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Characterization of deformation phenomena in polymers by rapid-scanning Fourier transform infra-red (FT i.r.) spectroscopy and mechanical measurements: 1. Orientation of isotactic polypropylene during uniaxial deformation

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INTRODUCTION

In recent years there has been steadily increasing interest in the effects of mechanical stress on the vibrational spectra of polymers and in the determination of spectroscopic orientation parameters which may provide some insight into the deformation mechanism. I.r. dichroism measurements of polymers under mechanical load reported previously[1–7] have been restricted to the application of conventional dispersive instrumentation. Owing to the long scan duration of dispersive instruments, the characterization of orientation in deformation processes has been limited so far to stepwise procedures. The orientation values derived from the i.r. dichroism of particular absorption bands then refer to the sample at the relaxed stress levels of the individual elongation steps which commonly differ signfiicantly from the corresponding unrelaxed stress levels of a continuously measured stress–strain curve. Thus, it has been demonstrated by rapid-scan X-ray diffraction that different changes in crystal orientation can be observed during stress relaxation of polyethylene dependent on the strain level under examination[8]. In so-called dynamic i.r. (d.i.r.) investigations of polypropylene, Wool and Statton[2–5] have detected changes in orientation during stress relaxation as a function of time by continuously monitoring the intensity of polarized absorption bands at constant wavenumber with dispersive instrumentation. However, this technique is not generally applicable – apart from the fact that it requires multiple experiments for various absorption bands – because the frequency shifts observed for stress-sensitive absorption bands[1,3,5] would severely bias the results of such investigations. Furthermore, it has been pointed out[2,3,5] that samples tested at the same strain level can have widely varying molecular mechanics as a function of strain history. Hence, strictly speaking, the structural conclusions derived on a microscopic scale from spectroscopic orientation measurements in stepwise elongation procedures should not be correlated with the macroscopic deformation properties reflected by continuously measured stress–strain diagrams. However, this situation has been largely improved by the introduction of rapid-scanning *FT* i.r. spectrometers. With such systems, intensity changes, dichroic properties, band shapes and frequency shifts of absorption bands can be monitored simultaneously with the deformation process over the entire mid-infrared region in very small strain intervals relative to the total elongation. Additionally, the influence of stress relaxation on particular absorption bands may be tested in the fast and slow decay region during short time intervals.

The effect of orientation on a particular absorption band in the i.r. spectrum of a polymer is generally expressed by the dichroic ratio R:

$$R = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances measured with radiation polarized parallel and perpendicular to the draw direction, respectively.

In order to characterize the chain alignment of a uniaxially oriented polymer, it is convenient to define an orientation function[9,10] f:

$$f = \frac{(3\langle\cos^2\Theta\rangle - 1)}{2} \tag{2}$$

with Θ representing the angle between the stretching direction and the axis of the chain segments. This function f has a value of unity for a sample whose polymer chains are completely oriented in the stretch direction. For perfect trans-

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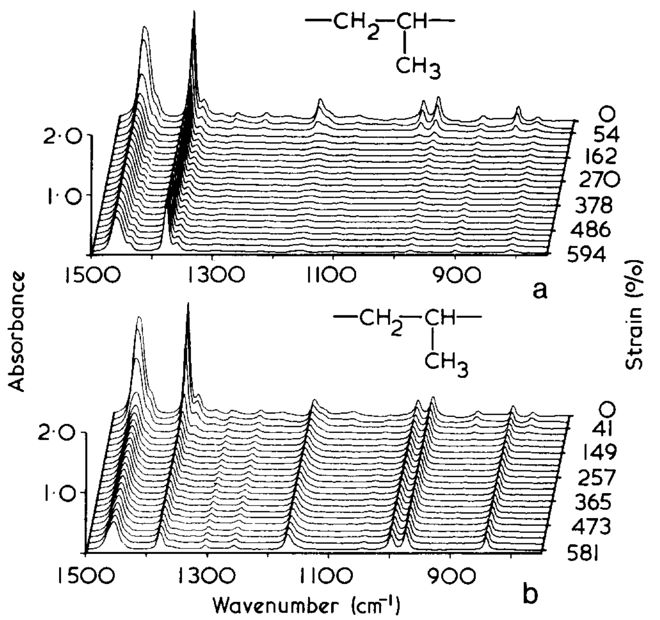

