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Study of polymer orientation and relaxation by polarization modulation and 2D-FTIR spectroscopy

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Abstract

Polarized Fourier transform infrared (FTIR) spectroscopy has been used extensively to study polymer orientation. The dichroic ratio and the dichroic difference are normally obtained from spectra recorded sequentially with the infrared radiation polarized parallel and perpendicular to a reference direction. To improve the sensitivity of this technique and to be able to follow accurately the dynamics of orientation, FTIR spectroscopy has been coupled with the polarization modulation (PM) technique. With this technique, the dichroic difference spectrum is recorded directly, thus minimizing instrumental and sample fluctuations. The results obtained demonstrate the high efficiency of polarization modulation infrared linear dichroism (PM-IRLD) to determine quantitatively the time dependence of the orientation function of several chemical groups during the orientation and relaxation processes. Examples of the application of this technique to study in situ the dynamics of orientation will be presented for both stretched films of polystyrene (PS) and poly(vinyl methyl ether) (PVME) blends and optically oriented copolymers containing azobenzene side chains. The use of the PM-IRLD technique has allowed the direct determination of the relaxation kinetics of the components in polymer blends. In the case of the azopolymers, the time-dependent spectra obtained by PM-IRLD have also been analyzed by two-dimensional Fourier transform infrared (2D-FTIR) spectroscopy. The results obtained with this technique show that the spectral resolution is significantly enhanced in the asynchronous maps that also provide valuable information about the relative movement of the different chemical groups of the polymers. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polarized Fourier transform infrared (FTIR) spectroscopy has been used extensively to study the orientation at the molecular level of samples showing optical anisotropy such as oriented polymers and thin films. Due to its intrinsic nature, this technique is particularly well-suited to study multi-component systems such as polymer blends, copolymers and semicrystalline polymers because the orientation of the different components of these systems can be determined independently.

The quantitative orientation of a given transition moment relative to a reference direction is normally

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determined from the dichroic difference, $\Delta A = (A_p - A_s)$, or from the dichroic ratio, $R = A_p/A_s$, where A_p and A_s are the absorbances when the incident infrared radiation is polarized parallel and perpendicular to the reference direction, respectively. Usually, ΔA and R are determined from separate measurements of A_p and A_s that are subject to instrumental and sample fluctuations occurring between the measurements. Consequently, linear dichroism has been used mostly to study highly oriented polymer samples and the dynamics of relatively slow orientation processes.

To overcome these limitations, we have shown that polarization modulation combined with FTIR spectroscopy (double modulation) can be used to measure static and dynamic linear dichroism of oriented polymer films with a high sensitivity [1,2].

In this paper, polarization modulation infrared linear dichroism (PM-IRLD) will first be briefly described. Then, examples of the application of this technique to study in situ the dynamics of orientation during the deformation and relaxation processes will be presented for both stretched films of polystyrene (PS) and poly(vinyl methyl ether) (PVME) blends and optically oriented copolymers containing azobenzene side chains. In the latter case, the time-dependent spectra obtained by PM-IRLD will also be analyzed by two-dimensional Fourier transform infrared (2D-FTIR) spectroscopy.

2. Theory

2.1. Orientation determination

In the case of an oriented system with uniaxial symmetry, the orientation of the transition moment of an infrared active vibration can be described adequately using the second Legendre polynomial, often called the order parameter [3]:

$$\langle P_2(\cos \gamma) \rangle = \frac{3\langle \cos^2 \gamma \rangle - 1}{2}.$$

This function is directly related to the dichroic ratio or the dichroic difference by the following expression:

$$\langle P_2(\cos \gamma) \rangle = \frac{R-1}{R+2} = \frac{\Delta A}{3A},$$

where $A = (A_p + 2A_s)/3$. In the case of a stretched polymer sample, A decreases with the draw ratio λ due to the diminution of the film thickness during the elongation. In the case of a homogeneous deformation, $A = A_0/\sqrt{\lambda}$ where A_0 is the absorbance of the unstretched isotropic sample. Under such conditions:

$$\langle P_2(\cos \gamma) \rangle = \frac{\Delta A}{3A_0} \sqrt{\lambda}.$$

When the transition moment of a given vibration makes a well-defined angle β with a structural unit, such as a chain axis, and is cylindrically distributed around this axis, the order parameter of the structural unit with respect to the reference direction can be calculated using the Legendre addition theorem:

$$\langle P_2 \cos \theta \rangle = \frac{2}{(3\cos^2 \beta - 1)} \langle P_2 \cos \gamma \rangle,$$

where θ is the angle between the structural unit and the reference direction.

