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Translocation of fluorescent probes upon stretching low-density polyethylene films. Comparison between 'free' and covalently-attached anthryl groups

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Fluorescence from (9-anthryl)methyl groups (AN-C) attached covalently to polymer chains has been used to study secondary α-, β- and γ-relaxation processes in two types of stretched and unstretched low-density polyethylene (LDPE) with different degrees of crystallinity and frequencies of branches in the temperature range 55–400 K. Plots of total fluorescence intensity or fluorescence intensity ratios at different wavelengths *versus* temperature indicate that the efficiency of radiationless deactivation processes is very sensitive to film stretching (i.e. micromorphological changes induced by macroscopically applied stress) and to secondary relaxation processes of LDPE (i.e. micromorphological changes induced by temperature). Also, since the efficiencies of intermolecular radiative energy transfer processes in LDPE suffered by AN-C and 'free' anthracene (ANH), doped into native films, are much different, the mode of 'reporter' incorporation into a film and its treatment thereafter can establish differing local concentration gradients. The results suggest that, although stretching reduces, on average, the amount of free volume available at guest sites and partially orients both AN-C and ANH probes, the AN-C (due to their being constrained to their original positions of incorporation) are more influenced by polymer relaxation processes, and the excited singlet states of both probes are more sensitive to temperature in stretched films than in unstretched ones. Overall, comparisons between the behaviour of the covalently-attached and free lumophores provide insights into how external perturbations, such as stress and temperature changes, affect specific aspects of polymer microstructure and mobility and what is the influence exerted by subtly differing environments on the photophysical properties of the probe.

(Keywords: polyethylene; stretching; relaxation processes)

INTRODUCTION

Macroscopic stretching of a semicrystalline polymer, such as low-density polyethylene (LDPE), induces significant changes in its structure and properties. These include distortion of the crystalline lamellae for higher yield processes, changes in optical anisotropy, and, in some other cases, an increase in the degree of crystallinity[1–4]. All of these are a consequence of both the partial orientation of polymer chains in amorphous regions and orientation of the crystallites in the drawing direction.

Whether introduced into LDPE by vapour diffusion or swelling protocols, guest molecules reside only in non-crystalline regions of unstretched and stretched films[5]. In most cases, the polymeric matrices have been used to obtain information about the structure and dynamics of the guest molecules. For instance, macroscopically-induced microscopic anisotropy from film stretching has been used for many years to obtain dichroic spectra of many guest molecules and to assign correctly the polarization of their vibrational and electronic absorption bands[6,7].

The source of dichroism in the spectra of guest molecules held in polymer matrices and of groups covalently attached to polymer chains in stretched LDPE is not completely clear. In one hypothesis, guest molecules in amorphous regions of unstretched films tend to translocate to the interfacial regions (between amorphous and crystalline domains) as a film is stretched; however, covalently attached groups in the amorphous region of stretched films are thought to be unoriented even though the chains surrounding them are at least partially oriented along the direction of draw[7]. In another hypothesis advanced by us[8–10], covalently attached probes, although somewhat less oriented on average than 'free' guest molecules, sense acutely their positions with respect to neighbouring polymethylene chains. Regardless, covalently attached probes are incapable of diffusing to more attractive sites after film stretching. They are subject to changes induced by (macroscopic) film stretching that occur to their initial (unstretched) environments[8,9,11,12].

Guests can also be sensitive probes of microscopic structural and dynamic properties of their LDPE hosts. As an example, results from studies of the photoreactions of guest molecules[11,12] and from fluorescence quenching by N,N-dimethylaniline (DMA) of pyrenyl and (9-anthryl)-methyl groups (AN-C) linked to LDPE chains that are not at a film surface[8–10,13] have indicated a surprisingly large decrease in the average free volume of *occupied* LDPE

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dopant sites upon film stretching. Positron annihilation studies confirm that the free volume at *all* sites, as they exist temporally in the absence of guests, is reduced drastically by film stretching[14,15].

Previously, we used the fluorescence from anthracene molecules (ANH) to study secondary α, β and γ polymer relaxation processes in both unstretched and stretched LDPE in the temperature range 15–400 K[16]. Plots of fluorescence intensity *versus* temperature exhibited slope changes near the microscopic relaxation transition temperatures that were ascribed to the cooperative influence of the polymer chain motions on the photophysical properties of anthracene excited singlet states. Temperatures for the polymer relaxation processes, as measured by the guest molecules, were almost the same for stretched and unstretched films. However, the greater magnitude of the slope changes observed in stretched films was explained by a net translocation of ANH molecules from amorphous to interfacial regions.

Here, we extend this study of probe-monitored polymer relaxation processes in two types of LDPE to include AN-C groups, where translocation of the fluorescent groups is not possible. In general, covalent attachment of groups like AN-C allows *quantitative* spectroscopic (diagnostic) measurements to be made *reproducibly* at elevated temperatures and under vacuum. Diffusion and evaporation (or sublimation) of noncovalently attached probes like ANH limit the utility of information obtained from them to lower temperatures. In this work, spectroscopic changes observed from externally applied variations in temperature or degree of stress (i.e. stretching) cannot be attributed to probe translocations. Comparisons between these data and those obtained with the 'free' guest, ANH, provide a more detailed picture of the micromorphological changes suffered by polymethylene chains in the amorphous and interfacial regions and allow a better separation of the lumophoric and environmental causes for fluorescence changes that occur.

EXPERIMENTAL SECTION

The low-density polyethylene films, BLDPE (an additive-free blown type film from Poliolefinas of Brazil) and NDLDPE (Sclair from Dupont of Canada), have been characterized in detail[17]. Each film piece was immersed in three fresh chloroform aliquots for one day each (to remove additives and/or impurities), and dried before being used.

Polyethylene films with AN-C groups were prepared from 9-anthryldiazomethane doped films by a procedure described previously[13]. After covalent attachment and removal of noncovalently attached species, films were cut into two strips and one was cold-stretched by hand over a mandrel to *ca.* 300% its original length.

Room temperature fluorescence and excitation spectra were first recorded at several wavelengths of excitation and emission using a Spex Fluorolog III spectrofluorimeter (linked to a PC) with a 150 W high pressure Xe lamp. Fluorescence measurements ($\lambda_{ex} = 360 \pm 10$ nm) at various temperatures were obtained using an instrument described previously[18]. Films were frozen to 15 K under vacuum in the chamber of a cryostat and then warmed progressively to 405 K. Spectra were recorded at temperature intervals of 10 degrees. Then, the films were recooled and progressively rewarmed while recording the spectra again.

Temporal fluorescence decay profiles and their analyses employed an Edinburgh Instruments FL900 single photon counting system using H_2 as the lamp gas. The film, AN-NDLDPE2 (*vide infra*), was placed in a Kimax flattened capillary tube (Vitro Dynamics) and immersed in methanol. The tube was flame-sealed after three freeze–pump–thaw cycles. It was oriented so that emitted radiation was collected from the back-face of the film.

