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Orientation in uniaxially drawn poly(ethylene terephthalate) (PET) film by two-dimensional ^{13}C n.m.r. and *FT* i.r. spectroscopy

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Two-dimensional magic angle spinning (2D-MAS) ^{13}C n.m.r. spectroscopy and *FT* i.r. microscopy have been used to measure the orientation in uniaxially drawn film as a function of draw ratio. Results obtained agree well with those obtained by optical birefringence measurements. *FT* i.r. microscopy is a powerful method for mapping the orientation across the film thickness with quick data collection and analysis. The strength of the 2D-MAS n.m.r. method lies in its chemical and phase selectivity while its weakness lies in the time-consuming data acquisition and analysis coupled with the lack of knowledge about the orientation of the chemical shift tensor in the molecular frame. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Rational improvement of a film production process, either in terms of increased efficiency or better film properties, requires a fundamental understanding of the relationship between the properties of a film, such as its mechanical strength and the manufacturing conditions. As part of the process–property relationship new spectroscopic approaches have been applied to the measurement of the orientation in poly(ethylene terephthalate) (PET) films. Routine measurement of the molecular orientation in PET films can be readily carried out using optical birefringence[1], while X-ray diffraction[2] provides the most complete picture of the orientation in a crystalline phase. The principal reason for turning to spectroscopic approaches is to provide a more detailed analysis at the molecular level, without the complexity of X-ray methods, through the use of the specificity of the i.r. bands[3] or n.m.r. chemical shifts[4], second moments[5] and relaxation times[6]. One aim of the current work has been to assess the relative merits of n.m.r. and *FT* i.r. spectroscopic approaches. One review has described the use of spectroscopic techniques for the determination of molecular orientation[7]; however, since its publication significant developments have been made in the use of n.m.r. techniques. In particular, a two-dimensional magic angle spinning (2D-MAS) experiment[8–10] has been developed which allows orientation measurements to be made using high resolution solid state n.m.r. spectroscopy. The feature of this experiment is that an ordered sample is spun, at the magic angle, with data acquisition synchronous with the rotor position. By incrementing the start of the data acquisition through the rotor period a two-dimensional spinning sideband pattern can be obtained in which one dimension corresponds to the n.m.r. frequencies and the second the order dimension. Calculation of the two-dimensional spinning sideband intensities then allows the order parameters to be derived. A further development has been a two-dimensional n.m.r. experiment involving flipping of a sample between two axes, which permits a far greater degree of sophistication in the data analysis[11]. However, any routine or general use of this method would appear to be severely limited by the long data acquisition times of nearly a day.

The strength of the 2D-MAS n.m.r. approach is that the orientational distribution function can be measured for each of the different resolvable nuclei within a molecule in a partially ordered sample. Assignment of the chemical shifts to specific nuclei within the molecule is usually straightforward and in most cases the resolution is adequate enough to observe the principal molecular environments. One essential requirement is that the components of the chemical shift tensor and its orientation in the molecular frame must be known. Such data can be obtained from independent experiments, and the difficulty is more one of actually having to determine these parameters from preliminary experiments rather than any intrinsic limitation on the applicability of the method[16]. A further argument put forward for the use of n.m.r. methods is that they give access to the higher moments of the orientation distribution function. Whilst this is undeniably true, little practical value has been attached to this benefit to date. In essence, the merits of

using n.m.r. to study the orientation in PET films must be found elsewhere.

In contrast to n.m.r., where all the resonances seen for PET can be used to study the orientation, few i.r. bands are at the same time dichroic, resolvable and identifiable with unique molecular groupings. On the other hand, the most significant advantage of i.r. spectroscopy is that it is quick, data collection and analysis taking less than 2 h per sample. Furthermore, i.r. microscopy allows the orientation to be mapped across the thickness of a sample. Larger scale mapping, though, with a spatial resolution on the millimetre scale can only be achieved like n.m.r. by the gross method of cutting appropriate samples from the larger object. Smaller scale orientation measurements have been made on ^{2}H enriched polyethylene using an n.m.r. imaging method[12].

