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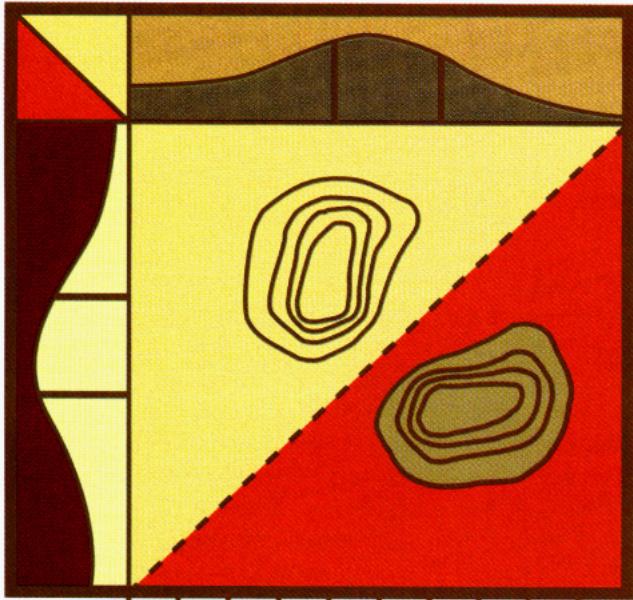


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Dynamic 2D IR spectroscopy can provide insights into polymer deformation mechanisms, identify interactions in polymer blends, and enhance the resolution of overlapping spectral features

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Dynamic Two-Dimensional IR Spectroscopy

The IR spectrum contains a tremendous amount of information that can be used to understand the nature of chemical systems. The large number of absorption bands, along with their peak frequencies, intensities, and lineshapes, often provides a unique signature for a particular chemical entity. In condensed-phase systems, individual spectral features are often highly overlapped because of the variety of submolecular environments experienced by the IR-absorbing functional groups. One way to distinguish subtle differences among molecules in locally different environments is to examine changes in a series of IR spectra as a function of a perturbation applied to the sample. Because IR spectra are, in general, extremely sensitive to subtle changes in the sample environment, any perturbation to the sample can influence the spectrum in a manner that may provide useful insights into the system. The differences observed among such a set of spectra can then be interpreted either as a response function to the applied perturbation or by correlation of the responses of individual spectral elements with each other.

The macroscopic properties of poly-

mers depend on the manner in which their submolecular constituents collectively interact and respond to external stimuli. IR spectroscopy is one of many analytical techniques commonly used to study polymers at the submolecular level. Dynamic IR linear dichroism (DIRLD) spectroscopy can be used to characterize polymers based on time-resolved rheo-optical measurements (1, 2). This technique, which looks at time-dependent IR responses to sinusoidal strain perturbations applied to polymer film samples, is well suited for the study of the local environment and dynamics of submolecular constituents. When the individual IR spectral responses are correlated with each other, rather than to the external perturbation, two-dimensional (2D) IR correlation spectra can be generated (3, 4). In this Report we will discuss both ways of looking at the time-dependent IR responses; the combination of the two approaches is referred to as dynamic 2D IR spectroscopy.

Dynamic IR spectroscopy coupled with 2D correlation analysis is a powerful analytical technique capable of providing insights into polymer deformation mechanisms, identifying submolecular interaction sites in polymer blend systems, and

enhancing the resolution of broad, overlapped spectral features. Measurements can be made on either dispersive or step-scanning FT-IR instrumentation. Dispersive instrumentation provides higher S/N over narrow spectral regions, whereas FT-IR spectrometers cover broader spectral ranges in less time.

Perturbation methods

The dynamic 2D IR spectroscopy experiment is shown in Figure 1. A variety of perturbation methods, including mechanical strain and electrical, thermal, magnetic, acoustic, chemical, and optical perturbations, can be used to induce dynamic variations in spectral intensities, which can later be represented as 2D correlation maps. In addition, the waveform, or specific time signature, of the perturbation need not necessarily be a sinusoid; it can vary from a simple step function or short pulse to more complex forms, including highly multiplexed signals and even random noise.

The use of electrical stimuli has been especially successful in studies of nematic liquid crystalline systems (5, 6), in which selective orientation of liquid crystals was observed under an alternating electric field. Electrochemical experiments modulated with an alternating electrical current have also been used to generate dynamic IR spectra suitable for 2D correlation analysis (7, 8). Recently, 2D photoacoustic spectroscopy (PAS) experiments have been conducted with a step-scanning FT-IR spectrometer to obtain depth profiles of layered samples (9, 10). The characteristic time dependence of PAS signals representing sample components located at different depths inside samples was successfully differentiated by 2D correlation analysis.

In each of these methods, a dynamic perturbation is applied to the sample and the time-resolved spectral response is measured as a function of IR wavenumber by using phase-sensitive detection (4). Although this approach is clearly quite general, we will focus on studies of polymer film samples undergoing a small-amplitude oscillatory strain perturbation.

Dynamic analysis methods

By definition, dynamic methods rely on changes in the measured quantity over

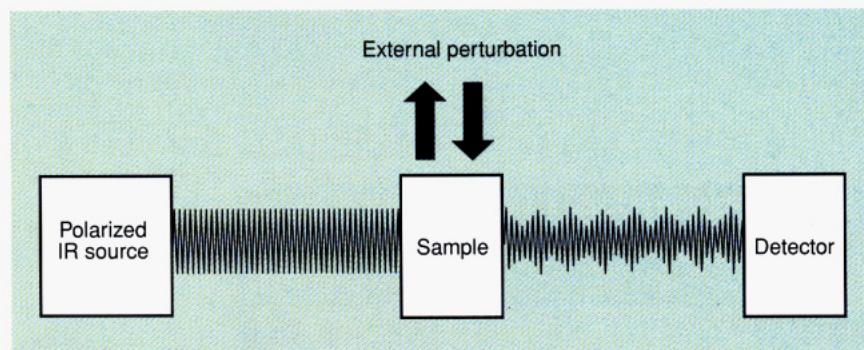


Figure 1. The dynamic IR experiment.

time. Dynamic mechanical analysis (DMA), dynamic IR spectroscopy, and dynamic 2D IR spectroscopy can all be used for polymer characterization.

DMA. DMA is widely used to characterize the properties of polymeric materials as a function of temperature and frequency (11). A small-amplitude oscillatory strain, typically fixed at a level < 1% of the sample length, is applied. The magnitude of the stress response, as well as the phase angle between the applied strain and the stress, can change as a function of temperature and frequency.

The complex modulus, which consists of both a real and an imaginary component, is often used to describe the viscoelastic state of a material at a particular temperature and frequency. The real component of the complex modulus, E' , is in phase with the applied strain, and the imaginary part of the complex modulus, E'' , is 90° out of phase with, or in quadrature to, the applied strain. If the polymeric sample behaves more or less elastically at a particular temperature and strain frequency, the stress response will be nearly in phase with the applied strain. Materials that are brittle or glassy will generally have high storage modulus (E') values. These materials do a good job of storing the supplied mechanical work as potential energy.

