

Dependence of relaxation processes in a low-density polyethylene with different crosslink densities investigated by fluorescence spectroscopy

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Abstract

Relaxation processes of one type of low-density polyethylene with three different degrees of crosslinking were studied using the fluorescence of 1-pyrenyl groups attached covalently to polymer chains. The average molecular weights between crosslinks (M_c) of the polyethylenes were 125, 76.5, and 7 kg mol⁻¹. As assessed by changes of the integrated fluorescence intensity and the full width at half maximum of the 0–0 emission band with temperature, chain mobility decreases with increasing crosslinking density. Chain mobility in the polyethylene with the smallest M_c value appears to be strongly inhibited up to 220 K, while motions of small segments of the polymer chains were observed for samples with lower crosslinking degrees at temperatures similar to those of the pristine (non-crosslinked) polymer. These data are discussed in terms of local versus bulk properties of the films.

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1. Introduction

Polyethylene is a generic name for polymers from ethylene monomers. Due to the various polymerization processes, polyethylenes with a variety of chemical structures and properties can be produced, each type targeting a specific application [1,2]. One specific use of polyethylene is the isolation of electrical cables because polyethylene combines good insulating, mechanical and thermal properties. In particular, crosslinked low-density polyethylene (XLPE) has been replacing low-density and high-density types of polyethylene for this purpose [3–6] because crosslinked polyethylene retains better its mechanical properties under shear and has better water treeing resistance.

Evaluation of the mechanical properties, thermal transitions and other relaxation processes in polymers can be studied by several techniques. Some are related to bulk properties (differential scanning calorimetry (DSC), dynamical-mechanical thermal analysis (DMTA), dielectric relaxation, etc.) and others (nuclear magnetic resonance, fluorescence spectroscopy, etc.) can investigate mechanisms for many relaxation processes at the molecular level [7,8]. In a recent publication, we compared the relaxation processes of an intrinsically fluorescent, conjugated polymer using DMA, nuclear magnetic resonance, fluorescence spectroscopy and thermal stimulated current depolarization. That study demonstrated that fluorescence data also recorded for this polymer are sensitive to all of the polymer relaxation processes expected, including some which occur at temperatures where the other techniques cannot be used [7,8]. Fluorescence spectroscopy is a very sensitive, non-destructive technique which can access secondary relaxation processes and phase transitions, such as melting

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of semicrystalline polymers and formation of glasses from rubbery states [7–16]. It is also a reproducible technique; when two polymer samples of the same kind are examined, plots of their fluorescence intensities (or related treatments of fluorescence data) versus temperature undergo slope changes at very similar temperatures. However, the magnitudes of the intensity changes may not be the same due to small variations in the distributions of the probes among their potential sites in different pieces of the polymer [7–16].

Relaxation processes of polyethylene involve several types of macromolecular motions. In the order of increasing temperature, the relaxation processes can be described as follows: $T_\gamma = 150$ – 200 K is attributed to the onset upon heating of motions of small segments of chains located in the amorphous phase or motions of folded chains in the interphase (i.e., amorphous–crystalline) regions [17,18]; the source of $T_\beta = 195$ – 280 K is still controversial, with some assignments as a glass transition and some as relaxation processes involving side chains at the lamellar interfaces [19,20]; $T_\alpha = 300$ – 350 K involves relaxation processes in the crystalline phase or shearing of lamellar surfaces [20]. In a recent report [21], some of us used dynamical-mechanical analyses (DMA) to demonstrate that the β -relaxation (240 – 270 K), as opposed to other transitions, was not affected by crosslinking density, indicating that the transition is related to the side chains of LDPE.

In some of our previous reports, all of the aforementioned relaxation processes of polyethylene were accessed using fluorescence spectroscopy, with a lumophore either as a guest molecule [14,16,23] or covalently attached to polymer chains [11,12,15]. One of the major advantages of fluorescence spectroscopy over DMTA, DSC, dielectric relaxation, and thermally stimulated current techniques for probing macromolecular transitions and relaxations is the exceedingly wide range of temperatures that can be used. Other advantages include (1) the ease of sample preparation, since samples of practically any size and shape can be studied, (2) the high sensitivity of the emission characteristics of appropriately selected lumophoric probes to local motions, as a result of the strong interactions between the electronically excited state of a lumophore and its local environment, and (3) the ability to investigate local chain motions as opposed to the bulk relaxations accessible from DMA and DMTA measurements. Any increase in thermal fluctuations or thermally activated motions of the environment near the lumophore will modify the electron–phonon coupling and, consequently, both increase the efficiency of non-radiative deactivation of the excited state and decrease the fluorescence intensity [7–16,22–25]. Conversely, changes of the environment emanating far from the lumophores will not be sensed by them. Fluorescence monitors local changes as opposed to bulk changes. Its sensitivity, therefore, depends on a convolution of the distribution of lumophores location and the places within the polymer where changes in chain motion occur.

Here, we extend our studies using the fluorescence of covalently attached pyrenyl groups to monitor relaxation processes in some crosslinked low-density polyethylenes [12,13,15].

To assure the ability to compare results directly, materials with three distinct crosslinking densities were produced chemically by the thermolysis of dicumyl peroxide in one type of polyethylene [26]. The polyethylenes are almost non-fluorescent materials under our experimental conditions. Pyrenyl is an efficient fluorescing group with well-characterized vibronic emission bands and an excited singlet lifetime in the range of 200 ns at room temperature when attached to polyethylene chains [12,27,28]. Therefore, its emission can be detected even at temperatures as high as 400 K.

2. Experimental

2.1. Materials

Low-density polyethylene (LDPE), from Polietilenos S.A. Brazil, had average $M_w = 135$ kg mol⁻¹, polydispersity = 9, density = 0.921 g cm⁻³, and melt index = 3.8 g/10 min according to data from the supplier. Data for the types and number of branches were not disclosed by the manufacturer. However, it is known that the polydispersity of this type of highly branched polymer is always very high. Although a complete and definitive characterization of this polyethylene would require a separate NMR study, we can estimate that ethyl and butyl side chain groups are separated on average by 30–40 carbon atoms along the main chain [29].

Samples of previously milled and sieved LDPE in powder form, containing 0.50, 1.00, and 1.50% w/w dicumyl peroxide (DCP), were molded in a model PHS 15 SHULZ press. Samples in the form of disks (diameter of 11 cm) were separated from the aluminum molds by cellulose acetate sheets. The thermal pressing was performed under a load of 4 tons during 5 or 15 min at 150 °C, 5 min at 160 °C, and 15 min at 170 °C [26].