RESULTS AND DISCUSSION

Characterization of the samples

LDPE films[17]. From elemental analyses of BLDPE and NDLDPE films that had been extensively brominated using 17 wt% bromine in chloroform, the concentrations of double bonds in the noncrystalline regions were approximated. Similarly, *FT*i.r. spectra in the region from 850 to 1000 cm^{-1} allow the total concentration of double bonds in the films to be calculated, and spectral intensities near 1350 cm^{-1} provided the frequency of methyl groups (number of CH_3 per 1000 CH_2). Degrees of crystallinity of the polymers were determined from the heats of melting as measured in d.s.c. thermograms.

The data, summarized in *Table 1*[17], show that the polymers have pronounced morphological and structural differences. BLDPE has the higher frequency of methyl groups, while the NDLDPE is the more unsaturated film. Also, the relative distributions of unsaturated groups in the two films differ.

We reported earlier that the degree of crystallinity of some types of LDPE increases upon stretching[16]. We also noted that the stretching process induces translocation of ANH guest molecules towards crystalline–amorphous interfacial regions (where they experience a much more rigid environment[16]). At the same time, the ANH become partially oriented, with their long axes aligned preferentially along the direction of film stretching[1–4,6,19].

Anthryl groups linked to LDPE – fluorescence spectra. The concentrations of AN-C groups linked to the LDPE (i.e. AN-NDLDPE and AN-BLDPE) were calculated from u.v. absorption spectra assuming that their molar extinction coefficients are the same as those of 9-methylanthracene (9-MA) in cyclohexane ($\epsilon = 9600$ at 368 nm). Five different measurements at different parts of each film were averaged. From optical densities and knowledge of the film thicknesses and densities, the concentrations of anthryl groups were found to be [AN-NDLDPE1] $\cong 10^{-5}$ M, [AN-NDLDPE2] $\cong 2.5 \times 10^{-4}$ M, and [AN-BLDPE] $\cong 1.7 \times 10^{-4}$ M. The very low concentrations and the absence of detectable excimer emissions from the films demonstrate that the AN-C groups are not *aggregated* in a few dopant sites[13].

Room temperature fluorescence and excitation spectra of AN-NDLDPE2 at several wavelengths of excitation and

Table 1 The percentage of crystallinity (χ) and melting temperatures from d.s.c. measurements and concentrations of various C=C bond types, their total (C_M), and of CH_3 groups expressed per 1000 CH_2 units from *FT*i.r. spectroscopy for the polyethylene films without additives[16]

Polymer	Vinylidene	Vinyl	trans-Vinylidene	C_M	CH_3	χ	T_m (K)
BLDPE	0.29	0.12	0.02	0.43	32	31	382
NDLDPE	0.08	0.37	0.04	0.49	25	42	389

emission are presented in *Figure 1*. The wavelength independence of the spectra and their shapes are consistent with the presence of only one type of lumophore, 9-alkylanthryl, being present. Excluding an intensity spike from reflected light, temporal decay curves from AN-NDLDPE2 could be fit to two exponential terms, of which the one with the shorter decay constant was dominant: at λ_{ex} = 389 nm (the maximum of the longest wavelength vibronic band) and λ_{em} = 414 nm (the wavelength of maximum emission intensity), τ_1 = 8.5 ns ($A_1 = 0.965$), τ_2 = 15.5 ns ($A_2 = 0.035$), and χ^2 = 1.037; at λ_{ex} = 369 nm and λ_{em} = 392 nm (the maximum of the shortest wavelength vibronic band), τ_1 = 8.2 ns (A_1 = 0.976), τ_2 = 21.2 ($A_2 = 0.024$), and χ^2 = 1.775. Considering its very minor contribution to the total fluorescence, the τ_2 component can be omitted from further discussion – the decays are essentially monoexponential. The decay constant from the dominant τ_1 component is consistent with emission from a 9-alkylated anthracene[20]. The absence of a significant second decay component signifies that the differing host sites provide very similar electronic environments to the anthryl groups (at ambient temperatures); all of the lumophores are surrounded by polymethylene chains.

Fluorescence spectra of the AN-C labelled polyethylene films at several temperatures are shown in *Figure 2*. The spectra are shifted hypsochromically relative to 9-MA dissolved in hexane, probably due to the higher polarizability of LDPE[21,22]. The intensity of fluorescence of AN-C groups in the three films decreased progressively with increasing temperature due to enhancement of rates of radiationless deactivation processes. Nevertheless, the shapes of the fluorescence spectra are much more dependent on AN-C concentration than on whether the films are unstretched or stretched (designated by the suffix S). The NDLDPE film with a lower concentration of AN-C groups, AN-NDLDPE1, has a vibronic band ratio which is similar to that (10^{-5} M) of 9-MA in nonpolar liquid solvents: the 0,0 emission band is the most intense, indicating that radiative energy transfer[21,22] among AN-C groups is not efficient[16]. This observation is further evidence for the disperse locations of the AN-C groups in the film.

Since the shapes (wavelengths and relative intensities) of the fluorescence spectra during two consecutive heating cycles are very similar, heating the samples in the vacuum chamber of the cryostat causes no apparent loss of the AN-C groups, as expected. By contrast, the same procedure with LDPE containing ANH led to a significant loss of signal due to probe sublimation[16].

Previously, we concluded from dichroic ratios derived from linear dichroism spectra that molecules of 9-MA dissolved in stretched LDPE are slightly more oriented, on average, than AN-C groups in a comparable stretched film. This observation supports the hypothesis that guest molecules tend to translocate when the host film is stretched. Alternatively, it may indicate the presence of orientational restrictions imposed by linking the anthryl moiety of AN-C groups to an LDPE chain. Regardless, 9-MA and AN-C do not reside in equivalent sites within an LDPE film, but both sense acutely the directing influence of neighbouring polymethylene chains[13].

Relaxation processes – unstretched and stretched films

Plots of the dependence of fluorescence intensity (I_F), integrated over the wavelength (λ) range of emission, *versus* temperature (T) and their corresponding Arrhenius-type curves for the first heating of unstretched and stretched films

