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Structure of the skin and core of ultradrawn polyethylene films by vibrational spectroscopy

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The molecular structure of ultradrawn films of polyethylene has been studied with a combination of different techniques of vibrational spectroscopy, namely attenuated total reflection at different angles of incidence (thus doing optical microtoming), infra-red absorption and Raman scattering in various geometries and polarizations. The experimental results are interpreted on the basis of the theoretical concepts of the lattice dynamics of ordered and disordered polymethylene systems previously worked out. A gradient of molecular and crystalline structures is found from the surface into the core. The skin is highly orthorhombic; moving inside the film, both monoclinic and orthorhombic lattices coexist. Moreover, in the core a new phase with 'isolated' *trans*-planar sequences is observed. Various kinds of collective and oriented or isolated conformational disorder are identified. From the experimental data collected, a molecular model is proposed for the process of orientation during drawing. A problem of general relevance in Raman scattering of polymers is presented by the fact that the scattering observed arises only from the upper skin of the sample.

(Keywords: polyethylene; molecular structure; films; vibrational spectroscopy; ultradrawing; skin; core)

INTRODUCTION

In recent years the preparation and characterization of ultra-oriented polymers showing ultra-high modulus has attracted the interest of several groups[1,2]. Polymeric materials with high modulus are of particular relevance in applied sciences. The origin of such properties and the process of formation of such materials must find an explanation in terms of the basic microscopic properties of the crystallites and/or of the molecules that make up such interesting systems in the solid ordered and disordered phases.

The problem of the preparation of the materials and the understanding of their morphology and structure has been treated in the literature[3–7]. The line of thought followed by various researchers is that of accounting for the peculiar macroscopic behaviour in terms of the physics of collective phenomena either treated with theoretical models or measured by techniques that substantially focus on collective properties (e.g. density, birefringence, calorimetry, sonic velocity, dynamic modulus, etc.), which are of interest to applied material science.

Not much work has been done focusing on the microscopic properties in terms of molecular structure and dynamics.

An analysis of the broad-line n.m.r. spectra of ultra-high-molecular-weight, ultradrawn polyethylene (hereafter referred to as UHMW-UD-PE) has been presented by Smith *et al.*[4]. These authors show the existence of three main structural phases, which are identified from the breadth of the observed n.m.r. spectral lines. These authors identify: (i) a crystalline region with high degree of molecular orientation in the ultradrawn material (broad line); (ii) a highly mobile fraction (with a narrow isotropic spectral component) assigned substantially to low-molecular-weight material that does not crystallize and, eventually, also to ends of the molecules rejected from the crystalline regions; and (iii) a fraction of high-molecular-weight material whose constrained ends do not allow much mobility to the whole chain. This less mobile fraction becomes oriented towards the draw direction to an extent depending on the draw ratio.

In this work we explore the structural properties of UD-PE at the molecular level using vibrational spectroscopy as a probe. The justification of such work is that recent theoretical and experimental studies of polymethylene chains have provided spectroscopic signals very characteristic of specific structural features of these molecules[8–14]. We decided to apply these spectroscopic methods to the study of UD-PE.

To our surprise, the infra-red spectra of UD-PE studied by us have presented additional and non-negligible features that could not fit the presently known spectroscopic signals.

The understanding of these new data has convinced us to analyse further the vibrational spectra of n-alkanes and of PE in order to disentangle spectroscopic details hidden in the complex convolution of several transitions in the CH_2 bending and CH_2 rocking frequency ranges. Further new concepts are thus derived from this work.

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In this work we shall use in a complementary way infra-red transmission and/or attenuated total reflection (ATR) spectra and Raman spectra, which are interpreted in terms of the current theoretical concepts of the molecular dynamics of chain molecules.

EXPERIMENTAL

Tapes of UD-PE of molecular weight M_w around 200 000 have been made as previously described[14]. The three samples analysed have draw ratios of 15, 20 and 25 and in the discussion that follows will be labelled as PE15, PE20 and PE25 respectively. The average thickness of the tapes is $\approx 80\,\mu$m.

Infra-red spectra were recorded with a Nicolet 7000 *FT* i.r. interferometer with an MCT detector. The absorption spectra are the results of 256 scans. Spectra of the tapes were also recorded in polarized light with suitable geometries and as a function of temperature in a commercial heating cell.

ATR spectra were recorded with 1536 scans on a KRS5 crystal at various angles (above the critical angle of $\beta = 39.18°$) with a Spectra-Tech reflection accessory. In order to increase the signal the film was placed at either side of the KRS5 crystal (index of refraction $= 2.39$); care was taken to keep the orientation of the film on both sides and to examine the same side of the film. Since the surface of the film is rough, great care was also taken to assure good optical contact between the film and the KRS5 crystal.

In this work use has been made of the method of 'band deconvolution' in order to 'zoom' at some spectroscopic details. However, owing to the arbitrariness in the choice of the parameters of the deconvolution, a cautious and critical use of the data has been made.

Raman spectra were recorded under different scattering geometries with a Dilor multichannel Raman spectrometer with the excitation wavelength of 514.15 nm (spectral resolution of 4–5 cm^{-1}, 200 scans).

Model molecules were also studied, namely $C_{36}H_{74}$, $C_{36}D_{74}$ and their mixtures at various concentrations. KBr pellets were used in the infra-red work and powders sealed in glass capillaries for Raman scattering.

VIBRATIONAL SPECTRA OF POLYMETHYLENE CHAINS AS A PROBE OF MOLECULAR AND LATTICE STRUCTURES

The study of the dynamics and spectra of polymethylene chains has progressed through the years and has become a useful probe for the detailed analysis of the structure of these systems. We limit our discussion here only to the spectroscopic data used in this work and refer to specialized review articles for a discussion of the spectroscopy of polymethylene chains[8–13].

Known probes

When a long polymethylene chain is considered as an isolated entity, free from intermolecular interactions, structurally relevant data from theory and experiment have already been collected, and their interpretation finds the agreement of most of the authors. We list below some of the spectroscopic features relevant to our work; they will be recalled in the text that follows.

(a) Band progressions in the infra-red of CH_2 rocking (medium strong) and CH_2 twisting–wagging (very weak) indicate that the molecule has a *trans*-planar conformation[15].

(b) The 'umbrella' deformation mode of the CH_3 groups at the end of the polymethylene chains occurs as a specific absorption at 1375 cm^{-1} (ref. 16) and its intensity is often used as an internal standard for the study of structural evolution when physical conditions are changed (e.g. temperature-dependent studies).

(c) Non-planarity is clearly indicated by the absorptions due to normal modes localized at specific conformational defects within the chain or at the end of the chain[17–20]. Weak absorptions at 1368 and 1306 cm^{-1} identify *GTG'* defects, which form a 'kink' in the chain without changing the overall trajectory of the chain; a weak absorption at 1353 cm^{-1} identifies higher-energy *GG* defects[21].

(d) The first overtones of CH_2 rocking modes (≈ 720 cm^{-1}) generate vibrational levels near 1440 cm^{-1}, which enter Fermi resonances with the CH_2 bending modes[22,23]. They borrow intensity from the fundamental transitions and generate characteristic Raman scattering near 1460 cm^{-1}. The shape of the scattering in this frequency range changes when the chains are isolated or in an orthorhombic lattice[23] and also when they are conformationally distorted[24].

(e) In the case of single-chain polyethylene considered as an infinite and perfect one-dimensional crystal, instead of the $q = 0$ modes of the band progressions one observes only the $q = 0$ modes that are i.r.- or Raman-active[8,9,25]. *Trans*-planarity is judged by the values of the frequencies in the infra-red spectra (with the complementary help from the Raman spectrum, which gives firmer evidence).