2.2. Polarization modulation infrared linear dichroism

The optical set-up and two-channel electronic processing used for the polarization modulation experiments are shown in Fig. 1. In a PM-IRLD experiment, the linear polarization of the infrared radiation is modulated at a frequency $2f_m$ (74 kHz) with a photoelastic modulator (PEM) so that the signal detected at the output of the detector is the sum of two components [1]. The first one, I_{DC}, carries only the intensity modulation induced by the moving mirror of the interferometer, while the second one, I_{AC}, contains, in addition, the polarization modulation induced by the photoelastic modulator. These two components are given by:

$$I_{DC} = CI_0(\omega_i)\left[(T_p + T_s) + J_0(\Phi_0)(T_p - T_s)\right]$$

$$I_{AC} = 2CI_0(\omega_i)\left[(J_2(\Phi_0)(T_p - T_s)\right]\cos(2\omega_m t),$$

where C is a constant accounting for the transmittance of the optical set-up and for the detection yield; $I_0(\omega_i)$ is the intensity of the p-polarized infrared radiation of frequency ω_i at the output of the polarizer before the PEM; T_p and T_s are the parallel and perpendicular transmittances, respectively; ϕ_0 is the maximum dephasing introduced by the PEM; ω_m is equal to $2\pi f_m$; $J_n(\phi_0)$ is the Bessel function of
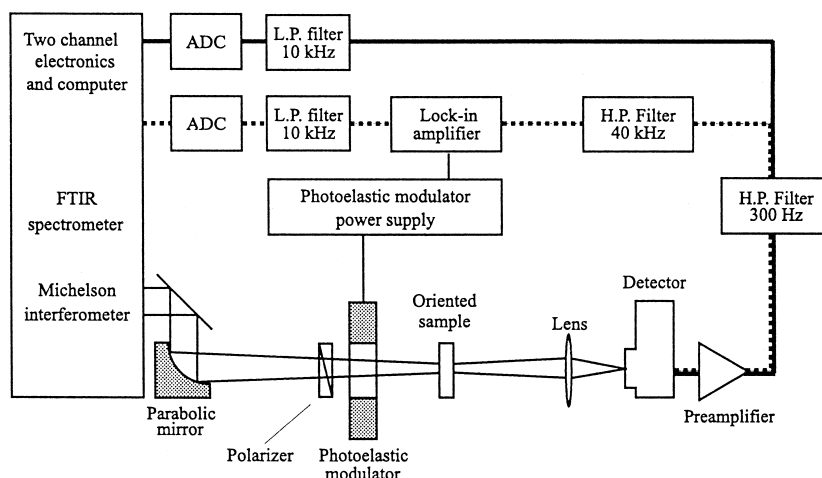
Fig. 1. Schematic diagram of the optical set-up and the two-channel electronic processing.

order n. After separation of the two signals using proper electronic filtering and demodulation of the I_{AC} signal with a lock-in amplifier referenced to $2f_m$, the two interferograms measured simultaneously are Fourier-transformed and ratioed to give the modulation spectrum S:

$$S = \frac{I_{AC}}{I_{DC}} = 2G \frac{J_2(\Phi_0)(T_p - T_s)}{(T_p + T_s) + J_0(\Phi_0)(T_p - T_s)},$$

where G is a factor accounting for the different gain and filtering of the two channels.

From calibration spectra obtained by replacing the sample by a linear polarizer oriented parallel (C_{pp}) and perpendicular (C_{ps}) to the polarizer positioned in front of the PEM, the dichroic difference spectrum can be obtained using the following expression [1]:

$$\Delta A = \log \left(\frac{C_{ps}\left(\dfrac{G}{G'} C_{pp} - S\right)}{C_{pp}\left(\dfrac{G}{G'} C_{ps} + S\right)} \right),$$

where G' is the gain used during the calibration.