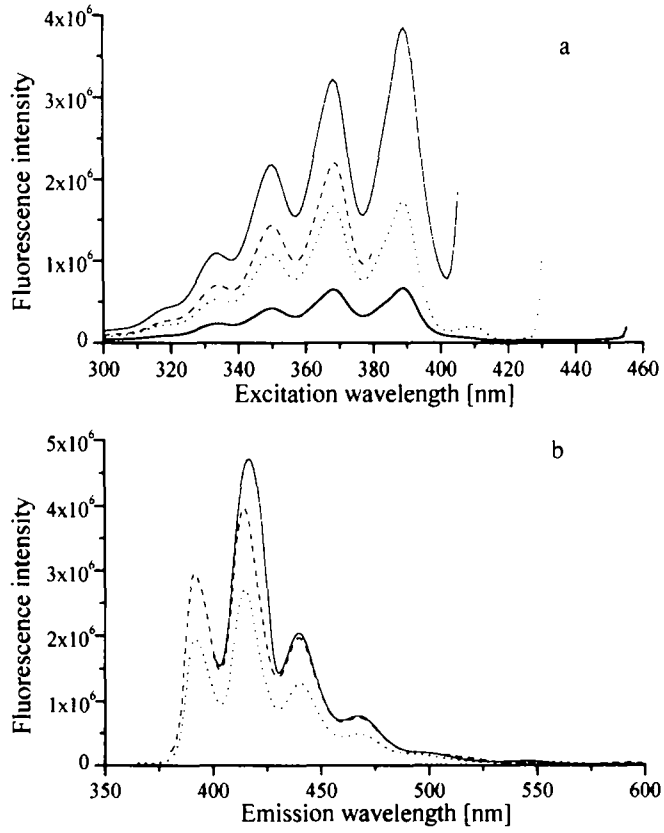

Figure 1 Room temperature excitation (a) and emission (b) spectra for AN-NDLDPE2 at λ_{em} = 392 (——), 415 (- - -), 440 (· · ·), and 467 nm (——) for (a) and λ_{ex} = 389 (——), 369 (- - -), and 351 nm (· · ·) for (b). The red-edge intensity increases in (a) are due to excitation radiation leaks to the detector and should be discounted

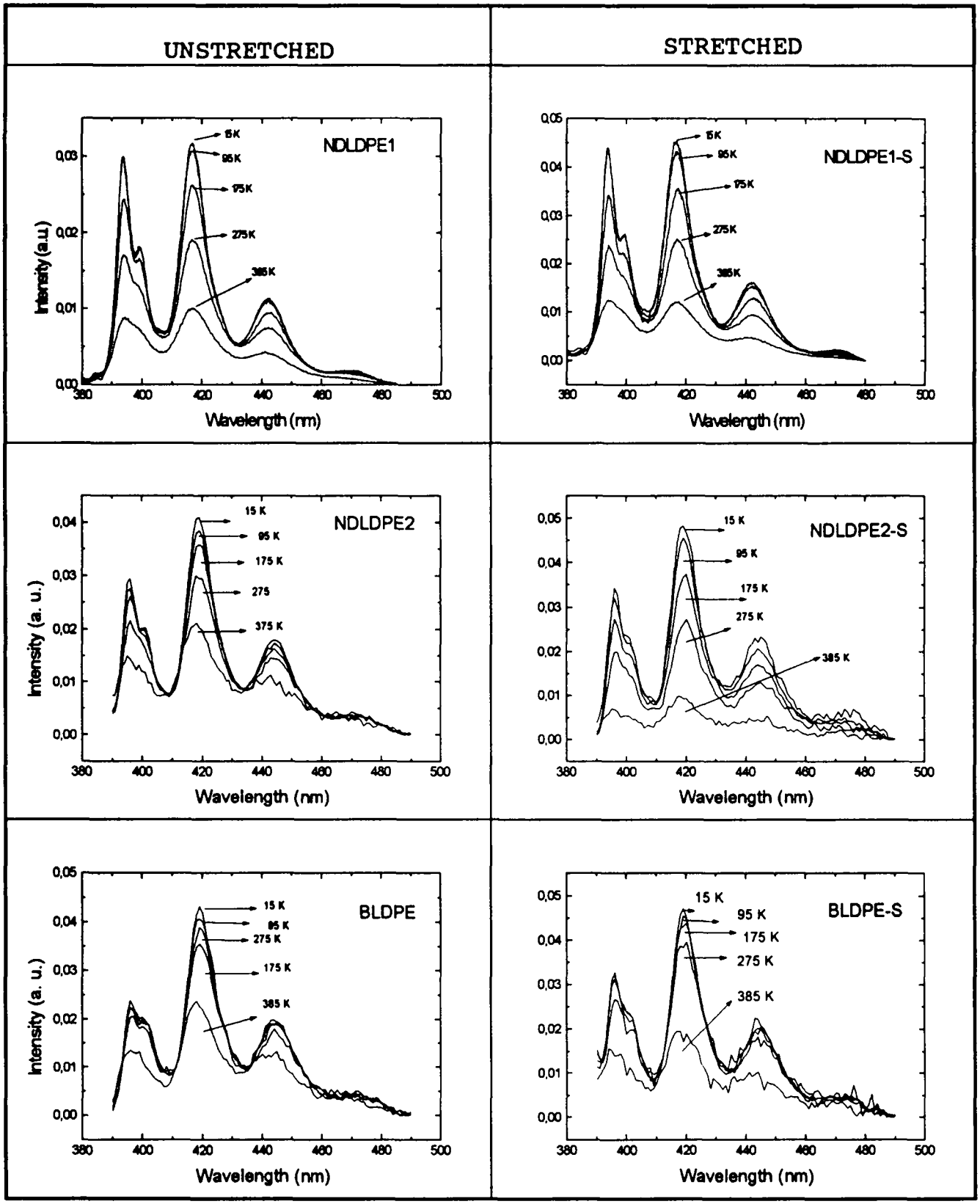

Figure 2 Fluorescence spectra for AN-C groups in LDPE films at several temperatures. First heating

are shown in *Figures 3 and 4*, respectively. The Arrhenius plots are not linear over the whole temperature range, but exhibit some pronounced slope changes at temperatures that can be correlated with the onset or cessation of relaxation processes of the host polymer. The only two somewhat nonlinear continuous segments are above the onset temperature of the fluorescence-based α-relaxation process T_α (*ca.* 320 K).

The method of calculation of transition temperatures from fluorescence intensity data involves interpolation of points of intersection between straight-line segments selected in *Figure 3* (and, in some cases, *Figure 4*) on the basis of correlation coefficients of fits over various temperature ranges; additionally, since data points are at 10 degree intervals, the intrinsic (minimum) error in the points of intersection is $\pm$ 5 deg. In several cases,