This protocol yielded samples with average molecular weights between crosslinks (M_c) of 125 kg mol⁻¹ (XLPE125), 76.5 kg mol⁻¹ (XLPE76), and 7 kg mol⁻¹ (XLPE7), respectively. The crosslinking level was evaluated by measurement of the gel content in the XLPE samples. Determination of the molecular weight between crosslinks is based on equilibrium swelling tests that are described in detail in Ref. [26]. Gel content determinations were performed using decalin (Vetec PA) as a solvent. Weighed samples of about 0.1 g and 20 mL solvent were placed in a 100 mL round-bottomed flask connected to a condenser. They were refluxed (190 °C) for 6 h. After drying to constant weight (about 16 h) at 70 °C, the extracted samples were re-weighed and the fraction of crosslinked material was calculated from the initial and final masses. Average film thicknesses were determined using a Mitutoyo micrometer. Other experimental details are described in Refs. [22,30] and some physical properties are summarized in Table 1.

Slices of the XLPE films were immersed in *n*-heptane and chloroform to remove residual DCP and its decomposition by-products, and subsequently left in a 10⁻⁴ mol L⁻¹ 1-pyrenyl-diazomethane [27,28,31,32] in *n*-heptane solution overnight in the dark. The films were then rinsed with ether to remove

Table 1
Some physical properties of the XLPE samples

Sample	M_c (kg mol ⁻¹)	L (mm)	T_m (K)	$W_{(XR)}$ (%)	$W_{(DSC)}$ (%)
XLPE125	125	0.954	385	47	50
XLPE76	76.5	0.929	385	45	54
XLPE7	7	0.957	383	46	54

M_c is the average molecular weight between crosslinks; L is film thickness; T_m from DSC; $W_{(XR)}$ (%) from X-ray diffraction is the ratio between the area of the crystalline diffraction peaks and the total area of the scattering; $W_{(DSC)}$ is the ratio between the melting enthalpy and the theoretical value from Ref. [1].

any 1-pyrenyl-diazomethane molecules from the surface, dried under a stream of nitrogen, sealed in a Pyrex flask under vacuum, and irradiated with a 450 W Hanovia medium pressure Hg arc lamp (filtered for $\lambda_{exc} > 300$ nm) during 1 h. After irradiation, the XLPE films were washed repeatedly in hexane and ether baths (to remove impurities and non-attached pyrene derivatives) until UV–vis absorption spectra of the last wash showed no evidence of pyrenyl moieties.

2.2. Methods

The concentrations of 1-pyrenyl groups covalently attached to the crosslinked polyethylene samples, $1-5 \times 10^{-5}$ mol kg⁻¹, were estimated by ultraviolet absorption spectroscopy at 343 nm using Beers law and assuming that their molar extinction coefficient is the same as that of 1-ethylpyrene in *n*-hexane (4.1×10^4 L mol⁻¹ cm⁻¹) [15].

Steady-state fluorescence emission and excitation spectra were recorded at room temperature using an ISS-PC1 single-photon counting spectrofluorimeter with a 300 W Xe arc lamp or from 20 to 410 K using an instrument described elsewhere [30] in which the sample is held under vacuum in a cryosystem. Excitation wavelengths (λ_{exc}) were 350–400 nm and emission wavelengths (λ_{em}) were 390–600 nm depending on λ_{exc} .

Dynamic fluorescence decays were recorded by the time-correlated single-photon counting (TCSPC) technique on a nF900 Edinburgh Analytical Instruments apparatus, operating with a pulsed H₂ lamp at a repetition frequency of 40 kHz and $\lambda_{exc} = 345$ nm and $\lambda_{em} = 397$ nm. Films for these experiments were flame-sealed at 10^{-4} Torr pressure in flattened Pyrex capillaries (VetroChem). The fluorescence decays $F(t)$ were analyzed by deconvolution of the lamp pulse, recorded using a solution of LUDOX™ (DuPont) with the impulse response of the sample. The data were analyzed by the exponential series method (ESM) [33–34]. The ESM uses a fixed set of lifetimes and fits to freely adjustable pre-exponential factors (B_i) that are constrained to be positive. Here, B_i represents the weight fraction of each exponential decay in our experiments. The search for the best fit uses the Marquardt algorithm to minimize the reduced χ^2 (goodness of fit).

X-ray diffractograms were obtained in the range $2^\circ < 2\theta < 50^\circ$ on a SHIMADZU-3A X-ray diffractometer employing a Cu K α source ($\lambda = 1.54$ Å) operating at 20 mA and 30 kV. Melting points of the films (T_m) were determined using a DuPont model v2.2A 90 differential scanning calorimeter, calibrated with indium as a standard. Samples initially at

room temperature were cooled to 150 K at 20 K min⁻¹ and then heated at 10 K min⁻¹ to 420 K. Three cooling–heating cycles were recorded.

3. Results and discussion

3.1. Polymer characterization

The T_m values from DSC measurements are based on the averages of three heating and cooling cycles per sample (Fig. 1). Measurements were performed on crosslinked films after photochemical attachment of pyrenyl moieties and cleaning as described in Section 2. As can be seen, the temperature at the maximum heat flow is practically independent of the scan number and is independent of the crosslinking degree (Table 1). The XLPE glass transitions were not detectable by DSC under our experimental conditions. The crystallinity degree can be determined using the ratio between the experimental enthalpy of melting and the enthalpy of melting of a 100% crystalline polyethylene estimated as 286 kJ g⁻¹ [1]. The probable reason for the lack of a systematic dependence of the crystallinity degree and melting temperature on the crosslinking density (Table 1) is that these samples were further manipulated after the crosslinking process.

X-ray diffractograms of the three films (the same samples for which we measured DSC) were recorded and the degree of crystallinity ($W_{(XR)}$, %) was calculated from the ratio of the area of the crystalline peaks and the area of the total diffraction and scattering bands [34]. These and the DSC data provided the final crystallinity of the samples used for the fluorescence measurements. Fig. 2 shows the diffraction pattern of XLPE7; the patterns of the other samples were very similar. As also observed from DSC data (Table 1), the calculated degree of crystallinity by X-ray diffraction is independent of the crosslinking level. Differences observed for the crystallinity degree obtained using DSC and X-ray diffraction can be attributed to the intrinsic differences of these two methodologies [15].

