Polymer Bulletin 23, 447–454 (1990)

Polymer Bulletin

Infrared linear dichroism spectroscopy by a double modulation technique

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Summary

A linear IR dichroism experiment has been devised using a FTIR instrument in combination with a photoelastic modulator. Based on the Mueller-Stokes calculus, a method to directly obtain the absorbance spectra $A(\nu)_{parallel}$ and $A(\nu)_{perpendicular}$ from the modulated interferogram is developped, which allows the sensitive evaluation of the dichroic ratio. The photoelastic modulator, in combination with a FTIR instrument, offers high sensitivity, high speed, excellent signal to noise ratio and a broad spectral range from 3300 to 850 cm^{-1}. First experimental results obtained from SBS block copolymer are reported.

Introduction

Linear Infrared Dichroism is a helpful tool to obtain information about oriented polymers that are stressed by external fields, i.e. a mechanical force field. Linear Infrared Dichroism can discriminate between the orientations of different compounds, which makes this method especially useful for studying blends and other multicomponent systems. The linear dichroic behaviour of the components may be observed if there are different specific absorptions $A^i(\nu)$ with sensitivity to orientation. The experiment usually is performed by putting a linear polarizer parallel (p) and perpendicular (s) to the stretching direction and measuring the absorbance spectra $A(\nu)_p$ and $A(\nu)_s$ of the polarized light beam (1). The ratio of these absorbances, $A^i(\nu)_p/A^i(\nu)_s$, called the linear dichroic ratio R, is related to the second Legendre polynomial P_2 of the orientation distribution function by the following equation:

$$P_2 = (R - 1)/(R + 2) \cdot (R_0 + 2)/(R_0 - 1) \qquad <1>$$

R_0 : linear dichroic ratio of a perfectly oriented sample.

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FTIR gives the possibility to take spectra over the whole frequency region of interest in a rather short time and with high accuracy. The limit in time resolution is given by the time to rotate the linear polarizer by 90° to get both absorbance spectra $A(\nu)_p$ and $A(\nu)_s$. There have been published several approaches to elliminate this problem. One possibility is to stop the deformation at certain deformation ratios, quench the sample to prevent relaxation, and taking the spectra in the glassy state (2). Another approach is two-dimensional IR spectroscopy by applying oscillatory deformations which gives very high time resolutions but works only for very small linear and reversible deformations of the sample (3). An enhancement of the time resulution also can be realized by using a photoelastic modulator which changes the polarization state of linear polarized light very quickly. In connection with a lock-in-amplifier and a low pass filter, a quantity proportional to the difference of the absorption spectra of two orthogonal polarization states is obtained, which would be $(A(\nu)_p - A(\nu)_s)$ in the case of linear dichroism (4). In connection with FTIR, where the primary signal is the interferogram, this method has not become very common because of the unconvenient data handling necessary to get the spectra from the modulated interferogram. However, this technique has been applied to circular dichroism measurements (4) and studies of surfaces (5) but never to the linear dichroic behaviour of polymers in uniaxial deformation fields with large strain ratios ($\alpha >> 1$). In circular dichroism, or surface orientation studies the sample thickness does not change during the experiment. Thus it is possible to calculate the absorbance spectra of the different orthogonal polarization states from the difference spectrum and the isotropic absorption spectrum. In the case of large uniaxial deformation, one has to deal with the problem, that the thickness of the sample changes during deformation. Thus, knowledge of the difference spectra $(A(\nu)_p - A(\nu)_s)$ is not sufficient for the determination of the linear dichroic ratio, the quantity that is related to the segmental orientation. In this paper the experimental setup for a linear IR dichroism experiment using a FTIR instrument in combination with a photoelastic modulator is given together with a short outline of the theoretical concept used for data analysis. The advantages of this technique are outlined and demonstrated on experiments using a SBS-triblock copolymer.

Experimental setup

The experiment was set up in conjunction with a BRUKER IFS 88 FTIR spectrometer. The stretching experiment was installed in a modified sample compartment originally designed for IR-GC coupling. The experimental setup is shown in Fig.1.