Near a viscoelastic transition, such as from glass to rubber, a large phase angle difference between the stress and strain is often observed. At temperatures or frequencies at which the viscoelastic state of the material changes, a large portion of the mechanical energy supplied to the sample is dissipated as heat. During the onset of a transition from a glassy to a rubbery state, for example, the loss modu-

lus, E'' , typically becomes large, whereas E' gets smaller.

Dynamic IR spectroscopy. Although DMA is an excellent method for measuring bulk macroscopic mechanical properties of samples, it provides little submolecular information useful for understanding actual deformation mechanisms. Dynamic IR spectroscopy is capable of correlating the IR responses of each functional group in the polymer with either the applied mechanical strain or the IR responses of other functional groups (1, 12). Instead of measuring only one macroscopic property (the time-dependent stress response to the applied strain in DMA), the dynamic IR technique measures the time-dependent component of IR absorbance at each wavenumber in the spectrum.

A molecule absorbs IR radiation when the frequency (i.e., energy) of the incident photon is in resonance with a particular vibrational energy-level difference in the molecule. A change in the permanent electric dipole moment occurs as a result of the vibrational transition.

Polarized IR light can provide additional information because electric dipole-transition moments are directionally sensitive (vectors). The IR intensity associated with a particular molecular vibration is proportional to the square of the electric dipole-transition moment, and only those components of the electric dipole-transition moments aligned parallel to the direction of the incident polarization can absorb the IR radiation. Therefore, the alignment of the electric field of the incident polarized radiation relative to electric dipole-transition moments in the molecule determines the extent of IR absorbance.

A sample that absorbs light of two orthogonal polarization states to different extents is said to be dichroic. Oriented polymer films are good examples of dichroic samples whose absorbance depends on the polarization direction of the incident light (13). If the orientation of a particular electric dipole-transition moment relative to a polymer chain is known, it may be possible to determine the predominant chain orientation direction in the film.

If a pair of orthogonal directional absorbances is measured with IR radiation polarized parallel and perpendicular to the strain axis, the time-dependent component of the DIRLD, which is related to the amplitude of both the dynamic absorbance and the dynamic dichroism, is obtained. The phase angle between the applied strain and the IR response is dependent on the wavenumber of the incident radiation.

Much of the unique information that comes from the measurement of a dynamic IR absorbance or DIRLD spectrum arises from the fact that not all bands in the IR spectrum of a polymer change in phase with each other. Functional groups that are interacting are more likely to reorient in phase with each other, whereas those tending to reorient independently are more likely to exhibit out-of-phase responses.

One of the original goals of DIRLD spectroscopy was to pinpoint the specific functional groups in a polymer sample primarily responsible for the observed mechanical property changes occurring as a function of temperature or frequency. For example, when the phase angle between the stress and strain begins to change at a particular temperature or frequency, functional groups whose IR bands change phase angle in a similar manner are most likely to be associated with that particular mechanical property change.

The molecular structure or morphology of the sample does not usually change when the viscoelastic state of the material changes. The normal (static) IR spectrum of a material, for example, is often virtually identical above and below the glass-to-rubber transition temperature. Dynamic absorbance and DIRLD spectra, on the other hand, are very sensitive to changes in the viscoelastic state of a material.

Dynamic 2D IR spectroscopy

DIRLD and dynamic absorbance spectra, both of which vary sinusoidally at a fixed frequency, are typically plotted as two separate (orthogonal) traces: one in phase with and the other quadrature to (90° out of phase with) the applied strain. The two traces contain all of the time-resolved information about the system. This representation emphasizes the relationship between the IR response and the applied strain perturbation.

However, the differences (or similarities) in the time-dependent behavior of dynamic absorbance and DIRLD signals at individual wavenumbers can be more effectively emphasized by constructing 2D IR correlation spectra (3, 4, 12). In 2D IR analysis, a cross-correlation function can

Dynamic IR spectra suitable for 2D correlation analysis can be obtained using a dispersive monochromator or FT-IR instrumentation.

be derived from time-resolved DIRLD spectra over an averaging period T to obtain correlation intensities as a function of two independent wavenumbers. For a given correlation time τ , this function is uniquely specified by the two independent wavenumbers, v_1 and v_2 . From the cross-correlation function, two types of 2D correlation spectra, synchronous and asynchronous, are derived.

When the perturbation is sinusoidal, as for DIRLD and dynamic absorbance experiments, simple expressions for the synchronous and asynchronous 2D correlation spectra involving only the in-phase and quadrature dynamic dichroism spectra (or dynamic absorbance) result. The synchronous spectrum shows a strong correlation intensity at wavenumber coordinates where the IR signal responses are fluctuating in phase with each other. A peak observed along the diagonal of a

synchronous 2D spectrum indicates that that particular absorbance changes as a result of the applied perturbation. Because not every absorbance in the IR spectrum of a material is necessarily susceptible to the perturbation, only a subset of all IR bands gives diagonal peaks. An asynchronous spectrum shows a strong correlation intensity at wavenumber coordinates where the IR signal responses have components out of phase with each other.

The apparent resolution of a normal IR absorbance spectrum can be significantly enhanced when the time-dependent responses of overlapped spectral elements are different. An asynchronous 2D correlation map, in particular, emphasizes any differences in the time-dependent responses lying underneath broad band contours. Although there is no increase in the intrinsic physical information in the 2D IR representation compared with the original time-resolved IR spectral data, representation of these data as 2D correlation maps can lead to insights into the interrelationships of individual spectral elements that may not have been otherwise apparent.

Instrumentation

Dynamic IR spectra suitable for 2D correlation analysis can be obtained using either a dispersive monochromator or FT-IR instrumentation (4b, 14, 15). Although well-designed dispersive spectrometers can achieve better S/N over small spectral regions, FT-IR measurements cover much broader spectral regions in less time and are available commercially. However, when the dynamic strain frequencies of interest are between 0.1 Hz and 10 kHz, conventional rapid-scan FT-IR measurements are not well suited for these measurements. Thus, we have used a step-scanning interferometer to make the measurements described here.

Extreme sensitivity is also required because the signals, which result only from the small dynamic strain applied to the sample film of interest, typically have maximum absorbances of 10^{-4} AU or less. Instrumentation with a substantial dynamic range is required to detect these small difference signals in the presence of a large total light flux at the detector. The optimum S/N for a dynamic IR band typically occurs when the normal IR absorp-

tion maximum of that band is between 0.4 and 1.0 AU. This makes the so-called multiplex advantage of FT-IR over dispersive spectroscopy less important, because it is often necessary to prepare several samples of varying thicknesses to get the peak absorbance of each band of interest to fall within this range.

Dispersive monochromator. A high optical throughput dispersive monochromator (Figure 2) is an excellent choice for dynamic IR spectroscopy (14). The incident IR beam, originating from a high-intensity source, is modulated at three places by a mechanical chopper, a photoelastic modulator (PEM), and DMA (i.e., polymer stretcher). An interferometer is substituted for the monochromator in the FT-IR experiment. The chopper (at ~ 400 Hz) labels photons originating from the source to distinguish them from background blackbody IR emission. The PEM, made of either ZnSe or CaF₂, immediately follows a fixed linear polarizer in the beam path. The combination of the polarizer and the PEM allows the polarization direction of the beam to be switched back and forth rapidly (at ~ 100 kHz) between directions aligned parallel and perpendicular to the sample strain direction. Fast liquid-nitrogen-cooled detectors are required to detect signals at these frequencies.