In a previous report with materials which were not manipulated after crosslinking, it was noted that the crystallinity degree increased with increasing gel content and that the melting endotherm in DSC thermograms became broader as crosslinking in polyethylene increased [21]. Nevertheless, other reports using electrons beam for inducing crosslinking showed that the crystallinity of low-density polyethylene was almost independent of the crosslinking density [4]. Similar results have been obtained by irradiating LDPE with lower energy photons than those employed here, but a change in the spatial distribution of the crystallites into the polymeric bulk is observed as the crosslinking degree is raised by irradiating with higher energy photons [15]. The major distinction among these experiments is that in some cases the crosslinking was performed using polymer films at room temperature while others employed melts. Therefore, the dependence of the crystallinity degree on the crosslinked ratio is still an interesting open question because of the variable experimental conditions.

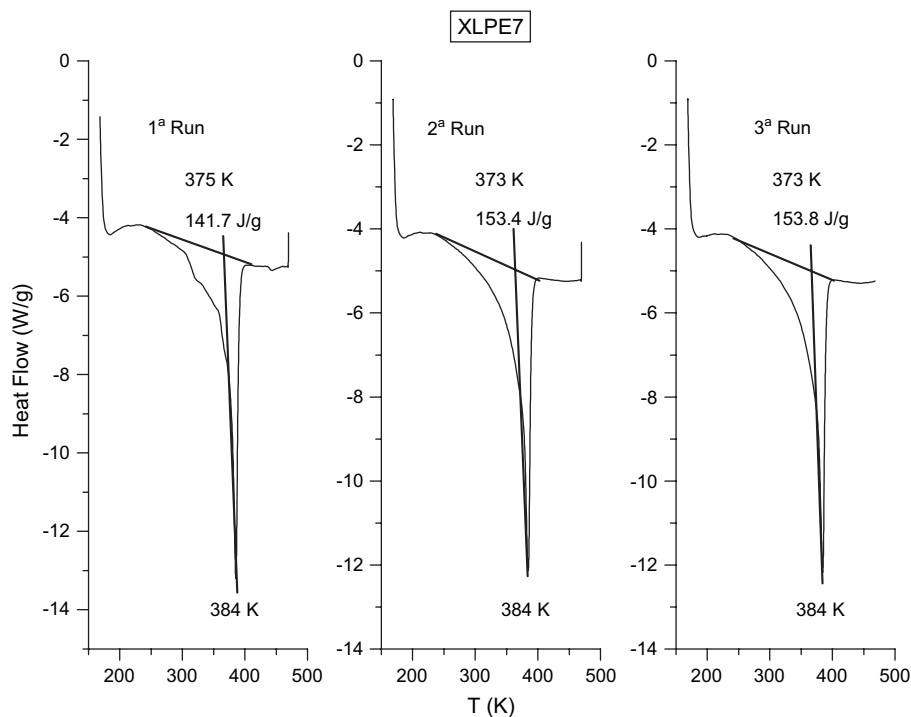


Fig. 1. Three successive DSC heating thermograms for XLPE7. Scan rate = 10 K min⁻¹.

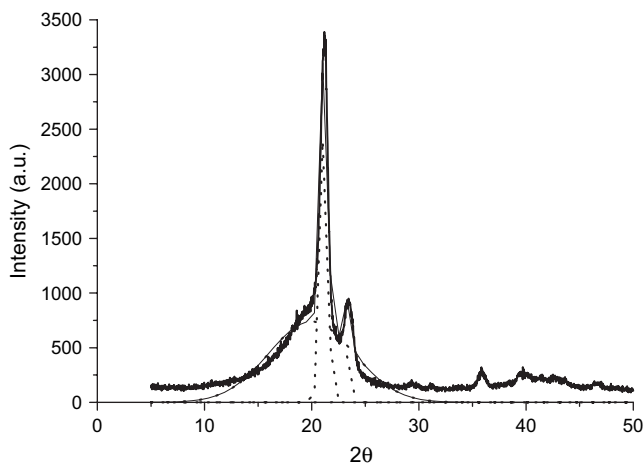


Fig. 2. X-ray diffraction pattern of XLPE7. Lines (...) represent the result of deconvolution of the total pattern into its amorphous and crystalline scattering components and (—) is the reconvoluted total pattern.

Nevertheless, we observe here by two independent methodologies that these three samples of very different crosslinking degrees have approximately the same crystallinity. Consequently, the results from the fluorescence data cannot be explained in terms of differences of the degree of crystallinity.

From prior work [12,15,31], it is known that neither the crosslinking reaction nor the photochemical attachment of 1-pyrenyl groups occurs within the crystalline parts of polyethylene because guest molecules cannot penetrate the interiors of the crystals [22,35–38]; pyrenyl moieties are attached to polymer chains in the amorphous regions and along the interfaces between the crystalline and the amorphous phases.

3.2. Steady-state fluorescence spectroscopy

The steady-state fluorescence spectra of pyrenyl moieties attached to the XLPE are very similar to those of 1-alkylpyrenes [11,15,27,28] (Fig. 3). The independence of the shapes of emission spectra profiles in relation to excitation wavelengths ($\lambda_{\text{exc}} = 328, 334, \text{ and } 345 \text{ nm}$) strongly suggests that one positional isomer of pyrenyl, 1-pyrenyl, is attached predominantly to the polymer chains. Also, the very low bulk concentrations of pyrenyl groups and the lack of detection of excimer emission lead us to conclude that if 1-pyrenyl groups are near each other, they are unable to interact within the lifetime of their excited singlet states, and, more likely, they are well separated from each other. Regardless, the efficiency of fluorescence of individual 1-pyrenyl groups must depend on the intrinsic molecular rate constants of their radiative and non-radiative processes [39,40].

