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A luminescence study of microstructure development and melting/crystallization processes in low density polyethylene (LDPE)

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Abstract

Pyrene, a fluorescent probe, was inserted in low density polyethylene and the emission spectrum was recorded during a cooling cycle from 150°C to -100°C and during isothermal crystallization at 105°C. Analysis of the temperature dependence of the fluorescence band at 365.5 nm reveals that, during dynamic crystallization, excited pyrene couples with vibrations which may correspond to crystalline defects. It was also found that pyrene emission increases about 10-fold during the final steps of the crystallization process, indicating that the interfacial cavity in which pyrene becomes lodged restricts its mobility. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In a previous article [1] we reported on the photophysical properties of a fluorescent probe, pyrene, when it is inserted in low density polyethylene and the temperature is increased from -100°C to 150°C. We found a small fluorescent band centered at about 365 nm, at energies above the 0-0 transition, whose intensity increased with temperature. The temperature variation of this band was interpreted in terms of electron-phonon coupling, and the fluorescent intensities were fitted to the Bose-Einstein equation (1):

$$\langle n_k \rangle = \frac{1}{\exp\left\{\frac{\hbar\omega}{kT}\right\} - 1}, \quad I_{365} \propto \langle n_k \rangle, \quad (1)$$

where $\langle n_k \rangle$ is the average number of phonons in mode k which vibrate at frequency ω above the zero-point energy at temperature T . We assumed the initial state for the emission process at 365 nm to be a high-energy vibronic state of the pyrene first singlet, and its mean thermal occupancy should increase with temperature following Eq. (1); consequently, if fluorescent intensity is a linear function of the population of the initial state of the transition, I_{365} should also increase with temperature. Two phonons were required to fit the experimental data. At lower temperatures, where the β relaxation is reported [2,3], excited pyrene was coupled with a high energy phonon of 2810 ± 35 cm⁻¹, whereas at high temperature (above 270 K) the energy of the phonon was 1437 ± 61 cm⁻¹. Both phonons correspond to fundamental vibrations of an infinite isolated polyethylene chain in extended conformation, as stated by its dispersion curve [4,5]. In this paper we report on

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the photophysical properties of pyrene inserted in LDPE during a cooling cycle from molten state and its relocation during the matrix crystallization process.

2. Experimental

Commercial low density polyethylene films of 0.4 mm thickness were obtained by pressing commercial LDPE of 4 mm thickness at 110°C for 30 min and cooling down to room temperature for a period of 2 h. Slices of about $20 \times 80 \times 0.4$ mm were cut, cleaned with chloroform for 4 h and vacuum dried at 50°C for 3 h. Pyrene was inserted into the LDPE slices according to the method reported elsewhere [1]; the pyrene concentration in the polymer matrix was 2×10^{-4} M.

Calorimetric measurements were performed on a differential scanning calorimeter (DSC) (Perkin Elmer 7) instrument. The sample was inserted in the calorimeter at room temperature and was allowed to equilibrate for 30 min under N_2 . The maximum temperature was reached at 2°C/min, it was kept constant for 5 min and a cooling cycle was run at -2°C/min until the low temperature limit was reached. Steady state fluorescence measurements were simultaneously performed using a fluorimeter (Perkin Elmer LS-50B). Details of the optical arrangement for coupling the two instruments and the fluorescence parameters can be found elsewhere [1,6].

In the crystallization experiments, the sample was kept at 150°C for 10–30 min and then quenched to 105°C at 200°C/min. Crystallization was monitored isothermally by recording the fluorescence spectra every 3 min for a period of time between 500 and 1000 min.

3. Results

3.1. Fluorescence results during the cooling cycle

The fluorescence spectra of pyrene at different temperatures during the cooling cycle between 150°C and -100°C are presented in Fig. 1. Only two bands will be discussed: the band at 365 nm,

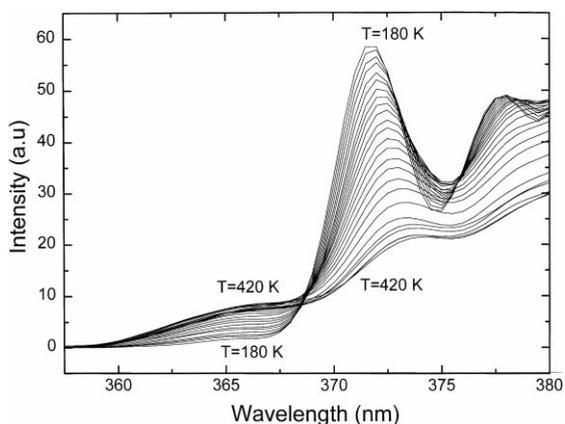


Fig. 1. High energy portion of the fluorescence spectra of pyrene in LDPE at different temperatures during a cooling scan from 420 to 180 K.

which corresponds to emission from a high-energy vibronic state of the pyrene first singlet [1], and the zero-phonon band, which appears at about 372 nm. As temperature is lowered, the 0–0 band shifts to higher energies, its width decreases and its intensity increases; these observations are common to all systems in which bandshape changes predominate over dispersion force variations [7].