Selective n.m.r. experiments based either on differences in the n.m.r. relaxation times or on chemical shift differences offer the possibility of measuring separately the orientation of different phases within a sample. These phases could be crystalline or amorphous ones for a semicrystalline polymer, components of a blend or different layers in a laminated film. Though the frequencies, intensities and bandshapes of certain i.r. bands are sensitive to the crystallinity of the sample the interpretation is not as clear cut as for the n.m.r. parameters. Perhaps the most severe limitation of n.m.r. is that it is not a sensitive technique; consequently, data acquisition for the two-dimensional experiment is time consuming, of the order of 8 h.

The purpose of this paper is to compare the ease of determination and degree of orientation found in uniaxially drawn, uncrystallized PET film using the 2D-MAS n.m.r. technique with i.r. and optical refractive index measurements.

EXPERIMENTAL

N.m.r.

The cross polarization ^{13}C MAS n.m.r. spectra were acquired on a Bruker MSL-200 n.m.r. spectrometer operating at 50.32 MHz. Samples of the drawn film were prepared by first cutting a 5 mm strip parallel to the draw direction and then cutting the strip into sections 4 mm long. These were then packed on top of each other into the rotor, maintaining the draw direction at an angle of 90° to the rotor axis. This angle was chosen to facilitate the sample preparation and should lead to the absence of intensity in the odd numbered slices in the ω_1-(order) dimension. The rotor was balanced by adding a small amount of laponite. Contrary to expectations stable MAS was readily managed for the film samples. Indeed, experience with a variety of sample forms has shown that the majority of films, fibres and objects with a uniform density can be spun without difficulty. Active control of the spinning speed was unnecessary owing to the stability of the nitrogen pressure. In fact most fluctuations in the spinning speed stemmed from poor regulation of the room temperature.

Data acquisition followed the procedure outlined by Harbison *et al.*[8] with the sample spun at 2692 Hz. The order dimension was defined by 16 time intervals, which, together with a recycle delay of 3 s and 1280 transients

per time interval, gave a total acquisition time for 17 h. Subsequent results suggest that this could be reduced by a factor of four by using only eight time intervals and 640 transients. Analysis of the two-dimensional data set consists of finding the order parameters, of order L, $P_L(\cos \theta)$ necessary to describe the experimental two-dimensional n.m.r. spectrum $S(\omega_1, \omega_2)$ in terms of a weighted superposition of sub-spectra $S_L(\omega_1, \omega_2)$[8] where

$$S(\omega_1, \omega_2) = \sum P_L(\cos \theta) S_L(\omega_1, \omega_2)$$

The sub-spectra depend on the chemical shift tensor, spinning speed and angle between the rotor axis and the draw direction. In principle, the order parameters can be determined for all the carbon environments found in PET; however, in practice there is a trade-off between the simplicity of the data analysis and the certainty with which the alignment of the chemical shift tensor in the molecular frame is known. For PET, simplicity in the calculations was preferred and thus the carbonyl resonance was chosen because it has an axial chemical shift tensor. The sideband intensities, $I_{M,N}$, were calculated using the program MAS2D based on equation (25) of ref. 8. The program was validated before use by test data kindly provided by Professor H. W. Spiess.

I.r.

Polarized i.r. spectra were obtained for each of the three sample axis directions using i.r. microscopy. In this procedure the 'thickness direction' i.r. spectrum is observed directly, using an i.r. microscope, from samples prepared by thinly microtoming sections cut parallel to the forwards draw and sideways directions of the film. Sideways and thickness direction spectra are obtained from sections cut parallel to the sideways direction while forwards and thickness direction spectra are found from the sections cut parallel to the forwards direction. Since the thickness direction spectrum is duplicated, absorbance values for all three directions normalized to the same section thickness may be determined. An essential requirement of this method is that any orientation or reorientation caused by microtoming is negligible in comparison with the intrinsic orientation. Sections of the film were prepared at room temperature using a Leitz 1700 base-sledge microtome fitted with a steel D profile blade. Before microtoming, the film sample was sandwiched in a high density polyethylene 'book'.