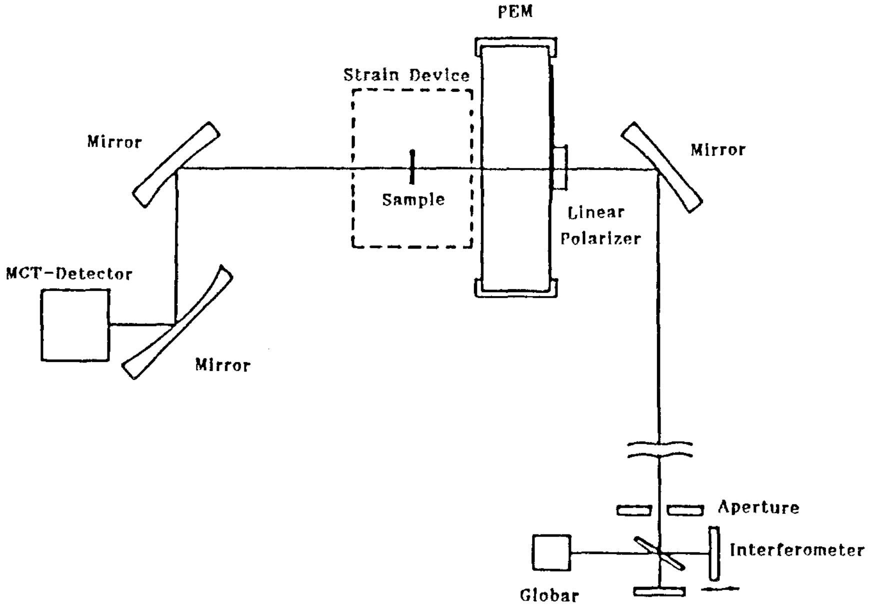

Figure 1: Schematic representation of the experimental set up: (light source, aperture, polarizer, PEM, sample, mirrors, detector)

The light coming from a Globar is modulated by a Michelson interferometer, passes an aperture and then is focussed onto a linear polarizer oriented at 90° with respect to the stretching direction. After the polarizer the light is modulated a second time by the photoelastic modulator (ZnSe, Hinds Intl. PEM 80) (oriented at 45° before passing the sample oriented at 0° and being focussed onto the MCT-detector by two parabolic mirrors. The problem is to determine not only the difference of the absorbance spectra $A(\nu)_p - A(\nu)_s$, but the absolute values $A(\nu)_p$ and $A(\nu)_s$ to be able to determine R by such an experiment. The formalism that allows the calculation of changes of the state of polarization and intensity of the incident light by optical elements like a polarizer, photoelastic modulator or sample is the Mueller-Stokes-Calculus (6). It allows the determination of the properties of the light going into the detector and from that it provides the procedure on how the signal has to be treated. The properties of the light are described by the Stokes-vector, which contains 4 elements. The first element represents the measured intensity. The optical elements are described by 4 X 4 matrices, the so called Mueller-matrices. The analysis is complicated by the two parabolic mirrors between sample and detector. The mirror-induced dichroism must be taken into account as well. The complete optical train thus is as follows:

$$S \text{ ->- } LP_{90} \text{ ->- } PEM_{45,\mu'} \text{ ->- } Sample_{0,\delta',\delta'} \text{ ->- } M_{0,\varepsilon',\varepsilon'} \text{ ->- } D$$

S : light from the source focussed on LP with the intensity I^0

LP_{90} : linear polarizer oriented at 90°

$PEM_{45,\mu'}$: photoelastic modulator oriented at 45° with the retardation $\mu' = A \sin(\omega t)$

A : amplitude

ω : frequency of the crystal (37 kHz)

t : time

$Sample_{0,\delta',\delta''}$: sample oriented at 0° with the retardation δ' and the extinction δ''

$M_{0,\epsilon',\epsilon''}$: both mirrors together oriented at 0° with the retardation ϵ' and the extinction ϵ''

D: detector

The retardation x' ($x = \delta$ or ϵ) is related to the birefringence dn':

$$x' = 2\pi D/l \bullet dn' \qquad \text{<2>}$$

D : thickness of the sample

l : wavelength

The extinction x'' is related to the dichroism dn'' in a similar way:

$$x'' = 2\pi D/l \bullet dn'' \qquad \text{<3>}$$

The dichroism dn'' allows the treatment of the dichroic properties which is alternative to the dichroic ratio R:

$$dn'' = n_p'' - n_s'' \qquad \text{<4>}$$

$$R = A_p/A_s = n_p''/n_s'' \qquad \text{<5>}$$

where n_p'' and n_s'' are the eigenvalues of the imaginary part of the refractive index tensor.

The general equation for the Stokes vector $\underline{S}'$ of the light incident on the detector is:

$$\underline{S}' = \underline{\underline{M}}_{0,\epsilon',\epsilon''} \bullet \underline{\underline{Sample}}_{0,\delta',\delta''} \bullet \underline{\underline{PEM}}_{45,\mu'} \bullet \underline{\underline{LP}}_{90} \bullet \underline{S} \qquad \text{<6>}$$

The first element of $\underline{S}'$ is the detected intensity I:

$$I = \tfrac{1}{2} \bullet a \bullet a_M \bullet [\, \cosh(\delta''+\epsilon'') + \sinh(\delta''+\epsilon'') \bullet \cos(\mu')\,] \bullet I^0 \qquad \text{<7>}$$

a : exponential, describing the isotropic part of the absorption of the sample

a_M : exponential, describing the isotropic part of the absorption of the mirrors between sample and detector

