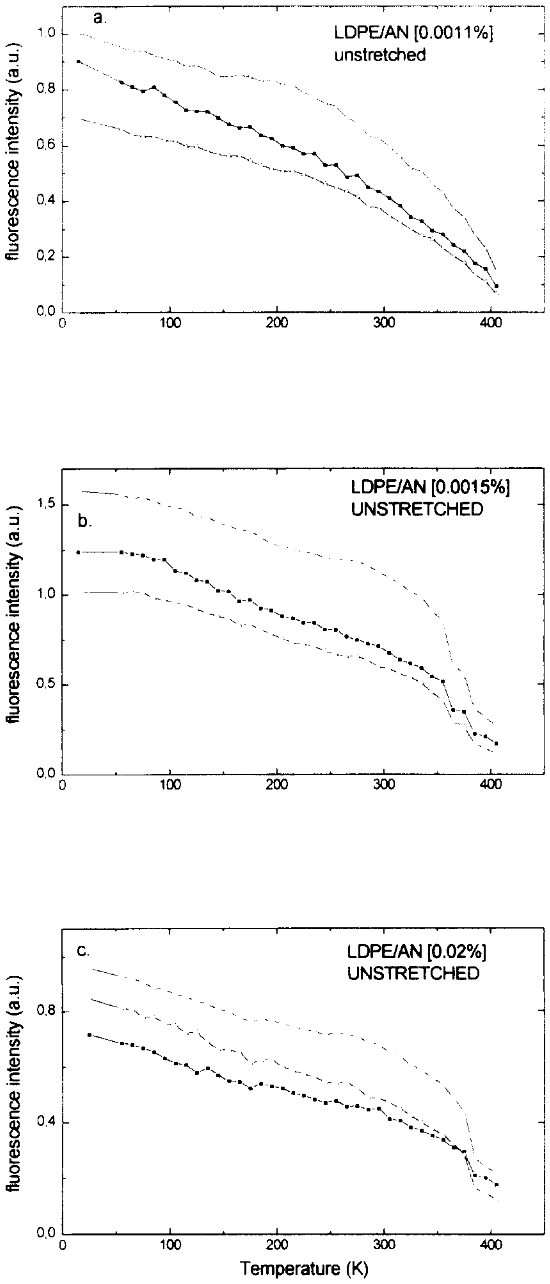

Figure 3 Relative fluorescence intensities for 0.0011% (a), 0.0015% (b) and 0.02% (c) AN in unstretched LDPE vs temperature: total integrated intensity, I_F (□); intensity at 382 nm (■) and at 402 nm (△)

In *Figure 3*, near 310–340 K, there are changes of the slopes of the three curves which become more pronounced at $T > 380$ K, the melting temperature of the polymer (*Figure 1*). As a consequence of these high temperatures and the low pressures to which the samples are subjected[25], we have noted a loss of AN in the films. The decreases in intensity above 380 K are not due primarily to changes in the unimolecular rate constants in equation (1).

Although the data in *Figure 3* are a convolution among concentration, bimolecular quenching and