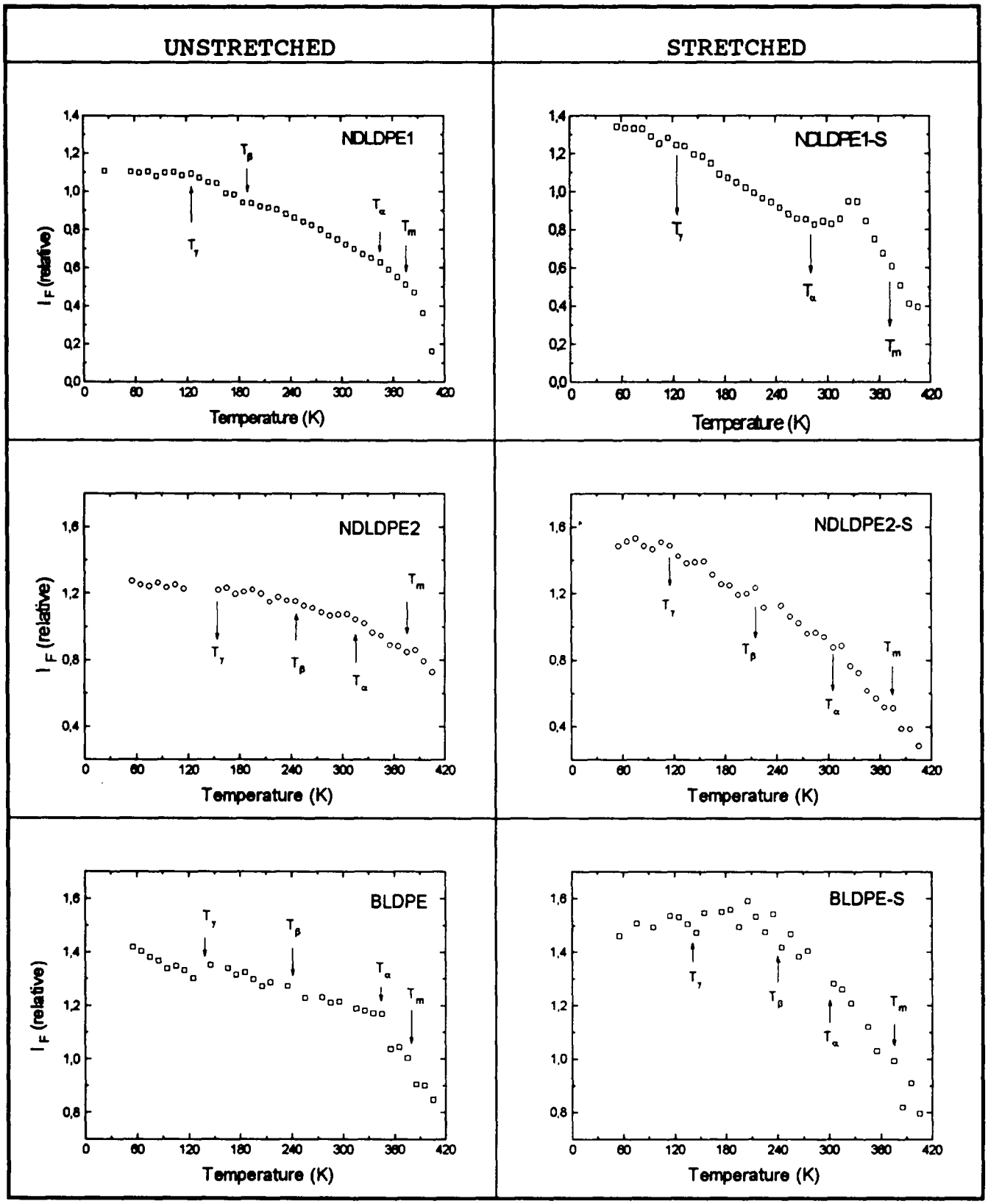

Figure 3 Fluorescence intensity (I_F) integrated over emission wavelengths *versus* temperature for AN-C groups in unstretched and stretched (S) LDPE films. First heating

especially for AN-BLDPE-S, the intersection points are not visually obvious. In such cases, for which the slope changes are small, the potential error is clearly larger.

The discrepancy between the melting temperatures (T_m) from differential scanning calorimetry (d.s.c.; *Table 1*) and fluorescence measurements (*Table 2*) is not surprising. First, the fluorescence-derived value is not very precise. More importantly, the fluorescence experiments report the relaxation at sites which contain, by necessity, a disturbing group. In essence, the presence of a probe group depresses the *locally monitored* T_m and, potentially, the temperatures of the relaxation processes occurring especially at the more ordered interfacial sites and/or in stretched films. AN-C fluorescence is a reporter of *microscopic* change, whereas

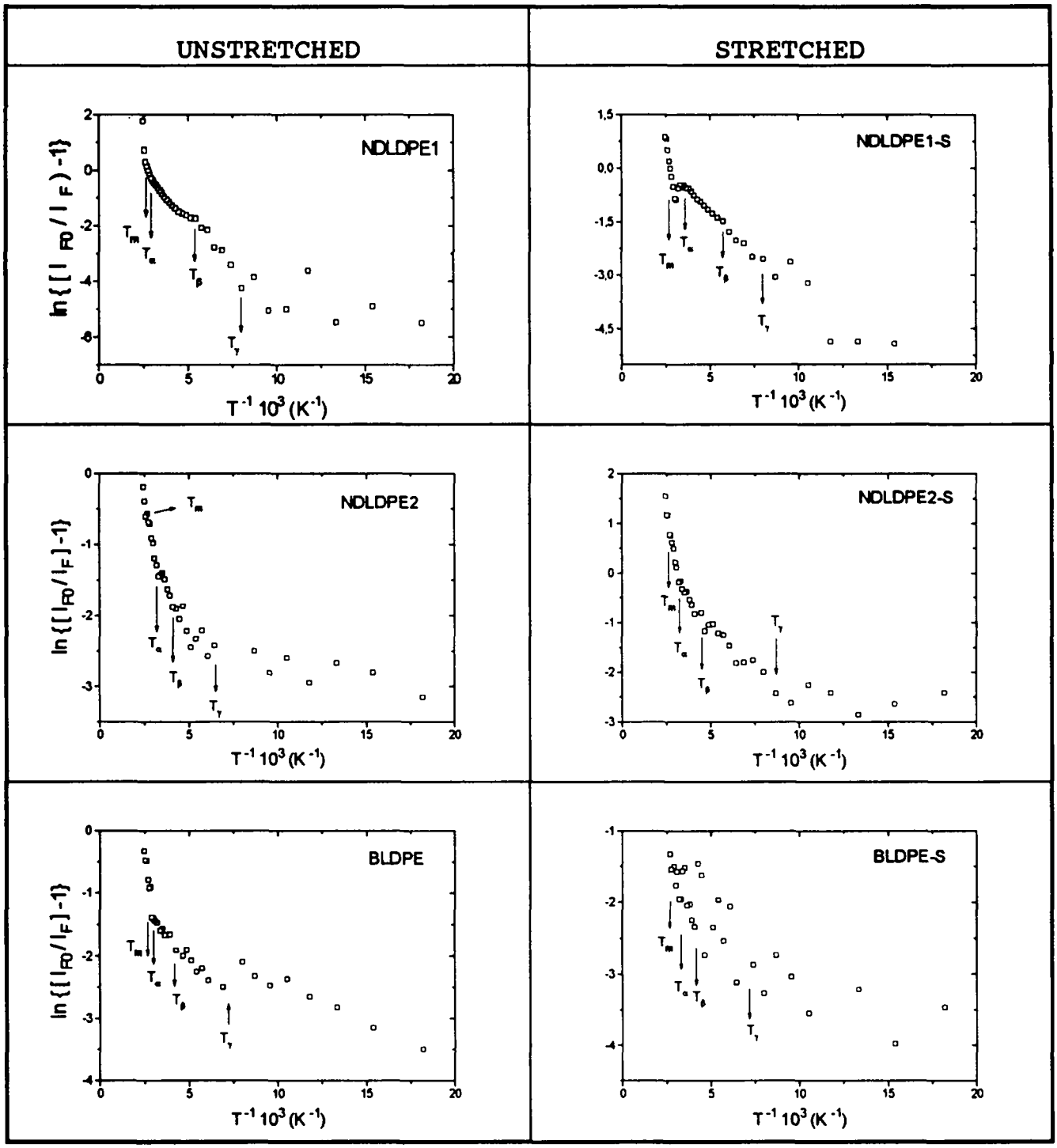

Figure 4 Arrhenius plots of the data in *Figure 3*. I_{F0} is defined as the fluorescence intensity at 55 K