Better results are generally achieved with InSb detectors when the process is operating above 1850 cm⁻¹, whereas mercury–cadmium–telluride (MCT) detectors perform well below 1850 cm⁻¹. Sam-

ple strain frequencies typically used in DMA are between 0.1 and 100 Hz. Each of the three modulations made to the IR signal is separated in frequency by at least 1 order of magnitude, which makes analysis of the individual signal components with lock-in amplifiers straightforward, although digital signal processing computer boards have also been used (16).

To obtain the important time-dependent dynamic absorbance and DIRLD responses, two-phase, or quadrature, lock-in amplifiers are used. These devices record signals both in phase and 90° out of phase with the sinusoidal strain reference signal. A combination of the in-phase and quadrature signals recorded over the entire spectral range contains all the time-resolved information about the IR response of the system. The monochromator is scanned one wavelength at a time through the spectrum, and data are collected on six separate channels (in-phase and quadrature dynamic dichroism, in-phase and quadrature dynamic absorbance, static dichroism, and normal IR absorbance) at each wavenumber until an acceptable S/N is achieved. Multiple scans of the entire spectrum can be collected to further improve the S/N and to average out longer term drift.

Step-scanning FT-IR spectrometer. The dynamic IR spectroscopy experiment can also be performed on FT-IR spectrometers (4b, 15–18). Like the dispersive monochromator, which scans through a spectrum one wavelength at a time, a step-scanning interferometer mea-

sures an interferogram one mirror retardation position at a time. In the step-scanning experiment, the moving mirror of the interferometer remains in a fixed retardation position while data are accumulated from the output channels of lock-in amplifiers tuned to the signals of interest (in-phase and quadrature dynamic absorbance as well as normal IR absorbance).

As in the dispersive experiment, signals are time averaged long enough to achieve an acceptable S/N, and multiple scans of the entire interferogram can be added to average out longer term drift. When a scan is completed, the resulting interferogram does not depend on the moving mirror velocity in the same way that an interferogram collected in rapid-scan mode does. The Fourier frequencies in a step-scanning experiment are typically in the sub-Hz range, where they are well separated from the polarization modulation and strain modulation frequencies, in contrast to a typical rapid-scan FT-IR experiment in which each IR wavelength is modulated at a different acoustic-range frequency.

Unlike a dispersive spectrometer, which uses a mechanical light chopper to label photons originating from the source, a rapid-scanning FT-IR spectrometer relies on the time-dependent appearance of constructive and destructive interferences generated by the moving mirror to modulate the IR signal. In a step-scanning FT-IR spectrometer the moving mirror is stopped while the measurement is being made. Some type of external modulation of the beam intensity is needed to make the signal of interest easier to detect in the presence of background blackbody emission, which has a large dc noise component.

When a mechanical light chopper is placed in the beam in a step-scanning FT-IR experiment, amplitude modulation of the IR signal occurs. The step-scanning interferometer, however, usually performs better when phase modulation is used to label the IR photons originating from the source. Phase modulation is achieved by dithering either the fixed or the moving mirror of the interferometer a small amount (typically 1.23 mm, or two He–Ne laser wavelengths) at a fixed frequency. This motion causes a modulation of the IR signal intensity through a

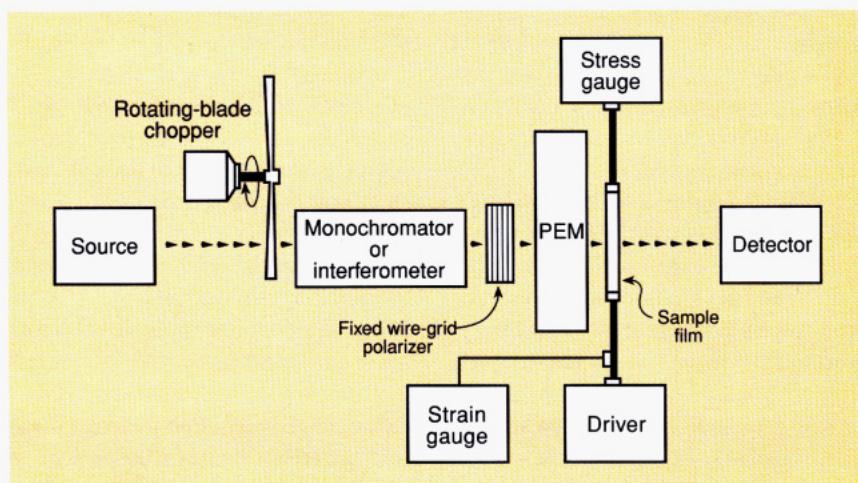


Figure 2. DIRLD spectrometer.

(Adapted with permission from Reference 2.)

change in optical path difference between the two arms of the interferometer. The amplitude of the signal detected is thus the slope of the actual interferogram at the average optical path difference. The entire interferogram is actually the first derivative of what it would be in a normal rapid-scanning or amplitude modulation step-scanning experiment.

Although most of the early measurements of DIRLD spectra on a dispersive spectrometer were made using a PEM to modulate the polarization rapidly between directions parallel and perpendicular to the dynamic strain axis, good results can also be obtained by simply placing a fixed polarizer in the beam oriented to pass light polarized parallel to the sample strain direction. Polarization modulation improves the S/N of dynamic IR spectroscopy by ~ 50% over that of fixed polarizer experiments, but a PEM adds complexity to the experiment. More lock-in amplifiers and careful optical alignment are required with polarization modulation.

When a PEM is not in use, the step-scan FT-IR experiment will work equally well with either a room-temperature deuterated triglycine sulfate (DTGS) detector or a liquid-nitrogen-cooled MCT detector. Although MCT detectors are typically an order of magnitude more sensitive than DTGS detectors, the full throughput of a commercial FT-IR spectrometer is enough to saturate the most sensitive MCT detectors. Unless a highly linear MCT detector is used, it is normally necessary to attenuate the beam by using smaller apertures, neutral density filters, or optical filters.

At present, dispersive dynamic IR experiments produce spectra with higher S/N over short spectral ranges than do FT experiments. The recent reintroduction of commercial FT-IR spectrometers with step-scanning capability, however, makes dynamic 2D IR spectroscopy accessible to many more laboratories and provides far broader spectral coverage in a single measurement than dispersive systems do.