$\cos(\mu')$ may be expanded as a sum of Bessel functions:

$$\cos(\mu') = \cos[A \bullet \sin(\omega t)] = J_0(A) + 2 \bullet \sum_{m=1}^{\infty} [J_{2m}(A) \bullet \cos(2m\omega t)] \qquad \langle 8 \rangle$$

From this it follows for the low pass filter signal I_{DC}:

$$I_{DC} = \tfrac{1}{2} \bullet a \bullet a_m \bullet [\, \cosh(\delta''+\epsilon'') + \sinh(\delta''+\epsilon'')\, J_0(A)\,]\, I^0 \qquad \langle 9 \rangle$$

The lock-in amplifier is set on $\cos(2\omega t)$. So the the lock-in amplifier signal I_{AC} is given by

$$I_{AC} = \tfrac{1}{2} \bullet a \bullet a_m \bullet \sinh(\delta''+\epsilon'')\, 2J_2(A)\, V\, I^0 \qquad \langle 10 \rangle$$

V is a gain factor of the lock-in-amplifier. I, I_{DC} and I_{AC} are intensities of interferograms and thus all quantities of these equations are functions of the position of the moving mirror in the interferometer. After phase correction and Fourier transformation spectra S_{DC} and S_{AC} are obtained, where all quantities are functions of wavenumbers.

$$S(\nu)_{DC} = \tfrac{1}{2} \bullet a \bullet a_m \bullet [\, \cosh(\delta''+\epsilon'') + \sinh(\delta''+\epsilon'')\, J_0(A)\,]\, S^0 \qquad \langle 11 \rangle$$

$$S(\nu)_{AC} = \tfrac{1}{2} \bullet a \bullet a_m \bullet \sinh(\delta''+\epsilon'')\, 2J_2(A)\, V\, S^0 \qquad \langle 12 \rangle$$

The functions $J_0(A)$ and $2J_2(A)V$, the mirror-induced extinction ϵ'', a reference spectra S^{ref} containing a_M and baselines for each polarization direction can be obtained by a calibration procedure. The details of this calibration procedure will be published in a following paper (7). Together with these calibration functions the spectra of the outputs of the low pass filter $S(\nu)_{DC}$ and the lock-in-amplifier $S(\nu)_{AC}$ yield $A(\nu)_p$ and $A(\nu)_s$ separately.

Results on SBS-triblock copolymer

The first results with this technique were obtained using poly(styrene-b-butadiene-b-styrene) block copolymer with 28% styrene (KRATON 1102 from Shell). A thin film (about 10 μm) was obtained by spin casting a solution of the polymer in cyclohexane. The film was stretched from a strain ratio $\alpha = 1$ to $\alpha = 5$ using a strain rate of 10 mm/min. Data aquisition took place at every $d\alpha = 0.125$ (every 15 sec). The time to take 7 scans with a resolution of 4 cm^{-1} was less than 5 seconds. There are several parameters that influence the measurement time. Further reduction of the measurement time is possible by taking less scans, increasing the scan velocity, reducing the spectral resolution or reducing the spectral range. In principle a measurement time of less than 1 sec for $A(\nu)_p$ and $A(\nu)_s$ is possible.

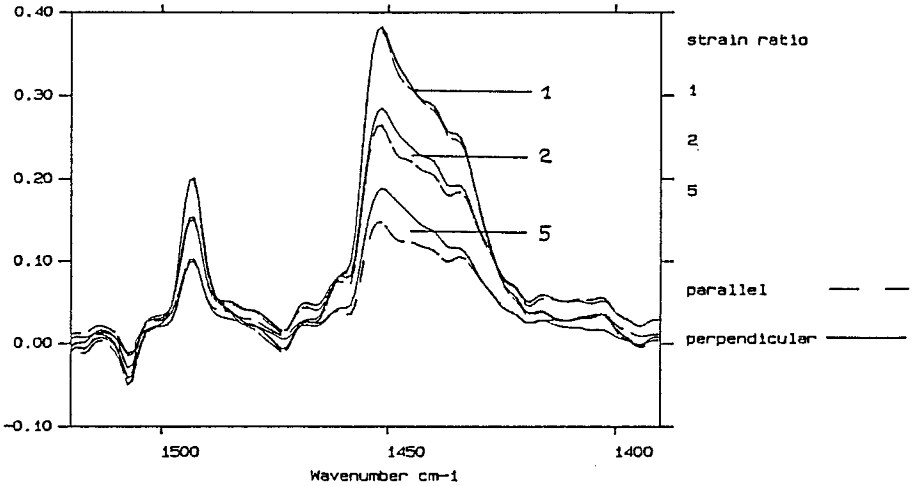

Figure 2: Section of the IR-spectra of SBS triblockcopolymer at resolution 4 cm^{-1} for α = 1.0, 3.0 and 5.0. Major absorptions correspond to PS (1490 cm^{-1}) and a complex PB (1440 cm^{-1}) vibration.