Table 2 Approximate temperatures of LDPE melting and relaxation processes from linear and Arrhenius plots of fluorescence intensity *versus* temperature for stretched (S) and unstretched films during first and second heating cycles. Values are determined from fluorescence intensity changes (*Figure 3*) unless noted otherwise. See text for details

AN-LDPE	Cycle	T_γ (K)	T_β (K)	T_α (K)	T_m (K)
NDLDPE1	1	125	190[a]	345	375
NDLDPE2	1	155	245	315	375
NDLDPE1-S	1	125[a]	180[a]	280[a]	375
NDLDPE2-S	1	115	215	305	375
NDLDPE2	2	155	215	315	375
NDLDPE2-S	2	165	245	305[a]	375
BLDPE	1	140	240	340	380
BLDPE-S	1	140	240	300	375
BLDPE	2	155	250	325[a]	375
BLDPE-S	2	155	213	325	375

[a] Values determined from Arrhenius plots (*Figures 4 and 5*)

d.s.c. detects *bulk* changes. On this basis, the values reported for onset temperatures by fluorescence intensity changes should be considered as lower limits to the T_m of unmodified films; the data reported here are most valuable when compared internally and analysed to obtain *qualitative* trends.

In the Arrhenius-like treatment, it is assumed that all radiationless deactivation processes for the fluorescent groups can be described by a unique activation energy. As a corollary, lumophores located in different site types of the polymers are required to suffer deactivation processes with the same efficiency and with the same temperature dependence. However, AN-C groups are located at sites within the amorphous and interfacial regions. Conceptually, they should influence somewhat differently the excited singlet state decay pathways, even within one temperature regime provided $T < T_m \simeq 380$ K[16,23,24]. Based on the wavelength independence of the excitation and emission spectra and the single decay constant from single photon counting experiments employing AN-NDLDPE2, the limiting temperature can be reduced further to below room temperature.

The chain orientation and mobility of the interfacial region are intermediate between those of crystalline and amorphous regions, and the chain density is assumed to be near that of the crystalline region[23]. The thickness of the interfacial region has been estimated experimentally and theoretically to be 10–30 Å[24]. As such, it represents a significant fraction of the polymer volume. Therefore, the experimental curves for the Arrhenius plot represent a weighted average of the temperature dependence of fluorescence intensity from AN-C groups in the two families of site types.

Significant changes in the shape of the fluorescence intensity and Arrhenius plots (*Figures 3 and 4*) occur when the films are stretched. In order to compare differences between unstretched and stretched films, the temperatures of slope changes between almost linear segments of the Arrhenius plots were compared with the onset temperatures of the various LDPE relaxation processes. Although the plots of fluorescence intensity dependence on temperature for the unstretched films follow almost the same profile (*Figure 3*), those for the stretched films are rather different. This implies that there are significant differences between the relative populations of AN-C groups in the amorphous and interfacial regions in NDLDPE and BLDPE films, and that the decay modes of anthryl excited singlet states are more sensitive to the more restrictive sites offered by stretched films.

Arrhenius curves for the fluorescence intensity of AN-C groups in the films during the first and second heating are shown in *Figure 5*. The shapes of curves from an unstretched film differ only slightly in consecutive runs; possibly, some strain present before heating is annealed during the first run[1]. The curves of the first and second runs using stretched films show important differences, and do not

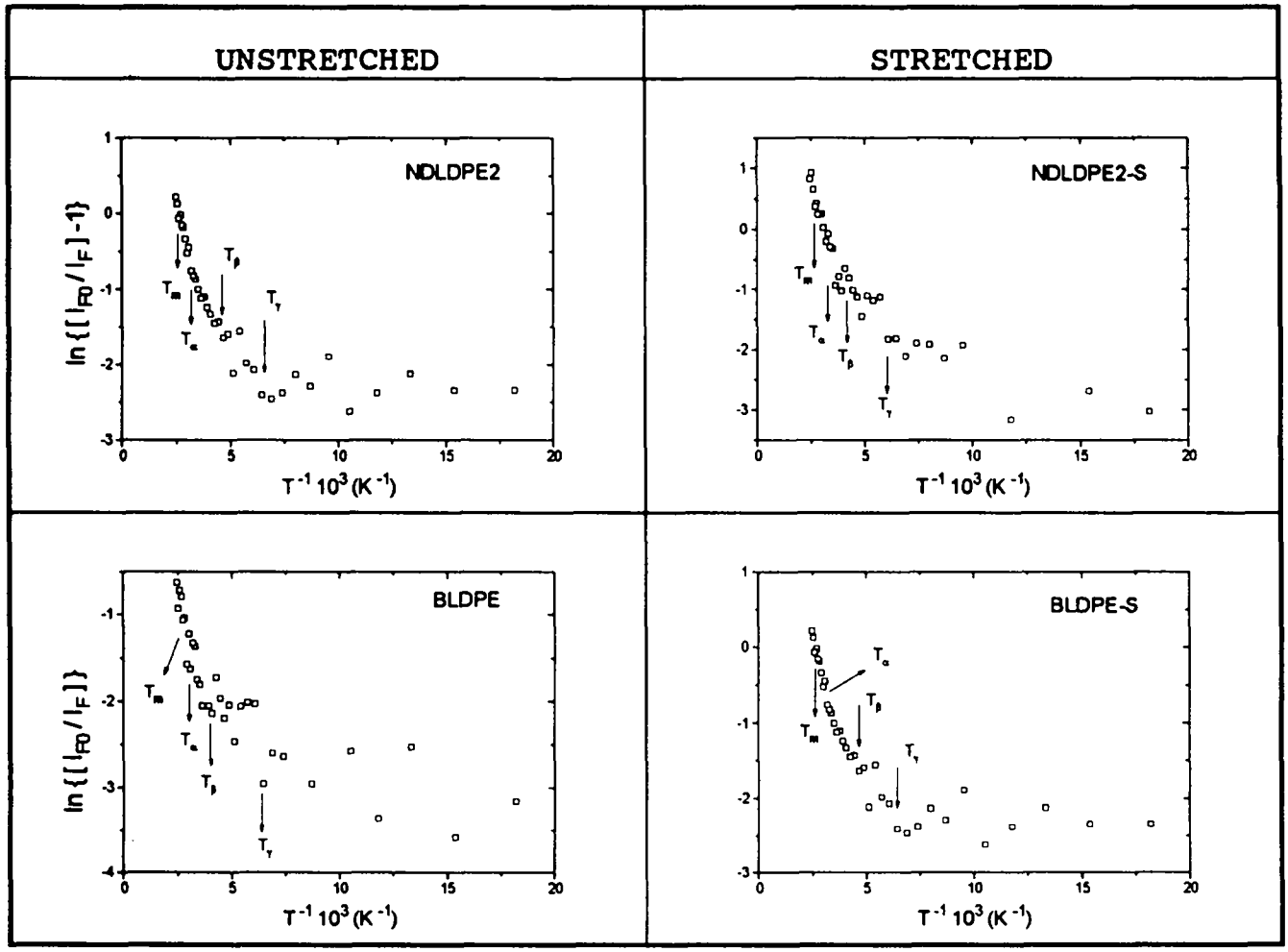

Figure 5 Arrhenius plots of the dependence of the integrated fluorescence intensity on temperature for AN-C groups in BLDPE and NDLDPE2 films as in *Figure 4*. Second heating

resemble the corresponding curves from unstretched films. There, the induced strain is initially very large, and the probe groups report its alleviation as temperature is raised. The major differences between the plots for the first and second scans appear at lower temperatures, where polymer relaxation processes involve only motions of short chain segments. The AN-C groups sense, on average, different environments in unstretched and stretched films since macroscopic stretching induces morphological changes in the polymer matrix, including movement of chain segments with attached AN-C groups.