3. Experimental

3.1. Materials

Monodisperse atactic polystyrene (Pressure Chemical) with $M_w = 942$ kg mol^{-1} and poly(vinyl methyl ether) (Polymer Scientific Products) with $M_w = 59$ kg mol^{-1} were used for the experiments on polymer blends. The polydispersity index of PVME was reduced to 1.3 by precipitation fractionation. The T_g of the pure PS and PVME was 105 and $-25°C$, respectively, as determined by differential scanning calorimetry. The films were cast on a glass plate from a 3% solution in benzene, and dried under vacuum at $T_g + 30$ for at least 48 h. The samples were cut into strips of 2 cm in length and 0.6 cm in width.

Random copolymers of 4′-[(2-(methacryloyloxy)-ethyl)-ethylamino]-4-nitroazobenzene (DR1M) and 4-nitrophenyl 4-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy] benzoate (BEM) were synthesized in Prof. Almeria Natansohn's laboratory at Queen's University [4]. To prepare thin films, the copolymers were dissolved in hot dimethylsulfoxide and the solutions were deposited onto hot (100°C) calcium fluoride disks. The films were dried under vacuum at 100°C for about 40 h in order to remove any trace of remaining solvent.

3.2. Experimental set-up

PM-IRLD spectra were obtained using a Bomem Michelson MB-100 spectrophotometer using the optical set-up and the two-channel electronic processing previously described [2]. Films of PS-PVME

blends were stretched to a draw ratio of 2 at $T_g + 8$ at a constant strain rate of 10 cm min^{-1} using a polymer stretcher fitted with ZnSe windows to allow the in situ recording of the PM-IRLD spectra during the orientation and relaxation periods. In the case of the poly(DR1M-co-BEM) films, the optical anisotropy was induced at room temperature in the spectrophotometer using a polarized frequency-doubled Nd:YAG laser (532 nm) with an irradiance at the sample of about 10 mW cm^{-2} [2].

4. Results and discussion

4.1. In situ study of the orientation and relaxation of PS in PS-PVME blends

As a first example of the use of PM-IRLD to study the dynamics of orientation of multi-component polymer systems, we have chosen the PS-PVME system, since it is an excellent model to study the deformation mechanisms in polymer blends [5]. First, it is completely amorphous, so that no complication due to the presence of a crystalline phase is expected. Second, this blend can be prepared in a miscible or heterogeneous state, depending on the solvent used and temperature. For PS contents between 65 and 100%, the T_g of the blends varies linearly with the composition from 30 to 105°C.

Real-time dichroic difference spectra recorded during the relaxation period for a blend containing 90% PS stretched at a draw ratio of 2 at $T_g + 8$ are shown in Fig. 2. The signal-to-noise ratio in these spectra is excellent, even though they were obtained from a limited number of scans and the maximum ΔA is less than -0.03. This demonstrates unambiguously the high sensitivity of the PM-IRLD technique to follow orientation dynamics. PS bands due to the ν_{17b} out-of-plane and ν_{18a} in-plane vibrations of the phenyl ring are well-resolved and observed at 906 and 1028 cm^{-1}, respectively. Both vibrations are insensitive to the conformation of the polymer and the angle β between their transition moment and the chain axis is 35° and 90°, respectively [6]. The band due to the C–O–C asymmetric stretching mode of the methoxy side chain of PVME is also observed at 1109 cm^{-1} as a shoulder on the band at 1070 cm^{-1} due to the ν'_{18b} vibration of polystyrene.
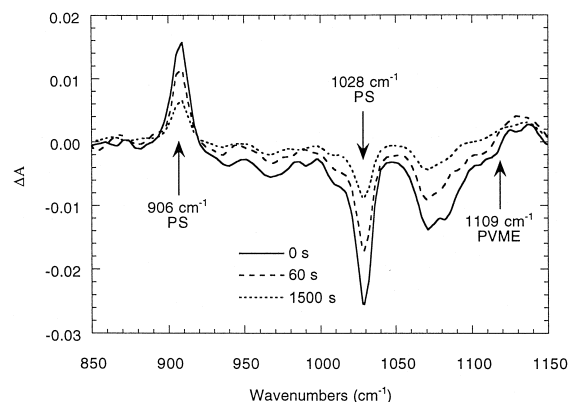