In agreement with the lack of dependence of the steady-state emission spectra on λ_{exc} and the crosslinking density, the fluorescence decay curves from time-correlated single-photon counting experiments could be fitted well to biexponential functions; the principal decay constant, representing >92% of the total, was between 180 and 220 ns and was independent of excitation wavelength (Fig. 4). As expected, these times are somewhat shorter than those obtained for pyrene as a non-covalently attached guest molecule in polyethylene matrices and are similar to the decay constants for other 1-alkylpyrenyl derivatives (Table 2) [11,27,28]. The second decay constant, ca. 40 ns, may result from (1) the effect of different polyethylene sites on the pyrenyl group, (2) formation of another weakly emitting species created by film irradiation,

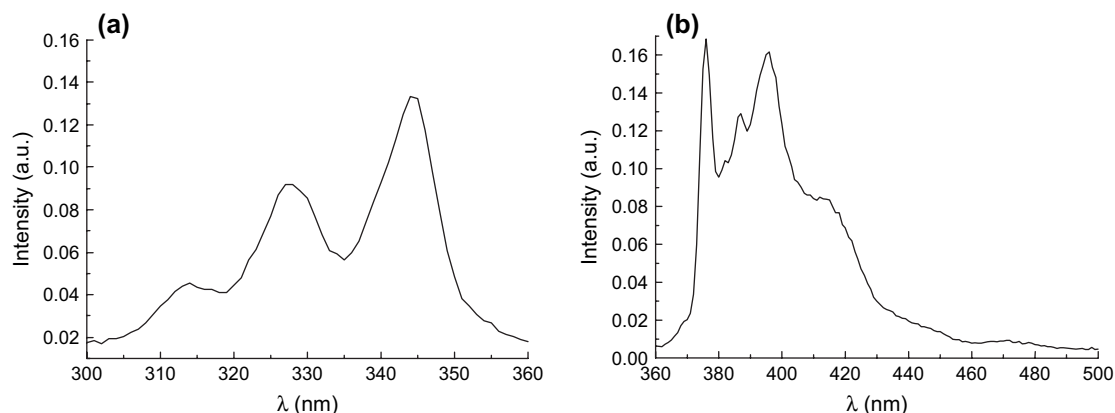


Fig. 3. Room temperature excitation (a) ($\lambda_{em} = 397$ nm) and emission (b) ($\lambda_{exc} = 345$ nm) spectra of 1-pyrenyl groups attached to XLPE125. Spectral shapes obtained for this film and for the other films at this and other λ_{em} and λ_{exc} were virtually the same.

(3) formation of a second pyrenyl derivative, and finally (4) by the presence of a small fraction of pyrenyl groups in sufficient proximity to allow intermolecular interactions without the ability to form a “relaxed” excimer. Fluorescence decay of a blank film ($\lambda_{exc} = 345$ nm; $\lambda_{em} = 377$ nm; crosslinked but without pyrenyl groups) shows an exceedingly weak emission with a time constant of ca. 65 ns. Consequently, we assume that the faster emission in the films with appended 1-pyrenyl groups (τ_2) arises from a species copolymerized with the polymer chains that cannot be removed by swelling and washing the films according to our experimental protocol. Furthermore,

Table 2

Fluorescence decay constants (τ_F) and fractional components (B) of 1-pyrenyl groups attached to XLPE films

Film	τ_{F1} (ns)	B_1 (%)	τ_{F2} (ns)	B_2 (%)	χ^2
XLPE125	180 ± 0.5	92	39.0 ± 0.4	8	1.186
XLPE76	222 ± 0.3	94	43.0 ± 0.6	6	1.227
XLPE7	217 ± 0.6	95	43.0 ± 0.5	5	1.067

$\lambda_{exc} = 345$ nm, $\lambda_{em} = 397$ nm.

we were unable to detect specific evidence for the presence of an excimer in the 1-pyrenyl appended film since no discernible emission was found by steady-state fluorescence at the expected emission wavelengths ($\lambda_{em} \approx 450$ nm); attempts to record TCSPC decays at 450 nm resulted essentially in ‘noise’, and no component of the decay curves with a protracted rise time was observed. On these bases, if an excimer is present, its concentration must be inconsequential mechanistically and the τ_{F2} components in Table 2 most likely are a result of species intrinsic to the crosslinked polymer. The absence of excimer emission is particularly important for the study of polymer relaxation processes using fluorescence spectroscopy because the photophysical descriptions are based on the temperature dependence of the non-radiative deactivation processes that include all sort of the uni- and bi-molecular events. Although unimolecular processes may be described by Arrhenius functions in the solid state, the dependence of bi-molecular energy transfer and excimer formation processes on the temperature are very complex and no analytical solutions are currently available. Therefore, a minimum contribution from bimolecular processes is necessary to accommodate our data. Furthermore, since no electronic absorption bands other than those intrinsic to pyrenyl monomers are available, we concluded that the population of ground state “dimers” is also very low.

The native crosslinked XLPE (i.e., without covalently attached or doped pyrenyl moieties) showed a residual weak emission that is detectable in TCSPC (time-correlated single-photon counting) experiments. It may arise from a larger concentration of copolymerized extraneous species with low emission quantum yields or a lower concentration with

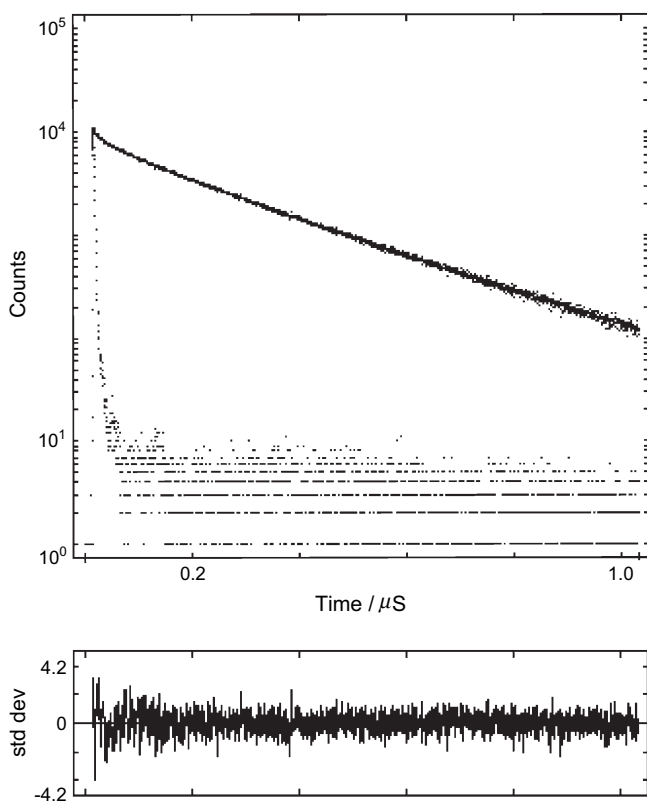


Fig. 4. Representative fluorescence decay curve for 1-pyrenyl groups attached to XLPE7 at room temperature. $\lambda_{em} = 397$ nm; $\lambda_{exc} = 345$ nm. A plot of the residuals is shown below and $\chi^2 = 1.067$ for a fit to a biexponential function.

a high quantum yield. Based upon the absence of new bands in the electronic absorption spectrum, we conclude that the concentration of these species is very low and their presence has no significant importance on the photophysical properties of the pyrenyl lumophores.