The γ-relaxation process. In the region between 55 and 150 K (*Figures 3 and 4*), the largest changes in fluorescence intensity occur in AN-NDLDPE1-S (i.e. the stretched film with the lowest AN-C concentration). Significant temperature dependence of the fluorescence intensity is noted above 130 K for the unstretched films and above 110–120 K for the stretched ones. Cooperative polymer–fluorophore relaxation processes are very insensitive to temperature in this range (i.e. far below the glass transition temperature, T_g) for the stretched films with low AN-C concentrations. In such rigid matrices, there is very little movement during the lifetime of excited singlet states of AN-C groups (*ca.* 8.3 ns) or the chain segments to which they are attached. Therefore, the most important contribution to changes in fluorescence intensity should be unimolecular internal conversion processes.

In a related study, we have found that the efficiency of radiationless internal conversion processes of dispersed ANH molecules is much lower in stretched than in unstretched films[16]. Using the hypothesis of stretching-induced translocation, this result can be explained on the basis of the fluorescence emanating from ANH molecules in different sites. Fluorescence intensity in the films reflects a weighted average of occupied site types convoluted with the quantum efficiency for emission from each. When a film is stretched, probe translocation alters the relative populations of the occupied sites, and the *normalized* fluorescence characteristics of the aggregates change. In unstretched films, where the mole fraction of ANH probes in the amorphous region is presumed to be higher than in stretched films, the fluorescence is weighted toward emissions from more disordered, more mobile environments. In stretched films, the mole fraction of ANH probes is increased in interfacial sites, where chains are presumed to be stiffer and more organized, and the available free volume is smaller[8–10,13]. Since molecules in the stiffer, more organized interfacial sites are less able than those in amorphous sites to move at a given temperature, their fluorescence is less sensitive to *changes* in temperature within a range that does not include a first- or second-order phase change.

In contrast, the changes in fluorescence intensity at or near relaxation temperatures for films with AN-C groups are more pronounced in stretched LDPE (*Figure 3*), revealing a greater sensitivity of the covalently attached anthryl excited singlet states to their local environments. Although AN-C groups are partially oriented by film stretching, they are forced to remain, to a greater extent than ANH probes, in more flexible domains (i.e. the amorphous region). Another consequence of their covalent attachment is that the AN-C groups are, on average, in a more stressed environment in stretched films. Increasing temperature within a range, therefore, has a greater tendency to alter AN-C environments in a stretched film than in an unstretched one.

The onset of γ-relaxation is known to involve motions of short segments (three to four methylene groups) within the noncrystalline regions of the LDPE chains[5,16,25,26]. We have suggested that the free volume generated by the γ-relaxation process is smaller than that necessary for diffusion or even rotation of ANH molecules and, consequently, the cooperative motions of the polymer chains affect unimolecular radiationless rate constants only to a small degree.

The β-relaxation process. The second nearly linear segment of the Arrhenius fluorescence plots occurs in the 150–250 K temperature range that includes the onset of the β-relaxation process. It is attributed to the mobility of the chain branches located in the amorphous region of polyethylene films[26]. Motions of chain segments whose dimensions are at least as long as an ANH molecule seem to be involved since the free volume generated is large enough to allow diffusion of ANH molecules and to cause temperature-dependent changes in the rates of bimolecular probe processes[16,25,26].

The chain motions should induce partial disruption of the order imposed by macroscopic stretching (*Figures 3 and 4*). Thus, AN-C groups, due to their linkage to chains, are able to sense β-relaxation processes, and the motions are sensed more acutely in (stressed) stretched films. Since ANH molecules can translocate upon film stretching to interfacial regions (where chain branches must be rare), they are expected and found to be less sensitive to relaxation in stretched than in unstretched films; very small slope changes are detected in their Arrhenius plots near 230 K.

The α-relaxation process. Besides the intrinsic increase in rates of nonradiative processes at higher temperatures, the fluorescence profiles in *Figure 3* above 320 K show that the intensity also depends upon whether the films are unstretched or stretched. In both the unstretched and stretched films, slope changes near 320–340 K and 380 K (the fluorescence-detected T_m) are discernible. In AN-NDLDPE-S, however, the lower temperature slope change is at 300–320 K and there is a pronounced intensity maximum at *ca.* 330 K. Given the low concentration of AN-C groups in this film, the source of the fluorescence intensity changes must be related primarily to unimolecular events caused by changes in chain motions near the occupied sites.

α-Relaxation of polyethylene is considered to be due to at least three types of different motions of chains below T_m, each of which is associated with the crystalline phase of the polymer[27]. As such, α-relaxation must also lead to increased chain mobility in the interfacial region, including the partial loss of anisotropy induced in long chain segments by film stretching.

The unexpected increase in fluorescence intensity observed for AN-NDLDPE-S may be due, in part, to the molecular alignment of AN-C groups since both electronic absorption and emission are polarized processes and the excitation radiation is probably somewhat linearly polarized. Then, only molecules or groups properly oriented will be excited. Once orientational order of the AN-C groups is lost due to α-relaxation processes, more anthryl groups may be excited (leading to a higher emission intensity) *if* the average initial film anisotropy places the lumophores in orientations that are less favourable for excitation than the relaxed (partially random) distribution. At still higher temperatures, where complete randomization is expected, the intensity of fluorescence decreases due to a combination of more efficient radiationless decay and, perhaps, a smaller

number of AN-C groups being oriented at any moment for excitation.

