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Two-Dimensional Correlation Spectroscopy Study of Polystyrene

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Summary: Two-dimensional (2D) correlation spectroscopy is a versatile technique suited for the study of polymers. The technique was originally developed for the examination of dynamic infrared linear dichroism spectra of polymer films. When a polymer film is subjected to a small-amplitude oscillatory strain, electric dipole transition moments associated with molecular vibrations of submolecular moieties undergo time-dependent reorientation processes, which can be monitored with a polarized IR probe. Dynamics of submolecular level reorientation turned out to be surprisingly complex even for a seemingly uniform amorphous polymer like polystyrene. Possible existence of highly localized molecular rearrangement, which cannot be explained by a simple polymer chain motion, is indicated. Such multiple and multi-staged reorientation processes can be effectively sorted out by applying the cross correlation analysis among time-dependent IR signals monitored at different wavenumbers to construct 2D IR correlation spectra.

Keywords: dichroism; infrared; polystyrene; two-dimensional correlation

Introduction

Two-dimensional correlation spectroscopy[1–3] is a technique well-suited for characterizing polymeric samples. The basic idea of 2D correlation spectroscopy itself actually is a relatively simple one. A sample under some spectroscopic observation is simultaneously stimulated by an external physical perturbation. Resulting variations of spectral intensities, reflecting various changes in the state and organization of system constituents induced by such a perturbation, are recorded and subjected to a cross correlation analysis to generate a set of correlation intensity maps useful for extracting pertinent information about the dynamics of the system. This type of analysis has been successfully applied to a number of polymeric systems under different types of perturbation methods, including mechanical, electrical, thermal, chemical, and many other forms of stimuli, by using various spectroscopic probes, like IR, NMR, x-ray, and fluorescence.[2]

Among many different types of experimental methods, a small amplitude mechanical deformation in the acoustic frequency range combined with IR measurement occupies a special place in the 2D correlation spectroscopy study of polymers.[4,5] The field of perturbation-based 2D correlation spectroscopy was indeed originated with the analysis of rheo-optical IR data obtained by mechanically stretching polymeric films to induce time-dependent molecular orientation changes, which can be probed by a polarized IR beam. It was discovered that submolecular or segmental dynamics of polymer samples can be effectively probed when the time-resolved IR data are displayed in the form of 2D correlation maps. The idea of combining the correlation analysis with perturbation-induced spectral intensity variations was later advanced to a much more generalized concept in analytical science.[1] However, the original form of 2D IR spectroscopy based on simple mechanical perturbation still remains one of the very popular topics

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in the field. In this study, 2D IR correlation analysis of a glassy polystyrene film undergoing small deformation is reported.

Dynamic Infrared Dichroism

Infrared dichroism spectroscopy is a well-established technique to probe molecular orientations, especially those of polymeric systems. In IR dichroism study, the absorbance values of IR beam polarized in the direction parallel ($A_{||}$) and perpendicular ($A_{\perp}$) to a selected reference direction, for example the direction of applied strain to the sample, are separately recorded. While an isotropic sample gives the same absorbance value for any direction, for an anisotropic sample, different absorbance values are observed depending on the direction of the polarization angle of light with respect to the sample optical axes.

For a uniaxially oriented system, the difference in the absorbance for IR beam polarized in the directions parallel and perpendicular to the optical axis of symmetry, so-called IR dichroic difference $\Delta A = A_{||} - A_{\perp}$, is often measured. This quantity is known to be proportional to the average (i.e., the second moment) of the orientation distribution function of the specific electric dipole transition moment associated with the molecular vibration responsible for the light absorption of the IR probe at the wavenumber. The overall average orientation of polymer chains with respect to the strain axis is characterized by the so-called Herman's orientation function $f = (3\langle\cos^2\theta\rangle - 1)/2$ based on the space average of the cosine squared orientation angles for all the molecular chain.

The classical theory of IR dichroism for uniaxially oriented polymers proposed by Fraser[6] relates the average orientation of individual electric dipole transition moment to the Herman's orientation function by a simple relationship $f = \Delta A/\Delta A_{\infty}$, where the ultimate dichroic difference ΔA_{∞} is the value of ΔA when the polymer chains are all fully aligned in the strain direction. This ultimate dichroic difference can be obtained by .$\Delta A\infty = 3A_0(2\cot^2\xi - 1)/(2\cot^2\xi + 2)$. The transition moment angle ξ is the average angle between the orientation direction of an electric dipole transition moment and the local molecular axis, and the structural absorbance $A_0 = (A_{||} + 2A_{\perp})/3$ corresponds to the orientation-independent absorbance of the system observed under the isotropic condition. This theoretical prediction was formulated by assuming a fixed angle ξ between the dipole transition moment and the molecular chain. It will be shown later by using 2D IR correlation spectroscopy that this assumption is not always strictly valid for some time-dependent reorientation processes of polymers.