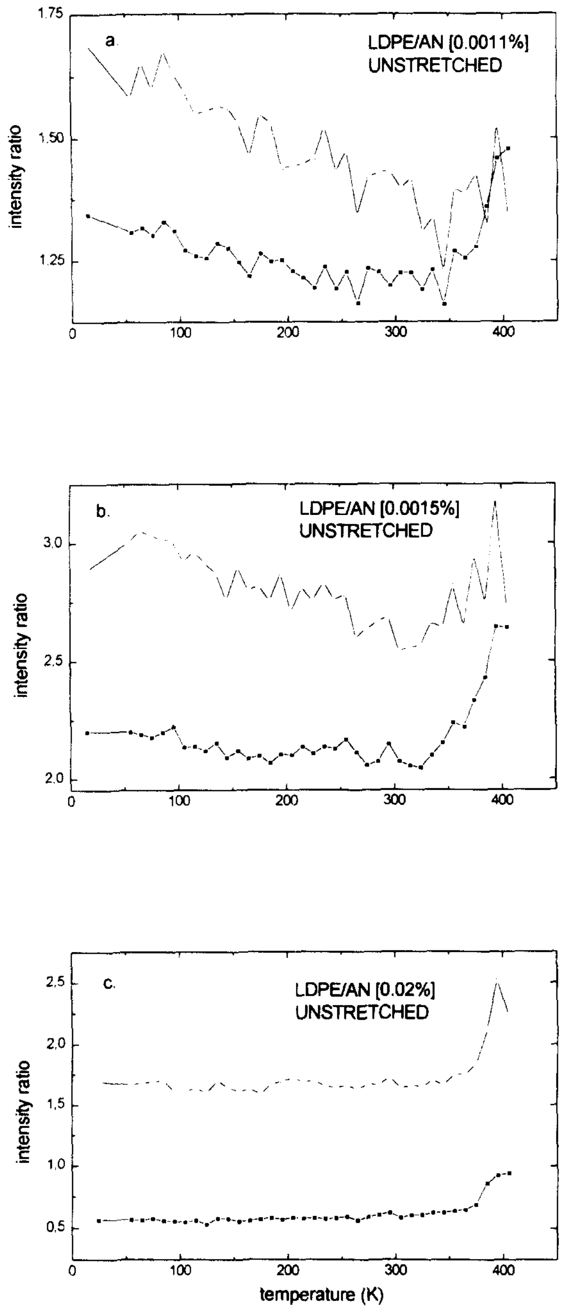

Figure 4 Fluorescence intensity ratios of 0.0011% (a), 0.0015% (b) and 0.02% (c) AN in unstretched LDPE vs temperature for I_I/I_{II} (□) and I_I/I_{III} (■)

unimolecular rate processes, those in *Figure 4* should be most sensitive to radiative energy transfer and unimolecular rate changes. AN concentration is important only in so far as it affects the probability of reabsorption of emitted radiation (equations (4) and (5)) and the distribution of AN molecules in amorphous and interfacial sites. The precipitous increases in I_I/I_{II} and I_I/I_{III} at $T > 350$ K in the two lower AN concentration samples indicate that the probe molecules are more evenly distributed throughout the polymer by α-relaxation. In the highest concentration sample (> 15-fold higher than the other two), the increase in the intensity ratios becomes apparent much nearer the melting temperature of the matrix, suggesting that the more aggregated systems are more difficult to disperse since a greater fraction of easily accessible host sites is occupied.

The results in *Figures 3* and *4* demonstrate that AN fluorescence can be used to follow mesoscopically the onset of various relaxation phenomena in unstretched polyethylene. Assuming that the changes in fluorescence intensity in the different temperature regimes can be treated separately and by equation (2), apparent activation energies have been calculated using total fluorescence intensities and temperature ranges that exclude (but are defined between) the onsets of relaxation processes (*Table 2*).

Relaxation processes in stretched films

Plots of AN fluorescence intensity vs temperature in stretched LDPE are shown in *Figure 5*. They should be compared with those in *Figure 3* for the unstretched films, where the intensity is much more dependent on temperature below ~ 310 K. The diminished dependence indicates that AN molecules in stretched LDPE are located on average in more rigid sites whose interactions with ^{1}AN vary with temperature to a smaller extent (i.e., sites in stretched LDPE lead to a smaller sensitivity of the unimolecular rate constants in equation (1) to temperature). However, the intensity changes associated with the onset of α-relaxation are more precipitous and more easily defined in the stretched films than in the unstretched ones. Since α-relaxation is associated with motions of chains at the surface of and in crystallites, we infer that a larger fraction of AN molecules is present at interfacial sites in the stretched polymers than in the unstretched ones. In fact, the data in *Figures 3* and *5* support the contention that translocation of guest molecules from amorphous to interfacial sites is a consequence of stretching LDPE[10,16].

As noted previously[11,12,22], there is a reduction in the average free volume at guest sites when LDPE films are stretched. The correspondent additional constraints on guest motion make unimolecular deactivation processes of AN singlets less sensitive to temperature; in essence, as temperature is changed in the low temperature regimes, the changes to local environments of the AN molecules are smaller in stretched than in unstretched LDPE. This conclusion is further borne out by the smaller changes in the I_I/I_{II} and I_I/I_{III} ratios below ~ 310 K for the stretched films (compare *Figures 4* and *6*).

From the very small changes in the slopes of the curves in *Figure 6* near 230 K, it is much more difficult to locate the onset of β-relaxation (i.e., the glass transition[5,6]). Again, this result is consistent with stretching causing the population of AN molecules in amorphous sites, where β-relaxation occurs, to be depleted. Although the 'unfreezing' of chain motions that accompanies β-relaxation should be at least as large in stretched as in unstretched LDPE, the former has fewer molecules occupying sites in the amorphous part to sense it.

