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Structural analysis of uniaxially oriented ^{13}C-labelled poly(ethylene terephthalate) films studied with solid-state ^{13}C nuclear magnetic resonance spectroscopy

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The structure of uniaxially oriented poly(ethylene terephthalate) (PET) with different draw ratios was studied in the solid state using ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy. All of the carbonyl carbons of the samples were isotopically labelled with ^{13}C, and therefore a detailed ^{13}C n.m.r. analysis, including the determination of the chemical-shift tensor for the carbonyl carbons, was possible. The chemical-shift tensor direction relative to the molecular symmetry axis was determined with the aid of semi-empirical quantum-chemical calculations by using the FPT-INDO (finite perturbation theory/intermediate neglect of differential overlap) method. The spectra of uniaxially oriented PET films observed by changing the angle between the draw direction and the magnetic field were analysed. Two components, one oriented and the other unoriented, were detected in the spectra of samples with draw ratios of 3 and 4. A highly oriented component was observed in addition to these two for samples having draw ratios of 5 (before and after heat treatment) and 5.66. The fraction of each component was determined by computer simulation of spectra that had been obtained as a function of sample orientation angle in the magnetic field. The angle θ between the phenylene *para* C–C axis and the chain axis was 16° ± 10° and 29° ± 5° for the oriented components, which is in agreement (within experimental errors) with the values reported previously by others. The angle-dependent spectra simulated with small p (characterizing the distribution of the fibre axis) confirm the presence of a highly oriented structure in the samples. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ^{13}C-labelled PET; solid-state ^{13}C n.m.r.; structural analysis)

INTRODUCTION

For crystalline solids, scattering of X-rays or neutrons by single crystals yields detailed diffraction patterns from which the structure can be derived in terms of atomic coordinates. However, if the material of interest is disordered, diffraction methods become progressively less useful because, with decreasing order, the diffracting patterns smear out, resulting in diffuse arcs and halos[1]. Numerous properties of materials, such as optical response, gas permeability and tensile or compressive strengths, are greatly influenced by the degree of order in the amorphous or partially ordered regions, as well as by order in the crystalline regions. Thus, it is very important to develop analytical methods for the structural determination of the amorphous or partially ordered regions of the material. Solid-state n.m.r. is one of the most powerful analytical methods capable of characterizing such partially ordered systems at the atomic level because of the angular dependences of the nuclear interactions detected in such experiments.

Poly(ethylene terephthalate) (PET) is a synthetic polymer widely used for fibres, films, bottles, injection-moulded parts and other products. Recently, orientational ordering in deuterated PET films drawn by necking was studied by ^{2}H n.m.r.[2]. Two types of samples of PET, one in which the benzene ring was deuterated and the other in which the ethylene groups were deuterated, were used to determine, in separate experiments, the orientations of the benzene ring and of the ethylene groups. By applying different 'waiting times' in the n.m.r. measurements, the orientation of chains of different mobilities was determined. The advantages of ^{2}H n.m.r. were discussed in comparison with other methods, as regards characterizing the amorphous regions.

Multidimensional 'direction exchange with correlation for orientation-distribution evaluation and reconstruction' (DECODER) n.m.r. experiments have been applied to determine molecular orientation distributions in PET

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thin films and fibres. This technique exploits natural-abundance ^{13}C resonances from different carbon sites to quantify oriented order[3]. For example, in PET fibres, direct reconstruction produces an orientation distribution that is at least bimodal, with 60% of the chains highly oriented with a full width at half-maximum (f.w.h.m.) of 20°. The angle between the phenylene *para* axis and the fibre axis is determined to be 18° ± 4°. For uniaxial films, the f.w.h.m. of the orientation distribution was measured to be 85°. The merit of the DECODER experiment is that it is not necessary to assume axial symmetry in the film samples.

On the other hand, ^{13}C CP/MAS (cross-polarization/magic-angle spinning) n.m.r. relaxation experiments have been applied to the determination of the molecular motions of PET samples by several researchers[4–9]. Most recently, on the basis of a relaxation study, Gabrielse *et al.*[9] proposed a three-region model for semicrystalline PET yarns, these being n.m.r. crystalline, rigid n.m.r. amorphous, and mobile n.m.r. amorphous regions.

In the present paper, ^{13}C solid-state n.m.r. spectra of uniaxially oriented PET films with different draw ratios are reported as a function of the angle between the machine draw direction and the laboratory magnetic field, in order to allow analysis of PET samples in terms of local structuring ordering. The basis of our studies is the orientation dependence of nuclear spin interaction tensors, which serve as probes of the relative orientations of specific bond vectors. Our attention is focused on the carbonyl carbons (which have large chemical-shift anisotropy) by the use of carbonyl carbon ^{13}C-labelled PET samples. Under these conditions, the contribution of the aromatic carbon peaks, which overlaps the carbonyl carbon peak in the natural-abundance ^{13}C CP spectrum, could be neglected in the analysis of ^{13}C n.m.r. results[3,9–11]. The ^{13}C n.m.r. analysis used here is essentially similar to the ^{15}N n.m.r. analyses that have already been applied to uniaxially aligned silk[12] and polyamides[13–17], except for the determination of the angles of the chemical-shift tensors relative to the molecular symmetry axis. In the present work, a finite perturbation semi-empirical molecular-orbital method (FPT-INDO, finite perturbation theory/intermediate neglect of differential overlap)[18] was used for the latter determination instead of the study of ^{13}C–^{15}N isotopically labelled model compounds[12–17].

THEORY

The ^{13}C chemical-shift anisotropy (*CSA*) principal axis system (PAS) is the reference frame in which the ^{13}C *CSA* tensor is diagonal with principal components $\sigma_{11} < \sigma_{22} < \sigma_{33}$. These tensor elements can be determined by observing the powder pattern arising from a randomly dispersed sample. The FAS (fibre axis system) is a reference frame fixed in the aligned sample, defined in such a way that the macroscopic fibre axis lies in the z direction (*Figure 1A*). Here, the macroscopic fibre direction is assumed to be the same as that of the machine draw direction (MD) of PET films. In addition, the sample is considered to have axial symmetry with respect to orientation. This has been concluded from the fact that there is no significant difference in the spectra when the angles of rotation about the draw axis are changed, as described later.

