Structural depth profiling in polyethylene films by multiple internal reflection infra-red spectroscopy

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The technique of internal reflection spectroscopy is used for the study of the structural gradient from the outer skin into the core in a commercial polyethylene film. A method is proposed for the quantitative evaluation of the relative amount of amorphous *versus* crystalline material. It is shown that the skin is highly crystalline and that an approximate amount of 40% amorphous material is found in the core of the film. The method used is of general validity for any polymer once bands characteristic of the amorphous and crystalline or regular structures are identified.

(Keywords: polyethylene; films; infra-red spectroscopy; structural gradient; internal reflection spectroscopy)

INTRODUCTION

The quantitative determination of the relative amount of crystalline and amorphous material in samples of polyethylene (PE) has been always carried out by transmission spectroscopy through thin films and not much attention has been paid to the fact that the distribution of the two phases may be topologically inhomogenous throughout the sample examined.

The availability of a precise vibrational assignment derived from theoretical calculations[1,3] and the possibility of recording spectra with multiple internal reflection infra-red spectroscopy (MIR) with varying angles of incidence[4] allows the study of the structural gradient of the film from the surface toward the core reaching (for this material) a depth of approximately 8–10 μm.

The experimental technique is well known[4] and accessories for MIR spectroscopy are commercially available. In this paper we wish first to report the theoretical methods we have used and the result obtained on a commercial film of polyethylene. This work has been extended to other samples of PE[5,6,14]. The results obtained are of general relevance in various fields of polymer science from technology to pure spectroscopy of PE.

EXPERIMENTAL

The sample used is a 56-μm thick film of commercial PE obtained from local sources. The film may contain some stabilizer which was not removed. Indeed in this paper our purpose is to show the usefulness of the method rather than to discuss the structural characterization of the sample.

The MIR cell was manufactured by Harrick Co. and consists of a crystal of KRS5 onto which we laid the film, taking care of a good optical contact. The angle of incidence can be varied at will within a certain range limited by the critical angle under which undesired band shifts and distortions take place.

Let the penetration depth d_p of the evanescent wave be given by the expression[4]:

$$d_p = \lambda/2\pi\sqrt{\sin^2\alpha - n_{21}^2}$$

where λ is the wavelength of the incoming radiation, α the angle of incidence measured from the normal to the surface, $n_{2,1} = n_2/n_1$ with $n_1 > n_2$, where 2 refers to the sample and 1 refers to the optical material (KRS5 $n_1 = 2.5$). A value of $n_2 = 1.5$ was assumed for PE.

The reflection spectra obtained as function of d_p in the spectral range of the CH_2 bending and rocking ranges are reported in *Figure 1*.

VIBRATIONAL SPECTRUM OF PARTIALLY AMORPHOUS PE IN THE CH_2 BENDING AND ROCKING REGIONS

On a qualitative basis a sample of solid PE can be considered as a two-phase system in which a crystalline phase coexists with an 'amorphous' phase[7]. It has been shown that while X-ray diffraction provides information on the 'crystalline' and 'amorphous' phases, vibrational spectroscopy generally distinguishes between one-dimensional periodicity (due to conformational regularity) and conformational irregularity or conformational disorder[8,1–3]. For orthorhombic PE and for a few other polymers tridimensional periodicity (hence crystallinity)[1,2,8] can be unequivocally detected.

It is well known that the doublets observed in infra-red near 1473–1463 (δ_a and δ_b) and 729–719 cm^{-1} (P_c and P_d), hereafter referred to as a, b, c, d respectively (*Figures 1* and *2*), originate from a factor group splitting due to the packing of two polymer chains per unit cell of an orthorhombic lattice[9,10]. It is also known that the setting angle θ between the planes defined by the transplanar C–C chain skeletons in the lattice is