Fig. 2. Dichroic difference spectra during the relaxation period of a PS-PVME blend containing 90% PS stretched to a draw ratio of 2 at $T_g + 8$. The spectra were recorded at 8 cm^{-1} resolution (0.4 s scan^{-1}). The number of scans per spectrum was 4 at 0 s and 60 s and 75 at 1500 s.

In the normal absorbance spectrum (not shown here), the opposite situation is observed, the 1070 cm^{-1} band appearing as a shoulder on the very strong PVME band. This implies that, after the deformation, the polystyrene chains acquire a significant orientation, while the chains of the soft PVME remains practically unoriented. Clearly, the dichroic difference of these bands decreases with time as the chains relax to their isotropic state. In this paper, only quantitative results obtained from the 1028 cm^{-1} band will be presented.

Fig. 3 shows the variation of the chain order parameter, $\langle P_2 \cos \theta \rangle$ of PS with the draw ratio for different blend compositions during the orientation process. A linear increase of $\langle P_2 \cos \theta \rangle$ with the draw ratio is found for all samples. It is important to stress out the very low dispersion of the data in these curves compared to the literature [5], even though each spectrum was obtained in only 1.6 s. This is due to the fact that the dichroic difference spectra are measured directly in PM-IRLD experiments without the artifacts potentially observed in the case of the independent measurements of A_p and A_s due to polymer relaxation, to the quenching of the polymer or to instrument instabilities. Fig. 3 shows that the PS chains are less orientated in the pure homopolymer than in the blends. At 65% PS, the measured order parameter is more than three times larger than that of the homopolymer. On the other hand, PVME,
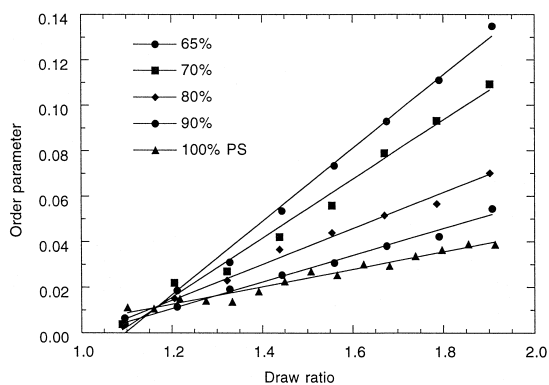
Fig. 3. Effect of the draw ratio on the PS chain order parameter $\langle P_2 \cos \theta \rangle$ calculated from the 1028 cm^{-1} band for different blend compositions during the orientation process. The stretching temperature was $T_g + 8$ and the spectra used to calculate the order parameter were obtained from four scans at a resolution of 8 cm^{-1} (0.4 s/scan). The time interval between the data points is thus 1.6 s.

which has a low T_g, remains poorly oriented. These results are in good agreement with those reported previously [5], and can be interpreted in terms of an increase of the friction coefficient between the dissimilar polymer chains. It has been suggested that the strength of the specific interactions between the methoxy group of PVME and the phenyl ring of PS is weak at low PVME content, but strong at compositions over 30% PVME. This could explain the step observed in Fig. 3 between the blends containing 80 and 70% PS.

Fig. 4 shows the relaxation kinetics of the same blends. To our knowledge, such a direct determination of relaxation curves in polymer blends has not been published before. As expected, a fast decay is observed for the short times, while a slow process due to chain reorientation occurs at longer times. A more quantitative treatment is underway, but it can be seen that the relaxation rate is faster for pure polystyrene than for the different blends, the increase of the PVME fraction leading to longer relaxation times. The step observed in Fig. 3 between the 80 and 70% PS blends is more apparent in the relaxation data. This behavior can be explained by the same arguments used for the orientation results. An increase of the friction coefficient should lead to a hindered relaxation of both the oriented polystyrene and PVME chains.