Applications

Data in the following examples were collected using both dispersive and step-scanning FT-IR instrumentation. The first example shows how the dynamic response of a single-component polymer can

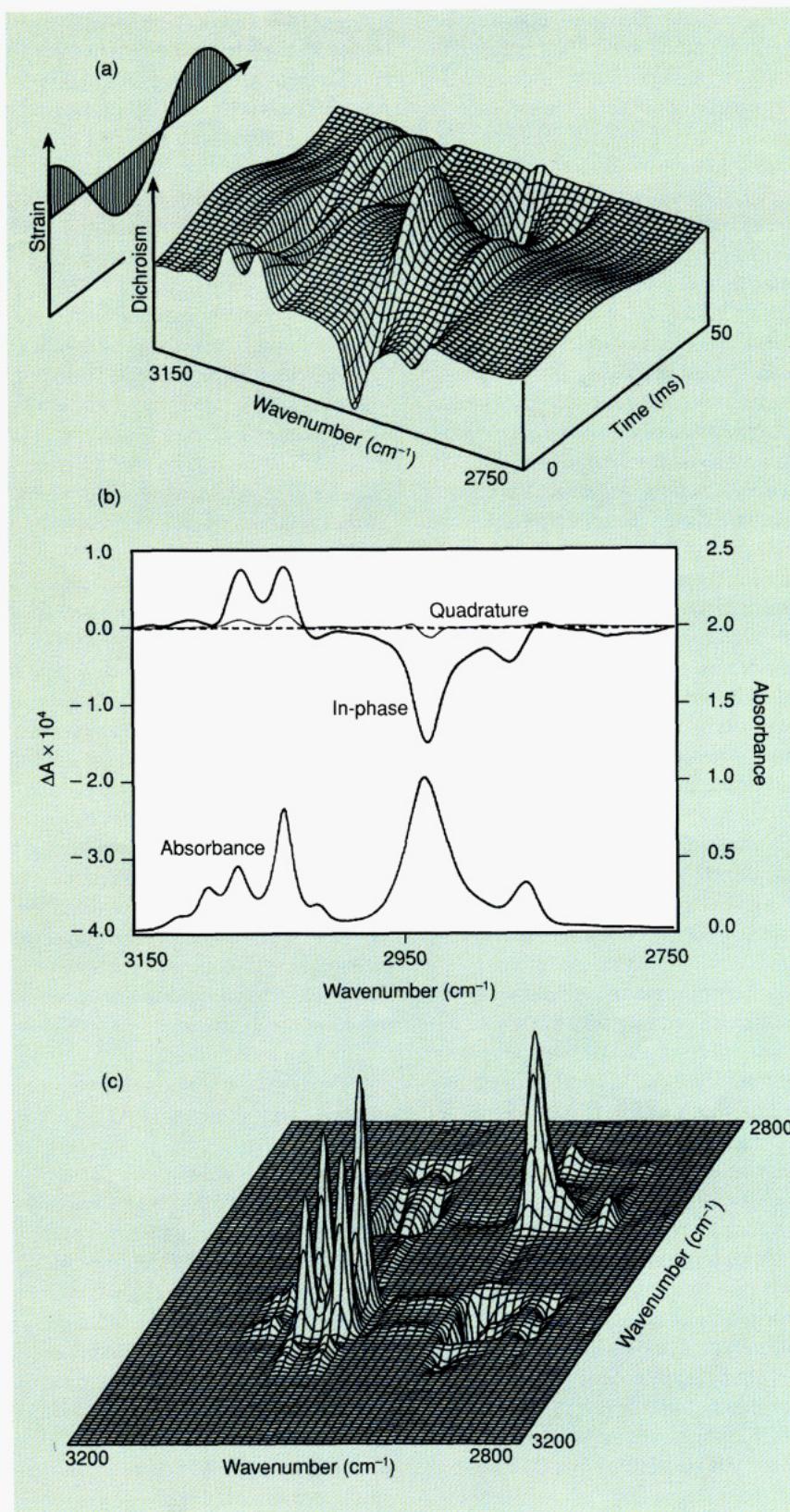


Figure 3. Dynamic 2D IR spectra of atactic polystyrene in the CH-stretching region.

(a) Time-resolved DIRLD spectrum. (b) In-phase and quadrature components of the DIRLD spectrum along with the normal IR absorbance spectrum. (c) Fishnet representation of the synchronous 2D IR correlation map of the DIRLD spectrum. (Adapted with permission from Reference 2.)

change dramatically at the submolecular level as a function of temperature. The next two examples show how immiscible polymer components respond independently of one another in response to a small-amplitude oscillatory strain perturbation. The fourth example illustrates how specific interacting sites in miscible polymer blend components can be identified using this technique. Each of these examples involves atactic polystyrene, an amorphous polymer, which minimizes complications in the data interpretation arising from crystallinity effects.

Atactic polystyrene near its glass-to-rubber transition temperature. Atactic polystyrene, like most polymeric materials, has different mechanical properties depending on temperature and the rate at which it is deformed. Although the properties of atactic polystyrene change dramatically as the temperature is raised above the glass-to-rubber transition temperature (T_g of $\sim 110^\circ\text{C}$), there is no corresponding change in either the molecular structure or the normal IR spectrum of the material. The DIRLD spectra collected above and below T_g , however, are dramatically different (19).

Figure 3a shows the time-resolved DIRLD spectrum of an atactic polystyrene film under a 0.1% 23-Hz oscillatory strain. This spectrum was recorded at room temperature on our dispersive instrument at a spectral resolution of 9 cm^{-1} between 3150 and 2750 cm^{-1} (19). The in-phase and quadrature DIRLD spectra used to generate the trace in Figure 3a, along with the normal IR absorbance spectrum, are shown in Figure 3b. Note that the dynamic dichroism signals induced by the strain perturbation are 4 orders of magnitude smaller than the normal IR absorbances. The bands above 3000 cm^{-1} are assigned to the CH-stretching vibrations in the phenyl side groups, whereas the bands at 2920 and 2854 cm^{-1} are assigned to the antisymmetric and symmetric aliphatic CH_2 -stretching vibrations of the backbone chains (13).

The electric dipole-transition moments of the two CH_2 -stretching bands are oriented roughly perpendicular to the chain propagation direction. Thus, the negative in-phase DIRLD signals associated with these bands strongly suggest that the

polymer chains are tending toward alignment with the stretch direction under the small-amplitude strain. A fishnet representation of the synchronous 2D IR correlation map of these data is provided in Figure 3c.

Figure 4a compares the in-phase and quadrature DIRLD spectra of atactic polystyrene recorded at room temperature with spectra recorded at 125°C , well above T_g (2, 19). The in-phase DIRLD signals associated with the two aliphatic CH_2 -stretching bands are somewhat weaker at 125°C than at room temperature, but their signs remain negative. This suggests that the backbone polystyrene chains still tend to dynamically reorient parallel to the stretch direction above T_g , when the sample is rubbery, just as they do at room temperature when the sample is in the glassy state. Note that the magnitudes of the quadrature DIRLD signals at 125°C are much larger compared with the in-phase signal than they were at room temperature. This behavior is similar to that of the storage and loss modulus measured in dynamic mechanical analysis, where E'' typically becomes large and E' gets small during a transition from a glassy to a rubbery state. In short, there is a direct correlation between the submolecular-scale dynamics of the polymer chain segmental motions as measured by DIRLD spectroscopy and the macroscopic rheological properties.

