Molecular orientation studies in polymer films by polarization modulation *FT*i.r. spectroscopy

T. Buffeteau and B. Desbat
Laboratoire de Spectroscopie Moléculaire et Cristalline (CNRS URA 124), Université de Bordeaux I, 33405 Talence Cédex, France

and S. Besbes, M. Nafati and L. Bokobza*
Laboratoire de Physico-Chimie Structurale et Macromoléculaire, ESPCI, 10 rue Vauquelin, 75231 Paris Cédex 05, France

(Received 20 September 1993; revised 3 December 1993)

Measurements of molecular orientation in stretched films of polydimethylsiloxane using infra-red linear dichroism have been improved by the introduction of polarization modulation of the incident electromagnetic field. This technique is able to measure small dichroic effects with high sensitivity, even for very small sample draw ratios.

(Keywords: polydimethylsiloxane; orientation; infra-red dichroism)

INTRODUCTION

Molecular orientation studies of polymeric systems are of particular interest since they provide valuable information on the mechanisms involved in polymer deformation. I.r. spectroscopy is one of the most useful tools to characterize this orientation.

The absorption of i.r. radiation is caused by the interaction of the electric field vector of the incident light with the electric dipole-transition moment associated with a particular vibrational mode. When a polymer film is drawn, the macromolecular chains tend to align in a specific direction. The absorption of an oriented film is sensitive to the state of polarization of the incident radiation with regard to a reference direction, usually defined as the stretching direction. This optical anisotropy induced by a simple stretching of polymers can be analysed by using i.r. linear dichroism.

Segmental orientation in a network submitted to uniaxial elongation may be conveniently described by the second Legendre polynomial:

$$\langle P_2(\cos\theta)\rangle = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) \tag{1}$$

where θ is the angle between the direction of extension and the local chain axis of the polymer.

Parameters commonly used to characterize the degree of optical anisotropy in stretched polymers are the dichroic difference, $\Delta A = A_{\parallel} - A_{\perp}$, or the dichroic ratio, $R = A_{\parallel}/A_{\perp}$ ($A_{\parallel}$ and $A_{\perp}$ being the absorbances of the investigated band, measured with radiation polarized parallel and perpendicular to the stretching direction, respectively).

The orientation function $\langle P_2(\cos\theta)\rangle$ is related to the dichroic ratio R by the expression:

$$\langle P_2(\cos\theta)\rangle = \frac{2}{(3\cos^2\beta - 1)}\frac{(R-1)}{(R+2)} = F(\beta)\frac{(R-1)}{(R+2)} \tag{2}$$

where $F(\beta)$ depends only on the angle β between the transition moment vector of the vibrational mode considered and the local chain axis of the polymer or any directional vector characteristic of a given chain segment.

The structural absorbance A, given by $A = (A_{\parallel} + 2A_{\perp})/3$ for a uniaxially oriented film, decreases owing to a reduction of sample thickness during elongation as $A_0/\sqrt{\lambda}$, where A_0 is the absorbance of the system under isotropic conditions and λ is the extension ratio ($\lambda = l/l_0$, where l_0 and l are the undeformed and deformed lengths, respectively). So, $\langle P_2(\cos\theta)\rangle$ is related to the dichroic parameters by:

$$\langle P_2(\cos\theta)\rangle = F(\beta)\frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} = F(\beta)\frac{\Delta A}{3A_0}\sqrt{\lambda} \tag{3}$$

Standard dichroism measurements require two different spectra of the sample to obtain the polarized absorptions parallel and perpendicular to the stretching direction, and form either the dichroic ratio R or the dichroic difference ΔA.

One of the problems in this static way of measuring i.r. linear dichroism is the lack of sensitivity in the determination of small dichroic effects, which is the case in films under low deformation or in polymers exhibiting slight orientation. In this case, the magnitude of ΔA is small and the dichroic ratio R is close to unity. A polarization modulation approach can then be used to measure small difference signals with high sensitivity.

---

* To whom correspondence should be addressed

0032-3861/94/12/2538–04

The main optical component in a polarization modulation experiment is a photoelastic modulator placed in a linearly polarized beam of light, which can rapidly alternate the state of polarization of the electromagnetic radiation between directions parallel and perpendicular to the stretching axis. This technique, which allows determination of a small difference signal in a single measurement, has been successfully applied in other i.r. experiments, including i.r. reflection-absorption spectroscopy (IRRAS)[1,2], vibrational circular dichroism[3], and i.r. linear dichroism under both static[4] and dynamic[5-7] conditions.