(f) When n-alkanes crystallize they can be packed in an orthorhombic (chains with an odd number n of C atoms), monoclinic ($n \geqslant 26$) and triclinic ($n \leqslant 26$) lattice. For the case of PE, while its orthorhombic structure is well established by unquestionable physical evidence[26], the existence of monoclinic and/or triclinic lattices is a matter of continuing work with various techniques (see also below).

When polymethylene chains pack in an orthorhombic lattice (with four CH_2 units in the unit cell with D_{2h} symmetry) the spectroscopic manifestations are clear and unquestionable, namely:

(g) CH_2 bending and CH_2 rocking $q = 0$ phonons of the one-dimensional lattice split into an infra-red-active 'factor group doublet' and a Raman-active doublet[8,9]. The selection rules of i.r./Raman mutual exclusion are due to the fact that the chain is centrosymmetric.

This concept is relevant for this work and needs further elaboration. Let the potential felt by the polymethylene chain be written as:

$$V_{\text{total}} = V_{\text{mol}} + V_{i,j} + V_{\text{sf}}$$

where V_{mol} represents the intramolecular potential, which we assume to be invariant in going from the isolated molecule into a crystalline environment, $V_{i,j}$ represents the non-bonded two-body atom–atom potential between molecules, which is a strong function of the $r_{i,j}$ distances, and V_{sf} represents the 'static field' potential felt by the molecule embedded in a given lattice. V_{sf} changes for different lattices[27–29]. The term $V_{i,j}$ originates the factor group splitting while V_{sf} displaces the 'centre of mass' of the doublet and makes the collapse of the doublet asymmetric. The problem is well known in spectroscopy and is sketched in *Figure 1*.

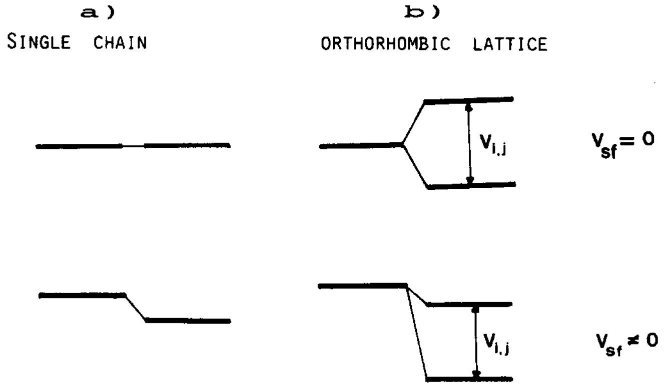


Figure 1 Scheme of the shifting and/or splitting of the vibrational levels in going from a molecule *in vacuo* to a crystalline lattice as a function of the static field effect V_{sf} and/or intermolecular potential $V_{i,j}$ for: (a) one molecule per unit cell and (b) two molecules per unit cell (see text)

When the crystal expands by heating, $r_{i,j}$ increase, the interactions weaken and quickly the factor group splittings decrease. The collapse of the factor group doublet is asymmetric because of the V_{sf} term.

(h) The intensity ratios of the two components of each factor group doublet (in both the Raman and i.r.) are related to the setting angle θ of the *trans*-planar chains within the unit cell[30]. Infra-red and Raman data agree with the X-ray and neutron scattering measurements on the fact that, for PE, $\theta = 42°$ (ref. 26).

It has to be pointed out that most of the time additional absorptions occur and overlap in the frequency ranges where CH_2 bending and rocking motions occur, thus altering the intensity ratio. It has already been shown that a band due to 'amorphous' PE (or more precisely conformationally distorted PE) lies below the factor group component near $1462\,cm^{-1}$. A similar, but not so distinct, situation occurs in the $720\,cm^{-1}$ range[31,32]. This problem will be discussed further below in this paper.

Less well known probes

The identification of the monoclinic crystalline phase has been the subject of work by a few groups. A general agreement exists among various authors that an infra-red line in the range $716–718\,cm^{-1}$ originates from the CH_2 rocking modes in a monoclinic packing[33–36]. For the bending range, Painter[34] has first proposed that the monoclinic lattice originates an infra-red line near $1473\,cm^{-1}$. This has recently been confirmed in a systematic study by Hagemann *et al.*[37]. The higher and lower frequencies of CH_2 bending and CH_2 rocking respectively with respect to the orthorhombic can be reasonably due to the V_{sf} term.

New probes

Additional structural probes can be identified in the CH_2 bending region where overlapping of several transitions occurs. The analysis of this section of the spectrum is relatively new. From spectroscopic correlations it is known that in this frequency range one observes the CH_2 scissoring modes overlapped with the CH_3 deformation modes[16].

The first experimental observations to be accounted for are the features occurring in the infra-red spectrum in the $1470–1400\,cm^{-1}$ range and their temperature dependence for both n-alkanes and PE. The *T*-dependent spectrum of PE initially in the 'orthorhombic' phase is shown in *Figure 2*. We identify in *Figure 2* the factor group splitting for the sample at room temperature, which narrows asymmetrically shifting the 'centre of mass' of the spectral pattern from $1465\,cm^{-1}$ to $1460\,cm^{-1}$. The increase of the intensity of the $1462\,cm^{-1}$ band originates from the onset of existence (or increase of an already existing fraction) of a conformationally disordered component[31,32]. Above the melting point, the peak broadens and moves towards lower frequencies with increasing temperatures, reaching a value near $1458\,cm^{-1}$ at 250°C. The same observations have been made for other systems containing polymethylene segments[38,39].

Since it is known that by increasing the temperature the originally *trans*-planar chain coils into rotational isomeric states mainly governed by Flory's statistics[40], we can associate the infra-red absorption near $1467\,cm^{-1}$ with the bending of the CH_2 groups organized in fully *trans*-planar segments, while they absorb at lower frequencies when they are involved in energy-allowed conformational defects such as e.g. *GG*, *GTG*, *GTG'*, etc. The smooth evolution with increasing *T* of the observed spectral pattern is then due to the increase in concentration of the conformationally distorted chains at the expense of the *trans*-planar chains.

An experimental verification that the CH_2 bending modes of a fully *trans*-planar chain absorb near $1465\,cm^{-1}$ can be obtained from the spectra of an alkane chain diluted into a crystal of its perdeutero derivative. This technique is well known for both small molecules[27] and polymers[9]. We have recorded the infra-red spectra of a solid solution (20/80) of $C_{36}H_{74}$ in $C_{36}D_{74}$ (*Figure 3*), which shows a clear and isolated peak at $1468\,cm^{-1}$. As already pointed out by many authors, the existence of the singlet in the spectrum of the solid isotopic