3.3. Temperature dependence of fluorescence emission intensity

Fluorescence spectra were recorded in the 20–410 K temperature range for the three films. Fig. 5 shows the spectra for

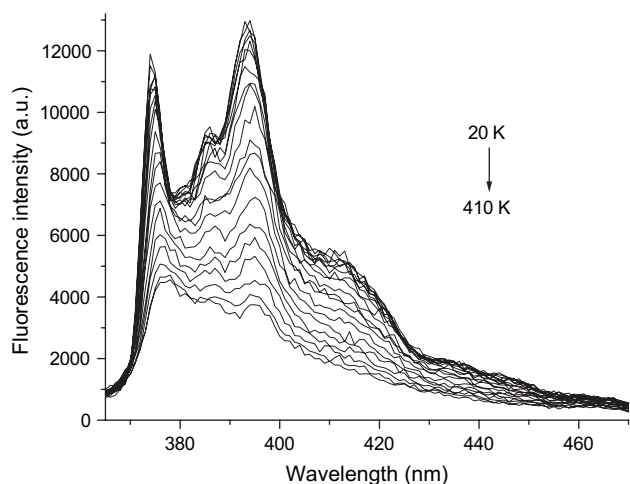


Fig. 5. Fluorescence spectra of 1-pyrenyl groups attached to XLPE125 films as a function of increasing temperature (20–410 K). ($\lambda_{\text{exc}} = 345$ nm). The arrow indicates the order in which the spectra were recorded.

XLPE125; the spectra of the other samples are very similar. As a result of the more rapid acceleration of non-radiative processes in relation to radiative ones with increasing temperature, the integrated emission intensity (n.b., the relative integrated area for emission between 360 and 470 nm, I_F) decreases as temperature is raised (Fig. 6). If the decrease of the intensity was due exclusively to unimolecular, non-radiative processes, the slope of this plot and for those of the other films would decay monotonically and exponentially with the increasing temperature [10,39,40]. They do not because the host matrix undergoes subtle changes at distinct temperatures (n.b., onsets of relaxation processes) and the effects of those changes are transmitted via phonon coupling to the excited singlet states of the 1-pyrenyl groups, regardless of the specific nature of their local perturbing influence [7,8,11–16,22,41].

The slope changes in the I_F plots in Fig. 6 can be ascribed to the influence of the onsets of particular polymer relaxation processes at distinct temperatures. We define the temperature of the relaxation process as where it is first observed during heating (i.e., the point of slope change). To be considered a valid slope change, we have adopted a protocol in which the new slope must be maintained at least along the next three higher temperatures. This methodology is intended to eliminate effects from small changes that originate from “noise” or from instrumental instabilities. In addition, as discussed below, we have compared the onset values from integrated fluorescence intensity measurements with those determined using changes in the full width at half maximum (FWHM) of the 0–0 emission band. Although the data arise from the same spectral measurement, they describe different phenomena: fluorescence intensity depends on the ratio between the

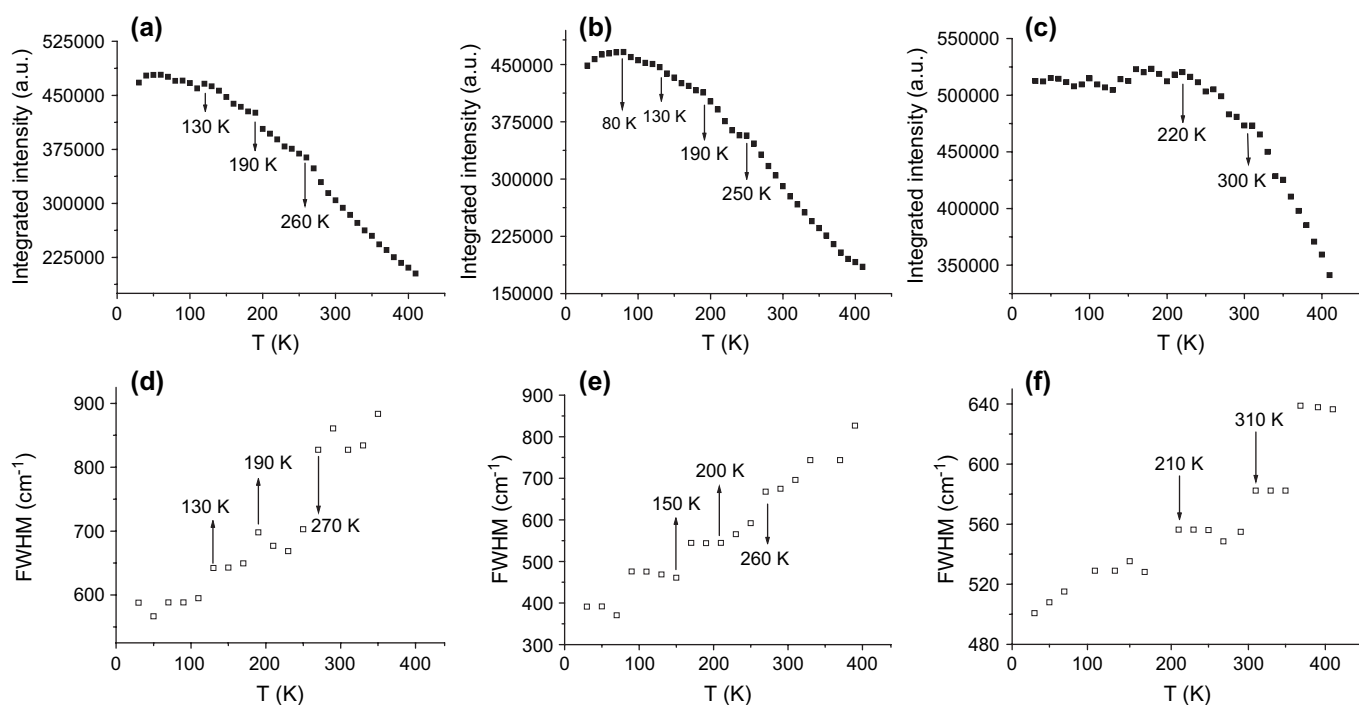


Fig. 6. Integrated fluorescence intensities (I_F) and full widths at half maxima for the 0–0 emission bands (FWHM, cm^{-1}) versus temperature for covalently attached 1-pyrenyl groups in (a,d) XLPE125, (b,e) XLPE76, and (c,f) XLPE7.

radiative and several non-radiative rate constants; the FWHM of the 0–0 emission band depends on the Franck–Condon state distribution of excited singlet pyrenyl environments as well as on the correlation among excited state deactivation rate constants, as they are affected by the relaxation processes of the medium around the fluorophore [25,40].