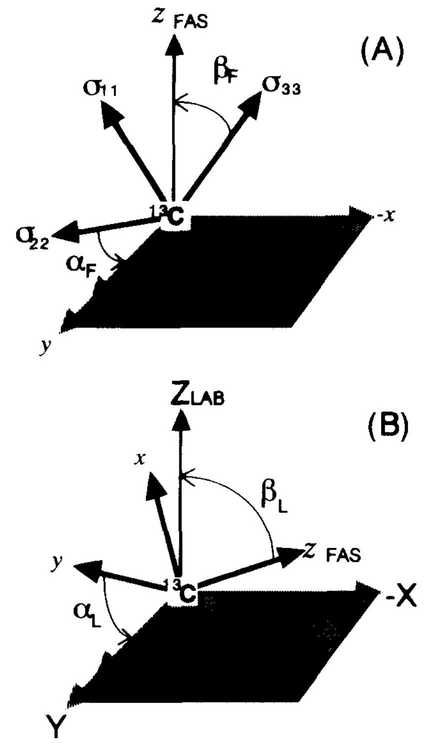


Figure 1 Transformations from the ^{13}C principal axis system (PAS) to the fibre axis system (FAS) (A) and from the FAS to the laboratory (LAB) frame of reference (B). The PAS is related to the FAS by the Euler angles α_F and β_F. The FAS is related to the LAB reference frame by the Euler angles α_L and β_L. The macroscopic fibre direction is assumed to be the same as that of the machine draw direction (MD) of the PET film

To transform the ^{13}C *CSA* tensor from the PAS representation to the FAS representation, the ^{13}C *CSA* tensor is first rotated about σ_{33} by α_F to bring σ_{22} into the xy plane (*Figure 1A*), followed by a rotation about σ_{22} by β_F to bring σ_{33} coincident with z_{FAS}. This position yields the convenient result that $\gamma_F = 0°$. The n.m.r. spectra are observed in the laboratory frame of reference (LAB), in which the magnetic field (B_0) lies in the Z direction. The angles α_L and β_L are the Euler angles that transform the FAS into the LAB frame of reference (see *Figure 1B*). Only two angles are required for this transformation because the n.m.r. experiment is sensitive only to the component of the tensor parallel to B_0. Therefore, the position of the FAS within the XY plane is arbitrary, and the Euler angle γ_L conveniently can be set to zero. The angle β_L is set in the experiment as an angle between z_{FAS} and Z_{LAB} (B_0). On the other hand, all values of α_L are equally represented in the spectrum ($0° < \sigma_L < 360°$).

The ^{13}C *CSA* tensor is rotated from the PAS through the FAS to the LAB frame of reference as follows[12]:

$$\hat{\sigma}_{PAS} \xrightarrow{\boldsymbol{R}_F(\alpha_F,\beta_F)} \hat{\sigma}_{FAS} \xrightarrow{\boldsymbol{R}_L(\alpha_L,\beta_L)} \hat{\sigma}_{LAB}$$

Here $\boldsymbol{R}_i(\alpha_i, \beta_i)$ represents the 3 × 3 unitary transformation matrix that rotates the original tensor to the i reference frame; i is a single-letter abbreviation denoting the frame to which the tensor is being rotated; (α_i, β_i) are the Euler angles as previously defined; and $\hat{\sigma}$ is the representation of the chemical-shift tensor in the reference frame denoted by its subscript. The general case for arbitrary relative orientations of the three reference frames is illustrated in *Figure 1*. The explicit form of the above net transformation is expressed as the following series of matrix multiplications:

$$\hat{\sigma}_{\mathrm{LAB}} = \boldsymbol{R}_{\mathrm{L}}(\alpha_{\mathrm{L}}, \beta_{\mathrm{L}}) \cdot \boldsymbol{R}_{\mathrm{F}}(\alpha_{\mathrm{F}}, \beta_{\mathrm{F}}) \hat{\sigma}_{\mathrm{PAS}}$$
$$\boldsymbol{R}_{\mathrm{F}}(\alpha_{\mathrm{F}}, \beta_{\mathrm{F}})^{\mathrm{T}} \boldsymbol{R}_{\mathrm{L}}(\alpha_{\mathrm{L}}, \beta_{\mathrm{L}})^{\mathrm{T}}$$

where $\hat{\sigma}_{\mathrm{LAB}}$ denotes the final representation of the *CSA* tensor in the laboratory frame, the superscript T denotes the transpose of the preceding matrix, and

$$\hat{\sigma}_{\mathrm{PAS}} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

$$\boldsymbol{R}_i(\alpha_i, \beta_i) = \begin{pmatrix} \cos\beta_i & 0 & -\sin\beta_i \\ 0 & 1 & 0 \\ \sin\beta_i & 0 & \cos\beta_i \end{pmatrix} \cdot \begin{pmatrix} \cos\alpha_i & \sin\alpha_i & 0 \\ -\sin\alpha_i & \cos\alpha_i & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The observed chemical shift corresponds to the component of the transformed chemical-shift tensor that is parallel to the magnetic field, which is the (3,3) component of the resulting $\hat{\sigma}_{\mathrm{LAB}}$ matrix.

For example, for the case where the fibre axis is parallel to B_0, $\alpha_{\mathrm{L}} = 0°$ and $\beta_{\mathrm{L}} = 0°$, and the observed chemical shift $\sigma_{\|}$ is given by:

$$\sigma_{\|} = \sigma_{11} \sin^2\beta_{\mathrm{F}} \cos^2\alpha_{\mathrm{F}} + \alpha_{22} \sin^2\beta_{\mathrm{F}} \sin^2\alpha_{\mathrm{F}} + \sigma_{33} \cos^2\beta_{\mathrm{F}}$$

For the case where the fibre axis is perpendicular to B_0, $\beta_{\mathrm{L}} = 90°$ and $0° < \sigma_{\mathrm{L}} < 360°$ (all values of α_{L} will be equally represented in the spectrum). The observed chemical shift $\sigma_{\perp}$ for this situation can be given by:

$$\sigma_{\perp}(\alpha_{\mathrm{F}}, \beta_{\mathrm{F}}, \alpha_{\mathrm{L}}) = F_{11} \cos^2\alpha_{\mathrm{L}} + 2F_{12} \cos\alpha_{\mathrm{L}} \sin\alpha_{\mathrm{L}} + 2F_{22} \sin^2\alpha_{\mathrm{L}}$$

where

$$F_{11} = \sigma_{11} \cos^2\beta_{\mathrm{F}} \cos^2\alpha_{\mathrm{F}} + \sigma_{22} \cos^2\beta_{\mathrm{F}} \sin^2\alpha_{\mathrm{F}} + \sigma_{33} \sin^2\beta_{\mathrm{F}}$$
$$F_{12} = (\sigma_{22} - \sigma_{11}) \cos\beta_{\mathrm{F}} \cos\alpha_{\mathrm{F}} \sin\alpha_{\mathrm{F}}$$
$$F_{22} = \sigma_{11} \sin^2\alpha_{\mathrm{F}} + \sigma_{22} \cos^2\alpha_{\mathrm{F}}$$

This equation represents a family of curves that are manifested in the spectral lineshape.