The reorientation dynamics of the phenyl side groups in atactic polystyrene are more complex than those of the main chain. As seen in Figure 4a, the in-phase dynamic dichroism signals associated with the phenyl CH-stretching vibrations above 3000 cm^{-1} change from being nearly all positive at room temperature to being entirely negative at 125°C . This result indicates that the local reorientation of some of the phenyl rings is different in the glassy and rubbery states of atactic polystyrene. This sign inversion in the DIRLD bands associated with the phenyl CH-stretching vibrations is characteristic of the glass-transition phenomenon in polystyrene and has been effectively used to probe the local viscoelastic state of complex multiphase systems such as block copolymer-based polymeric alloys (20).

Figures 4b and 4c show changes in the in-phase and quadrature DIRLD spectra at

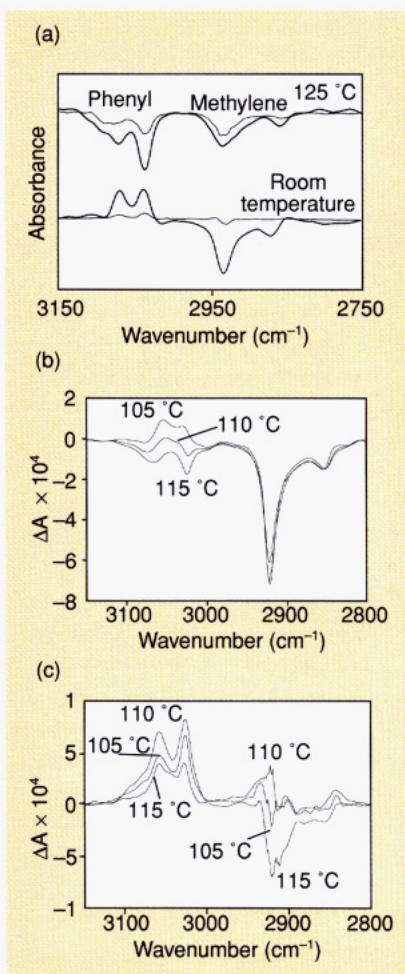


Figure 4. DIRLD spectra of atactic polystyrene above and below T_g .

(a) In-phase (bold) and quadrature (thin) DIRLD spectra at 125°C and room temperature. (b) In-phase DIRLD spectra recorded at 105°C , 110°C , and 115°C . (c) Quadrature DIRLD spectra recorded at 105°C , 110°C , and 115°C . (Adapted with permission from References 2 and 19.)

temperatures near T_g (105°C , 110°C , and 115°C). Note that the scale of the quadrature spectra (Figure 4c) has been amplified by a factor of 5 compared with the in-phase spectra (Figure 4b). The measurement conditions for these spectra are the same as for those shown in Figures 3 and 4a, except that wider slits were used in the monochromator, resulting in a spectral resolution of 16 cm^{-1} .

The wider slits provide two major benefits without a significant degradation in the bandshapes of the major spectral features. First, the spectra recorded at each temperature took < 10 min to collect, which minimizes any drifts in the system as a function of temperature, as evi-

denced by how well the baselines of these unsmoothed, unbaseline-corrected spectra overlay. Second, a higher S/N was obtained. The peak-to-peak noise level in these spectra is approximately 1×10^{-6} AU outside of the strongly absorbing band at 2920 cm^{-1} .

The spectra in Figures 4b and 4c clearly show that most of the differences between the DIRLD spectra of glassy polystyrene at room temperature and those of rubbery polystyrene recorded at 125°C (Figure 4a) occur over a very narrow temperature range near T_g . These spectra also suggest that the reorientation mobility changes observed for the backbone CH_2 groups do not occur at precisely the same temperature as the phenyl side groups. A maximum in the quadrature response occurs at 110°C for the phenyl CH-stretching bands, whereas the backbone CH_2 response at 2920 cm^{-1} has not yet reached its maximum negative excursion, even at 115°C . This observation has significant implications in terms of the nature of the glass-to-rubber transition in atactic polystyrene.

Polymer blend systems. One of the key applications of dynamic dichroism measurements in 2D IR correlation spectroscopy is the study of polymer blends. When a small-amplitude oscillatory strain perturbation is applied to a polymer film sample, interacting functional group components will reorient in phase with each other, whereas components that are not interacting may not. The raw data are collected as in-phase and quadrature spectra with respect to the applied strain perturbation. This representation of the data, as seen in the previous example, relates the response of each IR band to the applied strain. Although the relationship between the responses of individual functional groups can usually be seen in the raw in-phase and quadrature spectra, the 2D representation can often make these relationships easier for an untrained observer to see because the relative responses of each pair of IR bands are emphasized in a 2D map, without the need to mentally factor out the effect of referencing to the strain.

Immiscible blend of atactic polystyrene and low-density polyethylene. This system clearly illustrates how the relative responses of immiscible components can