4.2. 2D-FTIR correlation spectroscopy

Infrared spectra of multicomponent systems, such as polymer blends and copolymers, are often congested due to the superposition of the bands associated with each component. It has been shown by Noda [7] that the spectral resolution can be significantly enhanced in the asynchronous maps obtained by 2D-correlation analysis. In addition, this technique provides valuable information about the relative movement of the different absorbing chemical groups of the studied system. We have thus used the generalized formalism developed by Noda [8] in order to analyze the PM-IRLD spectra obtained from the real-time study of the light-induced orientation of copolymers containing azobenzene side chains.

It is well-known that amorphous high-T_g polymers containing azobenzene groups can undergo optically induced reversible molecular orientation. When such polymer films are addressed with linearly polarized light, the azobenzene groups orient perpendicularly to the polarization direction due to the photochemically induced *trans–cis–trans* isomerization of the azobenzene groups [9]. We have recently shown using PM-IRLD that, in copolymers containing azobenzene side chains and 'inert' rigid groups,
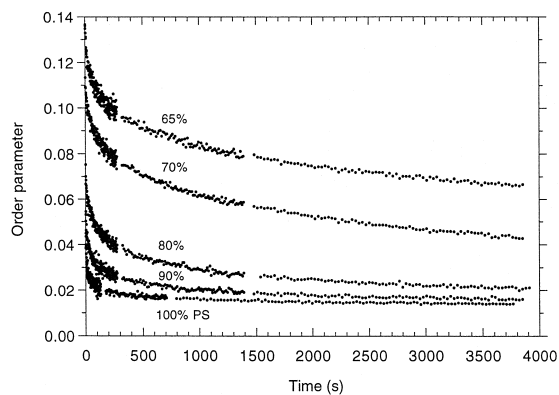

Fig. 4. Relaxation the PS chain order parameter $\langle P_2 \cos \theta \rangle$ calculated from the 1028 cm^{-1} band for different blend compositions. The films were stretched to a draw ratio of 2 at $T_g + 8$. The spectra used to calculate the order parameter were obtained from 4, 30 or 75 scans at a resolution of 8 cm^{-1} (0.4 s scan^{-1}) for short, intermediate and long times after the deformation, respectively.
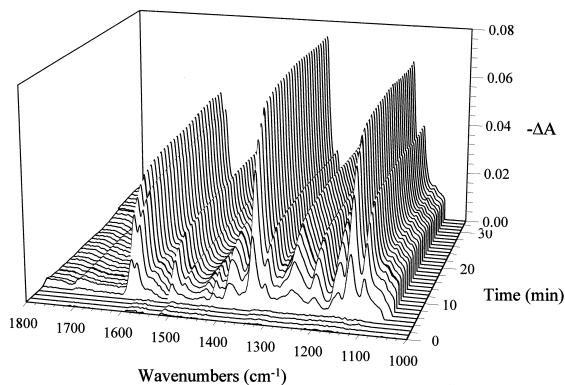
Fig. 5. Time dependence of the dichroic difference spectra for the optically induced orientation of a poly(DR1M-co-BEM) film with a DR1M mole fraction of 0.23. The time interval between the spectra is 52 s (50 scans at a resolution of 4 cm^{-1}).

there is a cooperative orientation of the inert groups with the azobenzene side chains [4].