The present work illustrates an application of the polarization modulation technique to the determination of segmental orientation in model networks of polydimethylsiloxane (PDMS). These nearly ideal end-linked networks present a small number of defects, such as dangling chains, loops or double connections. Their controlled polydispersity, as well as their junctions of almost constant functionality, allow a quantitative comparison with theoretical predictions. Testing the limits of validity of the various theoretical models requires precise experimental determination of segmental orientation. For this reason, together with the low level of orientation exhibited by the PDMS chains[8], the polarization modulation technique is particularly suitable in this case.

This technique has been successfully applied to IRRAS[9-11], and recently to i.r. linear dichroism[12]. Although the experimental procedure and quantitative analysis of the detected signal have already been described, we recall briefly the main features of the polarization modulation set-up.

POLARIZATION MODULATION SET-UP AND SIGNAL ANALYSIS

The optical set-up used in polarization modulation experiments is shown in *Figure 1*. At the output of the interferometer of a Nicolet 740 FTIR Spectrometer, the i.r. beam presents an intensity modulation at frequency ω_i (in the range 0.1–1 kHz), depending on the wavelength and on the velocity of the interferometer moving mirror. The beam is then polarized with a Specac ZnSe grid polarizer and passes through a Hinds ZnSe photoelastic modulator (PEM) which modulates, at a fixed $2\omega_m = 62$ kHz frequency, the polarization of the i.r. beam between the linear $\parallel$ and $\perp$ (parallel and perpendicular to the stretching direction, respectively) polarization states. The film is positioned in such a way that the direction of strain is parallel to the polarization of the incident radiation. After transmission through the sample, the beam is finally focused with a ZnSe lens onto the photoactive area of an InSb fast detector (Infrared Associated) cooled at 77 K.

If the electronic detection bandwidth is up-limited to $2\omega_m$, the intensity I_d detected at the output of the detector preamplifier can be written for an intensity modulation frequency ω_i:

$$I_d = \underbrace{C\frac{I_0(\omega_i)}{2}[(T_\parallel + T_\perp) + (T_\parallel - T_\perp)J_0(\phi_0)]}_{A} + \underbrace{CI_0(\omega_i)[(T_\parallel - T_\perp)J_2(\phi_0)\cos(2\omega_m t)]}_{B} \tag{4}$$

where $I_0(\omega_i)$ is the light intensity after the polarizer, ϕ_0 is the maximum dephasing introduced by the PEM between the i and j electric field components, $J_n(\phi_0)$ is the Bessel function of order n, $T_\parallel$ and $T_\perp$ represent the parallel and perpendicular transmittances of the sample, and C is a constant accounting for the transmittance of the optical set-up and for the detection yield and is assumed to be independent of polarization.

The detected signal I_d is the sum of two interferograms A and B. As only B has a double modulation, the two signals are separated into two different channels by means of an electronic filter with high-pass and low-pass outputs[12]. The B signal is demodulated with a lock-in amplifier, with the use of a reference signal at $2\omega_m$ coming from the PEM power supply.

The corresponding spectra are calculated by the Fourier transformation of the two interferograms and then ratioed. The resultant spectrum is given by:

$$I = \frac{2G[(T_\parallel - T_\perp)J_2(\phi_0)]}{[(T_\parallel + T_\perp) + (T_\parallel - T_\perp)J_0(\phi_0)]} \tag{5}$$

where G is an overall constant factor due to the different amplification and filtering on the two channels. This spectrum contains the $J_n(\phi_0)$ factors which can be determined by calibration measurements[12].