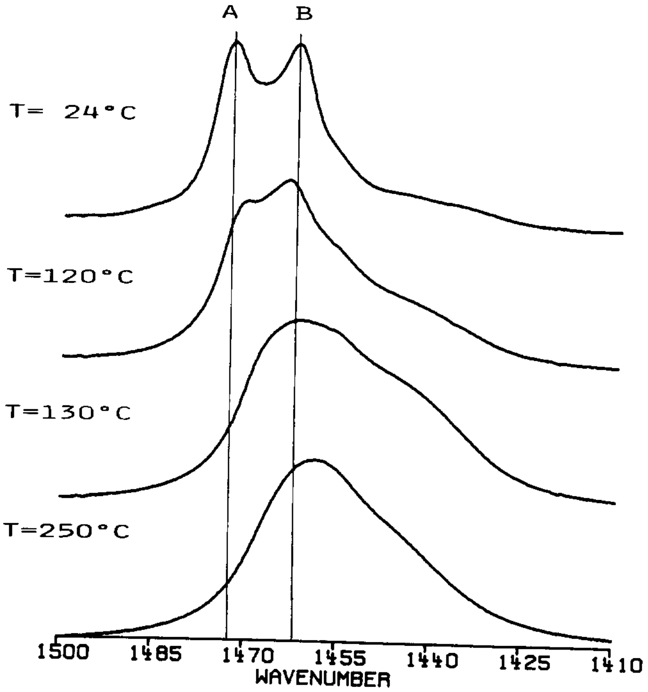


Figure 2 Temperature dependence of the infra-red absorption spectrum in the CH_2 bending region of 'normal' orthorhombic PE. The originally orthorhombic structure (bands A–B) evolves into a molten phase characterized first by a certain population of *trans*-planar segments which later coil with increasing temperature in conformationally disordered structures

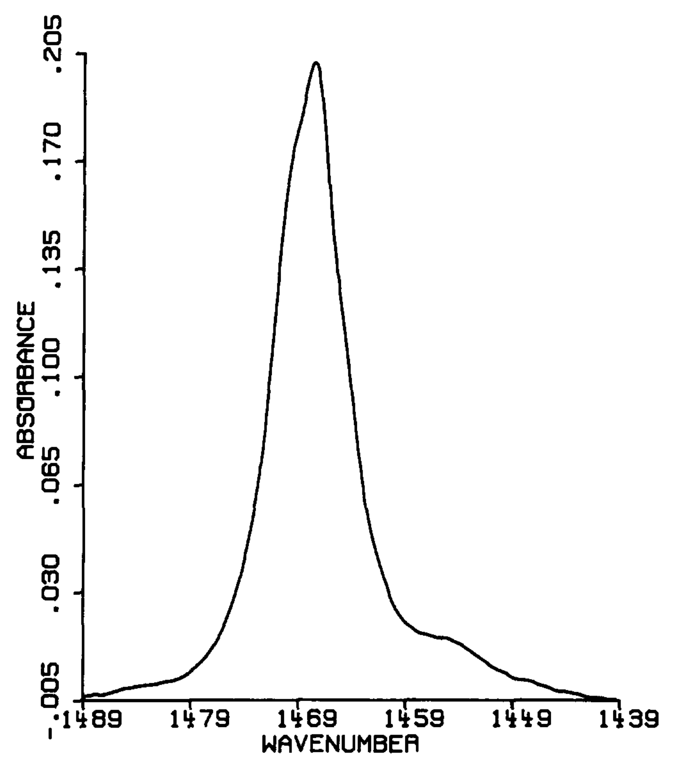


Figure 3 Infra-red absorption spectrum of an isotopic solid solution (20/80) of $C_{36}H_{74}$ and $C_{36}D_{74}$ in the CH_2 bending region

solutions confirms the assignment of the factor group doublet as well as the existence of the V_{sf} term.

We consider the experiments presented above as good experimental support for the assignment of the band near 1465–1467 cm^{-1} to *trans*-planar sequences of CH_2 units of an as yet undetermined average length. Our assignment differs from what has previously been proposed in the literature in which this band is assigned to an 'amorphous' component[32].

Independent information should come from the CH_2 rocking modes. From the spectra of the solid isotopic solutions we learn that the CH_2 rockings of the isolated chains absorb at 724 cm^{-1} but that the intrinsic absorption coefficient is smaller than (about a half of) that of the bendings[41]. If the concentration of *trans*-planar segments is not large it may not be easily seen in a more complex spectrum originating from mixtures of various morphologies. The same frequency range is complicated by the known fact that when *trans* segments are destroyed and conformationally distorted chains are formed a broad absorption occurs near 720 cm^{-1}.

The CH_2 deformation modes in conformationally distorted polymethylene chains originate broad absorptions near 1440 and 1456 cm^{-1}. Hagemann *et al.* assign the band at 1440 cm^{-1} uniquely to *G* conformation[32]. We shall obtain further information on the origin of these bands from the study of the spectra of UD-PE discussed below.

MULTIPLE INTERNAL REFLECTION SPECTRA

It is known that, in multiple internal reflection experiments, by changing the incidence angle φ it is possible to probe the material at different penetration depths (d_p)[42,43]. The formula currently used is:

$$d_p = [2\pi n(\sin^2\varphi - n_{21})^{1/2}]^{-1}\lambda$$

where λ is the wavelength of the incident radiation, φ is the incidence angle and $n_{21} = n_2/n_1$ (where n_1 is the index of refraction of KRS5 and n_2 that of PE).

Attention should be paid to the real physical meaning of d_p, namely d_p is the distance in the sample at which the amplitude of the incident field is reduced to 1/e of the value of the amplitude at the interface. Owing to this definition, the actual penetration depth is larger, but as a first approximation not much greater than d_p. What we are performing is an optical microtoming and the reflection spectra observed probe the average composition of the matter within d_p (for a thorough discussion see refs. 42 and 43).

It has already been shown that it is thus possible to probe in detail the structural gradient in a commercial PE film[31]. It was shown that the film is much more crystalline orthorhombic (see (g) and (h) in the subsection on 'known probes' above) on the surface and becomes more conformationally disordered in going into the core at approximately 10 μm (see (f) above).

We have repeated the experiment with UD-PE. The results are reported in *Figure 4* for PE25 (i.e. PE with draw ratio of 25) for the CH_2 bendings where the data are clearer (many other spectra have been recorded also for other draw ratios and they are available upon request). In *Figure 4* at $\varphi = 60°$ ($d_p \approx 1\,\mu$m) one immediately identifies the factor group doublet (labelled as A–B) due to the orthorhombic lattice (see (g) above) with approximately the theoretical intensity ratio I_A/I_B (see (h) above). The film is then highly crystalline on the surface. Going deeper ($\varphi = 35°$, $d_p \approx 10\,\mu$m) the ratio I_A/I_B decreases, indicating the onset of an absorption near

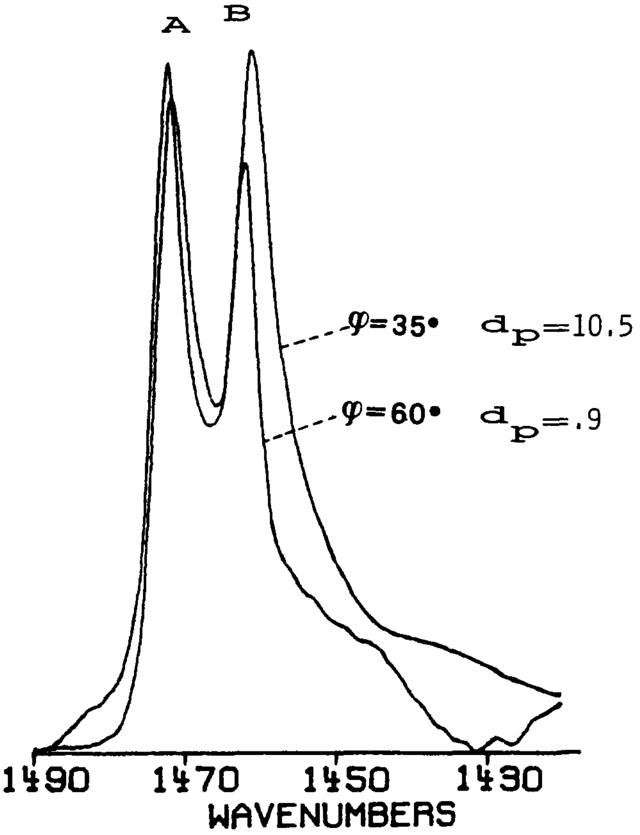


Figure 4 Multiple (infra-red) internal reflection spectrum of ultradrawn PE (PE25, i.e. $DR = 25$) in the CH_2 bending range at two angles of incidence φ (i.e. at two different penetration depths d_p)