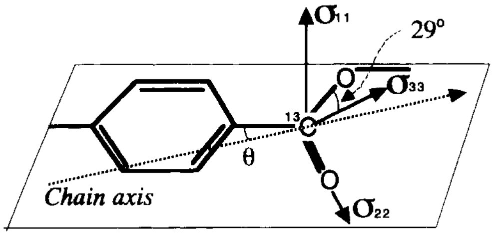


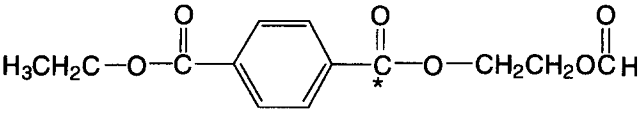
Figure 2 The principal axis system (PAS) orientation of the carboxyl carbon relative to the bonds of interest in PET. The σ_{11} axis corresponds to the normal of the carboxyl (O–C=O) plane. The σ_{22} axis is set parallel to the carbonyl direction (C=O) in the carboxyl plane. The σ_{33} axis is perpendicular to both σ_{11} and σ_{22} directions. These angles were determined from the results with FPT-INDO calculation for the appropriate model compound of PET. The angle θ between the phenylene *para* C–C axis and the chain axis is also shown

Since the samples usually have an orientational distribution around the fibre axis, a Gaussian distribution (around β_{L}) is assumed, with the distribution characterized by p, the standard deviation of the assumed Gaussian distribution, defined as follows[2,17]:

$$f(x) = [1/(2\pi p)] \exp[-(x - \beta_{\mathrm{L}})^2/2p^2]$$

where $f(x)$ is the probability of the oriented polymer molecules having angle x between the fibre axis and B_0.

The possible orientations obtained by the above method can be readily expressed in terms of bond angle orientations, provided the orientation of the ^{13}C PAS is known relative to the bonds of interest (*Figure 2*). The determination of the angles between the ^{13}C PAS and the molecular symmetry axis (MSA) frame of reference (the C–C bond of phenylene *para* axis, C–O and C=O bonds of PET molecule) was made by FPT-INDO[18]. In these calculations, the coordinates of PET reported by Daubeny *et al.*[19] were used as the coordinates of an appropriate model compound of the local structure as follows:



where the calculation of the chemical-shift tensor is performed for the carbonyl carbon marked by the star. It was found that the σ_{11} axis is approximately perpendicular to the O–C=O plane. The σ_{33} axis makes an angle of 29° with the C–O bond direction and σ_{22} is very close to the C=O bond direction in the O–C=O

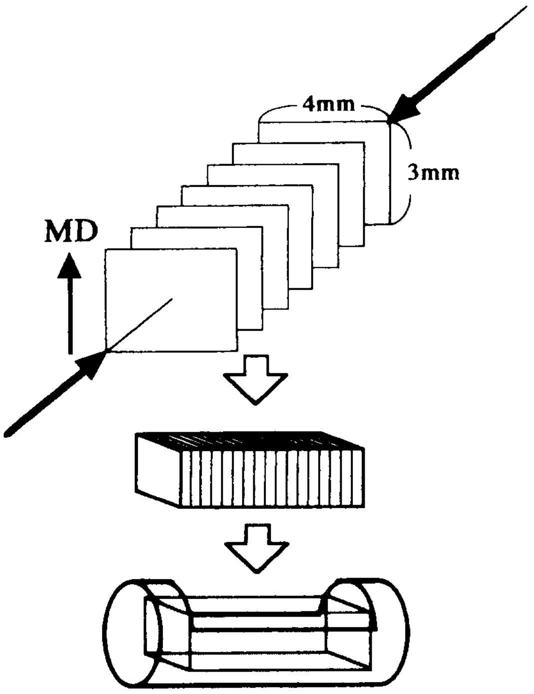


Figure 3 Preparation of a uniaxially oriented block sample of PET films for ^{13}C CP n.m.r. observations as a function of β_{L}, the angle between the machine draw direction (MD) and the magnetic field

plane (*Figure 2*). These angles determined in this way are very close to the values reported for protonated carboxyl groups[20,21]. The angle θ between the phenylene *para* C–C axis and the chain axis is also shown in *Figure 2*.

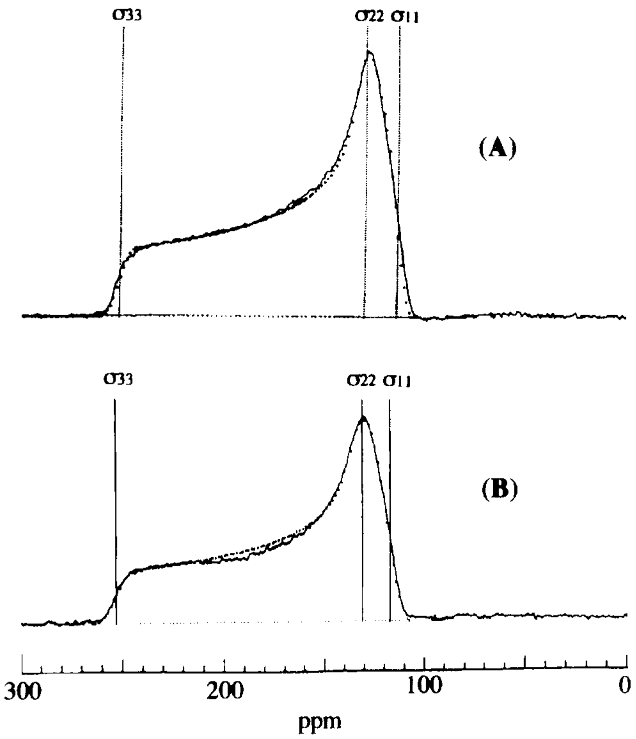


Figure 4 Comparison of observed (full curve) and calculated (dotted curve) ^{13}C powder patterns for randomly dispersed samples of carbonyl carbon ^{13}C-labelled amorphous PET film (A) and for the uniaxially oriented film with draw ratio 5 (B). The principal components of the ^{13}C chemical-shift tensor for the amorphous film (A) and the drawn film (B) are $\sigma_{11} = 114$, $\sigma_{22} = 130$ and $\sigma_{33} = 252$ ppm ($\sigma_{\rm iso} = 165.3$ ppm), and $\sigma_{11} = 117$, $\sigma_{22} = 131$ and $\sigma_{33} = 254$ ppm ($\sigma_{\rm iso} = 167.3$ ppm), respectively

EXPERIMENTAL

Materials

PET polymers were prepared by a stepwise melt polymerization process, which consists of transesterification, prepolymerization and finishing polymerization steps. In the transesterification stage, carbonyl carbon ^{13}C-labelled dimethyl terephthalate (98% enrichment, purchased from Shoko Tsusho Ltd, Japan) was used. Amorphous ^{13}C-labelled PET films (150 μm thick) were obtained by melt pressing for 5 min at 257°C under a maximum pressure of 100 kg cm^{-2} after the PET powder was dried for 2 h at 120°C. Uniaxial films with draw ratio 3 were prepared at a draw rate of 10 mm min^{-1} at 45°C[2]. The films (4 mm × 3 mm) were set as shown in *Figure 3*, and used in this form for ^{13}C n.m.r. observations. The 50 μm thick amorphous ^{13}C-labelled films were prepared at a draw rate of 500 mm min^{-1} at 80°C. Samples with draw ratios of 2, 3, 4, 5 and 5.66 were also used for n.m.r. observations. The sample with draw ratio 5 was also annealed at 170°C for 0.5 h.