The calibration measurements are performed by placing a linear polarizer as the sample oriented parallel ($C_{\parallel;\parallel}$) and perpendicular ($C_{\parallel;\perp}$) relative to the stretching

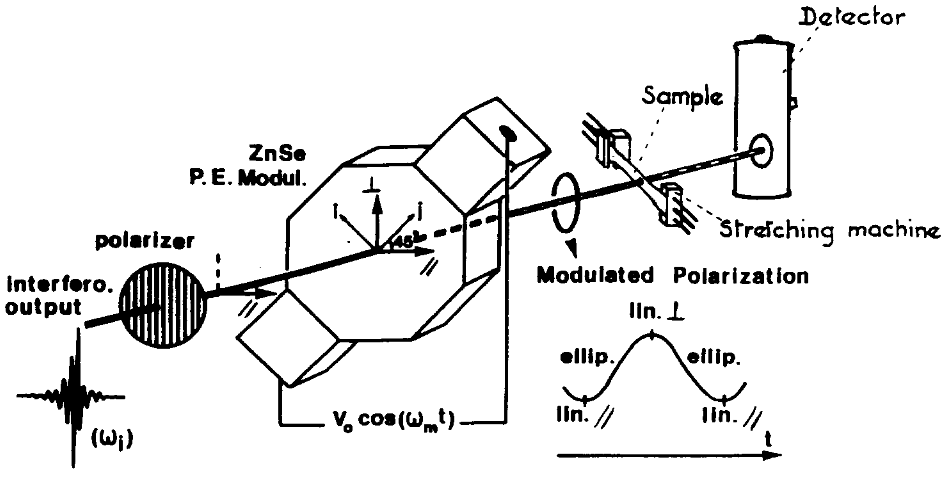

Figure 1 Schematic of the optical polarization modulation set-up

direction. Effectively, the polarizer represents a sample completely transmitting one polarization while totally absorbing the other. The respective calibration spectra, derived from equation (5) by suppressing $T_{\parallel}$ *or* $T_{\perp}$, lead to the two following expressions:

$$C_{\parallel;\parallel}=\frac{2G'J_2(\phi_0)}{[1+J_0(\phi_0)]} \qquad (6)$$

$$C_{\parallel;\perp}=\frac{2G'J_2(\phi_0)}{[1-J_0(\phi_0)]} \qquad (7)$$

where G' is the gain associated with the calibration measurements.

The dichroic difference ΔA, which is the convenient measure of the absorptive anisotropy of the system, is related to the transmittance by:

$$\Delta A=A_{\parallel}-A_{\perp}=\log\frac{T_{\perp}}{T_{\parallel}} \qquad (8)$$

Reformulation of equation (5):

$$\frac{T_{\parallel}-T_{\perp}}{T_{\parallel}+T_{\perp}}=\frac{I}{2J_2G-J_0I} \qquad (9)$$

and appropriate substitution in equation (8), which can be rewritten as:

$$\Delta A=\log\left\{\frac{1-[(T_{\parallel}-T_{\perp})/(T_{\parallel}+T_{\perp})]}{1+[(T_{\parallel}-T_{\perp})/(T_{\parallel}+T_{\perp})]}\right\} \qquad (10)$$

leads to the general expression:

$$\Delta A=\log\left[\frac{C_{\parallel;\perp}\left(\dfrac{G}{G'}C_{\parallel;\parallel}-I\right)}{C_{\parallel;\parallel}\left(\dfrac{G}{G'}C_{\parallel;\perp}+I\right)}\right] \qquad (11)$$

RESULTS AND DISCUSSION

In previous papers[8,13,14], molecular orientation in model networks has been investigated by Fourier transform (*FT*) i.r. dichroism according to the conventional method. We have pointed out the large scatter of the *FT*i.r. data ascribed to the low level of orientation and the small deformation range of the PDMS chains.

We have investigated the dichroic behaviour of the band located at 2500 cm^{-1} assigned to the overtone of the symmetrical bending vibration located at 1260 cm^{-1}. The transition moment associated with both vibrational modes lies along the CH_3–Si bond, which is a symmetry axis of the methyl group. We have determined the orientation function of the chain segment connecting two successive oxygen atoms, which is normal to the methyl axis.

In the polarization modulation experiments carried out on PDMS networks, the maximum dephasing ϕ_0 (corresponding to a retardation of $\lambda/2$) is adjusted in order to set the maximum $J_2(\pi)$ at about 2500 cm^{-1}.

As already mentioned, access to the dichroic difference requires a calibration procedure to be run. The spectra corresponding to $C_{\parallel;\parallel}$ and $C_{\parallel;\perp}$ are represented in *Figure 2*.