In the temperature range above the α-transition, there is a clear and precipitous increase in the I_I/I_{II} and I_I/I_{III} ratios that can be associated with the melting of crystallites (*Figure 6*). It is much more pronounced than in the unstretched films (*Figure 4*). These data suggest, again, that a large fraction of AN molecules is localized in interfacial sites below the α-transition temperature. As diffusion becomes more facile and the crystallites melt, the AN molecules become more evenly distributed within the film and trivial energy transfer is diminished. The results in *Figure 6C* suggest that at

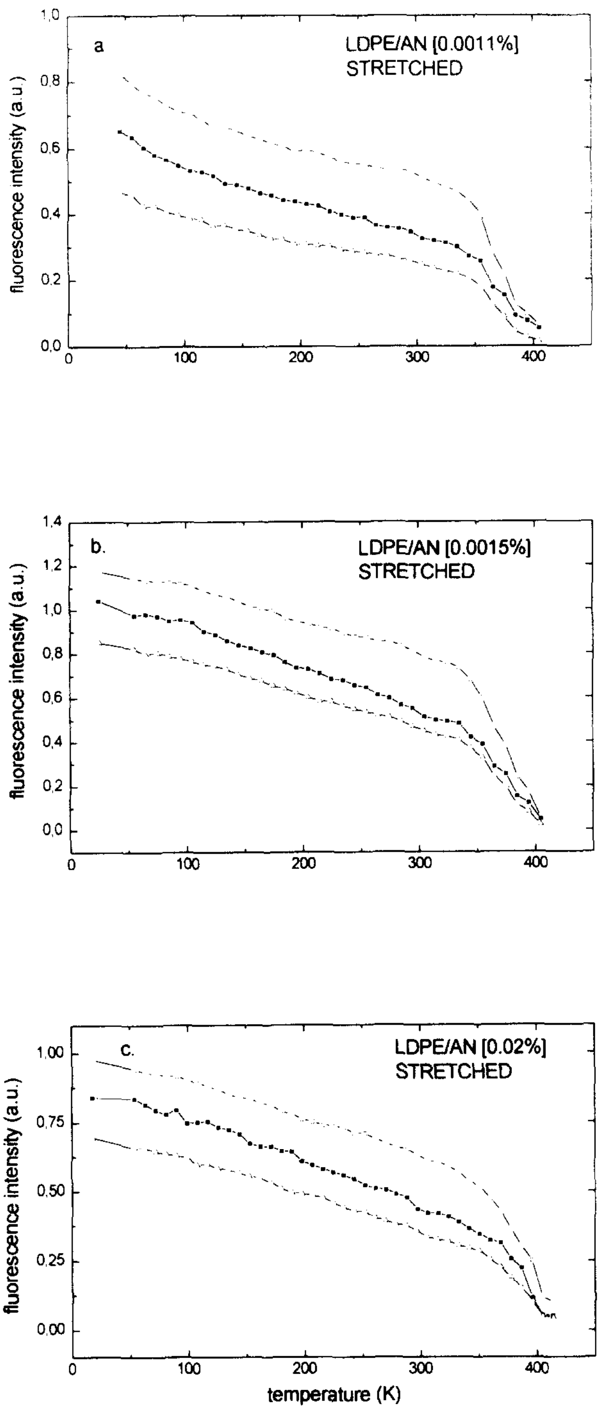

Figure 5 Relative fluorescence intensities for 0.0011% (a), 0.0015% (b) and 0.02% (c) AN in stretched LDPE vs temperature: total integrated intensity, I_F (□); intensity at 382 nm (■) and at 402 nm (△)