Figure 1 *FT* i.r. spectra recorded at 13.5% strain intervals during uniaxial deformation of an isotactic polypropylene film with radiation polarized alternately; a, perpendicular; b, parallel to the direction of stretch

verse orientation $f = -1/2$ and for random orientation $f = 0$. The relation between f and R for a particular absorption band has been derived by Fraser[11]:

$$f = \frac{R-1}{R+2} \times \frac{R_0+2}{R_0-1} \tag{3}$$

R_0 is the dichroic ratio for perfect parallel alignment and is given by:

$$R_0 = 2\cot^2\psi \tag{4}$$

where ψ is the angle between the transition moment direction of the absorbing group and the chain axis of the polymer. Hence, the dichroic ratio of an absorption band can be utilized for the estimation of the average chain orientation when the geometry of the transition moment of the corresponding vibration is known.

In the present report the application of rapid-scanning *FT* i.r. polarization spectroscopy is demonstrated with reference to the uniaxial deformation of isotactic polypropylene in combination with stress–strain measurements. The orientation data derived from the dichroism of various absorption bands of *FT* i.r. spectra taken in small strain intervals during the elongation procedure can be correlated with the various deformation stages observable in the stress–strain diagram and provide the basis for a more detailed understanding of the molecular orientation mechanism.

EXPERIMENTAL

The isotactic polypropylene film strips (20 x 5 mm) used in our studies were 30 μm thick and their density as measured in the gradient column (methanol/chlorobenzene) was 0.905 g cm^{-3}. The molecular weight derived from intrinsic viscosity measurements on solutions in tetralin[12] at 408K ($[\eta]$ = 74 ml g^{-1}) was about 90 000. X-ray studies revealed that the samples were in the smectic hexagonal modification and no spherulithic morphology could be detected by electron microscopy. In the d.s.c. diagram a melting endotherm was observed between 421K and 441K with the peak maximum at 435K.

For the spectrosopic measurements, a stretching machine had been constructed which allows a polymer film to be uniaxially drawn at a specified elongation rate (67% min^{-1} in the present study) while mounted in the sample compartment of the *FT* i.r. spectrometer (302K). Eight-scan spectra were recorded at 13.5% strain intervals on a Nicolet 7199 *FT* i.r. system with a resolution of 4 cm^{-1}. The polarization direction sequence of the radiation was alternately parallel and perpendicular to the drawing direction. Specific values for the dichroic ratio R of particular absorption bands at 13.5% strain intervals were obtained by relating the mean integrated absorbance value of two subsequent parallel polarization spectra to the absorbance value of the corresponding perpendicular polarization spectrum and *vice versa*.

As an improvement of the previously reported system[13] the electromechanical apparatus utilized for the mechanical measurements has been combined with the above-mentioned stretching machine so that the stress–strain diagram can be obtained simultaneously with the *FT* i.r. spectra on an identical sample. The specimen to be tested is held between two clamps which are movable by means of a spindle drive with adjustable velocity. One clamp is attached to a force measurement system and the distance travelled by the movable clamps is transformed into a voltage proportional to this distance. Thus, two voltages proportional to the two mechanical quantities – displacement and force – are recorded; and, taking into account the initial cross section of the sample under investigation, the typical stress–strain diagram shown in *Figure 2* has been obtained.

RESULTS AND DISCUSSION

In *Figure 1* the *FT* i.r. spectra recorded during the uniaxial deformation of a polypropylene film are shown separately for the parallel and perpendicular polarization directions as a function of strain. With increasing elongation several absorption bands exhibit significant parallel (π) and perpendicular (σ) dichroism. For the quantitative characterization of chain alignment during the deformation procedure, the 1378, 999 and 975 cm^{-1} absorption bands have been selected.