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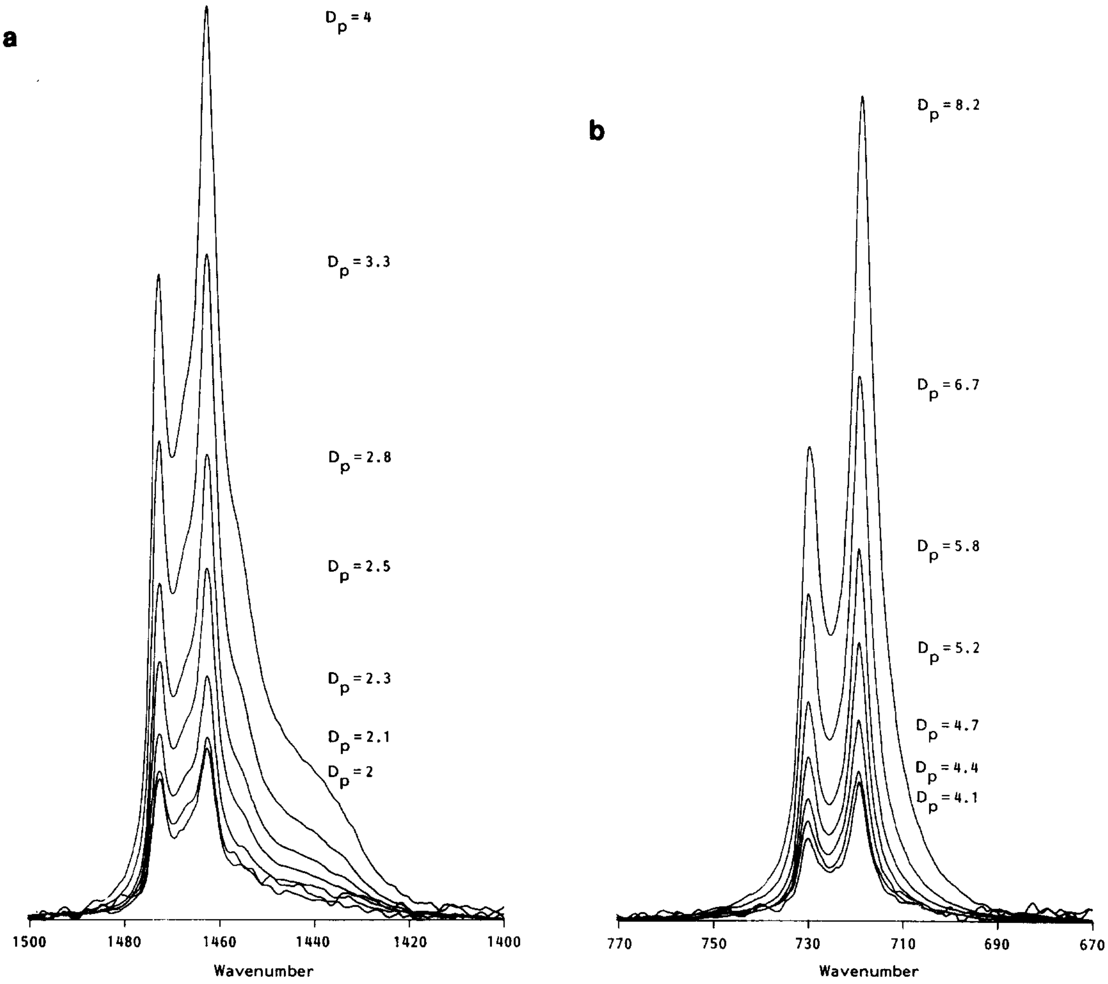

Figure 1 Multiple internal reflection spectrum at different angles of incidence of a 56-μm-thick film of commercial PE: (a) in the CH_2 bending region; (b) in the CH_2 rocking region