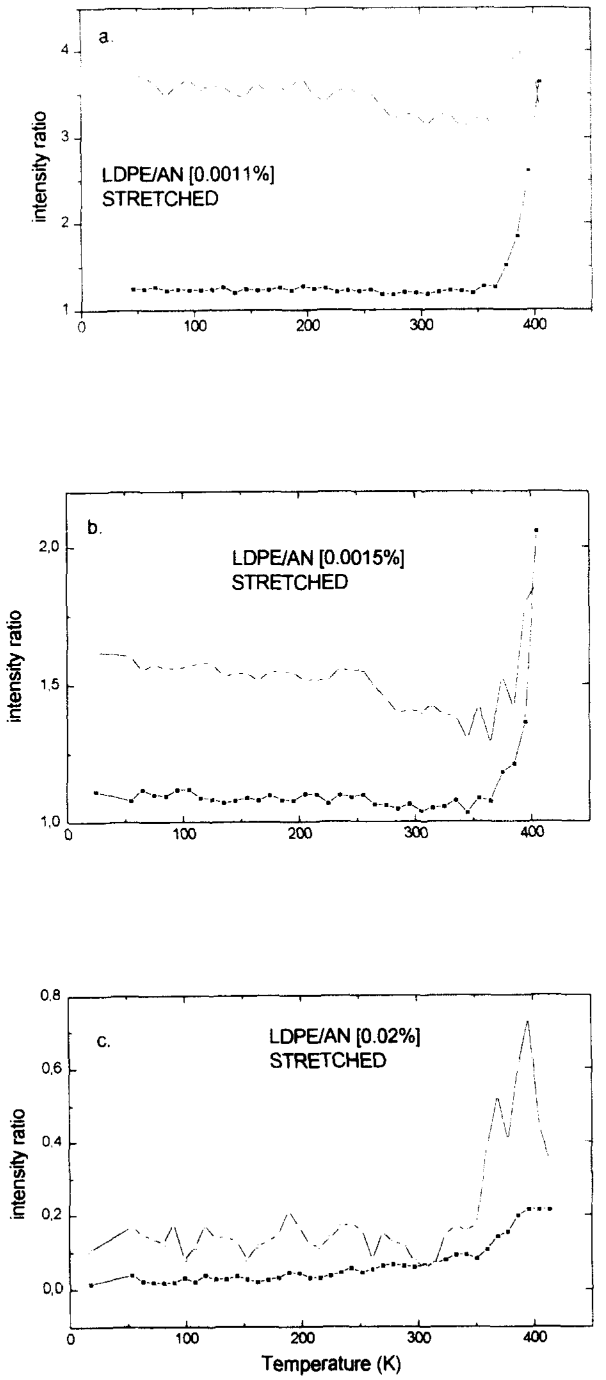

Figure 6 Fluorescence intensity ratios of 0.0011% (a), 0.0015% (b) and 0.02% (c) AN in stretched LDPE vs temperature for I_I/I_{II} (□) and I_I/I_{III} (■)

0.02% AN loading, virtually all of the accessible interfacial sites in stretched LDPE are filled; the remaining AN molecules occupy sites in the amorphous region.

Even at the lowest AN concentration, below the saturation limit of the interfacial sites, some guest molecules must occupy amorphous sites in stretched LDPE. However, as the concentration of AN increases, the *fraction* of AN molecules at amorphous sites must also increase. Thus, the smaller increase in the I_I/I_{II} and I_I/I_{III} ratios of *Figure 6c* as temperature is increased from ~350 K is a consequence of the fluorimeter sampling molecules in interfacial sites *and a considerable fraction still in amorphous sites.* The contribution to changes of fluorescence intensity by the latter during melting (and diffusion) is much smaller than by the former.

The apparent activation energies for the stretched films (*Table 2*) are similar to those for the unstretched films since the processes being interrogated are virtually the same.