It is possible to combine the conventional IR dichroism measurement using a polarized IR probe with simultaneous mechanical deformation applied to the polymer sample to monitor the real-time reorientation dynamics of polymer samples.[5] A schematic description of such a measurement is shown in Figure 1. A thin polymer sample film is stretched repeatedly in a sinusoidal fashion by a mechanical driver. The dynamic strain is continuously monitored by a gauge to assure the stable dynamic deformation with a constant amplitude and frequency, and the stress required to induce the strain is also

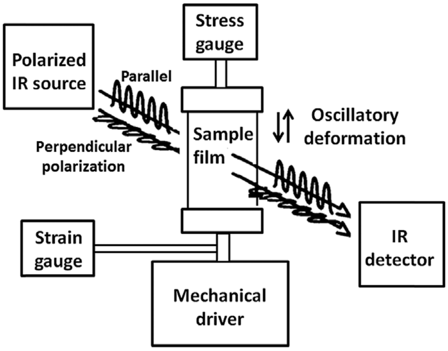

Figure 1.
A scheme to observe dynamic IR dichroism signals, reflecting the reorientation processes of submolecular constituents of a polymer sample undergoing a small-amplitude sinusoidal deformation, probed with IR beam polarized parallel and perpendicular to the deformation direction.

recorded for further analysis. The direction of the polarization angle of the incident IR beam is switched very rapidly between the parallel and perpendicular directions to provide an essentially instantaneous measurement of dichroic difference during the deformation. Temperature of the sample must also be carefully controlled in this experiment.

Two-Dimensional Correlation Analysis

Two-dimensional correlation is carried out by a pairwise comparison of spectral intensity signals measured at two different wavenumbers, which are both changing due to the perturbation applied to the system.[1,5] The comparison was made by calculating the complex cross correlation function between two IR signals along the time axis, which has the real and imaginary components. The real part of the complex cross correlation function, known as the *synchronous correlation* intensity, represents the simultaneous or coordinated changes in the spectral intensities while the perturbation is applied to the sample. The imaginary component of the cross correlation function, which is called the *asynchronous correlation* intensity, represents the out of phase changes of spectral intensities not occurring simultaneously.

Since the correlation analysis is carried out between spectral intensity variations observed at two different wavenumbers, the complex cross correlation function becomes a function of two independent wavenumbers, which is the origin of the two-dimensional nature of this particular data analysis method. It is customary to plot the distributions of synchronous and asynchronous correlation intensities in the form of contour maps defined by two independent wavenumber axes, which yield the 2D correlation spectra. Cross correlation intensities can take either positive or negative values. The regions of negative intensities are often indicated by shading in 2D correlation spectra.

Synchronous 2D correlation spectrum is symmetric with respect to the main diagonal, where the wavenumbers of two spectral axes are identical to each other. Positive peaks located at the diagonal positions are called autopeaks. They represent the magnitude of spectral intensity variations induced by the applied perturbation. For a 2D correlation spectrum constructed from the strain-induced time-dependent IR dichroism data, the autopeak intensity reflects the extent of dynamic reorientation of electric dipole transition moment for the molecular vibration at the given wavenumber.

Cross peaks located at off-diagonal positions of a synchronous map represent the coordinated or mostly simultaneous reorientation processes of dipole different transition moments for two different wavenumbers. Positive cross peak indicates that the reorientation directions of the dipole transition moments are the same, i.e., either both reorienting in the parallel direction or both in perpendicular directions to the applied strain. Negative peak, on the other hand, indicates that one is reorienting in a parallel direction, while the other in perpendicular direction.

Asynchronous spectrum constructed from the imaginary component of the cross correlation function is an anti-symmetric map with respect the main diagonal consisting of only cross peaks. A cross peak appears in an asynchronous 2D spectrum only if the reorientations of different electric dipole transition moments occur not simultaneously, i.e., one transition moment reorients before the other upon the application of the strain to the system. If the signs of the synchronous and asynchronous peaks at a given spectral coordinate are the same, the transition moment at the wavenumber of the horizontal axis reorients before that of the vertical axis. If the signs are different, the order is reversed.

Experimental Part

A film of atactic polystyrene (Aldrich, M_w 300 000) was cast from 1% toluene solution on a Teflon® sheet, which is transparent in the IR spectral region of current interest. The sample was annealed at 120 °C for 9 days, quenched, and then stored at −10 °C until being used.[7] Time-dependent IR dichroism spectra were collected with a home-built dispersive spectrometer equipped with a ZnSe photo-elastic modulator operated at 37 kHz to switch the IR polarization between parallel and perpendicular direction with respect to the stretching direction of the film. The details of this instrumentation and its operation are fully discussed elsewhere.[5] A 23 Hz dynamic strain was applied to the sample with an amplitude of 0.1%. A 2-mm x 2-mm narrow-band MCT detector with a 24-hour-hold liquid N_2 dewar was used. The temperature chamber holding the sample was controlled within 0.1 °C during the measurement.