GENERAL CONSIDERATIONS

The Arrhenius plots in *Figure 4* report temperature-induced changes in the *total* fluorescence intensity, integrated over all λ_{em} values. [A strictly rigorous calculation of the area under the emission curves should involve integration over $1/\lambda$, a quantity directly proportional to energy. However, the difference between the results in *Figure 3* and from rigorous calculations is small since the wavelength range of the integration is narrow.] Consequently, they are a convolution among concentration effects, bimolecular quenching, and

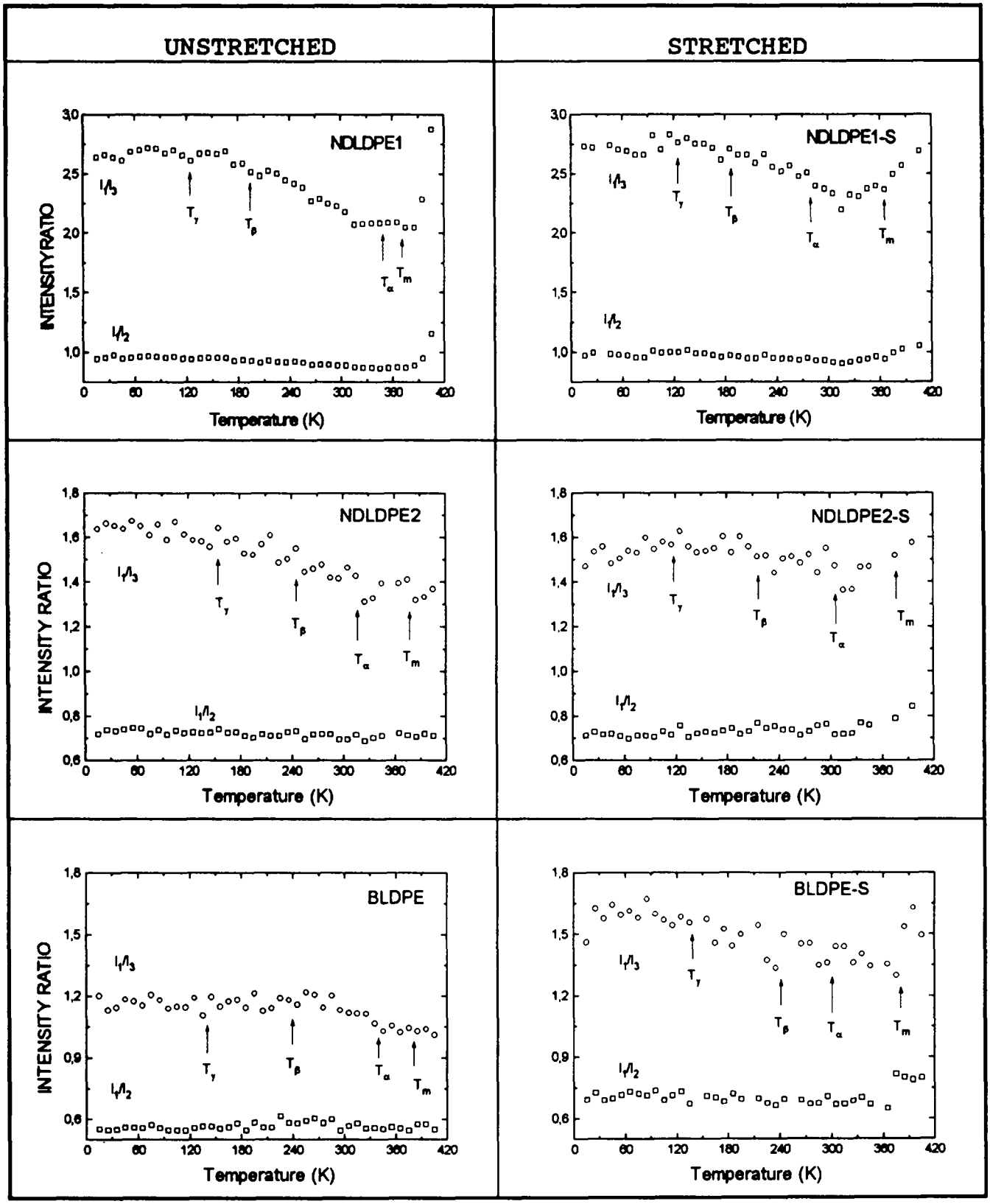

Figure 6 Intensity ratios of the vibronic bands I_1/I_2 and I_1/I_3 *versus* temperature for AN-C groups in LDPE. $\lambda_1 = 395$ nm, $\lambda_2 = 418$ nm, and $\lambda_3 = 442$ nm. First heating

unimolecular rate processes. The significant differences observed between plots from more dilute and more concentrated AN-NDLDPE films show that intermolecular energy transfer becomes important (at the higher concentration) as AN-C congregation increases. Since the method of AN-C attachment involves swelling of the LDPE by diethyl ether to introduce the precursor, 9-anthryldiazomethane, followed by removal of the swelling solvent prior to the thermal attachment reaction[13], there is a limited ability of the anthrylmethyl groups to select their positions within a film. As the 'preferred' sites for a guest in one region of the polymer become 'saturated', the remaining guests must find less attractive locations in another part of the polymer. At higher bulk concentrations, a larger fraction of the preferred sites in specific parts of a film has been occupied.

Figure 6 shows the dependence of ratios of emission intensities for vibronic bands at 395 nm (I_1) and at 418 nm (I_2) or at 395 nm and 442 nm (I_3). Since only the 395 nm band overlaps significantly the absorption spectrum of AN-C, changes in I_1 with respect to I_2 or I_3 provide a convenient measure of the relative contribution of *radiative* energy transfer[22]. Both ratios are much smaller in the more concentrated AN-NDLDPE2 film. Thus, radiative energy transfer is important even at *ca.* 10^{-4} M label even though it is negligible at these concentrations in isotropic liquid films. Similar results were obtained for ANH in LDPE[16]. The efficiency of *radiative* energy transfer depends on both concentration and sample thickness[22]. The *effective* distance travelled by a photon to traverse a semicrystalline film, like LDPE, is somewhat longer than the film thickness, d, due to diffractions. Regardless, the greater the distance that an emitted photon travels within a film with AN-C groups, the greater will be the probability of its reabsorption by another anthryl moiety.

The significant contribution of radiative energy transfer in AN-NDLDPE2 requires that the anthryl groups be congregated (but not aggregated) in specific regions of a film. Taking into account that the guests are precluded from entering the crystalline part of a film[5], the actual volume available to them is only 69% (for BLDPE) and 58% (for NDLDPE) of the total. Even with correction for this excluded volume, the concentrations employed, assuming an even distribution of guests, is inadequate to account for the observed energy transfer: from Beer's law, the optical density at the 0,0 absorption band (where significant overlap with the emission occurs) is < 0.1. Previous work points to the interfacial parts as regions where guests prefer to reside[4,6,7]. Whether additionally some of the amorphous parts tend to accept guests more readily than others cannot be determined with the data at hand.