CONCLUSIONS

The fluorescence intensity of AN dissolved in

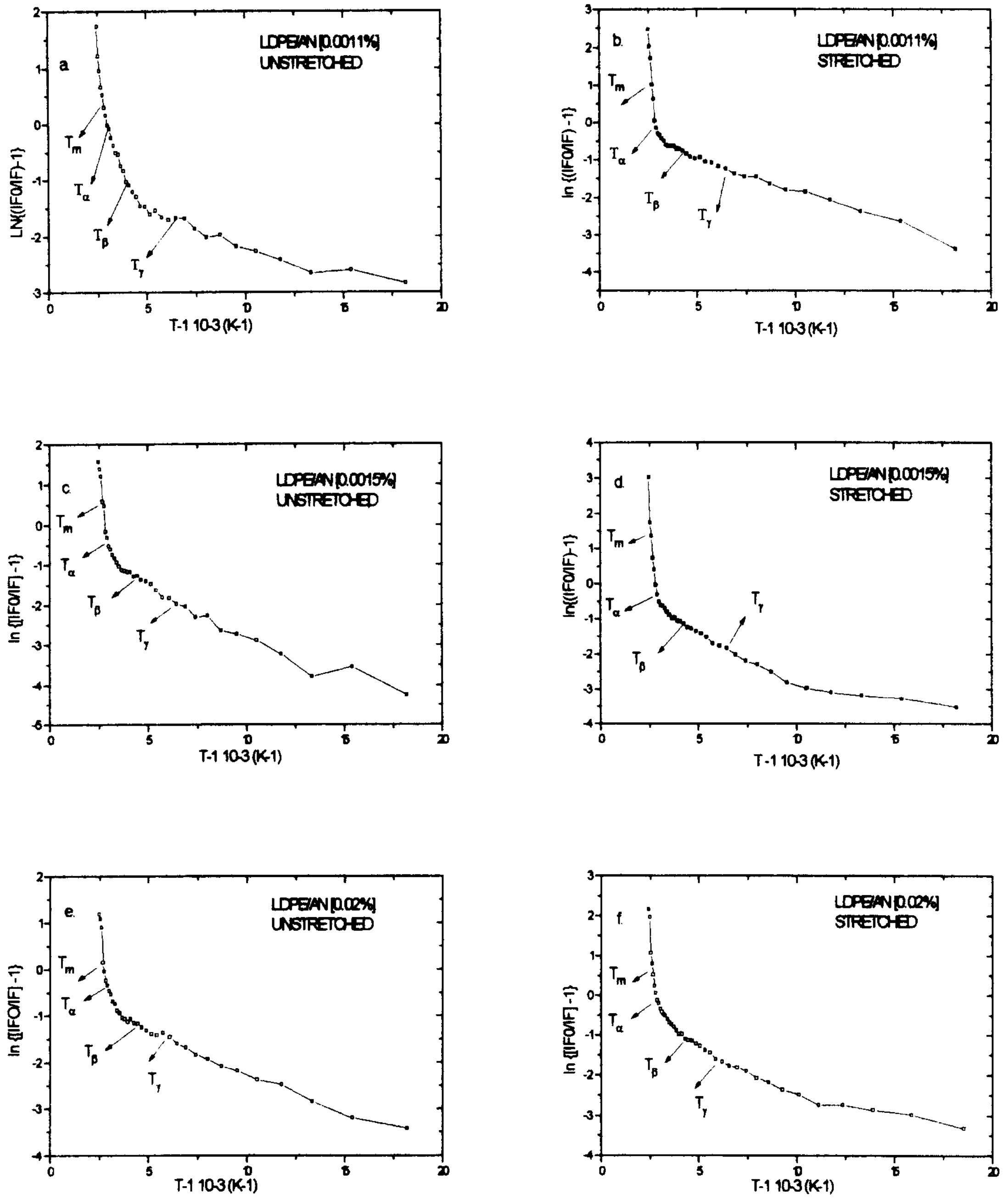

Figure 7 Arrhenius-type plots of AN fluorescence intensities in unstretched (a, c, e) and stretched (b, d, f) LDPE films for 0.0011% (a, b), 0.0015% (c, d) and 0.025% (e, f) AN. See equation (2)

unstretched and stretched LDPE decreases as the temperature is increased. However, plots of fluorescence intensity vs temperature exhibit slope changes which can be explained by the cooperative influence of polymer chain motions on the photophysical properties of excited singlet states of AN guest molecules. Arrhenius-type plots of fluorescence intensities (equation (2)) are shown in *Figure 7*. They exhibit distinct linear regions with changes in slopes at temperatures corresponding to the onset of characterized relaxation processes in unstretched and stretched LDPE. We have ascribed these changes to a combination of effects, including the conformational mobility of polymer chains (γ- and β- transitions) inducing increased non-radiative deactivation of AN molecules, and diffusional motions of the polymer chains (α- and melting transitions) leading to decreased trivial energy transfer among AN molecules.

Although significant changes in the onset temperatures for the relaxation processes are not caused by macroscopic stretching of the polymer, the Arrhenius-type curves show better defined slope changes in the stretched films (*Figure 7*). Using these slope values, we have calculated the apparent activation energy for the different segments of those curves for each sample, as shown in *Table 2*. From these data, and considering the experimental errors involved in the calculations from them, we believe that the activation energies are nearly independent of stretching. Only the E_a in the temperature range above the onset of α-relaxation motions is slightly higher in the stretched films, and the difference may well be within the limits of our experimental error. Even the largest E_a value calculated here is not measuring AN diffusion *per se* since diffusional activation energies for molecules of similar size are $> 6\,\mathrm{kcal\,mol^{-1}}$[11,12,35,38].

From analyses of X-ray diffraction and d.s.c. data, we find that stretching increases significantly the amount of crystallinity in NA-203 polyethylene, and that AN molecules are not incorporated within the crystalline parts of the films. Therefore, all of the phenomena probed in this work emanate in the amorphous part or at crystalline–amorphous interfaces.

These data, *in toto*, provide important insights into the temperature-dependent morphological changes that occur in LDPE when it is stretched. They also provide compelling evidence that film stretching promotes the translocation of guest molecules from amorphous to interfacial sites. It would be instructive to compare these results with those using other well-characterized polyethylenes of different degrees of crystallinity[39].

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39 See ref. 24 for the characterization of three other polyethylenes with greater degrees of crystallinity than NA-203