Since the temperature increment between measurements is 10 K, our onset temperatures cannot be more precise than ± 10 K. The effects of polymer chain motions from relaxation processes near a lumophore are additive; each additional process (occurring at higher temperatures) contains the contribution(s) of the one(s) that were initiated at lower temperature(s). As a result, the slope changes are larger at higher temperatures.

The observed profiles for curves I_F versus temperature for XLPE with lower crosslinking densities (Fig 6a,b) are very similar to those previously observed for other polyethylene samples [12–16,22,25]. Nevertheless, the profile for that with higher ratio is different. The confidence that these changes represent different types of polymer motions comes from several of studies with other polyethylene samples. They provide profiles of I_F versus temperature curves from different pieces of the same polyethylene in which the slope changes occur at virtually the same temperatures although the slope changes are somewhat different in magnitude. Therefore, fluorescence spectroscopy yields reproducible relaxation temperatures. Here, samples of the *same* polyethylene type but with *different* crosslinking densities behave differently.

In addition, the spectra in Fig. 5 show that the 0–0 emission band at 377 nm becomes progressively broader as temperature is increased. The full widths at half maxima (FWHM in cm^{-1}) of the bands at 377 nm were estimated by deconvolution of the 0–0 and neighboring bands using Gaussian functions, and the results are plotted versus temperature in Fig. 6 for the three XLPE samples. Above 340 K, precise FWHM measurements of the 0–0 bands could not be obtained because of their broadness and low relative intensity. In polymeric media, such as the ones employed here, broadening effects resulting from coupling between vibronic and rotational modes of the electronic excited state of the lumophoric group and its local environment, when there are new dipolar charge distributions within the excited state that promote reorganization by the polymer around the lumophore, and the rates of that reorganization and of excited state decay by the lumophore (ca. $1/200$ ns or 5×10^6 s^{-1} , at room temperature, for our 1-pyrenyl groups) are comparable. Spectra can also be broadened in the solid state if lumophores experience more than one microenvironment in which relaxation is much slower than the decay of the excited states [40]. In both cases, the observed envelope, which is a convolution of several slightly different spectra, is influenced by temperature because the electron–phonon coupling changes with the viscoelastic properties of the host [25,41]. At the lowest temperatures employed here, both factors contribute to the FWHM but the 0–0 band is somewhat narrower because the chain relaxation processes are much slower than the decay of the excited states [25]; as temperature is increased and the rates of relaxation of the chains become comparable to that of excited state decay, the changes

in the FWHM are due primarily to relaxation of the microenvironment.

The observation that the FWHM from fluorescence spectra in Fig. 5 for the covalently attached 1-pyrenyl groups are broader than those from pyrene guest molecules in LDPE [25] is a result of the inability of the covalently linked species to diffuse with time and temperature to different regions of the polymer that might be more amenable as guest sites. The covalently attached 1-pyrenyl groups are forced to remain in sites with a broader distribution of chain conformations [11–15]. The measured FWHM for 1-pyrenyl groups attached to polyethylenes are 150 – 180 cm^{-1} , while they are 130 cm^{-1} or less for pyrene doped polyethylene samples [15,26]. In both cases, the FWHM undergo changes at temperatures which are typical of the onset of the polyethylene relaxation processes [15,26]. This observation adds to our confidence that our fluorescence method provides valid measurements of the onsets of the relaxation processes because the microenvironments around the covalently attached and doped lumophores are not necessarily the same. In the three crosslinked XLPE studied here, there should be a correlation between the onset of the relaxation processes and abrupt changes of FWHM because the native polyethylene from which the crosslinked materials were prepared is the same, the photochemical process to attach the 1-pyrenyl groups is the same, and the samples were submitted to the same physical and chemical treatments. The crosslinking ratio is the only parameter that has been changed.

As noted, the emission spectra broaden in a fashion that is not monotonic because the host undergoes relaxation processes that begin at specific temperatures. The precipitous increases in FWHM noted in Fig. 6 are another manifestation of the initiation of polymer relaxation processes. Therefore, assignment of the onset of XLPE relaxation processes can be made from either the I_F or FWHM data in Fig. 6, but the best approach is to use both.

3.4. Detection of XLPE relaxation processes

We ascribe the smooth slope changes in Figs. 6 and 7 near 300–320 K to the onset of melting of crystalline portions of the XLPE films. At first glance, the DSC thermograms in Fig. 1 do not appear to be consistent with this attribution. However, the curved portions in the figure indicate that crystallites of different sizes are melting at different temperatures. Apparently, fluorescence intensity changes became sufficiently large to be detected only after melting of a fraction of the smallest, lower-melting crystallites, but certainly before melting of the larger crystallites is completed at 373 K. The melting onset is better defined in XLPE7 than in XLPE76, and is almost undetected in XLPE125. The onsets of the relaxation processes are expected to occur near 130 K (γ -relaxation), 190–220 K (β -relaxation), and 240–270 K (α -relaxation) [19,22,42].

There are at least three well-defined slope changes, at ca. 130 K, ca. 190 K, and 260–270 K, which can be identified in Fig. 6 for XLPE125. In analogy with other LDPE relaxation processes, the lowest temperature one is assigned to the onset of the γ -relaxation (i.e., to the freeing of motions of short

polymer chain segments) [11,12,14,19,20,22]. The second at 190 K is consistent with the onset of β -relaxations [11,12,14,19,20,22]. The excursion at 260 K can be attributed to the onset of α -relaxations (involving motions at interfaces between the amorphous and the crystalline regions) [11,12,14,15]. These processes are reasonably well defined in the curves for XLPE76 as well, but not in those for XLPE7 (the material with the highest crosslinking degree) for which only fluctuations of the integrated intensity are observed.