Spectra were recorded at 2 cm^{-1} resolution using a Spectra-Tech i.r. Plan microscope employing a Spectra-Tech Wileglid polarizer and coupled with a Bomem DA-3 FT-IR spectrometer. The sampling area was typically 150 μm × 150 μm. The two bands used in the analyses were the 1018 and 875 cm^{-1} bands. For accurate analysis a film needs to be less than 10 μm in thickness. Chips, fibres and objects can be treated in a similar manner.

Film samples

The PET films were prepared with a range of draw ratios from 1.0 to 3.5 on the Melinex^R stenter. Overall, the film crystallinity was low, reflecting the uncrystallized nature of the films, ranging from 0% in the undrawn

sample to 13% in the 3.5 draw ratio film as measured by density column and Raman spectroscopy.

ORIENTATION

Before we can compare the order parameters determined by n.m.r. and i.r. spectroscopy we need to consider the question of the relevant axes in the two cases. For both n.m.r. and i.r. the primary orienting feature is not the molecular chain, but rather the specific physical phenomenon being measured. That is the chemical shift tensor for n.m.r. and the vibration transition dipole moment for i.r. In view of this it is a disadvantage that the exact orientation of the PET carbonyl chemical shift tensor with respect to the polymer chain axis is not known. An argument has been put forward, based on amides, which suggests that the unique axis of the axial tensor lies within 5° of the chain axis[8]. However, even in this work on PET fibres there was evidence for a greater deviation of 20–30° in an amorphous phase. Further evidence for the tilting of the chemical shift tensor away from the chain axis has been provided by the ^{13}C DECODER n.m.r. experiments on PET fibres where a deviation of $18 \pm 4°$ was reported[13].

Turning to the vibration transition dipole moment, Cunningham et al.[14] have established that the $1018\,cm^{-1}$ transition dipole moment lies at 20° to the chain axis while the $875\,cm^{-1}$ band lies at 85° to the axis. Hence, to determine the order parameters measured by i.r. spectroscopy with respect to the polymer chain, $P_2(\cos\theta)$, we make use of the Legendre addition theorem[7]:

$$P_2(\cos\beta) = P_2(\cos\xi).P_2(\cos\theta)$$

where $P_2(\cos\beta)$ is the measured order parameter, and ξ is the angle between the transition dipole moment and the chain axis.

RESULTS AND DISCUSSION

Preliminary i.r. experiments were carried out on a nominally unoriented undrawn film which had been confirmed as being unoriented by refractive index measurements. The i.r. results show that a small degree of orientation is induced into the sectioning direction by microtoming, with $\langle P_2(\cos\theta)\rangle$ around 0.04 rather than the 0.00 expected in the absence of orientation; however, the absolute amount is rather small. Thus, we can be confident that microtoming does not significantly increase the orientation into the draw direction. Typical polarized i.r. spectra for oriented film are shown in *Figure 1*.