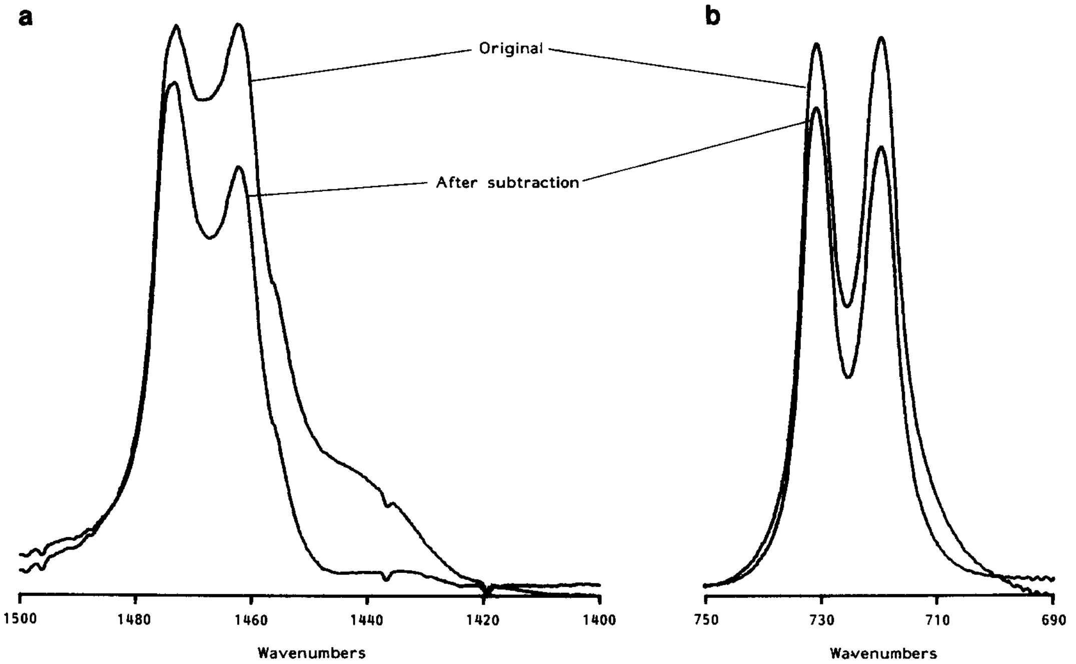

Figure 2 Infra-red absorption spectrum of the sample in *Figure 1* before and after subtraction of the spectrum of the amorphous component: (a) CH_2 bending; (b) CH_2 rocking. Subtraction has been made using the defect bands in the range 1365–1306 cm^{-1} as reference

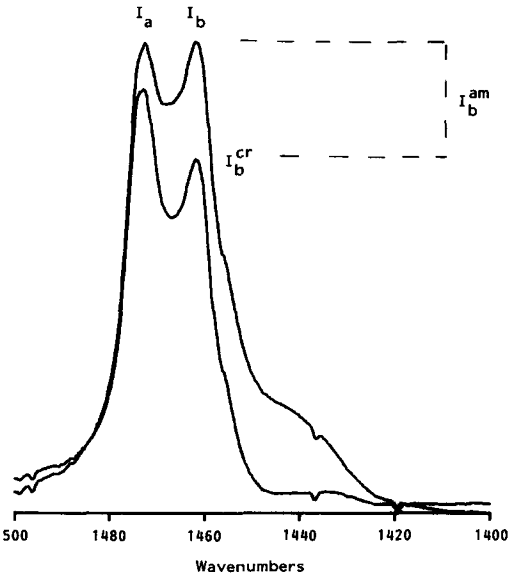

Figure 3 Infra-red absorption spectrum in the CH_2 bending region showing the experimental data used in the evaluation of crystallinity

approximately 42° (ref. 11). It has been shown from theoretical reasoning that for such a value of setting angle the intensity ratio I_a/I_b, R_{ab}, and I_c/I_d, R_{cd} must be 1.233 (ref. 12). This value has been verified experimentally in the infra-red (and Raman) spectra of highly purified and crystalline orthorhombic n-alkanes.

From *Figure 1* the following observations can be made: the observed R_{ab} and R_{cd} are opposite to what is expected, the components b and d being more intense than the partners a and c; it is indeed generally well known that R_{ab} and R_{cd} vary from sample to sample in many polymethylene systems; R_{ab} and R_{cd} are observed to continuously decrease when the penetration depth increases.

The last observation clearly indicates that both b and d bands must be the result of at least two overlapping absorptions, one of which increases with d_p. The increase of the band b is accompanied by a parallel increase of an absorption near 1442 cm^{-1} which is known to be associated with the existence of *gauche* conformers which exist in the material[13] and form the 'amorphous' phase. Thus, the δ and P modes of CH_2 groups in conformationally distorted *gauche* structures must show absorptions near 1463 and 719 cm^{-1}. We have confirmed the assignment by recording the spectrum of PE (and other n-alkanes) in the melt phase and indeed observed a broad band in the spectrum of the melt at the above frequencies. We have also recorded the Fourier transform infra-red (*FT*i.r.) spectrum of solid PE, subtracted the spectrum of a molten n-alkane and obtained the spectrum of the 'crystalline phase' (*Figure 2*) with a value R_{ab} and R_{cd} of ~1.3 satisfactorily close to the theoretical value of 1.23.

The quantitative evaluation has been carried out on the following principles. Let us discuss the spectrum in the bending range (*Figure 3*); the same conclusions can be drawn from the spectrum of P modes.

Let I_a+I_b be the total peak intensity of the CH_2 bending doublet. The peak intensities have been determined after suitable band separation and band fitting procedures in an *FT*i.r. experiment. We have postulated above that $I_b=I_b^{cr}+I_b^{am}$, the last two quantities indicating the contributions by the crystalline and amorphous components to the band b, respectively. Since $I_a/I_b^{cr}=1.233$ $I_b^{am}=I_b-I_b^{cr}=I_b-(I_a/1.233)$. The per cent fraction x of amorphous material is then obtained by suitable normalization, i.e. $x=100I_b^{am}/(I_a+I_b)$.