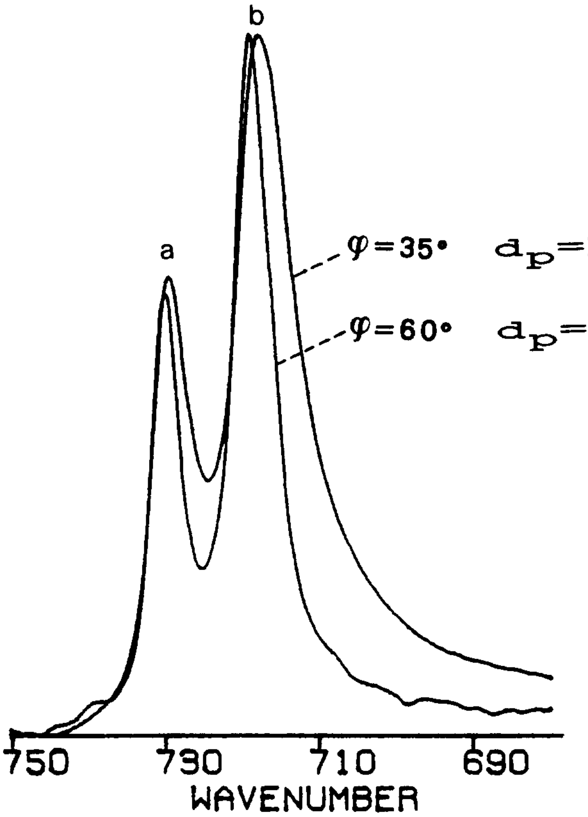


Figure 5 Multiple (infra-red) internal reflection spectrum of ultradrawn PE in the CH_2 rocking range at two angles of incidence φ (i.e. at two different penetration depths d_p)

1455–1460 cm^{-1} due to conformationally distorted structures. The existence of a structural gradient is clearly shown for UD-PE at various draw ratios by our ATR experiments.

By increasing the wavelength of the incident radiation one can probe the material at larger d_p. The ATR spectrum in the CH_2 rocking range (*Figure 5*) shows again that, at $\varphi = 60°$, $d_p \approx 2\,\mu m$, the material is highly orthorhombic (peaks a, 730 cm^{-1}, and b, 719 cm^{-1}). For $\varphi = 35°$, $d_p \approx 20\,\mu m$, peak a shifts towards lower frequencies (near 717 cm^{-1}) and becomes a convolution of the orthorhombic component, the absorption that originates from the monoclinic lattice (see subsection on 'Less well known probes' above) and the absorption from the conformationally distorted structures. Further evidence will be collected from the absorption spectrum in both the CH_2 bendings and CH_2 rockings.

INFRA-RED ABSORPTION SPECTRA OF UD-PE

The survey infra-red absorption spectra of the three samples of UD-PE (*Figure 6*) are limited to the 1800–400 cm^{-1} range since the intensity of the C–H stretching is too strong and cannot be studied at the thickness of the actual samples. Any attempt to reduce the thickness would modify the morphology of the as-prepared samples that we wish to study.

The spectra of *Figure 6* identify three main absorptions, which we examine in detail below, namely (i) the CH_2 bending range centred near 1460 cm^{-1}, (ii) the CH_2 rocking near 720 cm^{-1} and (iii) the weak and structured absorption near 1360 cm^{-1} assigned to the wagging of CH_2 within conformational defects.

CH_2 bending

The spectra in polarized light (α = angle of polarization) of the oriented sample PE25 of *Figure 7* show an unusual structure, which needs to be understood. The corresponding deconvoluted spectra are given in *Figure 8*. The peaks are identified here again by letters. In the geometry of absorption as indicated in *Figures 7* and *8*, the doublet A–B, (A, 1472 cm^{-1}; B, 1461 cm^{-1}) clearly shows a transition moment perpendicular to the drawing direction and is ascribed (as in the case of the reflection spectra of the previous section) to the factor group doublet of the $q = 0$ phonons of CH_2 bending in an orthorhombic lattice, in agreement with the commonly accepted assignment (see (f) in the subsection on 'Known probes'). From $\alpha = 90°$ to $\alpha = 0°$ the contribution by the A–B doublet almost disappears and a clear absorption (C) is left in between A and B with the most prominent feature centred at $\approx 1467\,cm^{-1}$ for $\alpha = 0°$.

The striking fact is that band C does not exist in the ATR spectrum of *Figure 4*, indicating that an additional molecular structure exists in the core of the film.

Using the concepts presented in the subsection above entitled 'New probes', the absorption has to be assigned to a fraction of the material in which chains are *trans*-planar. This information is new and has to be reconciled with the whole view of the morphology of these samples of ultradrawn PE.

The fact that peak C and the corresponding *trans*-planar morphology are peculiar to PE in the ultradrawn state is proven by the spectrum of *Figure 9*. If UD-PE

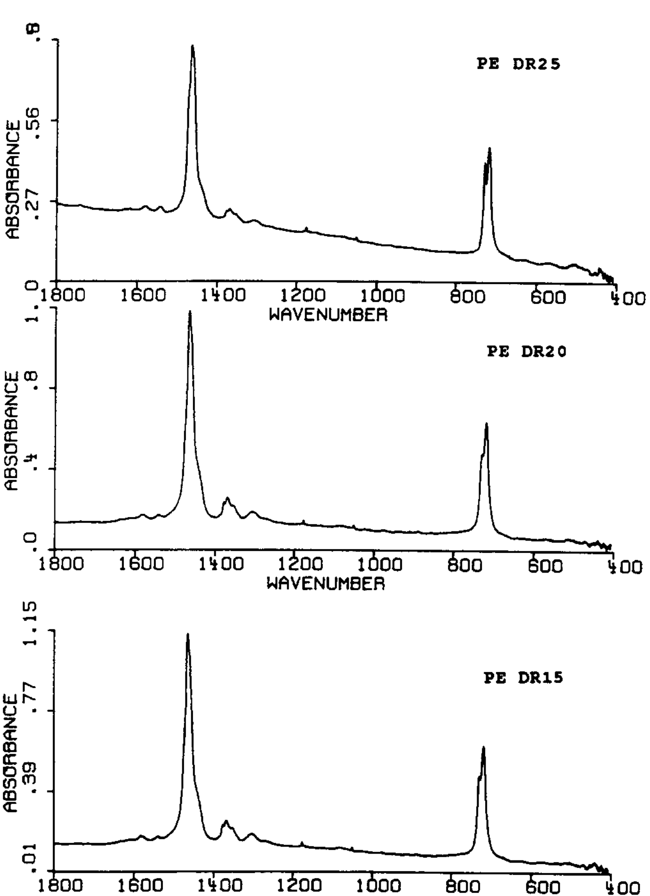


Figure 6 Survey infra-red absorption spectra (1800–400 cm^{-1}) of ultradrawn polyethylene tapes at different draw ratios