In the i.r. spectrum of crystalline, isotactic polypropylene, the absorption bands can be assigned to A- or E-mode vibrations whose transition moment directions are oriented parallel and perpendicular to the 3_1 helix axis, respectively. The σ-dichroic absorption band at 1378 cm^{-1} has been predominantly assigned to the $\delta_s(CH_3)$ E-mode[14–17]. The σ-dichroism of this absorption band, however, is weakened as a consequence of partial overlap by the less intense π-dichroic $\delta_s(CH_3)$ A-mode[14]. The potential energy distributions of the π-dichroic 999 and 975 cm^{-1} A-mode absorptions have been calculated by several authors[15–17]. Thus, the 999 cm^{-1} band belongs to strongly coupled $\gamma_r(CH_3)$, $\nu(C{-}CH_3)$, $\delta(CH)$ and $\gamma_t(CH_2)$ vibrations while the 975 cm^{-1} absorption involves strongly coupled $\gamma_r(CH_3)$ and $\nu(C{-}C)$ backbone vibrations. In a recent *FT* i.r. absorbance subtraction study of isotactic polypropylene, Painter *et al.*[18] have isolated i.r. bands which are characteristic of the regular 3_1 helical and irregular conformations in the ordered and amorphous

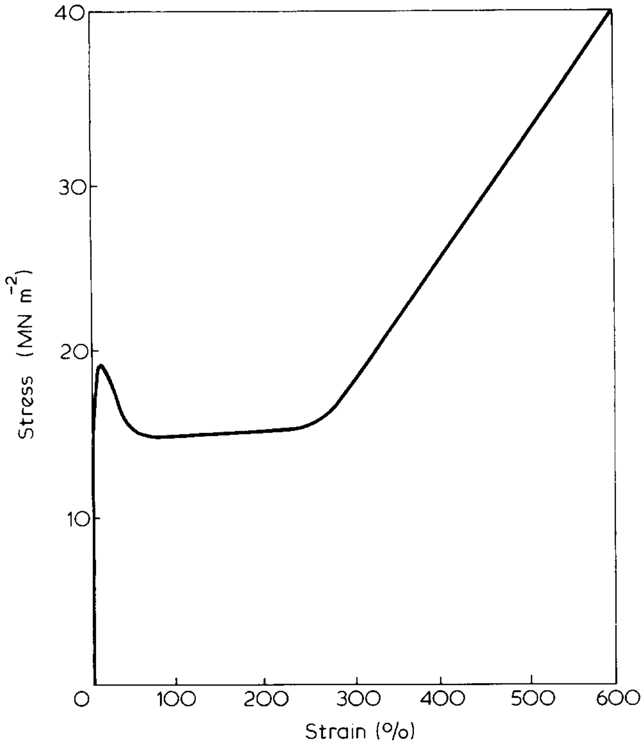

Figure 2 Typical stress–strain diagram of isotactic polypropylene

phases, respectively, from the spectrum of the semicrystalline polymer. Hence, the 1378 and 975 cm^{-1} absorptions have been shown to contain contributions of both phases, while the 999 cm^{-1} band is characteristic predominantly of conformationally regular chains in the ordered domains.

The typical stress–strain diagram corresponding to the polarization spectra of *Figure 1* is shown in *Figure 2.* The formation of a neck which propagates through the specimen is indicated by the yield point at 20% strain and the subsequent plateau region up to 250% strain. Beyond 250% strain a linear increase of stress with strain is observed in the so-called strain hardening region[19–21].