^{13}C n.m.r. measurements

A JEOL EX-270 spectrometer operating at 67.8 MHz for ^{13}C observation was used. Samples were examined at 25°C. The cross-polarization (CP) technique (Hartmann–Hahn matched conditions) with $CP_{\rm mix} = 2$ ms was used with a recycle delay of 5 s and the spin-locking field strength was 1.2 mT. Phase cycling was used to minimize artifacts. A goniometer was used to adjust the sample to different angles $\beta_{\rm L}$ between the draw direction (MD) and the magnetic field; the angles examined included 0°, 15°, 30°, 45°, 60°, 75° and 90°. In addition, in order to examine axial symmetry with respect to MD, two spectra of the uniaxial films with draw ratio 5.66 were observed by changing the angle of rotation about MD when MD is parallel to the magnetic field. Typically 350 free induction decays (FIDs) were accumulated for each spectrum. Chemical shifts are represented in ppm downfield from tetramethylsilane (TMS); the chemical shift of the methyl peak of hexamethylbenzene was used as an external chemical-shift reference and converted as 17.3 ppm from TMS. All the peak simulations were

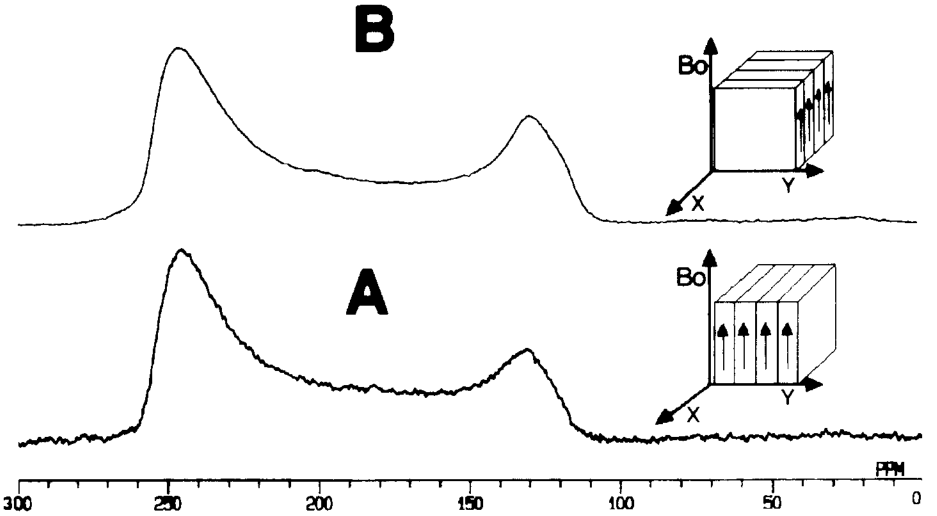


Figure 5 The ^{13}C CP n.m.r. spectra of carbonyl carbon ^{13}C-labelled uniaxially drawn (×5.66 at 80°C) PET film obtained by changing the angle of rotation around MD when MD is parallel to the magnetic field

performed with the programs made by us[12] using a MIPS RS 3230 work station or an NEC PC-9801 personal computer.

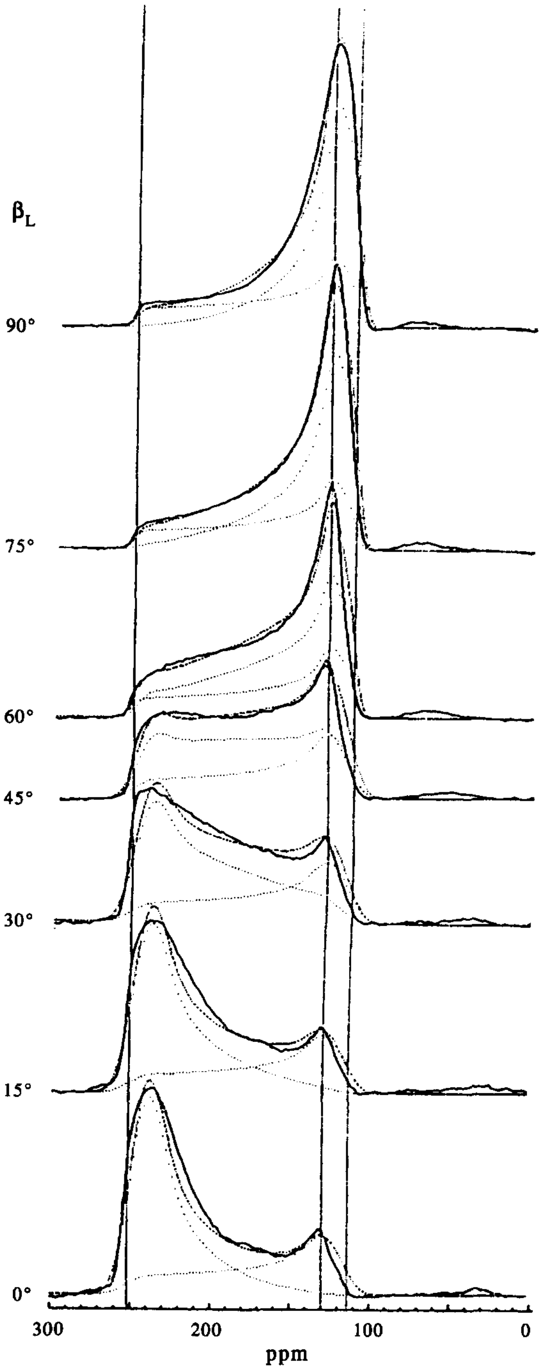


Figure 6 The ^{13}C CP n.m.r. spectra of carbonyl carbon ^{13}C-labelled uniaxially drawn (×3 at 45°C) PET film as a function of β_L, the angle between the draw direction and the magnetic field. Full and dotted curves show observed and calculated spectra, respectively. The fractions of the two components, amorphous (35%) and oriented (65%), were determined by computer simulations of the observed n.m.r. lineshapes. The structural parameters $\alpha_F = 90°$, $\beta_F = 18° \pm 6°$ and $p = 22°$ were found to be characteristic of the oriented component, while the chemical-shift tensor elements are $\sigma_{11} = 114$, $\sigma_{22} = 130$ and $\sigma_{33} = 252$ ppm