A typical 2D n.m.r. spectrum is shown in *Figure 2* for a sample with a draw ratio of 3.5. Nine inner slices of the spectrum are shown, although significant intensity is only seen in the $M = \pm 2$ slice. Orientation in a sample is indicated by intensity in the ω_1-dimension; hence, the n.m.r. data are consistent with a low degree of order. As expected no sideband intensity is seen in the odd slices, $M = \pm 1, \pm 3$, confirming that the order director lies along the draw direction, though one cannot rule out that misalignment of the film strip parallel to the draw direction exactly compensates for a deviation in the order director from the draw
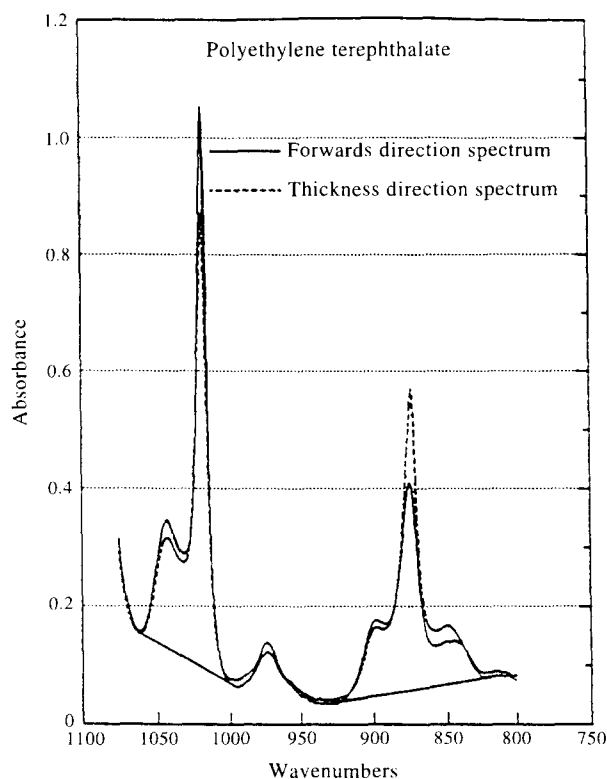
Figure 1 Typical polarized i.r. spectra taken from a section cut in the forwards draw direction from an oriented PET film. Setting the polarization parallel to the forwards direction generates the 'forwards direction spectrum'. Rotating the polarizer by 90° generates the 'thickness direction spectrum'
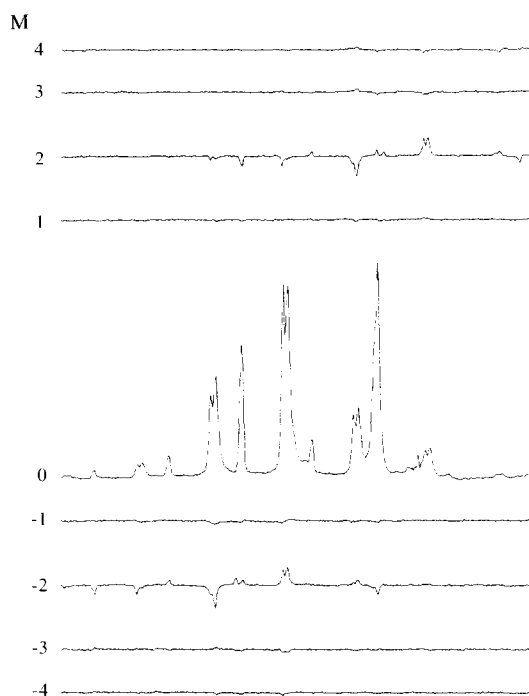
Figure 2 Cross-sections from the 2D ^{13}C CP/MAS orientation n.m.r. spectrum of the uniaxially drawn PET film with a draw ratio of 3.5. The M slices correspond to the order direction, while $M = 0$ slice is equivalent to the unoriented n.m.r. spectrum. A spinning speed of 2692 Hz was used together with a contact time of 2 ms

direction. In view of the low degree of order the data analysis was restricted to $P_2(\cos\theta)$. Note that in the fitting procedure the order parameters are implicitly determined with respect to the chain axis

through the defined orientation of the chemical shift tensor.