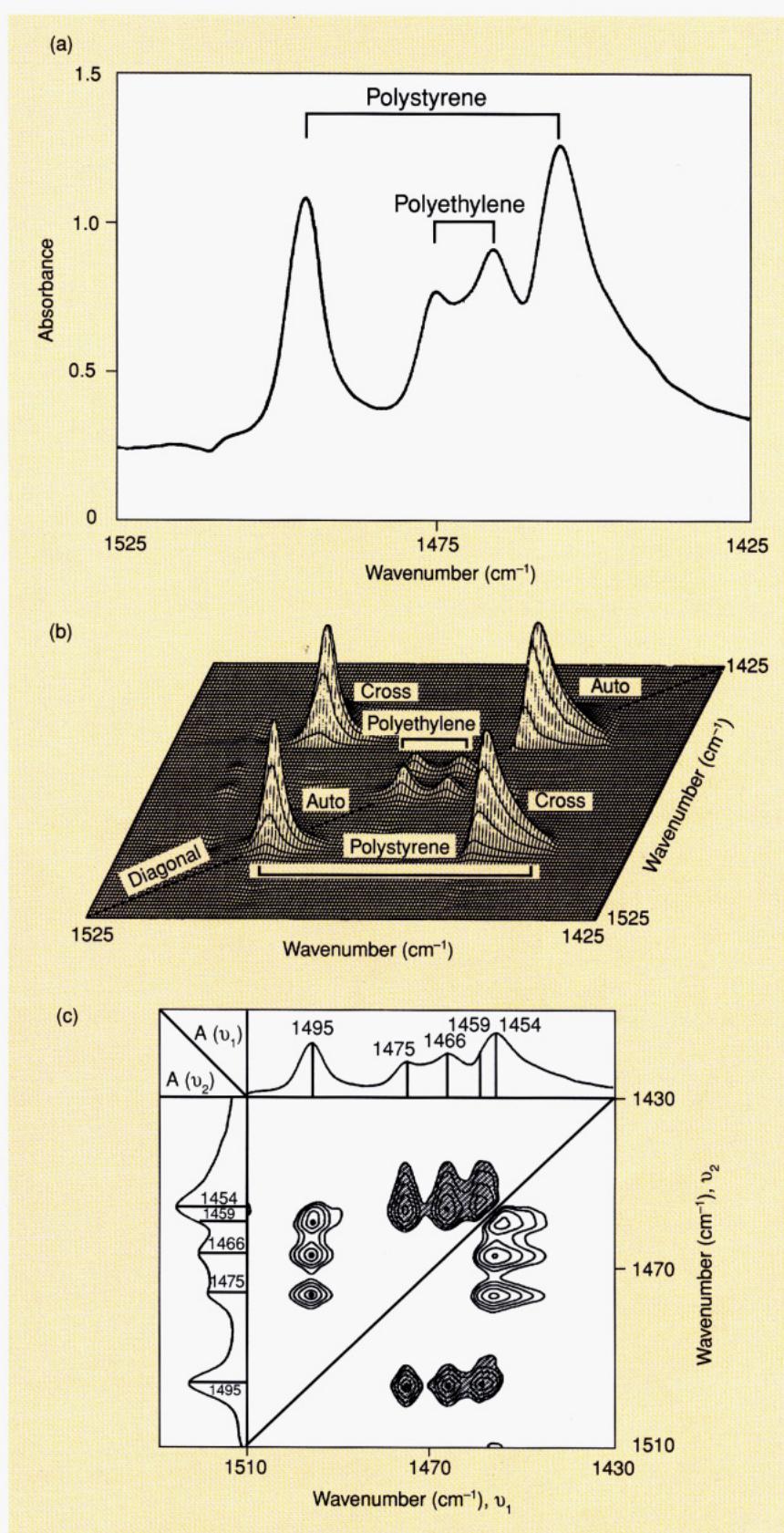


Figure 5. Dynamic 2D IR spectra of a polystyrene/polyethylene blend.

(a) Normal IR absorbance spectrum of a $25\text{-}\mu\text{m}$ film of atactic polystyrene cast on top of a $25\text{-}\mu\text{m}$ film of low-density polyethylene. (b) Fishnet representation of the synchronous 2D IR correlation spectrum. (c) Contour map representation of the asynchronous 2D IR correlation spectrum. (Adapted from Reference 21.)

be distinguished using this technique (21). Figure 5a shows the normal IR absorbance spectrum of a 25- μm film of atactic polystyrene cast on top of a 25- μm film of low-density polyethylene in the region between 1525 and 1425 cm^{-1} . The phenyl ring semicircle stretching mode absorptions of atactic polystyrene at 1495 and 1454 cm^{-1} are cleanly separated from the absorptions of the crystalline and amorphous low-density polyethylene CH_2 -deformation modes at 1475 and 1466 cm^{-1} .

In-phase and quadrature dynamic IR absorbance spectra were collected on our dispersive spectrometer at room temperature while the sample was undergoing a 0.1% sinusoidal strain at 23 Hz. Figure 5b shows a fishnet representation of the synchronous 2D IR spectrum obtained from the raw in-phase and quadrature dynamic IR absorbance spectra, which were collected at a spectral resolution of 4 cm^{-1} . Autopeaks observed on the diagonal of this plot at 1495 and 1454 cm^{-1} indicate that the absorbances of these two polystyrene bands change dynamically as a result of the strain perturbation applied to the sample. A pair of intense cross peaks appearing at the off-diagonal positions of the spectral plane near 1495 and 1454 cm^{-1} indicates the existence of a strong synchronous correlation between these two polystyrene bands. Similarly, autopeaks corresponding to the dynamic intensity fluctuation of IR bands associated with the CH_2 -deformation modes are observed near 1475 and 1466 cm^{-1} . A pair of cross peaks clearly correlates these IR bands attributable to the polyethylene component.

A contour map representation of the asynchronous 2D IR spectrum is shown in Figure 5c. The development of cross peaks differentiating the polystyrene and polyethylene bands indicates that, even under an identical macroscopic perturbation, the time-dependent behavior of the IR intensity fluctuation for the polystyrene component of the sample is substantially different from that for polyethylene. Note the development of additional cross peaks in the asynchronous 2D IR spectrum correlating a polystyrene spectral feature at 1459 cm^{-1} , which is not a resolved peak in the normal IR spectrum, with the polystyrene phenyl ring semicircle stretching mode absorptions at 1495 and 1454 cm^{-1} .

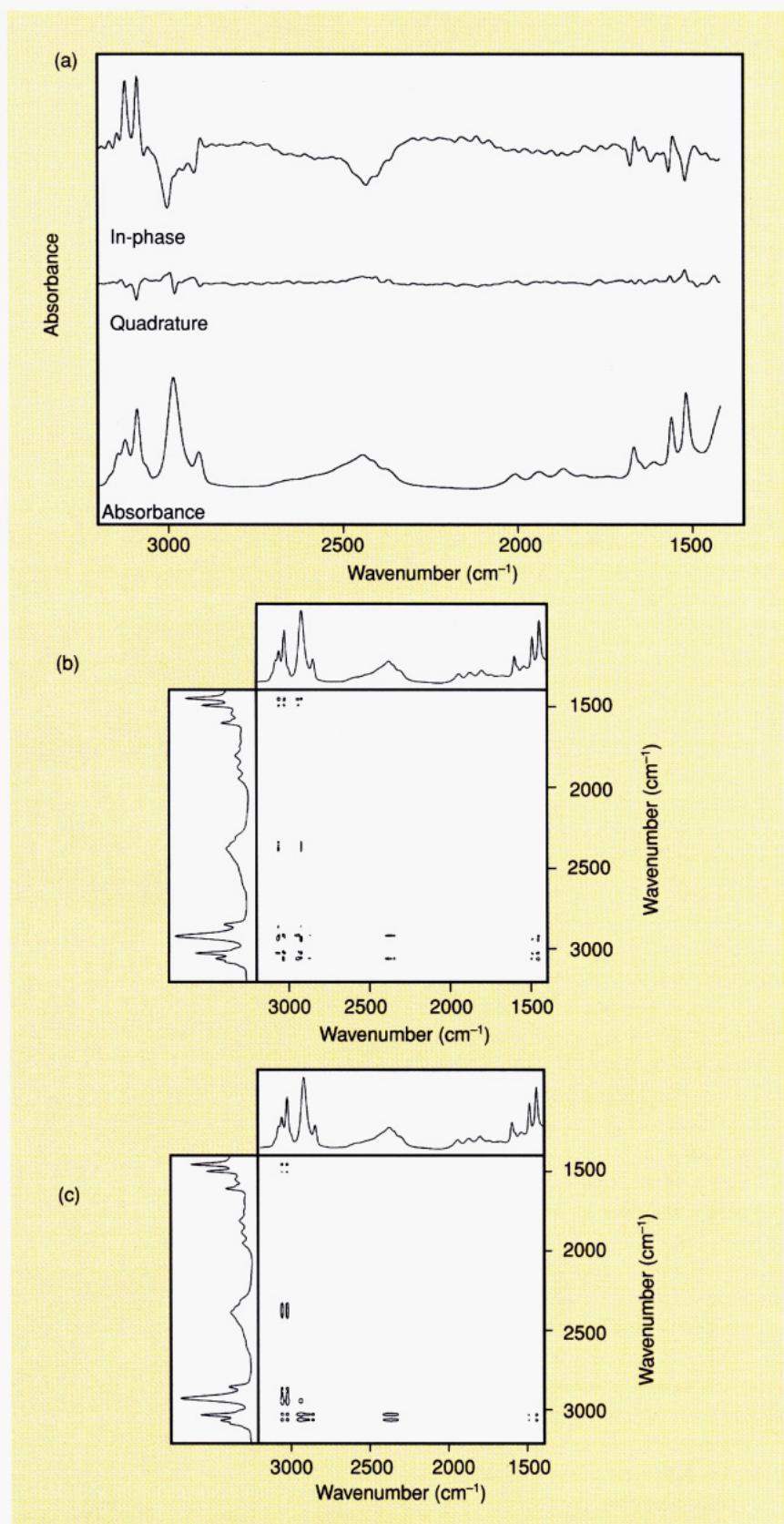


Figure 6. Dynamic 2D IR spectra of a polystyrene/Teflon blend.