RESULTS AND DISCUSSION

^{13}C CP powder pattern spectra

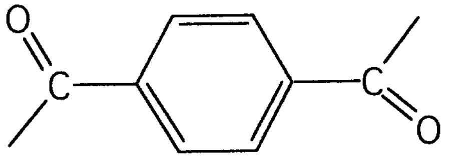
Figure 4A shows the ^{13}C CP n.m.r. spectrum (full curve) of carbonyl carbon ^{13}C-labelled amorphous PET powder with the corresponding peak simulation (dotted curve). The simulation includes a line-broadening factor (*LB*) of 4 ppm. It is clear that only carbonyl carbon signals contribute to the spectrum[3]. The chemical-shift tensor elements obtained by means of the simulation[12] were $\sigma_{11} = 114$ ppm, $\sigma_{22} = 130$ ppm and $\sigma_{33} = 252$ ppm. Values for these elements of the carbonyl carbon have previously been reported as $\sigma_{11} = 122$ ppm, $\sigma_{22} = 122$ ppm and $\sigma_{33} = 250$ ppm by Murphy *et al.*[10], and as $\sigma_{11} = 113$ ppm, $\sigma_{22} = 126$ ppm and $\sigma_{33} = 252$ ppm by Chmelka *et al.*[3] for natural-abundance PET samples. Our values are very close to the latter values. The powder pattern spectrum of PET powder prepared from uniaxially drawn films with draw ratio 5 is also shown in *Figure 4B*. Simulation of the result yields $\sigma_{11} = 117$ ppm, $\sigma_{22} = 131$ ppm and $\sigma_{33} = 254$ ppm, with $LB = 5$ ppm. Thus, slightly larger tensor values were obtained than with the former case. The σ_{iso} value was 167.3 ppm for PET powder prepared from the film (draw ratio 5), while the value was 165.3 ppm for amorphous PET powder. This is in agreement with the ^{13}C CP/MAS observation of PET where the carbonyl peak from the crystalline region is shifted slightly upfield from the corresponding resonance of the amorphous region[9]. The chemical-shift tensor values determined here will be used for the structural characterization of the oriented components in the PET samples below.

Axial symmetry of ^{13}C CP spectra around the draw axis

As is shown in *Figure 5*, two spectra of the sample with draw ratio of 5.66 were observed by changing the angle of rotation around MD. Here, MD is parallel to the magnetic field. There is no significant difference between the spectra A and B. A similar observation was obtained for the sample with draw ratio 5 after heat treatment at 170°C. These results indicate axial symmetry around the draw direction of the oriented films.

^{13}C CP spectra of oriented sample (draw ratio 3) drawn at 45°C

The ^{13}C CP n.m.r. spectra of uniaxially oriented PET films (draw ratio 3, and drawn at 45°C) are shown in *Figure 6* as a function of the angle β_L between the machine draw direction (MD) and the magnetic field. The glass transition temperature T_g of PET has been reported to be about 68°C[3,22]. Thus, the oriented PET film used here was drawn at a temperature lower than T_g. It is clear from the angle-dependent spectra that the spectra cannot be explained by assuming only a single angular-dependent component in the material examined. For example, the small peak at about 130 ppm between $\beta_L = 0°$ and 30° indicates strongly the presence of an angle-independent powder pattern component in this sample. By use of spectral simulation (dotted curves in *Figure 6*), the fraction of the powder pattern and the oriented components in the obtained spectra were determined as 35% and 65%, respectively. For the latter component, the structural parameters were determined as $\beta_F = 18° \pm 6°$ with $p = 22°$. The appearance of a series of simulated spectra as a function of β_L is strongly dependent on the angle β_F and, therefore, the angle β_F can be determined with good precision by simulation. Chmelka *et al.*[3] determined the angle (β_P in their paper) between the chain axis and the σ_{33} direction at the carbonyl carbon site from the two-dimensional (2D) ^{13}C DECODER spectra of drawn PET fibre as 18° ± 7°. Since β_F as defined for our work has the same direction as β_P, there is agreement between the two studies with regard to the angle between the chain axis and the σ_{33} direction at the carbonyl carbon site. On the other hand, the spectral change as a function of β_L is insensitive to the angle α_F in the simulation. Walls applied attenuated total reflectance infra-red spectroscopy (a.t.r.-i.r.) to the examination of the conformational change by sample orientation in uniaxially drawn PET films[23]. A remarkable increase in the absorbance of the PET vibration at 1340 cm^{-1} (CH_2 wagging vibration from the glycol segments of the polymer chain in the *trans* conformation) and decrease in the absorbance at 1370 cm^{-1} (*gauche*) are observed for uniaxial draw ratio between 2 and 3. The most significant changes in extended *trans* content occur with samples in this uniaxial draw ratio range. In addition, the conjugated system:



is substantially planar[19]. Thus, the chain axis is considered to be in the plane. As is shown in *Figure 2*, with β_F = 18° ± 6°, the value 22° ± 6° is obtained as the

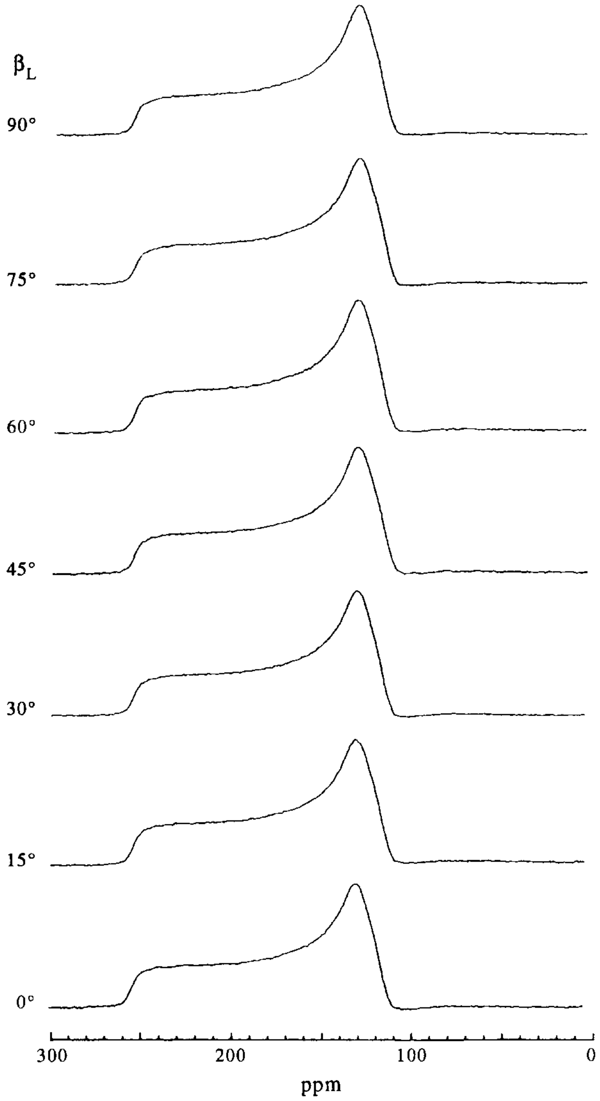


Figure 7 The ^{13}C CP n.m.r. spectra of carbonyl carbon ^{13}C-labelled uniaxially drawn (×2 at 80°C) PET film as a function of β_L