At about 368.5 nm an isoemissive point linking bands at 365.5 and 372 nm, can be observed for the temperature range below 93°C. On cooling from 150°C to 93°C, the intensity of the 372 band increases but the 365.5 band remains constant. It is noteworthy that in the temperature range in which dynamic crystallization occurs (362.5–387.5 K, as revealed by Fig. 2) the isosbestic point is not present.

3.2. Fluorescence results during isothermal crystallization

In Figs. 3 and 4, the scattering intensity, I_{SC} , and the fluorescence intensity at 384 nm, I_{384} , are presented as a function of crystallization time. Three time ranges can be observed in both figures. Less than 80 min, I_{SC} is constant up to the first 45 min of the crystallization process, then decreases continuously to 40% of its initial magnitude. Between 100 and 130 min, the scattering intensity

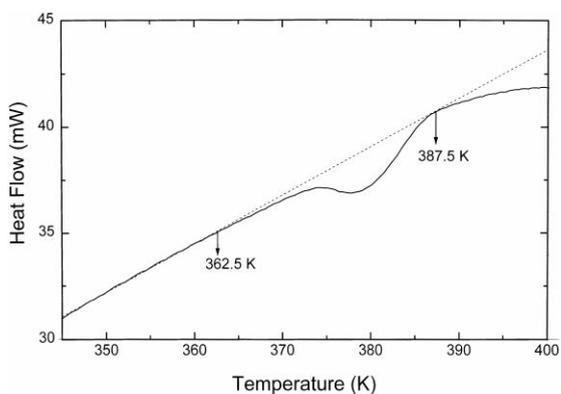


Fig. 2. Crystallization exotherm of LDPE on a cooling scan at $-2^{\circ}\text{C}/\text{min}$. The dotted line represents the base line. The temperature points denote the crystallization range, which coincides with the temperature range in which the isosbestic point is no longer maintained (see text and Fig. 1).

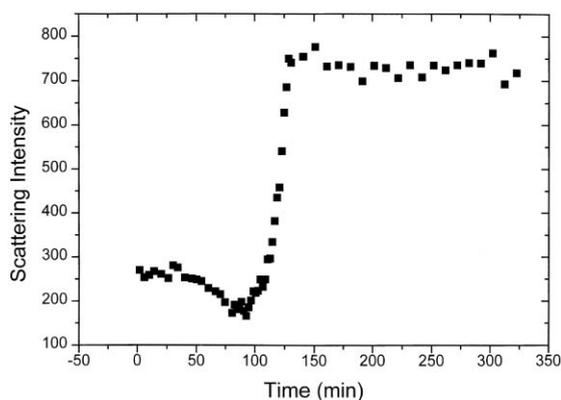


Fig. 3. Variation with time of the scattering intensity at 350 nm during isothermal crystallization of LDPE at 378 K.

increases about 500%; above 130 min, I_{SC} remains approximately constant.

I_{384} follows a similar trend to I_{SC} , but some differences can be noted: (a) in the initial regime, where I_{SC} begins to decrease, I_{384} increases gradually, (b) at 130 min, fluorescence intensity increases about 1000%, (c) at longer crystallization times, fluorescence intensity decreases linearly with time. This last result may be due to pyrene photodegradation or sublimation since it is subjected to high temperature and long irradiation time.

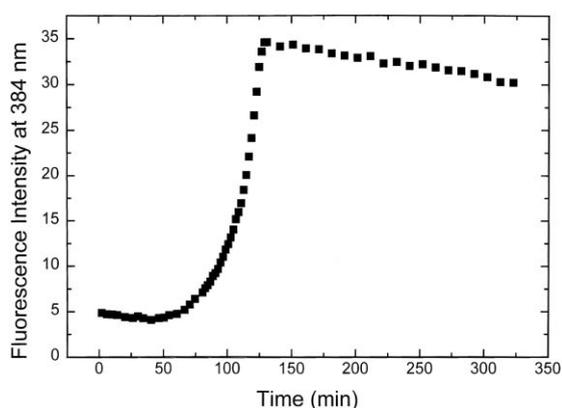


Fig. 4. Variation with time of the fluorescence intensity at 384 nm during isothermal crystallization of LDPE at 378 K.