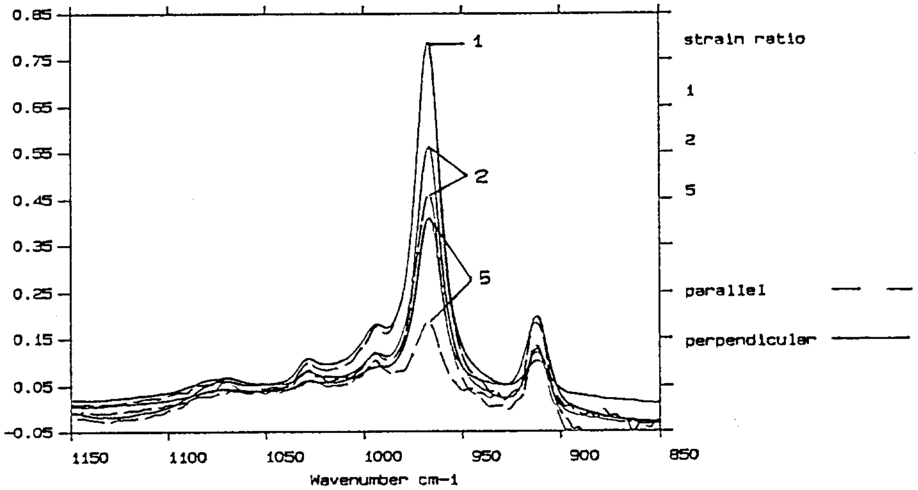

Figure 3: Section of the IR-spectra of SBS triblockcopolymer at resolution 4 cm^{-1} for α = 1.0, 3.0 and 5.0. Major absorption corresponds to trans-CH_2-wagging vibration of PB (965 cm^{-1}) vibration.

At room temperature only the poly-butadiene (PB) of this phase separated system is rubbery while poly-styrene (PS) is in the glassy state. One question is, whether the PS domains deform upon stretching already at room temperature (r.t.) well below the glass transition of the PS domains. In Figs. 2 and 3 two sections of the spectra are shown for $\alpha = 1.0$, 3.0 and 5.0. As an example, the absorption band of PS at 1490 cm^{-1} shows no linear dichroism, while the strongly overlapping absorption region of PB at 1440 cm^{-1} (which also hides a PS-line) and the CH_2-wagging-vibration of the trans-1,4-part of PB at 965 cm^{-1} show strong linear dichroisms. The parallel and perpendicular absorption spectra obtained by the modulation technique have practically identical baselines which are difficult to realize in the conventional technique using a rotating polarizer. Thus, even rather weak dichroism at low strains can be detected. The results on the SBS block copolymer clearly demonstrates that only the PB chains are deformed upon stretching at room temperature.

Conclusions

The previous results show that the spectra $A(\nu)_p$ and $A(\nu)_s$, and thus the linear dichroic ratio can be determined by using FTIR spectroscopy in connection with a linear polarizer and a photoelastic modulator. One major advantage of the modulation technique is the increased sensitivity due to the fact that the anisotropic part of the signal, which is usually small compared to the overall signal, is selectivly amplified by the lock-in amplifier and so the whole binary resolution of the adc of the FTIR may be used to resolve the small dichroic part of the measured signal. Since the measurement time is much shorter than in the conventional case, the increase of deformation has not to be interrupted in order to measure the linear dichroic ratio.

Acknowledgements

The authors are grateful to the Bundesministerium für Forschung und Technologie (BMFT project 03M4011)) and to the Deutsche Forschungsgemeinschaft (Gerhard Hess program for R. S.) for financial support. One of us (V.A.) would like to thank "Graduiertenkolleg Polymerwissenschaften" and Deutscher Akademischer Austauschdienst (DAAD) for financial support.

References

1. H.W.Siesler, Adv. Polym. Sci. 65, 1 (1984)

2. J.P.Faivre, B.Jasse, L.Monnerie, Polymer 26, 879 (1985)

3. I.Noda, A.E.Dowrey, C.Marcott, Appl. Spectrosc. 42, 203 (1988)

4. L.A.Nafie, N.-S.Lee, G.Paterlini, T.B.Freedman, Mikrochim. Acta III, 93 (1987)

5. W.G.Golden, D.D.Saperstein, M.W.Severson, J.Overend, J. Phys. Chem. 88, 574 (1984)

6. W.A.Shurcliff, "Polarized Light", Harvard University Press, Cambridge, Mass., (1962)

7. V. Abetz, G. G. Fuller, R. Stadler, Appl. Spectrosc., submitted

Accepted January 26, 1990 C