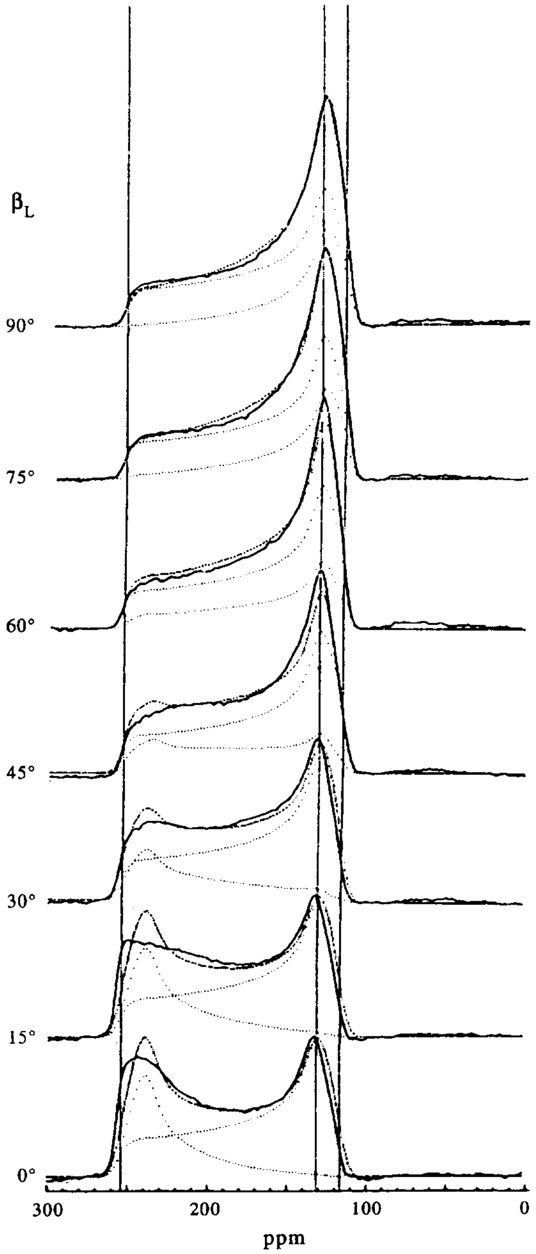


Figure 8 The ^{13}C CP n.m.r. spectra of carbonyl carbon ^{13}C-labelled uniaxially drawn (×4 at 80°C) PET film as a function of β_L, the angle between the draw direction and the magnetic field. Full and dotted curves show observed and calculated spectra, respectively. The fractions of the two components, amorphous (70%) and oriented (30%), were determined from simulations. The structural parameters were $\alpha_F = 90°$, $\beta_F = 20° \pm 10°$ and $p = 24°$ for the oriented component when the chemical-shift tensor elements are $\sigma_{11} = 117$, $\sigma_{22} = 131$ and $\sigma_{33} = 254$ ppm

angle θ between the phenylene *para* axis and the chain axis in the oriented chain of uniaxially aligned PET films (draw ratio of 3, drawn at 45°C). In this case, α_F is determined to be approximately 90° (refs 12, 13, 17). Within experimental error, the value of θ is in agreement with the reported values: 20° by Arnott and Wonacott[24]; 24° by Rober and Zachmann[2] and Harbison *et al.*[11]; and 18° by Chmelka *et al.*[3].

^{13}C CP spectra of oriented samples (draw ratios 2, 3, 4, 5 and 5.66) drawn at 80°C

Figure 7 shows the ^{13}C CP n.m.r. spectra of a PET sample (draw ratio 2) as a function of the angle β_L. The spectra are independent of the angle and are typical powder patterns. Thus, with a draw ratio of 2 when the sample is drawn at 80°C (above T_g), the structure is found to be a completely disordered one.

On the other hand, an angle-dependent component is observed in the spectra of a PET sample with draw ratio of 3. Since the spectral pattern is similar to the case of the sample with draw ratio of 4, except for the fraction of the powder pattern, the detailed spectral simulations are shown for the latter sample (*Figure 8*). The appearance of the oriented component in the uniaxially oriented PET chains in samples with draw ratios of more than 3 corresponds to the conformational change from *gauche* to *trans* in the glycol segments of the polymer chain[23]. In the simulation (dotted curves), the powder pattern spectrum (*Figure 4B*) of uniaxially oriented PET film with the ^{13}C chemical-shift tensor values $\sigma_{11} = 117$ ppm, $\sigma_{22} = 131$ ppm and $\sigma_{33} = 254$ ppm was used. The angle α_F was considered to be 90° as mentioned above. The angle β_F is 20° ± 10° and the distribution parameter p is 24°. Although the character of the spectral change with orientation angle is considered to be roughly reproduced in the simulations, the agreement between the observed and calculated spectra is not good in the lower-field portion of the spectra when $\beta_L = 0°$ to 45°. The disagreement might come from the deviation from the assumed symmetry distribution of the chain axis or from the assumption of a Gaussian distribution as well as the presence of small amounts of other components. The fraction of angle-dependent component increases from 20% when the draw ratio is 3 to 30% with a draw ratio of 4.