For a correlation of the mechanical deformation behaviour with the spectroscopic results, the dichroic ratios of the 1378 cm^{-1} and 999 and 975 cm^{-1} absorption bands – determined from the integrated absorbances – have been plotted as functions of strain in *Figures 3* and *4*, respectively. As a common feature to all profiles, significant σ-dichroism (*Figure 3*) and π-dichroism (*Figure 4*) increases are observed in the region from 50 to about 175% strain. These drastic changes, indicative of a preferential perpendicular alignment of the CH_3 side groups and a parallel alignment of the polymer helix axes with reference to the direction of stretch, correspond to the propagation of the neck past the sampling area. They may shift slightly on the strain scale in different experiments, depending on the position of the initial formation of the neck relative to the sampling area. The dichroism measured in this region represents the average orientation of the inhomogeneous sample area exposed to the i.r. beam. Once the neck has moved past the sampling area (at about 175% strain in the present experiment), no significant changes in orientation can be detected spectroscopically until the onset of the strain hardening region.

Different polarization phenomena for the absorption bands under examination are observed beyond 250% strain where the complete specimen has been reduced to uniform cross-section. While the σ-dichroic ratio of the 1378 cm^{-1} band tails off at higher draw ratios with only a minor increase at about 350% strain, the 975 and 999 cm^{-1} bands reflect further significant π-dichroism increases. An interpretation of these effects has to take into account the above-mentioned assignment of the absorption bands under investigation. Thus, the experimental results support the view that, in the necking region, the polymer chains of the amorphous as well as the crystalline domains are oriented by a rigid-body mechanism involving translation and rotation of the entire chains with respect to the direction of stretch[19,20]. In the strain hardening region beyond about 250% strain, however, further orientation is reflected only by the absorption bands which involve vibrations of the polymer backbone or which belong to conformationally regular sequences. The polarization properties of the skeletal vibrations can best be accounted for by a type of extensional orientation mechanism proposed by Wool[4]. In the strain hardening region where further chain orientation becomes exceedingly difficult, such a mechanism considers changes of transition moment vectors of backbone vibrations by homogeneous deformation of linear, load-bearing segments. Additionally, the polarization behaviour of the 999 cm^{-1} band reveals that in the strain hardening region further chain alignment is also observed preferentially for conformationally regular segments.

For a more quantitative representation, the dichroic ratios R, orientation functions f and corresponding angles Θ have been calculated for the absorption bands under discussion for selected strain levels based on the simplified assumption of parallel and perpendicular transition moment directions of A- and E-mode vibrations, respectively (*Table 1*). The initially negative orientation functions indicate that the original sample shows a slightly preferential orientation perpendicular to the direction of subsequent elongation. The largest decrease in angle Θ during elongation has been observed for the 999 cm^{-1} band. Thus, a value of 16° was derived for the 500% strained sample. From the azimuthal

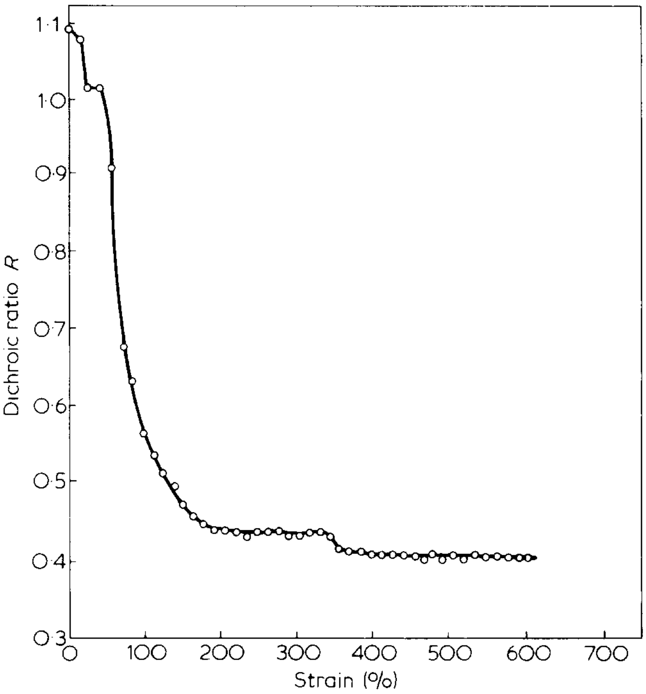

Figure 3 Dichroic ratio R of the 1378 cm^{-1} absorption band as a function strain