(a) In-phase and quadrature dynamic IR spectra and normal IR absorbance spectrum of atactic polystyrene cast from toluene onto an amorphous Teflon substrate. (b) Synchronous 2D IR correlation plot. (c) Asynchronous 2D IR correlation plot. (Adapted with permission from Reference 4.)

This 1459-cm^{-1} band is attributable to the CH_2 -deformation modes of the polystyrene backbone chain, suggesting a difference in the mobilities of polystyrene backbone and side-group functionalities. These results are completely consistent with results discussed in the previous section, where different responses were observed for the phenyl CH-stretching and backbone CH_2 -stretching modes of a single-component atactic polystyrene sample.

Immiscible blend of atactic polystyrene and amorphous Teflon. Figure 6a shows the in-phase and quadrature dynamic IR spectra along with the normal IR absorbance spectrum of a thin film of atactic polystyrene cast from toluene onto an amorphous Teflon substrate recorded on a step-scanning FT-IR spectrometer. A 13-Hz, 50- μm -amplitude sinusoidal strain was applied to the sample, and the spectral resolution was 16 cm^{-1} (4b). The in-phase and quadrature spectra have been expanded by a factor of $\sim 10^4$ compared with the normal IR spectrum. A significant in-phase response attributable to the Teflon band substrate is observed at 2300 cm^{-1} . The high wavenumber side of the strong Teflon peak centered at 1204 cm^{-1} is starting to show up on the right-hand edge of the absorbance spectrum. All the other bands are attributable to atactic polystyrene. These in-phase and quadrature spectra are in good agreement with results obtained previously on a dispersive system in two separate measurements at $3150\text{--}2750\text{ cm}^{-1}$ (Figure 3b) and $1525\text{--}1425\text{ cm}^{-1}$ (14). Although the S/N is significantly better for spectra recorded on dispersive instrumentation, much broader spectral ranges are covered in the FT-IR measurements.

Figure 6b shows a synchronous 2D IR correlation plot of the dynamic IR spectra of atactic polystyrene shown in Figure 6a. The strongest cross peaks occur among the phenyl CH-stretching modes and between these bands and the phenyl ring stretches at 1450 and 1495 cm^{-1} . Figure 6c shows the corresponding asynchronous 2D IR map of the dynamic spectra of atactic polystyrene. Cross peaks between the Teflon substrate band at 2300 cm^{-1} and the CH-stretching bands of polystyrene, as well as between the phenyl modes and the aliphatic CH_2 -

stretching bands at 2920 and 2855 cm^{-1} , are observed. This plot illustrates that the IR spectrum of the polystyrene film is changing out of phase with the IR bands of the Teflon substrate spectrum. This is not surprising, because these two compo-

nents are immiscible and segregated from each other. Once again, we see that the phenyl side groups of polystyrene are apparently reorienting out of phase with the aliphatic backbone component of polystyrene.

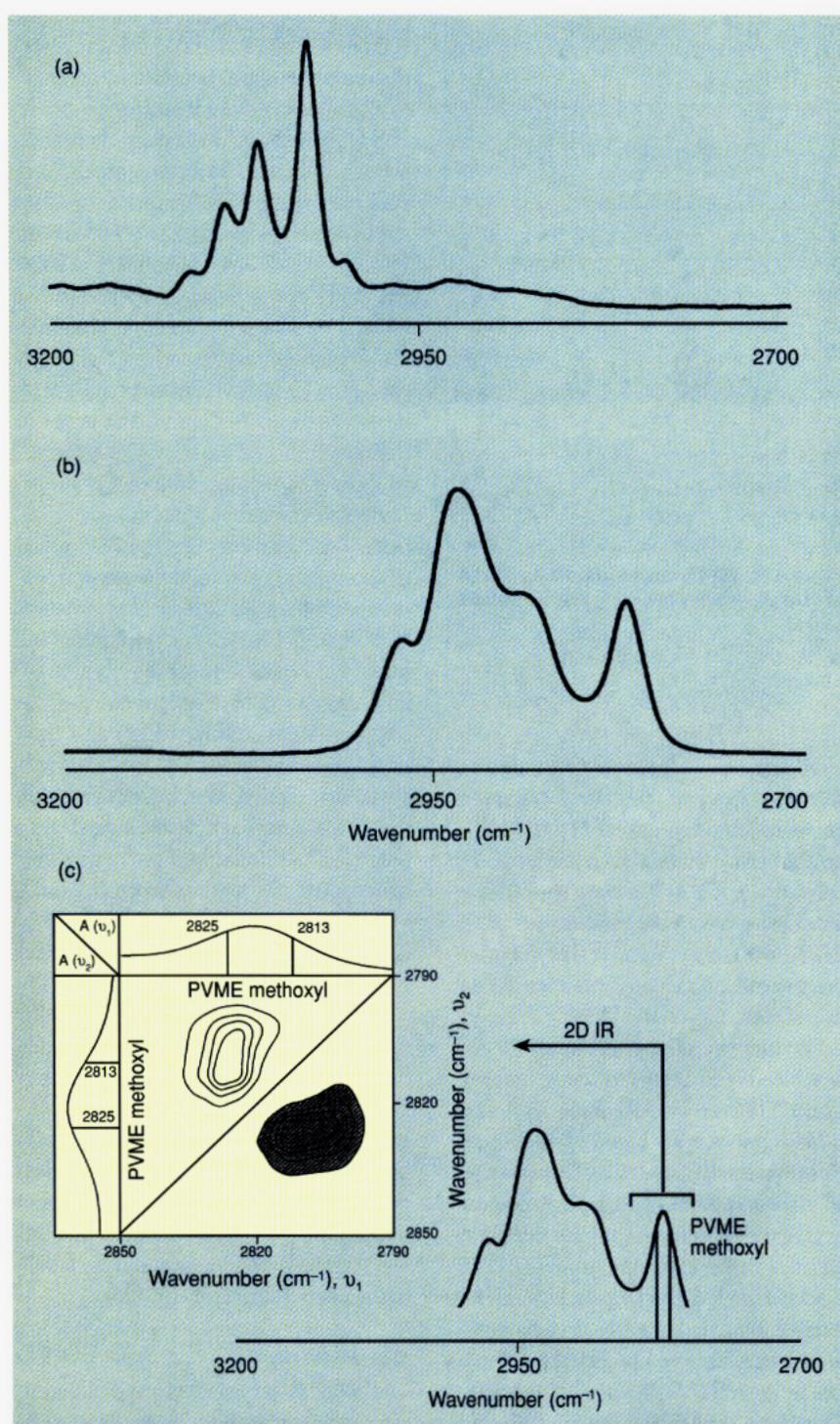


Figure 7. IR spectra of the d_3 -PS/PVME blend system in the CH-stretching region.