The assumption of two components can no longer be retained when considering spectra obtained with a PET sample with a draw ratio of 5 (*Figure 9*). There are additional broad peaks in these spectra (marked by arrows) for $\beta_L = 15°$ to 60°, indicating the presence of a highly oriented component in addition to the oriented component observed in the spectra of the samples with

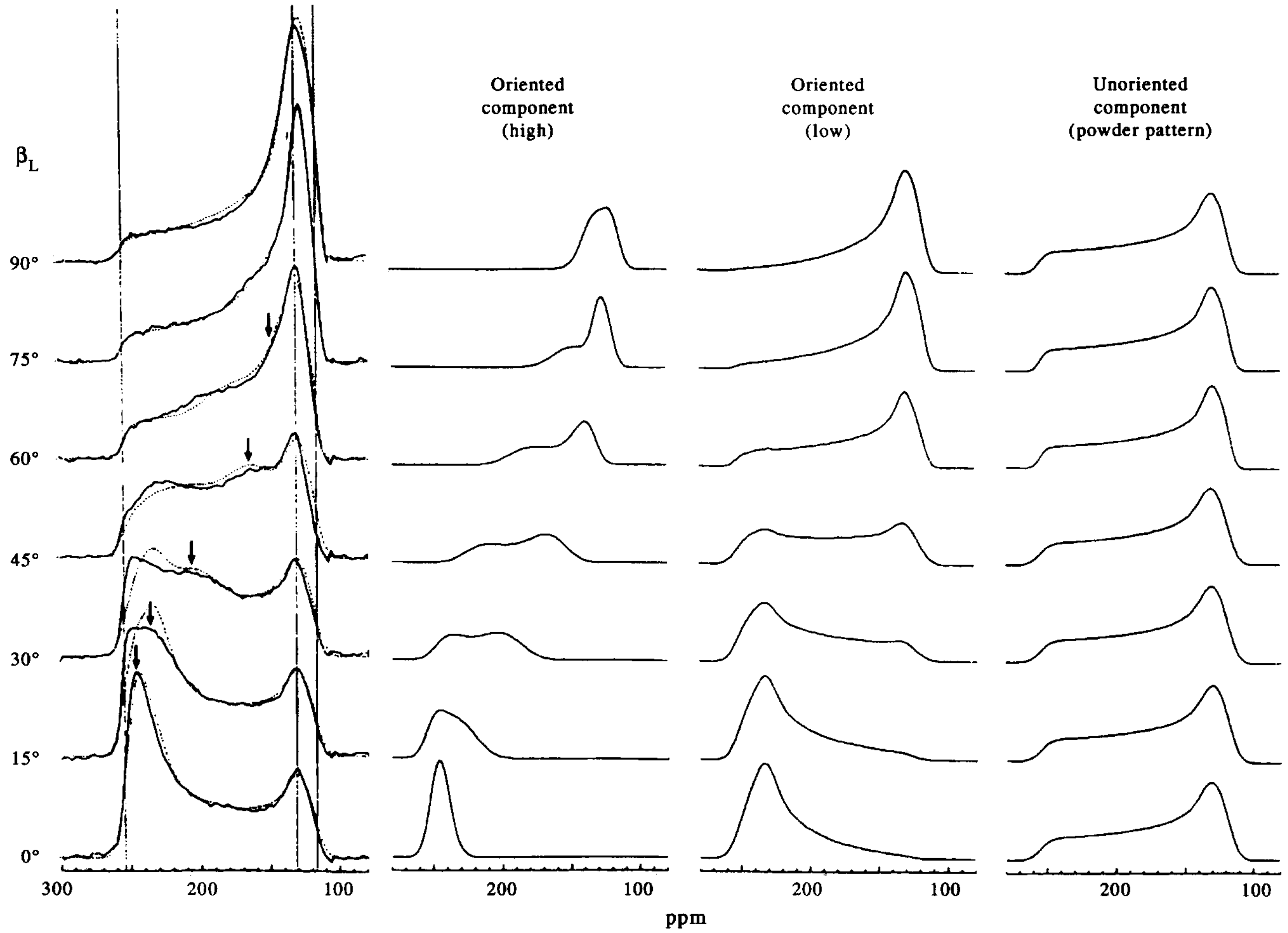


Figure 9 The ^{13}C CP n.m.r. spectra of carbonyl carbon ^{13}C-labelled uniaxially drawn (×5 at 80°C) PET film as a function of β_L, the angle between the draw direction and the magnetic field. Full and dotted curves show observed and calculated spectra, respectively. The fractions of the three components, amorphous (55%) and two oriented (33% and 12%) ones, was determined by simulation. The structural parameters were $\alpha_F = 90°$, $\beta_F = 24° \pm 10°$ and $p = 24°$ (low oriented component) and $\alpha_F = 90°$, $\beta_F = 16° \pm 6°$ and $p = 5°$ (high oriented component), respectively, when the chemical-shift tensor elements are $\sigma_{11} = 117$, $\sigma_{22} = 131$ and $\sigma_{33} = 254$ ppm