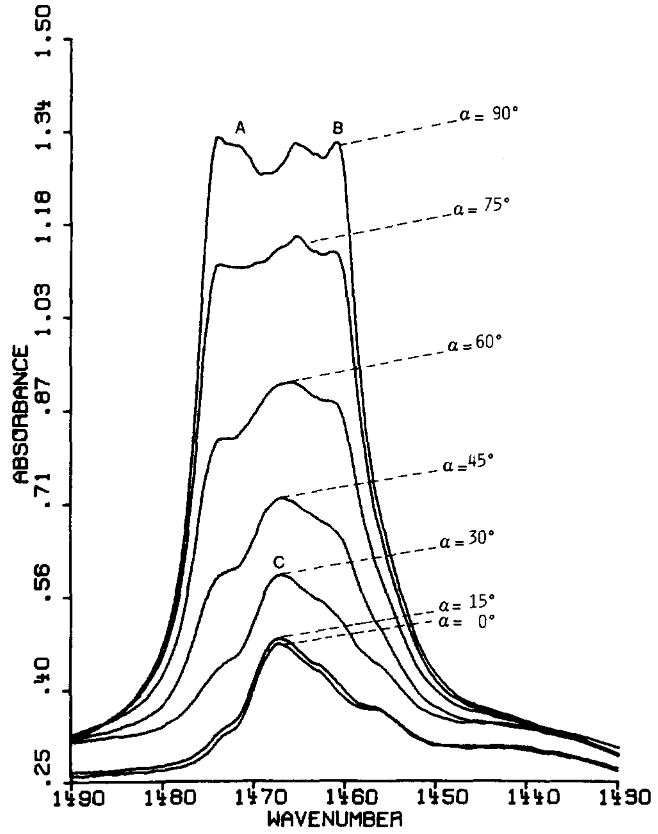


Figure 7 Infra-red absorption spectra in polarized light of PE25; α = polarization angle with respect to the direction of drawing. Peaks A and B identify the absorption due to the orthorhombic lattice; C is assigned to all-*trans* isolated sequences

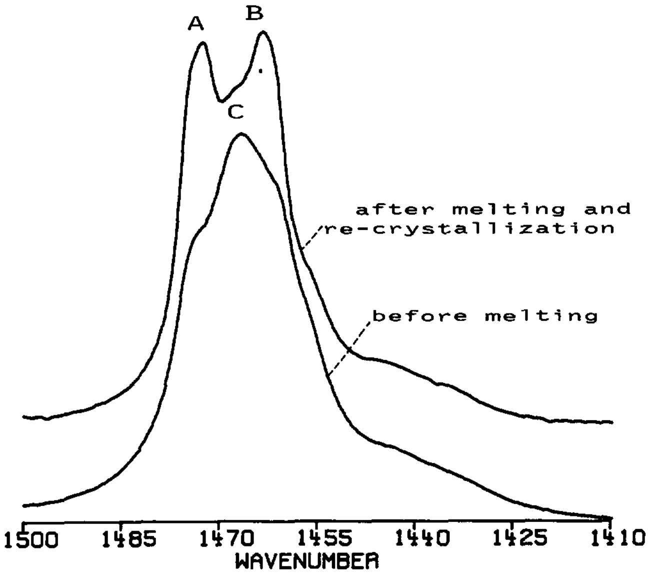


Figure 9 Infra-red absorption spectrum of PE25 films as prepared and after melting and recrystallization (+8 h annealing). The spectrum shows that the *trans*-planar isolated sequences (band C) are peculiar to ultradrawn samples

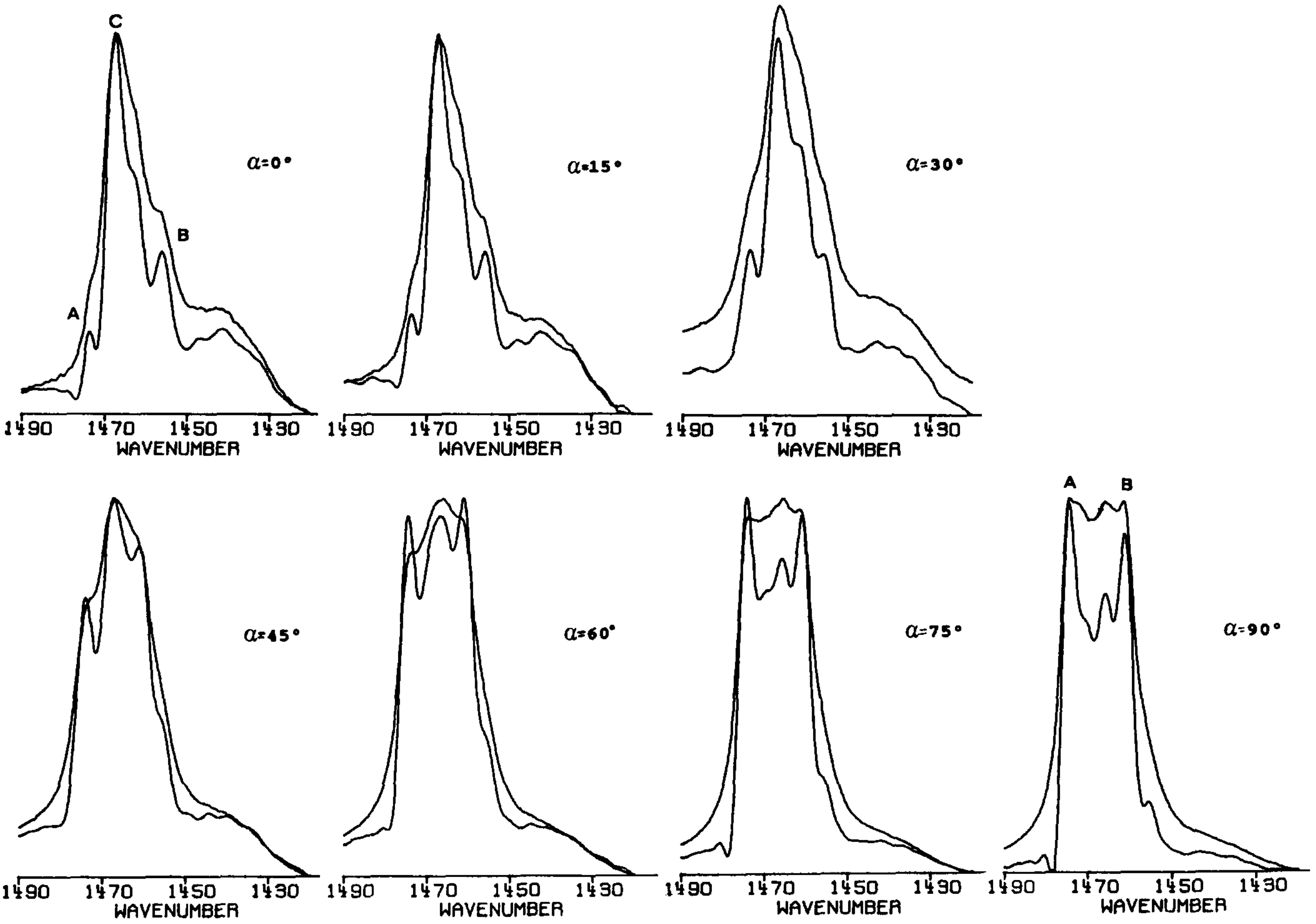


Figure 8 Infra-red absorption spectra of PE25 in polarized light as recorded and after band deconvolution. For the meaning of the symbols see *Figure 7*. To help in the comparison, for each value of α two spectra are superimposed with an artificial readjustment of the intensities. For the same reason there are no correlations between the intensities at two different values of α. The physically meaningful trend of intensities with α is that of *Figure 7*

is melted and cooled, the crystalline PE obtained after melting is shown to be orthorhombic (peaks A and B (see (f) above)) and partially conformationally disordered (see (g) above); the strong C peak of UD-PE has disappeared.