The dichroic difference can be determined from the experimental spectrum and the calibration measurements according to equation (11). Each spectrum has been obtained within a few minutes by co-addition of 100 interferograms at 4 cm^{-1} resolution. *Figure 3* represents, as a typical example, the strain dependence of the dichroic difference ΔA for a PDMS network with molecular weight between crosslinks equal to 12000. Qualitatively, it is satisfactory to see that the dichroic difference increases with the draw ratio λ. On the other hand, the polarization modulation technique is able to detect a dichroic effect for a draw ratio as low as 1.05 while the standard method leads to significant measurements only for $\lambda = 1.5$.

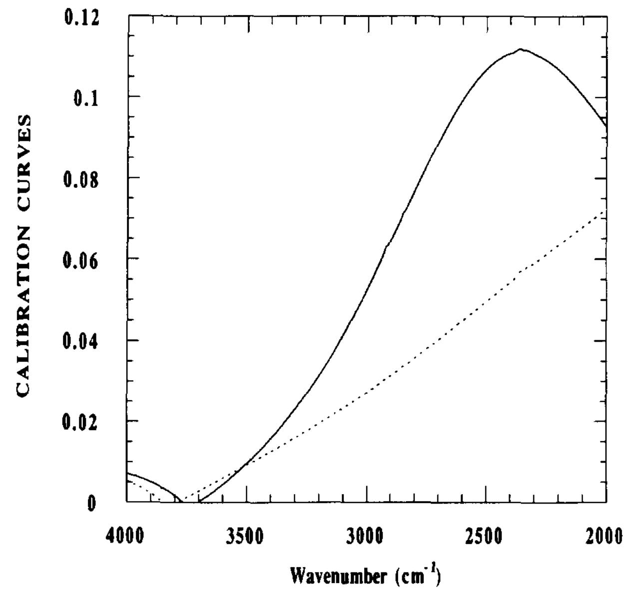

Figure 2 Calibration spectra: $C_{\parallel;\parallel}$ (——) *and* $C_{\parallel;\perp}$ (– – –)

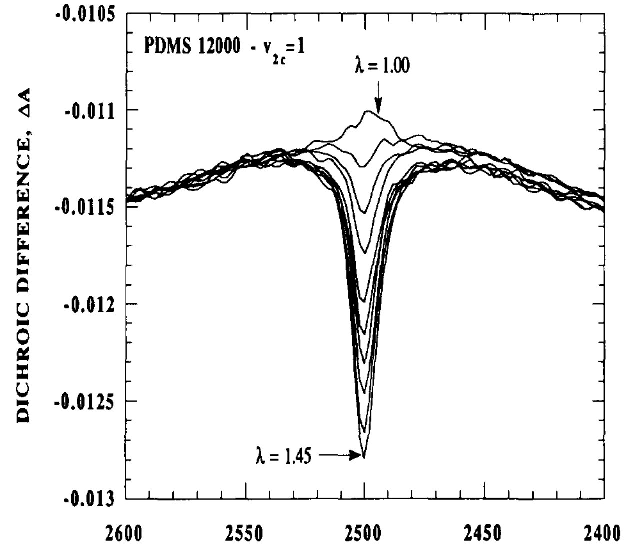

Figure 3 Strain dependence of the dichroic difference for a PDMS network stretched at draw ratios ranging from 1.0 to 1.45

Values of the orientation function $\langle P_2(\cos\theta)\rangle$ derived from the dichroic difference according to equation (3) are plotted against the strain function $(\lambda^2-\lambda^{-1})$ in *Figure 4* for two different networks, crosslinked in the bulk for $v_{2c}=1$ or in solution for $v_{2c}=0.6$ (v_{2c} being the volume fraction of polymer during the crosslinking process). This way of plotting the data arises from the proportionality between the orientation function and the strain function, which generally appears in the theoretical models of