Fig. 5 shows the time-dependent behavior during the orientation period of the dichroic difference spectra of a copolymer containing azobenzene (DR1M) and 'inert' phenyl benzoate (BEM) side chains of similar shape and polarity. When the polarized writing laser is turned on, the intensity of the bands observed in the dichroic difference spectra increases for approximately 15 min and then remains constant. Most bands observed in the difference spectrum are negative and come from both the azobenzene or the phenyl benzoate side chains. For example, the bands due to the ν(N=N) (1388 cm^{-1}) and ν_a(C–O–C) (1211 cm^{-1}) vibrations associated to DR1M and BEM groups, respectively, are well-isolated and can thus be used to probe the orientation of the two
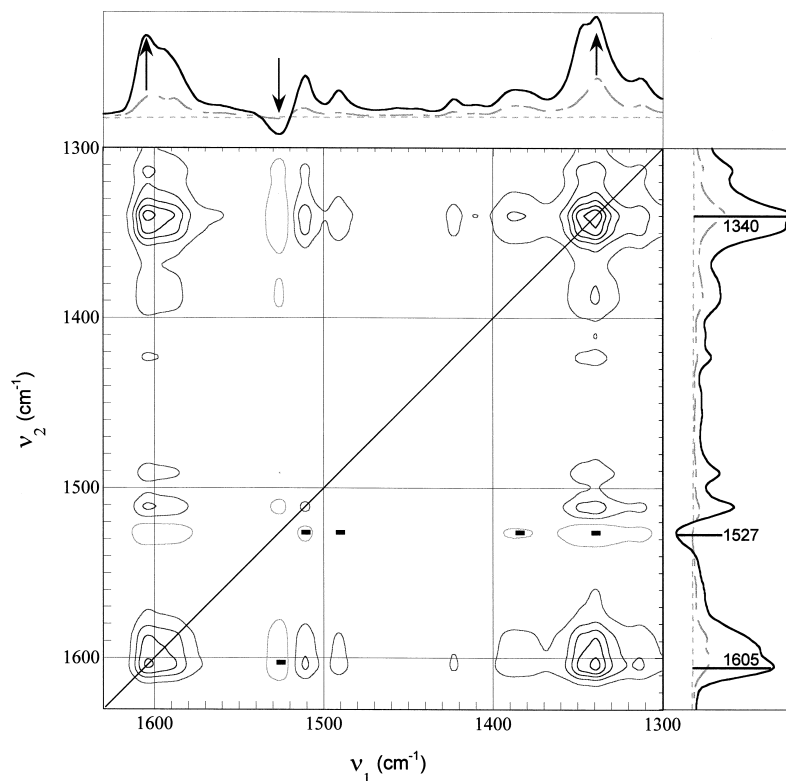

Fig. 6. Synchronous 2D-FTIR correlation map of poly(DR1M-co-BEM) with a DR1M mole fraction of 0.23 during the photoinduced orientation process. In this figure, the negative peaks are indicated by a minus sign and the one-dimensional spectra are the dichroic difference spectra recorded after 5 min (dashed line) and 60 min (solid line) of irradiation.

structural units of the copolymers. Since the vibrations associated with these bands have their transition dipole moment essentially parallel to the long axis of the azobenzene or phenyl benzoate groups, the dichroic difference spectra clearly demonstrate that the irradiation of the copolymer produces a preferred orientation of the DR1M and BEM groups perpendicular to the writing polarization direction. Since the BEM groups are not involved in the photoisomerization process, their orientation has to come from a cooperative motion of the BEM and DR1M groups, thus proving unambiguously that the photoactive and nonphotoactive side chains move in concert when the copolymer is irradiated. On the other hand, the bands due to the symmetric stretching vibration of the NO_2 groups (around 1340 cm^{-1}) and those associated with the ν_{8a} and ν_{8b} C=C stretching vibrations of the *para*-substituted phenyl rings (around 1600 cm^{-1}) of the DR1M and BEM

groups strongly overlap in the spectrum of the copolymer.