The time-dependent dichroism spectra were converted to the corresponding synchronous and asynchronous 2D correlation maps by using a home-built software based on the algorithm reported elsewhere.[2] The levels of contour lines used for the 2D spectra were set such that equal increment is calculated from the maximum value of the correlation itensity of the map. The negative intensity region of the map was marked by shading.

Results

Figure 2 shows a 48-millisecond segment of the time-resolved IR dichroic difference spectrum of polystyrene film observed at room temperature under a 23-Hz sinusoidal tensile strain with the maximum strain amplitude of ca. 0.1%. The reorientation processes of various electric dipole transition moments associated with molecular vibrations of polystyrene are clearly reflected by the changes in dynamic IR dichroic difference signals.

Time zero in this plot is set to the maximum stretching point of the applied dynamic strain. Negative dichroism intensities, indicating the reorientation of dipole transition moments in the direction perpendicular to the sample strain direction, are observed for IR absorption bands around 2860 and 2930 cm^{-1} at time zero. They correspond, respectively, to the symmetric and antisymmetric methylene stretching vibrations of the backbone of polystyrene. This result makes sense if the polymer chain is indeed reorienting in the

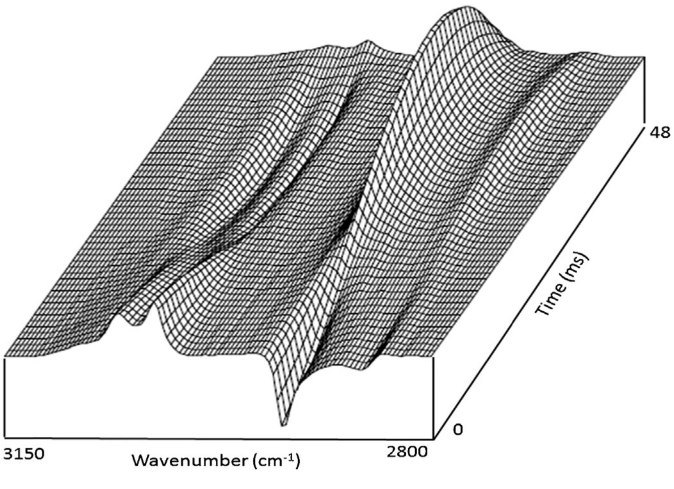

Figure 2.
Time-resolved IR dichroism spectrum in the CH-stretching region of a polystyrene film under a small-amplitude (ca. 0.1%) sinusoidal deformation with the frequency of 23 Hz at room temperature.

direction of the applied tensile deformation, since both transition moments are believed to be more or less aligned perpendicular to the backbone of polystyrene.[7]

Synchronous and asynchronous 2D correlation spectra constructed from the time-resolved IR dichroism result are shown in Figure 3. Autopeaks located at the diagonal positions of synchronous map indicate the dynamic dichroism signals reflecting the strain-induced reorientations of electric dipole transition moments associated with the molecular vibrations of various constituents of the polymer. It is noted that positions and the number of correlation peaks do not always completely match those of the peak maxima of the ordinary IR absorption spectra, which are provided at the top and side of the 2D maps for reference purpose. It shows that dynamic dichroism signals represent only the portions of IR spectrum which are changing due to the reorientation of dipole transition moments.

Synchronous cross peaks located around the spectral coordinate (2860, 2930 cm^{-1}) and (2930, 2860 cm^{-1}) are mostly positive, which is consistent with the fact that both methylene stretching transition moments are reorienting in the same (perpendicular to the tensile deformation) direction.[7] In contrast, some of the cross peaks observed between these backbone methylene bands and side group phenyl bands located at higher wavenumbers above 3000 cm^{-1} are negative. It suggests that some of the electric dipole transition moments associated with the CH-stretching vibrations of the phenyl group must be realigning in the direction parallel to the deformation axis. Such reorientation behavior of phenyl group actually is indicative of a locally constrained submolecular deformation observed for glassy polystyrene.[7] The direction of strain-induced reorientation of side group phenyl is known to change at a temperature above the glass-to-rubber transition with less constrained molecular environment.