The existence and length of the *trans*-planar segments should be given by the observation of the so-called 'LAM modes' in the Raman spectrum at small shifts. For the reason discussed in the later section of this paper on 'Raman spectra', the Raman scattering seems to arise mainly from the upper skin of the sample. For this reason we do not expect to observe LAM scattering due to the isolated *trans* chains which exist in the core of the sample.

CH_2 rocking

In the complex spectral pattern of *Figure 6* one notices that the higher-frequency component is the result of two overlapping absorptions. The highest feature is evidence of the existence of the monoclinic lattice. This is also supported by the reflection spectra in the CH_2 rocking range (see last paragraph of section entitled 'Multiple internal reflection spectra').

CH_2 WAGGING OF CONFORMATIONAL DEFECTS

Information on the conformational disorder in UD-PE is given by the 'defect modes' in the infra-red in the 1375–1300 cm^{-1} range. As stated in paragraph (c) in the section on 'Known probes', each peak originates from a localized mode pinned at a specific conformational defect. As shown in *Figure 6* these materials do contain conformational defects; their intensity relative to the other $q=0$ modes of the perfect part indicates that their concentration is small if compared with the case of 'normal' crystalline PE. The spectrum of *Figure 10* indicates the following local structures.

CH_3 groups

The band near 1375 cm^{-1} indicates the existence of CH_3 groups, which we mainly ascribe to end-groups and not to branching. It is known that when the CH_3 group is surrounded by a structurally ordered environment, its frequency occurs at 1375 cm^{-1}; if the environment is disordered or somewhat 'distorted', the frequency shifts to 1378 cm^{-1} (ref. 44), as observed in our cases. The end-groups of such chains then rest in a disordered domain of the material. If this is true, we should observe the defect mode due to *gauche* end CH_3 groups near 1345 cm^{-1}. A shoulder is indeed observed, but it is too weak to be taken as a meaningful signal. Since the concentration of CH_3 groups does not change when the material is subject to mild physical treatments, the intensity of such a band can be taken as a reference. Moreover, if the domains in which CH_3 groups rest are disordered they should be isotropic when examined in polarized light as 'liquid-like droplets' embedded in the material.

GTG′ *kinks*

The absorptions at 1368 and 1307 cm^{-1} indicate the existence of *GTG′* defects. These defects can be easily hosted within the stretch-aligned morphology of the material since the trajectory of the polymethylene chain is not altered. It is known that the *GTG′* kink is energetically favoured for a chain *in vacuo*, but it is very likely that it is also preferred in a solid since it does not much perturb the surrounding medium and can easily pack to form domains of collective kinks.

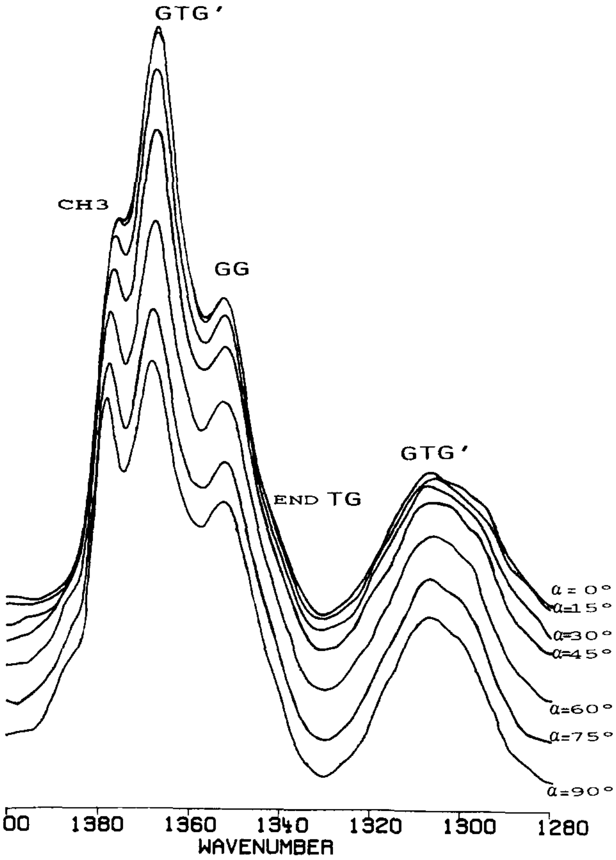


Figure 10 Infra-red absorption spectra in polarized light (as a function of α) of PE25 in the spectral range where absorption occurs due to specific conformational defects

The band at 1368 cm^{-1} of the oriented samples showed noticeable optical anisotropy with maximum absorption at $\alpha = 0°$, i.e. with the transition moment parallel to the stretching direction. Since the motion considered is a linear combination of CH_2 wagging, one concludes that the *GTG′* kinks are preferentially oriented. This fact can only be justified if the kinks are not isolated within *trans* chains but feel a cooperative driving force during drawing which generates oriented domains of *GTG′* kinks.

GG *defects*

The absorption at 1353 cm^{-1} shows the certain existence of *GG* defects, which indicate the existence of more disordered 'liquid-like' structures embedded in the material either around the CH_3 groups and/or somewhere else where chain folding takes place.

The intensity of the *GG* band relative to that at 1368 cm^{-1} due to *GTG′* kinks provides further information relevant to our work. If *GG* defects were associated with liquid-like droplets, the intensities of the 1368 and 1353 cm^{-1} lines should be similar to those observed in the spectrum of a liquid n-alkane or in the spectrum of our materials in the molten state (*Figure 11*). *Figure 11* clearly shows that the population of *GTG′* kinks relative to that of *GG* defects is much larger in solid UD-PE than for the same material in the molten state. This observation is further support for the existence of organized *GTG′* domains in UD-PE samples.

As a by-product of this work, the excess of *GTG′* kinks over *GG* defects in UD-PE has allowed us to find the

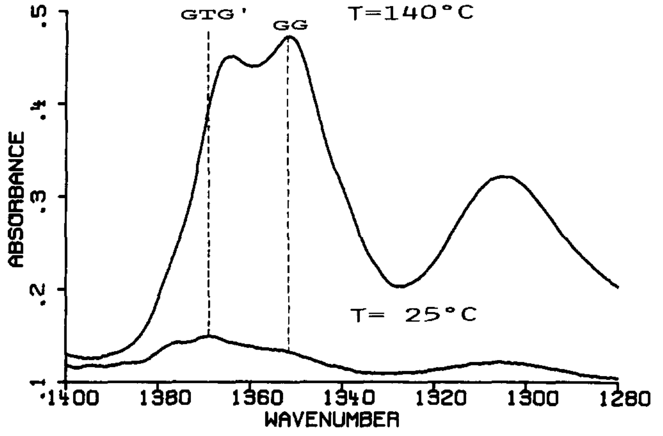


Figure 11 Comparison of the infra-red absorption spectra of PE25 in the solid phase (as prepared) and in the molten state showing that the relative concentration of *GTG'* kinks with respect to *GG* defects is larger for the ultradrawn material

origin of the broad absorption centred near 1450 cm^{-1} constantly observed in all polymethylene systems and which has been a puzzle in spectroscopic circles. By difference spectroscopy, (spectrum of UD-PE) – (spectrum of molten PE), when the *GTG'* absorptions are taken as the reference band to be compensated, unquestionably negative valleys develop near 1353 cm^{-1} (*GG* defect) and 1450 cm^{-1}. This shows that the 1450 cm^{-1} absorption originates from *GG* structures[45]. The negative features are consistent with the fact that the concentration of *GTG'* kinks in the solid UD-PE is larger than that of *GG* defects; by zeroing the *GTG'* absorption, an overshooting of the *GG* absorption must necessarily occur.