4. Discussion

It is currently assumed that the microstructure of a semicrystalline polymer such as polyethylene can best be explained in terms of a three-phase model which incorporates the amorphous/crystalline interfaces as the third phase [2]. When PE is put in contact with a solvent such as hexane, only the amorphous regions and amorphous–crystalline interfaces are accessible to the solvent molecules; however, if a solution of a low-molecular-weight solute is used instead of a pure solvent, it would be reasonable to assume that these two regions will also be accessible to the solute. If a polymer sample doped with pyrene is heated to a temperature greater than its melting point, the crystalline surface cavities disappear and all the pyrene molecules may be considered as impurities in a viscous amorphous environment. On cooling, a crystalline microstructure develops and, because of the different chemical properties of pyrene and polyethylene, the former should be excluded from the crystallites and should diffuse through higher surface free energy regions such as the crystal fronts. It is precisely in these “ordered” regions where excited pyrene may couple with representative vibrations of the environment, giving rise to the emission at 365 nm. Analysis of the temperature dependence of the fluorescence intensity at 365 nm appears in Fig. 5. Data were fitted to Eq. (1) and the frequency of the representative

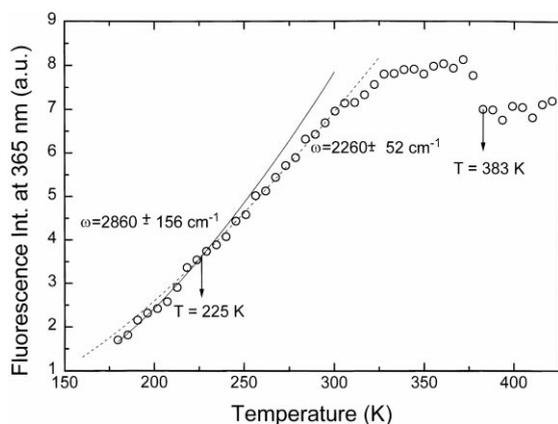


Fig. 5. Fluorescence intensity at 365 nm as a function of temperature. Lines denote the best fit of data to Eq. (1) using w as an adjustable parameter. $T = 225$ K represents the crossing of the two fitting lines and $T = 383$ K denotes the melting point obtained by DSC.

vibration with which excited pyrene is coupled has been left as an adjustable parameter. Two phonons were required to fit the data. At low temperature the energy of the phonon coincides with that obtained when pyrene was inserted by solvent diffusion [1] (about 2860 ± 160 cm^{-1}) and corresponds to an internal mode of linear polyethylene [4]. At temperatures above 225 K, a different vibration (energy about 2260 ± 60 cm^{-1}) couples with excited pyrene. This vibration does not correspond to a fundamental vibration of a fully extended all *trans* polyethylene chain [4], suggesting that pyrene may be located near a crystallization defect which manifests itself at the outer side of the crystalline lamellae. The presence of crystallization defects may be due to the non-isothermal conditions at which PE was crystallized.

The location of pyrene at the crystalline/amorphous interfaces can be investigated by analyzing the changes in fluorescence spectra during the crystallization process. A similar problem is associated with the annealing of latex films and has been elegantly discussed in terms of the photon diffusion theory [8]. According to this theory and considering the optical arrangement used in this paper – excitation and emission are parallel and the sample is located inside a reflecting aluminum pan – during

the first 45 min (Fig. 3) scattering essentially comes from the excitation light reflected from the back of the aluminum pan, which remains almost constant. As the crystals grow, the sample becomes less transparent and backscattered light decreases, as can be seen between 45 and 90 min in Fig. 3. At the same time the mean free path of the photons, i.e. distance covered by a photon between two consecutive collisions with the scattering surfaces (crystal surfaces), decreases but the overall distance covered by the photon increases and, therefore, the optical path also increases. Consequently, the probability of collision of the photon with a pyrene molecule increases and, as noted in Fig. 4, the fluorescence emission begins to increase. The increase of I_{384} and the decrease of I_{SC} are of the same order of magnitude (40%). This entire process may correspond to primary crystallization.

As crystals grow, the intercrystallite length decreases. When this length becomes very small, the mean free path of the photons also becomes very small (of the order of molecular dimensions) and I_{SC} begins to increase rapidly with time. However, the pyrene emission intensity does not decrease but, rather it begins to increase and doubles in scattering intensity. This trend can be justified if we assume that the pyrene is located just at the interfacial cavities between crystals. These non-fluid regions cannot act as heat sinks for pyrene and, therefore, non-radiative processes become inhibited.

5. Conclusions

During isothermal crystallization of LDPE, pyrene emission intensity increases more strongly than scattering emission. This result can be explained in terms of the photon diffusion theory by assuming that pyrene locates mainly at crystalline/amorphous interfaces. During non-isothermal crystallization, pyrene emission at 365 nm is associated with a vibration which does not appear in the dispersion curve of all-*trans* polyethylene linear chains.

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