Values of $P_2(\cos\theta)$ against the draw ratio determined by n.m.r., i.r. and optical refractive index measurements are shown in *Figure 3*. It must be borne in mind that the order parameters have been determined for different groups since the carbonyl i.r. band is not sufficiently dichroic while the non-axial character of the aromatic carbon chemical shift tensor leads to a more complex analysis. Good agreement is seen on the whole, though the n.m.r. measurements tend to give a higher degree of order. This may be related to a movement of the unique axis of the chemical shift tensor away from the chain axis. For example, if the unique axis is 20° from the chain axis this would reduce $P_2(\cos\theta)$ by a factor of $p_2(\cos 20°)$, i.e. 0.82, which would bring the n.m.r. data into line with the other techniques. As mentioned above such a shift in the unique axis of the carbonyl chemical shift tensor has been proposed to explain an inconsistency in the order parameters seen for PET fibres. Naturally, the question arises, does the change in orientation of the chemical shift tensor reflect a different conformation for the carbonyl group with respect to the chain axis or is it a consequence of variations in the electronic structure? Matters are complicated by the paucity of data concerning the alignment of the chemical shift tensor in the molecular frame. Indeed, in contrast to the view expressed by Harbison *et al.*[8], there does not appear to be a consensus on the orientation of the carbonyl chemical shift tensor in ester compounds, as witnessed by the angle of 69° found for dimethyl oxalate[15], but 15-25° in amides.

In the absence of firm independent data on the molecular frame orientation of the carbonyl chemical shift tensor the results reported here can only be used as evidence that the unique axis of the carbonyl tensor lies 20° or so from the draw direction. Only when more accurate information is available, describing the tensor orientation in the molecular frame, can the molecular orientation be deduced from the carbonyl resonance. Similar difficulties do not arise in the analysis of the i.r. results because more work has been carried out validating the orientation of the vibration transition dipole moment.

CONCLUSIONS

Two-dimensional MAS n.m.r. and i.r. microscopy give the same degree of orientation in uniaxial films as optical birefringence measurements, confirming that the different techniques give a consistent picture of the order within the PET films. N.m.r. experiments, though more time consuming than i.r. spectroscopy, in principle, allow a fuller description of the molecular orientation. Even for uniaxial films where the spectroscopic approaches seemingly provide little advantage over conventional optical birefringence in terms of defining the degree of orientation the molecular view carries important additional information. In particular, clear experimental evidence is obtained for the orientation of the molecular units. This is readily overlooked because of the weight attached to intuitive ideas about how a polymer chain will align with an orienting influence. The present studies have provided invaluable experience in the methodology associated with n.m.r. and i.r. spectroscopic techniques and have demonstrated the validity of the approach. Having established a procedure for a given film, which can take a considerable time, subsequent routine use is limited by the spectrometer time for n.m.r. and personnel time for i.r.

Extension of these ideas to biaxially drawn films where the analysis of optical birefringence is difficult has already been carried out for i.r. microscopy. However, progress in the application of the 2D-MAS n.m.r. method has been limited by the more complex data analysis required for biaxially oriented samples.

Figure 3 Comparison of $P_2\langle\cos^2\theta\rangle$ with respect to the aromatic ring axis as determined by n.m.r., i.r. and refractive index measurements for various draw ratios λ

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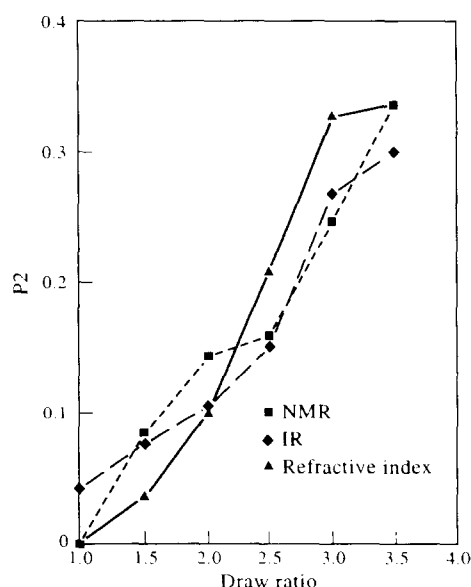
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