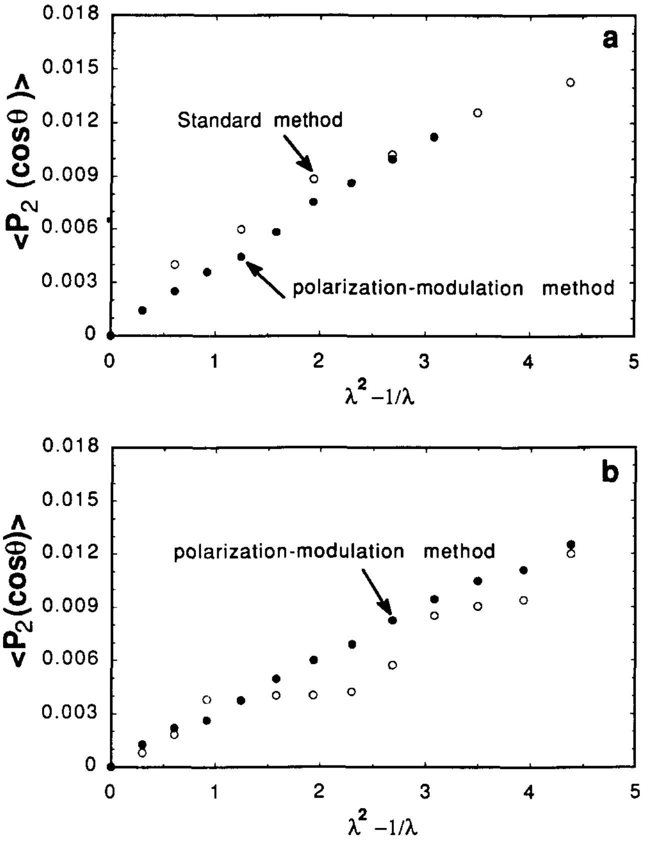

Figure 4 Strain dependence of the orientation function $\langle P_2(\cos\theta)\rangle$ obtained by the conventional method (○) and by the polarization modulation technique (●): (a) network crosslinked in the bulk; (b) network crosslinked in solution

rubber elasticity. The results obtained with the standard method are also reported in *Figure 4*. A large scatter of data is observed for the standard method of measuring linear dichroism, especially for the network prepared in solution. The results obtained with the polarization modulation approach show that this technique is able to detect precisely the onset of orientation, and leads to perfect linear dependences of the orientation function.

CONCLUSION

This paper demonstrates that the polarization modulation technique can provide a higher precision in the characterization of segmental orientation occurring during stretching of polymer networks.

By improving the signal-to-noise ratio and minimizing errors generated by repositioning the sample or the polarizer for a second measurement, this method leads to more precise determination of the dichroic effects. This technique should be exploited in order to obtain more reliable experimental results, thus allowing more extensive comparisons between theory and experiment.

REFERENCES

1 Dowrey, A. E. and Marcott, C. *Appl. Spectrosc.* 1982, **36**, 414
2 Golden, W. G., Saperstein, D. D., Severson, M. W. and Overend, J. *J. Phys. Chem.* 1984, **88**, 574
3 Nafie, L. A. in 'Advances in Applied Fourier Transform Infrared Spectroscopy' (Ed. M. W. Mackenzie), J. Wiley, Chichester, 1988
4 Marcott, C. *Appl. Spectrosc.* 1984, **38**, 442
5 Noda, I., Dowrey, A. E. and Marcott, C. *J. Polym. Sci., Polym. Lett. Edn* 1983, **21**, 99
6 Noda, I., Dowrey, A. E. and Marcott, C. Proceedings of an International Conference on Fourier and Computerized Infrared Spectroscopy, SPIE, 1985, Vol. 553, p. 56
7 Noda, I., Dowrey, A. E. and Marcott, C. *Appl. Spectrosc.* 1988, **42**, 203
8 Besbes, S., Cermelli, I., Bokobza, L., Monnerie, L., Bahar, I., Erman, B. and Herz, J. *Macromolecules* 1992, **25**, 1949
9 Buffeteau, T., Desbat, B. and Turlet, J. M. *FT-IR Spectral Lines, Nicolet* 1990, **11**, 2
10 Buffeteau, T., Desbat, B. and Turlet, J. M. 'Les Cahiers de Spectra 2000, Spectrométrie', 1991, supplement to no. 159, p. 8
11 Buffeteau, T., Desbat, B. and Turlet, J. M. *Appl. Spectrosc.* 1991, **45**, 380
12 Buffeteau, T., Desbat, B., Pezolet, M. and Turlet, J. M. *J. Chim. Phys.* 1993, **90**, 1467
13 Besbes, S., Bokobza, L., Monnerie, L., Bahar, I. and Erman, B. *Polymer* 1993, **34**, 1179
14 Bahar, I., Erman, B., Besbes, S., Bokobza, L. and Monnerie, L. *Polymer* 1993, **34**, 1858