Normal IR spectra of (a) d_3 -PS and (b) PVME. (c) Normal IR spectrum and asynchronous 2D IR correlation spectrum of a 25:75 (by weight) blend of d_3 -PS and PVME.

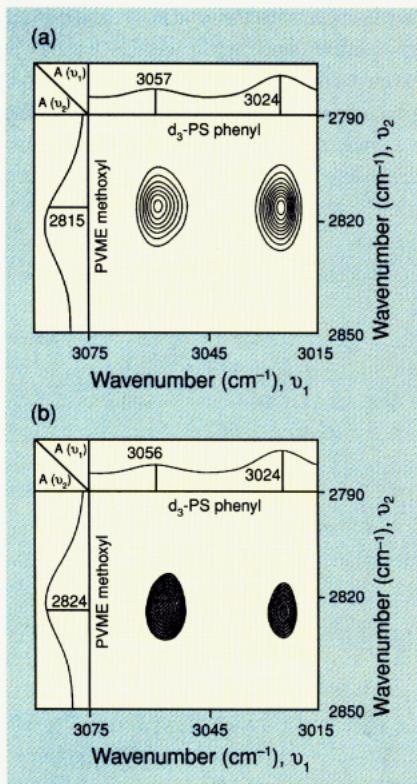


Figure 8. 2D IR correlation spectra of the d_3 -PS/PVME (25:75) miscible blend.

(a) Synchronous spectrum and (b) asynchronous spectrum.

Miscible blend of atactic polystyrene and poly(vinyl methyl ether). The polystyrene/poly(vinyl methyl ether) (PS/PVME) system represents a classical miscible polymer blend that has been studied in detail using a variety of techniques (22–24). These studies suggest that the primary site of interaction is between the lone pair of electrons on the PVME methoxyl group and the phenyl group of PS. We have used DIRLD spectroscopy coupled with 2D IR correlation techniques to study a 25:75 (by weight) blend of d_3 -PS and PVME in the CH-stretching region, where all of the backbone aliphatic hydrogen atoms in the PS component have been substituted with deuterium atoms (25, 26). Because the PVME component was left totally protonated, the CH-stretching region is virtually free of spectral overlap between the PS and PVME components. The clean separation between the aliphatic CH-stretching bands in PVME and the aromatic CH-stretching bands of PS can be clearly seen in Figure 7.

Figure 7c shows the asynchronous 2D

IR map of a film of a miscible 25:75 blend of d_3 -PS and PVME in the region of the symmetric-methyl stretching band of the PVME methoxyl group. Although this band appears to be a single peak at 2820 cm^{-1} in the normal IR absorbance spectrum, the 2D spectrum shows that it clearly consists of two components. The splitting of the 2820 cm^{-1} peak suggests the existence of two populations of methoxyl groups in different environments.

Figure 8 shows the synchronous and asynchronous 2D IR cross-correlation spectra of the PVME methoxyl CH_3 -stretching band around 2820 cm^{-1} and the PS aromatic CH-stretching bands at 3024 and 3057 cm^{-1} of the 25:75 PS/PVME blend. Cross peaks in the synchronous 2D IR map suggest that an interaction between the PS phenyl ring and the PVME methoxyl group is a significant factor in the miscibility of these two polymers, which is in agreement with previous work (24). Note the strong synchronous cross peaks occurring between the PS aromatic CH-stretching bands and the low-wavenumber side of the 2820 cm^{-1} symmetric methyl stretch (2815 cm^{-1}) of the PVME methoxyl group. The strong asynchronous cross peak between the two d_3 -PS aromatic CH-stretching bands and the high-wavenumber side of the 2820 cm^{-1} symmetric methyl stretch (2824 cm^{-1}) of the PVME methoxyl clearly indicates that only the PVME methoxyl group component contributing to the absorbance on the low-wavenumber side of the 2820 cm^{-1} band is interacting with the PS phenyl group.

The sign of the cross peaks in 2D IR time-correlation spectra can provide additional submolecular-level insight into the interaction between the PVME methoxyl group and the PS aromatic ring in this blend. Using our knowledge of the local orientation of the electric dipole-transition moments (13), we can determine that the O–C (methyl) bond lies in a plane parallel to the phenyl ring of PS (25, 26).

Conclusions

The ability to provide improved understanding of the interactions and interrelationships among chemical components is one of the key strengths of 2D correlation analysis of perturbation-induced dynamic responses. A sample perturbation that in-

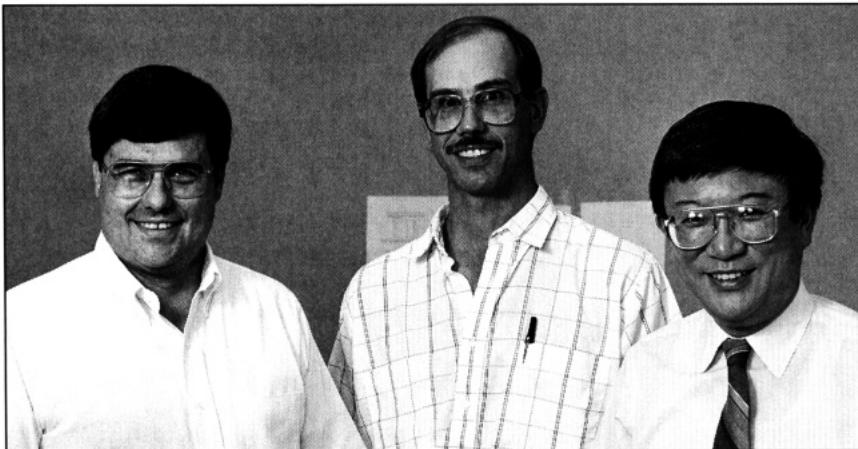
duces a time-dependent spectroscopic response can add substantially to the information available in the IR spectrum of a material. When individual spectral elements respond differently to the applied perturbation, useful spectroscopic features often emerge that were previously buried under broad spectral contours. Although these examples have focused on insights into polymeric systems that can be gleaned from using dynamic 2D IR spectroscopy, this approach can also be extended to nonpolymeric samples and other types of perturbations, such as electric field, ultrasonic, or temperature (5–10), with a variety of different waveforms (sinusoidal, exponential, pulses, or random noise) (4, 25, 27, 28).

Useful insights into the behavior of any sample can result if the time-dependent spectroscopic responses induced by the applied perturbation differ as a function of the wavelength of light being absorbed by chromophores in the sample. Finally, although these examples involved IR spectroscopy, any type of electromagnetic probe could be used (12, 29). The idea of applying a time-dependent perturbation to a sample and examining the spectroscopic response to some type of electromagnetic probe is one that could be re-applied in many other areas of analytical chemistry.

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