RAMAN SPECTRA

The Raman spectra of PE25 (i.e. PE with $DR=25$) in various scattering geometries have been recorded with the main purpose of identifying the symmetry species of the $q=0$ Raman-active phonons of such ultradrawn materials. The spectra obtained (*Figure 12*) are in agreement with those previously reported in the literature[44,47] and do not exhibit unusual features to be ascribed to the processes of ultra-orientation. For the assignment of the various symmetry species specific to each scattering geometry, see ref. 46.

Of particular interest to us is the factor group doublet at 1446 cm^{-1} (band A') and at 1425 cm^{-1} (band B') of the experimentally determined B_{1g} and A_g species respectively.

The reason for our interest is to verify in the Raman spectrum of UD-PE the existence of short *trans*-planar CH_2 sequences. As discussed above for the case of the infra-red spectra, we should also observe in the Raman spectra a singlet between the two components of the factor group doublet due to the orthorhombic lattice.

We have recorded the Raman spectra of the same solid isotopic solutions of $C_{36}H_{74}/C_{36}D_{74}$ studied by infra-red methods. The spectrum of *Figure 13* shows that the scattering of CH_2 bendings occurs at 1442 cm^{-1} asymmetrically placed in between the A'–B' doublet. The spectrum is also modified at higher frequencies near 1465 cm^{-1}. The difference in scattering in the 1465 cm^{-1} range is due to the changes in Fermi resonances for a chain in an orthorhombic lattice and for one chain isolated in its isotopic matrix[23].

Even if we have experimentally determined where the scattering occurs for the CH_2 bending of isolated *trans*-planar sequences, the Raman spectrum of UD-PE tapes does not give any scattering corresponding to the isolated *trans* structures seen in absorption spectroscopy.

The situation is similar to that observed in the ATR spectra discussed above; this leads to the conclusion that with the Raman spectrum we are probing substantially the surface of the sample, which we know is highly crystalline and orthorhombic.

This fact is quite relevant in the spectroscopy of polymers. Indeed, from this experiment it seems that the exciting radiation does not penetrate much into the sample and that the scattering volume is located at the surface of the sample within the first 10 μm layer as determined from ATR studies (see above). More detailed studies specifically aimed at this very important problem are required for a generalization of the phenomenon.

CONCLUSIONS: A MOLECULAR MODEL FOR THE STRUCTURE OF UD-PE FILMS

The vibrational data collected in this paper describe the structural situation of a UD-PE film at the molecular level in the following way:

(i) The skin of the film within $\sim 10 \mu m$ is highly crystalline and orthorhombic. We cannot yet distinguish whether the skin explored is only that between the grooves of the rough surface or includes also a thin layer of the core.

(ii) UD-PE film is a multiphase system with the topological distribution of the phases changing in going from the surface into the core.

(iii) The orthorhombic phase exists both on the surface and in the core, while the monoclinic phase starts at $d_p > 10 \mu m$.

(iv) The orthorhombic and monoclinic phases are highly anisotropic and are oriented along the draw direction.

(v) An additional phase is identified from $d_p > 10 \mu m$ into the core. This phase consists of sequences of CH_2 groups in *trans* conformation; their average length and their orientation in space with respect to the orthorhombic chains are still undetermined.

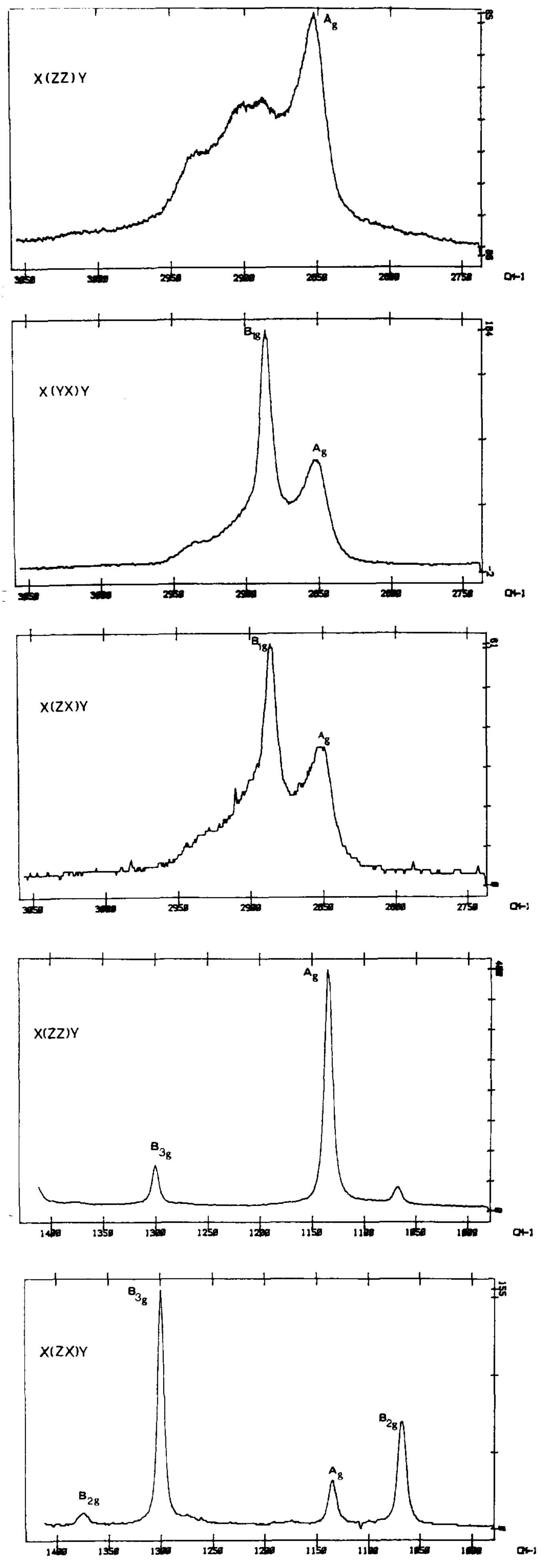
(vi) The additional *trans*-planar phase exists already by $DR = 15$ and qualitatively decreases its concentration at higher draw ratios with respect to the orthorhombic component.

(vii) *GTG'* kinks are organized in anisotropic domains seemingly as a result of collective phenomena of orientation during stretching. Oriented domains of *GTG'* kinks are likely to exist.

(viii) The concentration of *GTG'* kinks relative to *GG* defects is certainly larger than in the Flory's type situation encountered in molten PE or in liquid n-alkanes.

(ix) The chain-end methyl groups find themselves in a disordered environment with the same spectra as those observed for liquid n-alkanes. The existence of 'liquid-like' droplets or of 'disordered domains' around the CH_3 groups may be envisaged.

(x) Conformational defects of the type *GG* are observed and may originate from intrinsic 'liquid-like' structures, from the disorder around the CH_3 heads and from some kind of chain folding between crystallites or within polymer lamellae.