These assignments are facilitated by the fact that the onset temperatures for the XLPE and non-crosslinked LDPE are found at similar temperatures [11,12,14,15]. At the beginning of this study, it was not obvious that they would be. Furthermore, after the well-defined I_F slope change at 260 K for XLPE125 and at 250 K for XLPE76, there is a marked decrease of I_F , followed by an increase in the spectral broadening. These changes require the appearance of new large amplitude motions in the vicinity of the 1-pyrenyl groups, perhaps involving very long chain segments of the polymer chains.

As noted, the response of the emission from XLPE7 to temperature was different from that of the other two XLPE films: the onset of the first clear intensity decrease, at 220 K, is higher than the onset temperature of the β -relaxation processes of LDPE ($T = 180$ K), XLPE125 ($T = 190$ K), and XLPE76 ($T = 190$ K). The second, larger I_F change was observed at 300–310 K, a temperature also higher than those observed for the onsets of the α -relaxation processes of XLPE125 ($T = 260$ K) and XLPE76 ($T = 250$ K). The higher temperatures indicate that the mobility of the chains in the XLPE7 polymer is reduced as a result of the more frequent intersections of chains (i.e., higher degree of crosslinking). The lack of detection by pyrenyl moieties of a lower temperature relaxation process in XLPE7 suggests that these probes are located in rather rigid cavities at temperatures as high as 190 K. This observation is also indirect evidence that the pyrenyl groups are not attached very near to the ends of polymer chains or to smaller branched segments which are strongly involved with the γ -relaxation processes [18]. Pyrenyl groups attached to polymers with a lower degree of crosslinking are able to detect γ -relaxation processes, even though they may not be attached to branched segments, because the environments

around the electronically excited groups through which electron–phonon coupling is transmitted are somewhat disturbed.

Recently, the onsets of two relaxation processes in XLPE, one between 240 and 270 K (assigned to a β -relaxation) and other around 200 K (assigned to a γ -relaxation), that were apparent only in aged samples, have been detected by DMA [21]. The onset temperatures of both were nearly independent of the crosslinking degree (gel content). Our fluorescence-based results are at variance with these observations. Our onset temperatures for the α -relaxations in the 240–270 K region move to higher temperatures in the order, XLPE125 (260 K) \sim XLPE76 (250 K) $<$ XLPE7 (310 K) (Fig. 6), and indicate that the environment around the 1-pyrenyl groups becomes stiffer with increasing gel content (and crosslinking density). This conclusion is supported by similar changes in onset temperatures for the β -relaxations: 190 K for XLPE125 and XLPE76 and 220 K for XLPE7. Whereas DMTA measures a weighted average of motions occurring in all regions of a polymer, our fluorescence techniques report only on local regions that are near a lumophoric group. The information from the two techniques is complementary. Another representation of these changes is provided by Arrhenius-type plots of the integrated intensities using the formula, $\ln(1 - I_F/I_{F20}) = A - E_a/RT$ (Fig. 7). Here, I_{F20} is the integrated intensity at 20 K, the lowest temperature where measurements have been made.

The decrease of intensity observed at T_γ can be explained by an increase of the non-radiative rate constants when smaller segments of the polymer chains gain some mobility and, thus, are able to aid in the non-radiative decay of the excited singlet states of nearby 1-pyrenyl groups. The onset of the γ process is a change from a nearly completely frozen state of the polymer host to a partially mobile one. Radiative transitions of the electronically excited 1-pyrenyl groups below T_γ are from non-relaxed Franck–Condon vibronic states; the solvent organization associated with the vertical electronic transition is preserved and the resultant emission spectra are narrower than above T_γ . The agreement between the temperatures of the slope changes from the I_F and FWHM curves for each polymer in Fig. 6 demonstrates that radiationless deactivation of the excited states and solvent relaxation are physically linked phenomena.

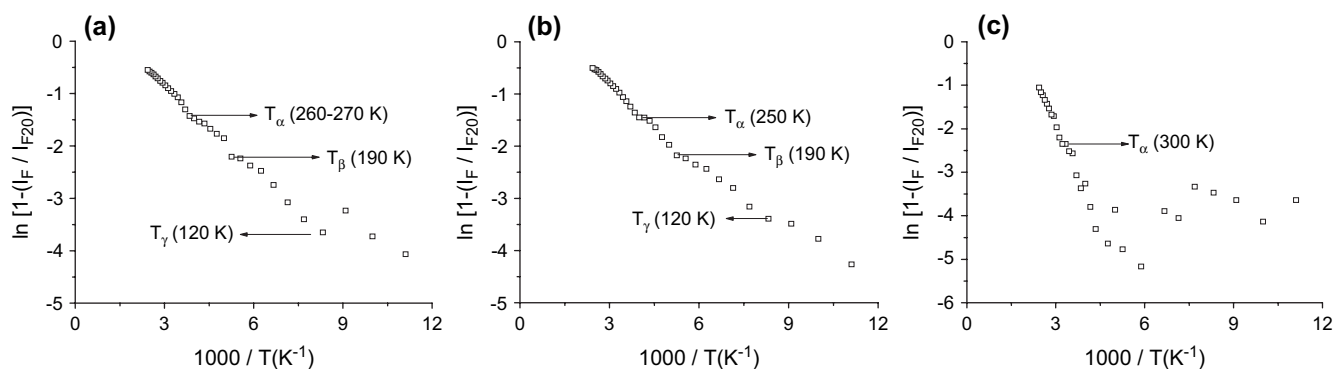


Fig. 7. Arrhenius-type plots of $\ln(1 - I_F/I_{F20})$ versus reciprocal temperature for (a) XLPE125, (b) XLPE76, and (c) XLPE7. Data from Fig. 6. The larger data scatter at the lower temperatures is due to small differences between I_F and I_{F20} .

For a clearer interpretation of these results, it is necessary to discuss the exact nature of the photophysical data. The photophysical properties of some lumophores are strongly dependent on their local environments. In these cases, the lumophores are a probe of events occurring in their immediate proximity. Consequently, polymer motions occurring far from the sites where the lumophores reside will have a negligible effect on their photophysical properties (unless those motions can propagate efficiently to the polymer chain segment where the lumophore is attached). Since the lumophores are not located within the crystalline regions of the XLPE films, they do not sense well events occurring there, and the curves in Fig. 6 respond to melting of the crystallites by a very smooth change of slope. This smooth change is also consistent with the aforementioned discussion of crystallite melting based on the DSC thermograms in Fig. 1. However, the much less drastic motional changes associated with the onsets of the α -, β -, and γ -relaxations are detected because the lumophores are located in the immediate vicinity where initiation of these chain motions occur.