The accuracy of the quantitative measurement is not great, but gives a very acceptable estimate of the concentration of the amorphous component.

RESULTS AND DISCUSSION

We have applied the method described above for the measure of the percentage concentration of the 'amorphous' phase as function of the penetration depth for a 56-μm film of PE. The results are plotted in *Figure 4*. Reliable quantitative data were obtained from the CH_2 bending for a penetration depth of 6 μm. The change in wavelength from δ to P modes allows a larger penetration. As seen in *Figure 4* the data from the bending overlap with and are continued by the data from the rocking modes.

Our study shows that the outer skin of the film is highly crystalline (with two molecules per unit cell in an orthorhombic surrounding); one then observes a continuous change in the structure with an increase of the concentration of the amorphous component (~40%) when penetrating into the core; the value of 40% is reached at approximately 9–10 μm.

A few observations need to be stated:

(1) the method of evaluation of the percentage amorphous phase has general validity both in reflection and in absorption spectroscopy and can be applied for any sample of PE. The method can be extended to other polymers once characteristic signals of the 'crystalline' and 'amorphous' components are clearly identified;

(2) the quantitative measurements of crystallinity so far obtained by transmission spectroscopy, or other physical techniques, provide values which are an average of what the beam probes in crossing the skin and the core of a sample. The possibility of obtaining two independent sets of data from the skin and the core may be quite relevant in the development of new technological

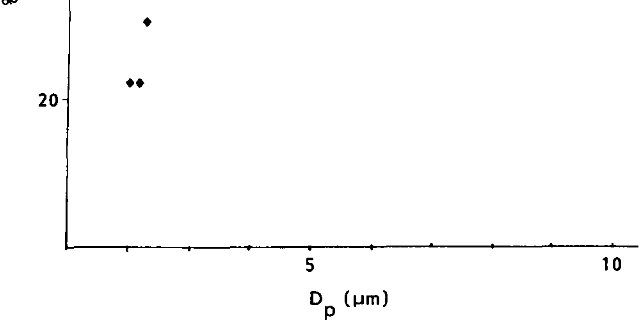

Figure 4 Percent concentration of amorphous component as function of penetration depth of the samples in *Figure 1*. ◇, Rocking; ◆, bending

processes which try to improve the physical properties of polymeric objects;

(3) we have also observed the factor group doublet of the bending modes in the Raman spectrum and the value R_{a*b*} is very close to the value of the crystalline material with no amorphous component (a and b refer to only infra-red active modes; with a* and b* we label the corresponding modes active only in the Raman). This observation is in agreement with the results from infra-red since it is known that the penetration of the laser beam into the polymer sample is very small. We then derive the important conclusion that the Raman spectrum of polymers is that of the first few microns of the skin of the sample. This information may be relevant for structural studies of polymers using Raman spectroscopy. Further studies are required on other samples.

Based on the same principles we have already studied the structure of the skin and the core in several samples of ultradrawn PE[6,14].

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REFERENCES

1 Zerbi G. Molecular Vibrations in High Polymers in: 'Applied Spectroscopy Reviews' (Ed. E. G. Brame), Vol. 2, 1963, p. 193

2 Zerbi, G. in: 'Advances in Chemistry' (Ed. C. D. Craver), American Chemical Society, Washington, 1982, p. 487

3 Zerbi, G. The Vibrations of Large Molecules in: 'Advances in Infrared and Raman Spectroscopy' (Eds. R. J. H. Clark and E. Hester), Vol. 11, Wiley-Heyden, New York, 1984, p. 301

4 Harrick, N. J. Internal Reflection Spectroscopy, Interscience, New York, 1967

5 Zerbi, G. Proceedings of the Symposium on Macromolecules, Kyoto, 1988

6 Zerbi, G. and Gallino, G. to be published

7 *Faraday Discuss. Chem. Soc.* 1979, 68

8 Zerbi, G., Ciampelli, F. and Zamboni, V. *J. Polym. Sci. C* 1964, **7**, 141

9 Krimm, S. *Adv. Polym. Sci.* 1960, **2**, 51

10 Snyder, R. G. *J. Mol Spectrosc.* 1961, **7**, 116

11 Avitabile, G., Napolitano, R., Pinozzi, R., Rouse, K. D., Thomas, W. and Willis, B. T. M. *Polym. Lett.* 1975, **13**, 371

12 Abbate, S., Gussoni, M. and Zerbi, G. *J. Chem. Phys.* 1979, **70**, 3577

13 Hagemann, H., Strauss, H. L. and Snyder, R. G. *Macromolecules* 1987, **20**, 2810

14 Gallino, G. *PhD Thesis* University of Milano, 1988