The synchronous 2D-IR map of poly(DR1M-co-BEM) between 1300 and 1630 cm^{-1} (Fig. 6) contains several correlation peaks. Except for the negative peak at 1527 cm^{-1}, all remaining peaks are positive, showing that the bands in the dichroic difference spectra all increase in intensity in the same direction. The $\nu_s NO_2$ vibration of the DR1M and BEM side chains gives a strong and unresolved autopeak around 1339 cm^{-1}. The negative peak at 1527 cm^{-1} is assigned to the antisymmetric stretching vibration of the NO_2 group, its transition moment being perpendicular to that of the $\nu_s NO_2$ vibration at 1339 cm^{-1}. The intensity of the bands associated with these two vibrations should thus change in opposite directions. A strong and highly asymmetric positive cross correlation peak between the $\nu_s NO_2$ vibrations and the ν_{8a} and ν_{8b} C=C stretching
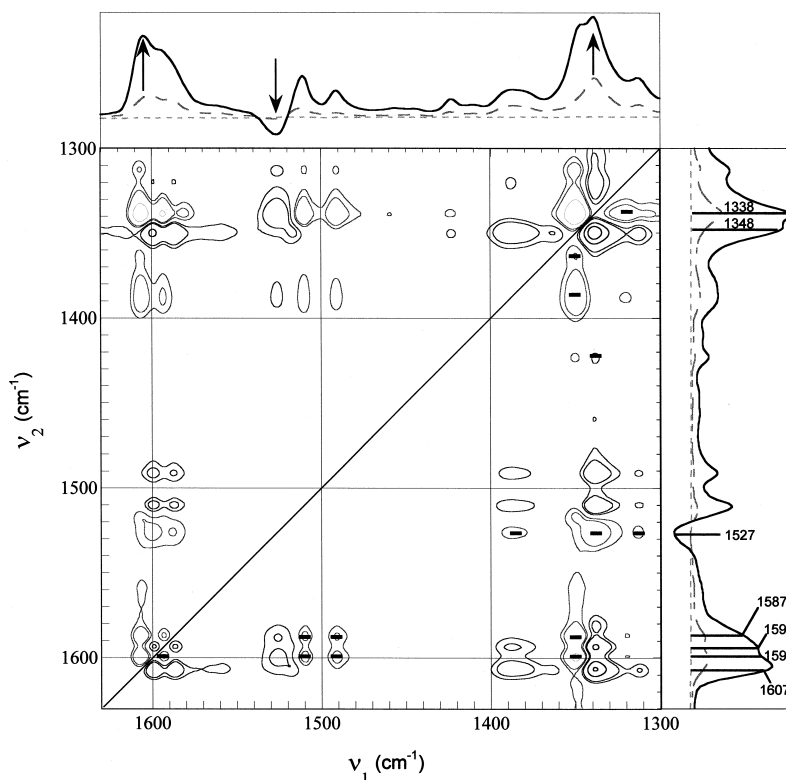

Fig. 7. Asynchronous 2D-FTIR correlation map of poly(DR1M-co-BEM) with a DR1M mole fraction of 0.23 during the photoinduced orientation process. In this figure, the negative peaks are indicated by a minus sign and the one-dimensional spectra are the dichroic difference spectra recorded after 5 min (dashed line) and 60 min (solid line) of irradiation.

vibrations of the *para*-substituted phenyl rings of the DR1M and BEM side chains is also observed at around 1339–1600 cm^{-1}, showing clearly that the DR1M and BEM groups move as rigid rods when the polymer is irradiated with polarized visible light.

Fig. 7 shows that the spectral resolution is markedly enhanced in the asynchronous map of the copolymer. It is characterized by several cross peaks that provide further insight into the reorientation rates of the two types of side chains in the copolymer. It reveals that the $\nu_s NO_2$ band contains two components located at 1338 and 1348 cm^{-1}, frequencies that match exactly those observed in the spectra of DR1M and BEM homopolymers, respectively [4]. Since the cross peak at 1338–1348 cm^{-1} is negative above the diagonal, Noda's rules [7] indicate that the component at 1338 cm^{-1} grows more rapidly than that at 1348 cm^{-1} and that the absorbing DR1M side chains orient more rapidly than the inert BEM ones. The two pairs of peaks at 1587 and 1599 cm^{-1} and 1594 and 1607 cm^{-1} are assigned to the ν_{8a} and ν_{8b} C=C stretching vibrations of the *para*-substituted phenyl rings of the DR1M and BEM side chains, respectively. As for the $\nu_s NO_2$ bands, the frequency of these bands is in perfect agreement with those of the homopolymers and their sign show that the DR1M groups orient with a faster rate constant than the BEM side chains. The quantitative analysis using a biexponential function of the intensity of the different components after

band decomposition shows that for 23 mole% DR1M content, the fast rate constant of the DR1M groups is at least five times larger than that of the phenyl benzoate side chains [4].

Acknowledgements

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