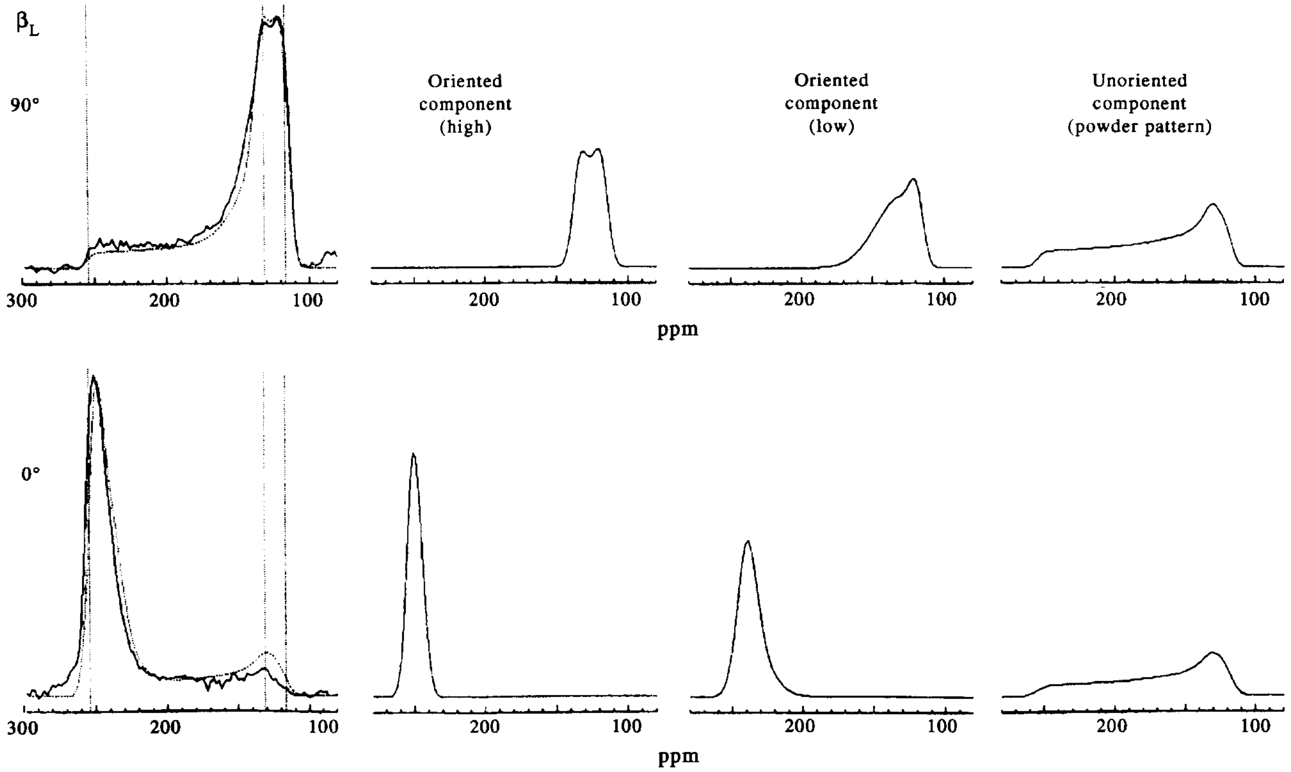


Figure 10 The ^{13}C CP n.m.r. spectra of carbonyl carbon ^{13}C-labelled uniaxially drawn (×5 at 80°C) PET film after heat treatment at 170°C. The angle β_L between the draw direction and the magnetic field is set as 0° and 90°. Full and dotted curves show observed and calculated spectra, respectively. The fractions of the three components present, amorphous (30%) and two oriented (35% and 35%), were determined by simulation. The structural parameters are $\alpha_F = 90°$, $\beta_F = 20° \pm 10°$ and $p = 8°$ (low oriented one) and $\alpha_F = 90°$, $\beta_F = 11° \pm 5°$ and $p = 2°$ (high oriented one), respectively, when the chemical-shift tensor elements are $\alpha_{11} = 117$, $\sigma_{22} = 131$ and $\alpha_{33} = 254$ ppm

Table 1 Fraction (%) of disordered and ordered components for uniaxially oriented PET films determined from ^{13}C CP n.m.r.

	Drawn at 45°C	Drawn at 80°C					Heat treatment
	(×3)	×2	×3	×4	×5	×5.66	(×5)
Disordered	35	100	80	70	55	47	30
Ordered[a]	65	0	20	30	33 (l)	38 (l)	35 (l)
					12 (h)	15 (h)	35 (h)

[a] (l) = low ordered component; (h) = high ordered component

Table 2 Structural parameters (degrees) of the ordered components for uniaxially ordered PET samples determined from ^{13}C CP n.m.r. (α_F was assumed to be 90°)[a]

		Drawn at 80°C			Heat treatment (×5)	
	Drawn at 45°C (×3)	×3 & ×4	×5 & ×5.66			
			Low	High	Low	High
p	22	24	24	5	8	2
β_F	18 ± 6	20 ± 10	24 ± 10	16 ± 6	20 ± 10	11 ± 5
θ	22 ± 6	20 ± 10	16 ± 10	24 ± 6	20 ± 10	29 ± 5

[a] The definition of the angles α_F and β_F is shown in *Figure 1A*; p = orientational distribution around the fibre axis (chain axis or MD); θ = angle between the phenylene *para* C–C axis and the chain axis (or MD) of PET film

draw ratios of 3 and 4. By assuming three components (one angle-independent, the other two with spectra that are orientation-angle-dependent), the spectra of the PET sample with a draw ratio of 5 could be simulated, as shown in *Figure 9*. The contribution of the powder pattern to the spectrum was thus determined to be 55%. The oriented component which corresponds to the oriented portion of samples with draw ratios of 3 and 4 was found to be 33%, with $\alpha_F = 90°$, $\beta_F = 24° \pm 10°$ and $p = 24°$. The fraction of highly oriented component of the sample was 12% with the structural parameters $\alpha_F = 90°$, $\beta_F = 16° \pm 6°$ and $p = 5°$. The spectral character of the third component reproduces very well the presence of the peaks marked by the arrows in *Figure 9*. The fraction of this component was found to increase with heat treatment of the PET sample, as will be described below. The structural parameters obtained by analysis of ^{13}C spectra are the same for samples with draw ratios of 5 and 5.66 (data are now shown). However, the fraction of each component changed to 50% for the powder pattern, 38% for the component with low orientation and 12% for the highly oriented component.

^{13}C CP spectra of oriented sample (draw ratio 5) after heat treatment at 170°C

Figure 10 shows the ^{13}C CP n.m.r. spectra of a sample of PET with a draw ratio of 5 after heat treatment at 170°C for 30 min at orientation angles of $\beta_L = 0°$ and $\beta_L = 90°$, along with the corresponding spectral simulations (dotted curves). These spectra clearly indicate that after heat treatment the sample is well oriented. For example, the doublet of sharp peaks in the spectrum at $\beta_L = 90°$ is highly consistent with this conclusion. By spectral simulation, the fraction of powder pattern contributing to these spectra was determined to be 30%. The low oriented component ($\alpha_F = 90°$, $\beta_F = 20° \pm 10°$ and $p = 8°$) was 35%, while the highly oriented one ($\alpha_F = 90°$, $\beta_F = 11° \pm 5°$ and $p = 2°$) was also found to be 35% of the sample. The small p values for the latter two components coincide with the well oriented character of the sample. The angle θ between the phenylene *para* C–C axis and the chain axis of the component is determined at 29° ± 5°.

The structural parameters obtained for uniaxially oriented PET films are summarized in *Tables 1* and *2*. The three components observed in the spectra of well oriented PET samples might correspond to the three-region model proposed by Havens and VanderHart[6] and Gabrielse *et al.*[9] on the basis of ^{13}C CP/MAS n.m.r. relaxation experiments: n.m.r. crystalline, rigid n.m.r. amorphous and mobile n.m.r. amorphous regions in their experiment correspond to highly oriented component, low oriented component and unoriented component, respectively, in our experiment.

CONCLUSIONS

The ^{13}C CP n.m.r. method coupled with ^{13}C isotopic labelling of the carbonyl carbon site of the samples provides quantitative information on the molecular orientations in uniaxially oriented PET films. The presence of two components (one unoriented and another oriented) for the samples with draw ratios of 3 and 4 was detected from the spectral changes observed as a function of the angle between the draw direction and the magnetic field. For the samples with draw ratios of 5 (before and after heat treatment) and 5.66, an additional highly oriented component was clearly observed. The fraction of each component was determined by simulation of the spectra obtained at seven angular orientations relative to the magnetic field. Structural parameters such as the angle between the phenylene *para* C–C axis and the chain axis, and the distribution of the chain axis, are also determined for the oriented components through the simulations. Thus, ^{13}C CP n.m.r. observations coupled with ^{13}C isotopic labelling is very useful for the structural and compositional analysis of heterogeneous polymer samples.

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