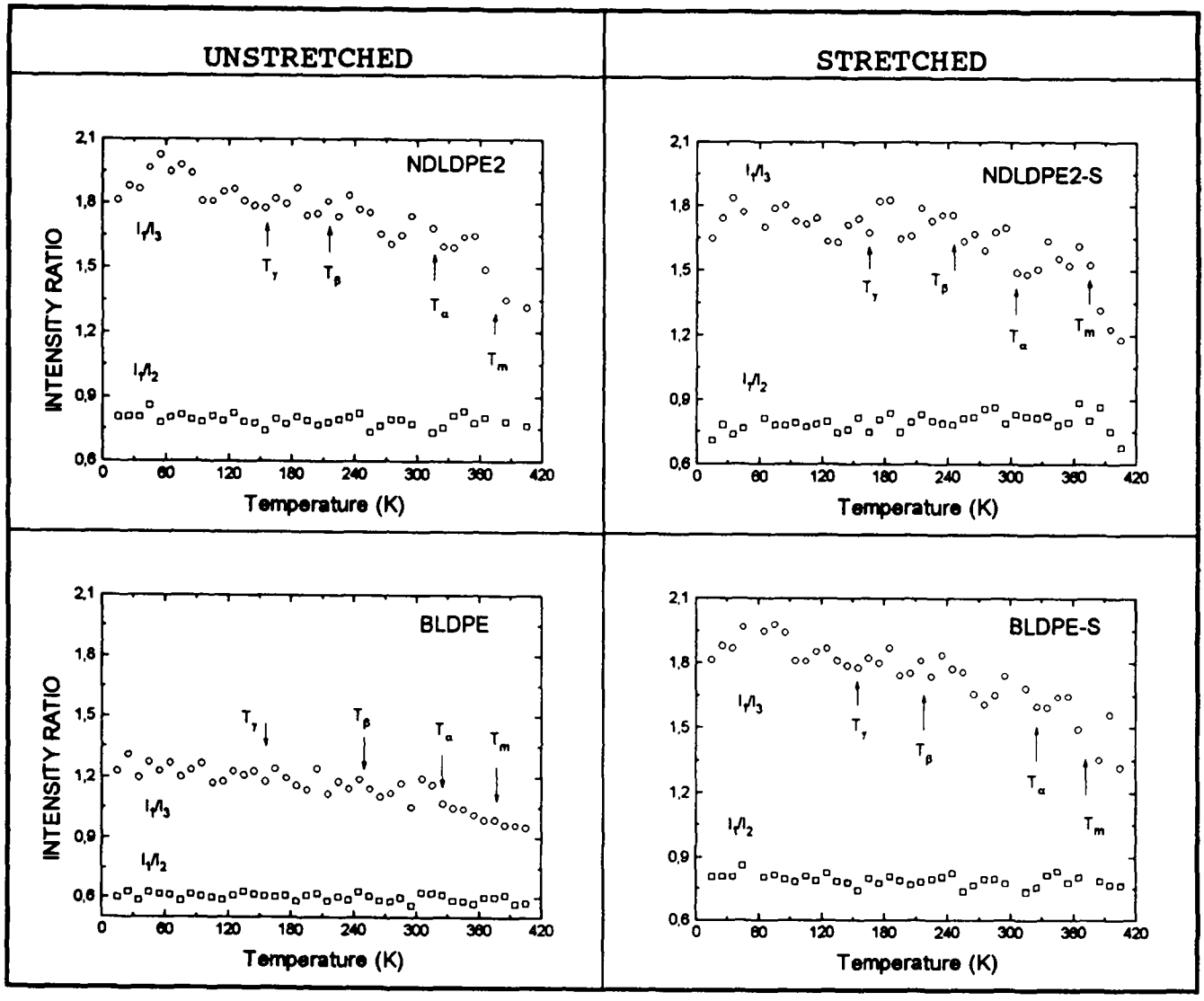

Figure 7 Intensity ratios of the vibronic bands I_1/I_2 and I_1/I_3 *versus* temperature for AN-C groups in LDPE films as in *Figure 6*. Second heating

There is a slight increase of the intensity ratios for the stretched films with covalently attached anthryl groups at temperatures above 380 K, the onset of LDPE melting. The increase is larger for the more concentrated AN-NDLDPE2-S and AN-BLDPE-S films (*Figure 6*). However, the intensity ratio changes are rather different from those obtained from ANH in LDPE[5,16,25,26], where there is an abrupt increase above T_m due to the reduction of ANH concentrations as a result of sublimation. We hypothesize that initially parallel (or nearly parallel) AN-C groups are able to relax, making the electric vector of their emitted photons lie in planes that are less likely to lead to reabsorption by other AN-C groups. As expected from the arguments above, only the stretched films have significantly differing intensity ratios for first and second heating runs (*Figure 7*). During the second heating, the orientation of AN-C groups induced by stretching is lost (in the first heating run), and the ratios are similar to those expected from a thinner unstretched film.

CONCLUSIONS

Although the LDPE films in this work have some chemical (structural) and morphological (degree of crystallinity) differences, the temperatures (especially in the subambient range) at which fluorescence from AN-C groups and ANH probes exhibit large changes are similar and can be associated with the onset of polymer relaxation processes. On this basis, we conclude that the AN-C are linked to the same site types in NDLDPE and BLDPE, and that the number (but not distribution) of site types occupied does not change with increasing anthryl concentration (in the range explored). However, fluorescence spectra of AN-C groups are strongly dependent on probe concentration and film crystallinity due to a combination of medium-based factors (e.g. site distributions) and photophysical factors (e.g. the efficiency of radiative energy transfer).

Since fluorescence intensity *versus* temperature plots are different for unstretched and stretched films of the same polymer type, film stretching must influence the factors mentioned above. Specifically, stretching partially orients AN-C groups, allowing radiative energy transfer to occur more easily. These data and the conclusions derived from them support conclusions from other studies employing dichroic absorption and fluorescence quenching as experimental tools.

A specific advantage of AN-C groups is that they are not removed from the film at high temperatures and they are not able to diffuse within a film independent of the polymer chains to which they are attached. ANH probes are lost at high temperatures and *do* diffuse independent of the polymer chains.

Plots of integrated fluorescence intensity of AN-C in LDPE *versus* temperature exhibit slope changes that can be correlated with the *relaxation* of chain segments of the polymer hosts. Arrhenius-type plots for the fluorescence intensities from AN-C in unstretched or stretched films exhibit distinct, almost linear regions with slope changes at temperatures near the onset of the γ-, β- and α-relaxation processes and melting of LDPE. The influence of macroscopic stretching is greater on AN-C groups than on ANH probes, further supporting the hypothesis that stretching induces translocation of guest molecules toward interfacial regions.

Plots of the vibronic band intensity ratios of AN-C and ANH emissions *versus* temperature are quite different. These differences can be ascribed to the ability of the ANH probes to undergo diffusional motion in the LDPE matrices at higher temperatures and the inability of the AN-C groups to do so, coupled with the effects that diffusion (or a lack thereof) has on the efficiency of radiative energy transfer.

Although *significant* changes in the onset temperatures for the polymer relaxation processes for stretched and unstretched films, as monitored by ANH probes, are not observed, they are always lower for stretched than unstretched films when monitored by AN-C groups. Moreover, the temperature dependence of integrated fluorescence intensities for AN-C groups and ANH labels in the same type of LDPE are rather different for both unstretched and stretched films; the fluorescent reporter groups do not appear to be distributed in the same way between amorphous and interfacial sites in unstretched and stretched films. The data suggest that AN-C groups are both oriented by nearby polymer chains and their motions are controlled by the polymer chain segments to which they are linked. Therefore, their radiationless deactivation processes are strongly affected by the cooperative motions of the polymer matrix[28–30].

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