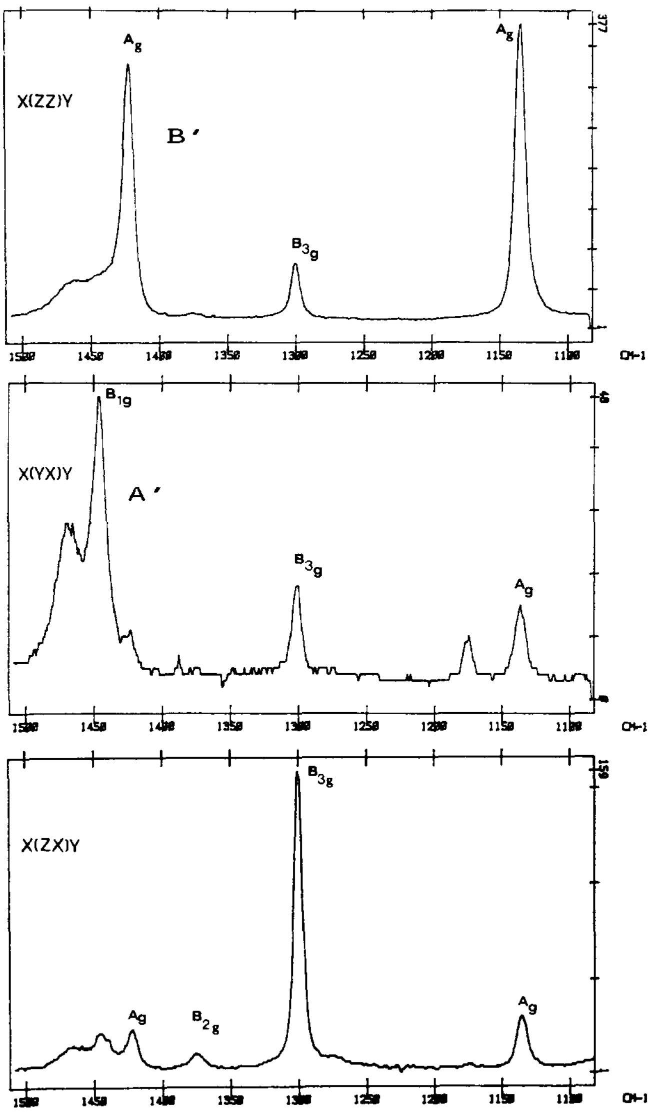


Figure 12 Raman spectra of PE25 in different scattering geometries (the traditional notation is used; see for instance ref. 46). In our experiment Z coincides with the stretching direction of our samples. This experiment provides the symmetry species of the $q=0$ phonons as indicated. The 'residual' unwanted scattering in the various geometries may be due to: (i) optical scrambling and/or bleeding, (ii) lack of perfect orientation of the chains (mosaic spread and/or imperfect alignment of the sample) and (iii) intrinsic lowering of the symmetry within the sample because of conformational disorder

(xi) The concentration of conformational defects decreases when the draw ratio increases, thus showing that conformationally disordered and coiled chains unwind towards a better alignment and perfection of the *trans*-planar molecules.

DISCUSSION

The comparison of our model with the ones proposed in the literature (see for instance refs. 3–6) is not easily feasible since most of the models focus on morphological (i.e. supermolecular) structures and avoid zooming in to more microscopic molecular details. Our experiments reveal several microstructures variously localized macroscopically in the samples. Some kind of correlation can be drawn between our data and the results of the broad-line n.m.r. experiments by Smith *et al.*[4]. The

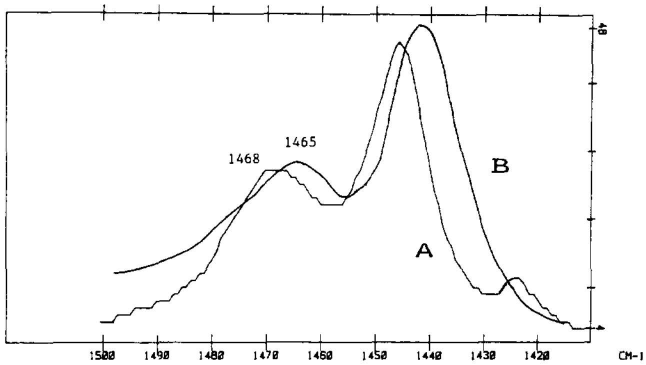


Figure 13 Comparison of the Raman spectrum of PE25 in $X(YX)Y$ scattering geometry (A) with the Raman spectrum of a 20/80 solid isotopic solution of $C_{36}H_{74}/C_{36}D_{74}$ (B)

orthorhombic and monoclinic structures may correspond to the 'less mobile' fraction detected by Smith *et al.*[4]. The 'highly mobile' matter corresponds to our 'disordered structures' existing around the CH_3 groups, within the 'liquid-like' domains or between and within lamellae. The 'intermediate component which does not crystallize' proposed by Smith *et al.* may correspond to our *trans*-planar sequences. These authors indicate a preferential orientation of the 'intermediate component' while we have not yet been able to determine an average orientation of the *trans* isolated chains with respect to the drawing direction. Moreover a quantitative estimate of the relative amount of '*trans*-planar sequences' has not yet been made, even if it is estimated to be relatively small, but sizeable. The mobility seen by n.m.r. cannot be revealed by i.r. (or Raman) since the timescales are different in the two experiments. The 'motions' detected by n.m.r. are much slower ($<10^8$ Hz) than the vibrational modes (10^{12} Hz). The optical spectra see an instantaneous average structure with respect to n.m.r.

This spectroscopic work is based on the use of spectroscopic markers specific to particular crystal or molecular structures; some of these probes are known and some have been identified for the first time. While some of the structures identified in ultradrawn PE are peculiar to UD-PE some, instead, are commonly found in solid and liquid n-alkanes and normal polyethylene.

We think that the information most relevant to the physics of ultradrawing is the generation of a certain population of 'isolated' *trans*-planar chains whose orientation within the oriented material may not coincide with the drawing direction. The most relevant problems in this field are to ascertain the following:

(i) Are the exceptional macroscopic mechanical properties of these ultradrawn polymer samples determined by the existence of the 'isolated *trans*-planar chains'? One could imagine (but with no evidence) that such *trans*-planar chains originate from 'tie molecules' joining lamellae or crystallites and tying them in such a way as to increase the macroscopic strength.

(ii) Are the isolated *trans* chains just an intermediate phase formed during the process of drawing? They necessarily exist since they originate from the unwinding of disordered chains as an intermediate step in the formation of a more stable crystalline phase. If this is the case the measure of the intensity of the infra-red band at 1467 cm^{-1} in polarized light on oriented samples could be used to monitor at the molecular level the process of drawing.

At the molecular level the qualitative model of the process of orientation for materials inside the core which seems to account better for observations (v), (vi) and (xi) in the previous section is the following. During drawing, conformationally disordered chains unwind and form *trans*-planar segments whose orientation progressively tends to align parallel to the drawing direction. The isolated segments later become organized in the orthorhombic and/or monoclinic lattice. One could also envisage that the monoclinic structure is the intermediate phase formed by the originally coiled chains which became *trans*-planar. The monoclinic phase transforms then into the final more stable orthorhombic phase.

The observed fact that the structure of the skin is almost totally orthorhombic (in contrast to the core) may be qualitatively explained in terms of a larger freedom of motion (i.e. conformational flexibility and translational mobility) of the chains on the surface. The instantaneous (temperature-dependent) inter- and intramolecular interactions (i.e. viscous forces) during drawing are certainly different on the skin and in the core. At the temperature and drawing rate chosen for the preparation of the samples, molecular chains on the skin of the film move faster and more efficiently towards the thermodynamically more stable orthorhombic structure. In the same experimental conditions the molecular motions inside the core are more hindered.

The discussion above refers to the problems of structure and morphology of ultradrawn polymers. This work has relevance also in the pure spectroscopy of polymers and in the structural results that have previously been derived on many polymers. This work seems to indicate that the scattering observed for polymers is that arising from the upper skin of the samples. Since we show here that the skin has a structure different from that of the core, many spectroscopic structural determinations on polymers may need to be revised. More specific studies on this problem are, however, required.

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