Table 1 Orientation parameters of isotactic polypropylene derived from *FT* i.r. spectra taken during uniaxial elongation

Strain (%)	Dichroic ratio			Orientation function			Θ (°)		
	R_{1378}	R_{999}	R_{975}	f_{1378}	f_{999}	f_{975}	Θ_{1378}	Θ_{999}	Θ_{975}
0	1.09	0.85	0.82	−0.06	−0.05	−0.06	57	57	57
50	0.98	1.4	1.3	0.01	0.12	0.09	54	50	51
100	0.56	5.9	3.4	0.34	0.62	0.44	41	30	38
150	0.47	11.8	4.9	0.43	0.78	0.56	38	22	33
200	0.44	12.5	5.1	0.46	0.79	0.58	37	22	32
250	0.44	13.1	5.3	0.46	0.80	0.59	37	21	31
300	0.43	18.0	6.4	0.47	0.85	0.64	36	18	29
400	0.41	22.1	7.4	0.49	0.87	0.68	35	17	28
500	0.40	23.2	7.7	0.50	0.88	0.69	35	16	27
575	0.40	23.6	7.9	0.50	0.88	0.70	35	16	27

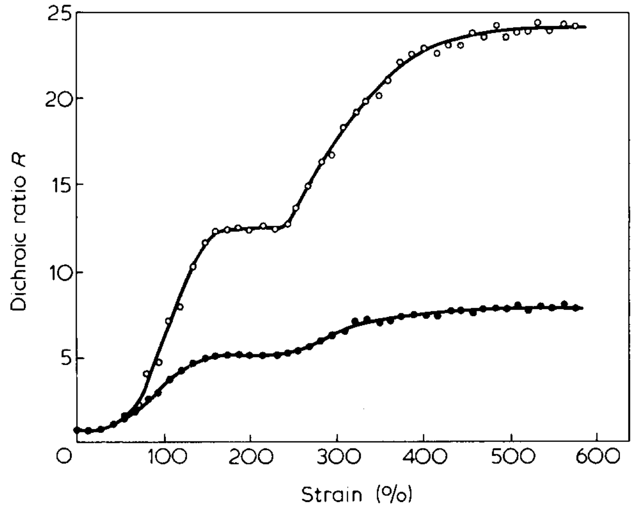

Figure 4 Dichroic ratios *R* of the 975 (●) and 999 cm^{-1} (○) absorption bands as functions of strain

intensity distribution of the equatorial wide angle X-ray reflex of a 500% drawn sample at relaxed stress level, a value of about 8° was obtained for the average angle of disorientation of the polymer chains in the crystalline regions[22,23]. These experimental results indicate strongly that portions of conformationally regular sequences also occur in the less oriented amorphous domains[24]. The polarization data of the 1378 and 975 cm^{-1} absorption bands which contain contributions both from the amorphous and crystalline phase yield significantly larger angles Θ than the 999 cm^{-1}. This suggests that the polymer chains in the amorphous regions are on the average less regularly aligned in the direction of stretch than the polymer chains in the crystalline domains[25]. The orientation effects of the 1378 cm^{-1} band are further reduced by the above-mentioned superposition of this E-mode vibration with the less intense A-mode vibration[14].

In conclusion, the outlined *FT* i.r. technique provides a rapid method for monitoring orientation changes in polymeric materials in small strain intervals during deformation and has already proved of special value for the study of cyclic loading and unloading procedures[13]. Contrary to dispersive i.r. spectroscopic investigations of stepwise elongation processes, the data derived from the *FT* i.r. technique can be interpreted unambiguously in terms of the macroscopic deformation behaviour reflected by the continuously measured stress–strain diagram.

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