Similar phenomenon of reorientation direction change near the glass-to-rubber transition temperature was also observed in the past for the ring semicircle stretching vibration bands around 1495 and 1455 cm^{-1}.[7] By taking advantage of the coordinated changes of temperature-dependent reorientation directions of transition moments, further insight might be obtained for the molecular vibrations of polystyrene phenyl groups. It is almost tempting to assign the five specific bands appearing in the CH-stretching vibration

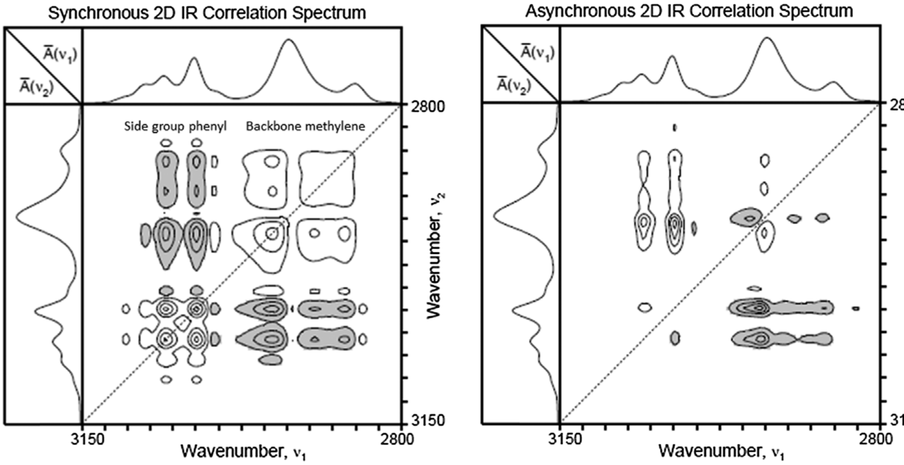

Figure 3.

Synchrnous and asynchronous 2D IR correlation spectra of polystyrene constructed from the time-resolved IR dichroism data of Figure 2. Regions of negative intensities are indicated by shading.

region of the phenyl group to well-defined local modes with the aid of 2D correlation spectroscopy. However, merely correlated behavior of IR bands probably will not be a sufficient justification to make such definitive assignments.

A very interesting result is observed for the asynchronous 2D correlation spectrum. First of all, a number of asynchronous cross peaks are clearly observed, indicating that reorientation processes of different electric dipole transition momemnts of polystyrene are not completely synchronized. Some dipole transition moments reorient before others when a strain is applied. This result should be surprising if one simply assumes that the alignment angle of a transition moment with respect to the polymer chain is fixed as a constant throughout the deformation process, which is the key premise of the classical theory connecting IR dichroism and unidirectional orientation of polymer chain.[6] Obviously, the asynchronous nature of reorientation processes of different transition moments observed here places a serious doubt about the validity of this well-accepted assumption, at least for relatively fast time-dependent reorientations of polymer chains in the range of millisecond time scale.

Furthermore, it is intriguing to note that the signs of asynchronous cross peaks between the phenyl bands and methylene bands indicate that the reorientation process of polystyrene at room temperature occurs in the order such that the side group reorients before the backbone. This result is almost counterintuitive, since one may expect the through-bond connected polymer chains to reorient first upon deformation, which then drag the side groups along for further realignment. The result from the asynchronous 2D correlation analysis, in turn, suggest a possibility that a different deformation mechanism may be in place. It can be speculated that the load-bearing initial response of polystyrene matrix in the glassy state may involve extensive through-space interactions of a number of aromatic rings, which then induces the subsequent realignment of the backbone chain.[7] In such a view, the glassy state of polymers may not be that much different from those of low molecular weight inorganic glasses without molecular chain connectivity.

Conclusion

Two-dimensional correlation analysis of time-dependent IR dichroism signals obtained for a glassy polystyrene film perturbed with a small-amplitude dynamic sinusoidal tensile strain reveals several interesting points. Upon stretching of a film, the polymer chain seems to be indeed reorienting in the direction parallel to the deformation. This conclusion is deduced from the positive synchronous cross peak between methylene bands arising from the simultaneous perpendicular reorientations of the corresponding dipole transition moments. Negative synchronous cross peaks between backbone methylene bands and side group phenyl shows the parallel reorientation of dipole transition moments for the aromatic ring arising from the locally constrained deformation.

The appearance of asynchronous peaks is a definitive indication that reorientation processes of individual dipole transition moments are not occurring simultaneously. It is, therefore, difficult to relate the overall polymer chain orientation dynamics to the behavior of individual IR dichroism signals under time-dependent deformation condition. Sequential order analysis based on the signs of cross peaks of 2D IR correlation spectra indicates that the side group phenyl of glassy polystyrene reorients before polymer backbone during the tensile deformation. The result suggest the primary transmission of load bearing stress occurs by the through-space interactions of phenyl groups instead of the through-bond backbone connectivity of polymer chain.

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