Comparison of the plots in Fig. 6 shows that the pyrenyl moieties are more sensitive to the lower temperature processes in the XLPE with lower degrees of crosslinking (i.e., longer distances between interconnecting points on chains) than in those with higher degrees of crosslinking. Since the 1-pyrenyl concentrations of the three XLPE are similar, we assume that the efficiency of 1-pyrenyl attachment is independent of the degree of polymer crosslinking. We also assume that the 1-pyrenyl groups attached to the polymer chains are not aggregated (at least in the amorphous and interfacial regions) for reasons already discussed. On these bases, we conclude that suppression of chain motions in XLPE7 is the most probable explanation for the absence of a slope change (Fig. 6) in the temperature regime where the onset of γ -relaxations is expected.

Also, fluorescence changes attributable to the onset of motions of side chains (i.e., γ -relaxations) were not detected for the sample with the highest crosslink density. The most plausible explanation for this observation is that motions of short macromolecular segments are completely inhibited for this sample or that the 1-pyrenyl moieties are far from the sites where the relaxation processes are occurring. These site types are very difficult to distinguish by fluorescence methods when the polymers are not crosslinked or have low crosslinking densities. If 1-pyrenyl is attached to shorter segments which are relaxing at T_γ , there will be an increase in the efficiency of the non-radiative processes in the same way as when the emitting groups are attached to longer segments; the motions of shorter segments in non-crosslinked polymers are partially coupled to the motions of the chain backbones. Because the 1-pyrenyl moieties are randomly attached throughout the amorphous and interfacial regions of the polymers and γ -relaxations are found usually in these regions when the polymer chains are not (heavily) crosslinked, the photophysical properties of the lumiphoric groups will be modified. However, when polymers are crosslinked, the coupling between motions of short segments and the main chains should be decoupled

because there are strong hindrances to the propagation of main chain motions. Consequently, if the 1-pyrenyl groups are not attached to the remaining short segments, they will be weakly disturbed by the γ -relaxations.

Moreover, the temperature for the onset of the β -relaxation process ($T_\beta \approx 220$ K) in the XLPE with the highest crosslink frequency (XLPE7) is also higher than that for films with lower crosslink density (XLPE125 and XLPE76). By contrast, DMTA data for distinct samples of the same polymer reveal no apparent dependence on the crosslinking density [21]. Our tentative explanation for the different observations is based on what each technique measures. Whereas fluorescence spectroscopy reports the sum of individual events occurring locally and is able to separate them in wavelength and time, DMTA evaluates bulk properties of a material. Thus, the data from each are not in conflict; they are complementary. Together, they provide a more detailed picture of the dynamic processes occurring in the polyethylenes than either can alone.

In addition, at lower fluorophore concentrations, the disturbance of the fluorophore on bulk properties is also reduced. Previously, we have used DSC, DMA, and fluorescence spectroscopy to determine the temperatures of macroscopic relaxation processes of acrylic copolymers with different concentrations of covalently attached anthryl moieties [11]. In that study, the relaxation processes were found to be the same as those observed for the acrylic polymer without anthryl groups up to an [anthryl]/[acrylic unit] ratio of 1:35. For higher ratios, the glass transition temperature increased gradually. Therefore, at the very low lumophores loadings used in the current study, changes to *bulk* properties are beyond the sensitivity of conventional techniques, such as DSC and DMA. However, there must be *local* disturbances caused both in this study and the one employing acrylates by the presence of the lumiphoric probes. Such disturbances have been investigated by theory using molecular dynamics and Monte Carlo simulations of the influence of benzene incorporated in polyethylene [43]. They indicate conformational changes of the polymer chains that increase their rigidity in the vicinity of the benzene molecules [43]. As the content of *transoid*-like conformations increases, chains can pack more densely (as in the crystalline phase) and, thus, be stiffer. In addition, a molecular dynamics with Monte Carlo simulation of 1,3-di(1-pyrenyl)propane in polyethylene predicts a maximum probability of excimer formation at 375 K, very near the experimentally observed temperature (373 K). Both of these investigations indicate that although probes will disturb their local environments, they do not change the macroscopically determined melting temperature as long as their concentrations are low [44]. Whether these calculation have relevance here is unclear because the concentration of our attached pyrenyl groups are much lower than those employed in the benzene study and our pyrenyl groups are spatially separated as opposed to the 1,3-di(1-pyrenyl)propane study; the specific nature of the perturbing influence of attached 1-pyrenyl groups in our crosslinked XLPE samples remains to be ascertained. However, as long as physical communication (especially via electronic coupling) is maintained between excited singlet states of the 1-pyrenyl groups and their

neighboring polymer chains, the former should be able to report on changes suffered by the latter. In fact, there is an expectation that the perturbations caused by the presence of the probes will depress slightly the onset temperatures of relaxation processes registered via fluorescence. Given that our precision for the onset temperatures is, as mentioned previously, ± 10 K, these depressions are not observed.

4. Conclusions

Studies comparing the temperature dependence of the fluorescence emission of 1-pyrenyl groups covalently attached to one type of low-density polyethylene with three distinct cross-linking ratios are reported. In this case, that comparison is internal—it is used to evaluate differences among polyethylene films that differ only in the degree to which they are cross-linked. Based on the integrated fluorescence intensities and the FWHM of the 0–0 emission bands, films with higher average molecular weights between crosslinks exhibit onsets for relaxation processes which are similar to those of low-density polyethylene. However, the polyethylene with the lowest molecular weight between crosslinks (i.e., the highest crosslinking density) exhibits very different onset temperatures for its relaxation processes, and its fluorescence intensity is almost constant up to 220 K, where its β -relaxation commences. Additionally, the melting of crystallite portions of the polymer is nearly undetected by changes in the pyrenyl fluorescence properties, although it is well defined by DSC.

These observations demonstrate that no one technique is best for observing onsets of all of the transitions of these (and other) polymers. However, a combination of techniques that includes measurements of changes in fluorescence from covalently attached lumophores can provide a more comprehensive and self-consistent picture of the relaxation processes.

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