

A Faster Approach to Infrared Rheo-optics Using a Planar Array Infrared Spectrograph

CHRISTIAN PELLERIN,* SIMON FRISK, JOHN F. RABOLT, and D. BRUCE CHASE

Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716-3106 (C.P., S.F., J.F.R.); and DuPont Experimental Station, DuPont Inc., Wilmington, Delaware 19880 (D.B.C.)

Infrared rheo-optics combines dynamic mechanical analysis with infrared spectroscopy to provide molecular level information about the segmental reorientation and the changes in local environment associated with the dynamic deformation of polymers. Up to now, the application of this technique has been limited by the amount of time necessary to perform the experiments. In this article, we demonstrate that the use of a planar array infrared (PA-IR) spectrograph can accelerate the acquisition time by as much as two orders of magnitude while maintaining a signal-to-noise ratio (SNR) similar to that obtained using step-scan Fourier transform infrared (FT-IR) spectrometry, and by more than three orders of magnitude at the expense of a reduced SNR. The advantages and drawbacks of this new technique are discussed.

Index Headings: Polymer deformation; Infrared rheo-optics; Planar array infrared spectrograph; Time-resolved spectroscopy.

INTRODUCTION

Dynamic mechanical analysis (DMA) is a widely used technique to characterize the viscoelastic properties of polymers.¹ In a typical DMA experiment, a sample is subjected to a reversible cyclic deformation and its dynamic stress response is measured both in phase and 90° out of phase with respect to the applied strain. These two stress components are related to the elastic (storage modulus) and the viscous (loss modulus) properties of the polymer, respectively. By performing a temperature or frequency sweep, it is possible to obtain a mechanical spectrum that contains distinctive features associated with the viscoelastic transitions, such as the glass transition temperature (T_g) or the brittle-to-ductile transition. The main limitation of DMA is that it only provides a macroscopic response, stress, which cannot be directly related to the molecular origin of the observed phenomena.^{2,3} This becomes particularly significant for the study of multicomponent and/or multiphase systems such as polymer blends, copolymers, and semi-crystalline homopolymers.

To overcome this limitation, DMA has been coupled with various spectroscopic probes in what are usually known as “rheo-optical” techniques. Among those probes, infrared spectroscopy is a tool of choice because it can simultaneously provide molecular information about the conformation and orientation of the different components of the system.² Infrared rheo-optics have been applied to study a wide range of samples, including homopolymers,^{3–17} polymer blends,^{3,18,19} copolymers,^{20–27}

and biopolymers.^{15,28} Marcott and coworkers first developed infrared rheo-optics using a dispersive infrared spectrometer^{3,8,16,17,19,29} but, because of their multiplex advantage and high signal-to-noise ratio performance, Fourier transform infrared spectrometers (FT-IR) in the step-scan^{13–16,18} or the asynchronous sampling modes^{7,23,24} have now become standard instrumentation for infrared studies.

While the early experiments required hours of acquisition to probe a narrow spectral range, the development of modern instruments and of new demodulation schemes has significantly reduced the experimental timescale for obtaining a full spectrum. Step-scan FT-IR measurements typically require about 30 min for the acquisition of a single scan, while single scan measurements in only 5 min have been reported using the asynchronous sampling mode.^{23,24} In these examples, however, three scans had to be averaged to improve the signal-to-noise ratio. Despite these improvements, the repetitive deformation of samples, even for a few minutes, still imposes limitations on the widespread use of infrared rheo-optics (*vide infra*) and new developments further reducing the acquisition time could further extend its reach.

In this paper, we report the first rheo-optical application of a newly designed planar array infrared spectrograph (PA-IR), which couples a Czerny–Turner diffraction element with an infrared focal plane array (FPA) detector.³⁰ Isotactic polypropylene (iPP) is used as a model sample because its dynamic deformation has been widely studied before.^{12–15,17,25} We show that the PA-IR spectrograph has the potential of creating a breakthrough in this field by reducing the experimental measurement time by as much as three orders of magnitude as compared to FT-IR based techniques.

EXPERIMENTAL

The design of a PA-IR spectrograph that allows acquisition of infrared spectra in the fingerprint region of the mid-infrared has been recently described.³⁰ The infrared beam from an air-cooled global source (Surface-niter Corporation, Chagrin Falls, OH) was focused on the polymer sample through a 200 μm entrance slit (Model 1451X, SPEX, Edison, NJ), diffracted by a 50 grooves/mm grating (Thermo RGL, Rochester, NY), and was finally focused on a liquid-nitrogen-cooled 256 \times 256 mercury cadmium telluride (MCT) focal plane array (FPA) (EGL2333, Santa Barbara Focalplane, Goleta, CA) equipped with a Ninnox multi-element lens (Janos Technology, Townshend, VT). A long-pass optical filter with a 5 μm cut-off was used to reject the second and higher

Received 22 January 2004; accepted 27 February 2004.

* Author to whom correspondence should be sent. E-mail: pellerin@udel.edu.

diffraction orders from the grating. For the *p*-polarized experiments, a KRS-5 wire-grid polarizer with its transmitting axis parallel to the stretching direction was introduced before the slit. All the PA-IR experiments were recorded under ambient conditions (without purge) as a series of 600 single-frame images at a frame rate of 114.89 Hz.

The sample used in this work was an $\sim 18 \mu\text{m}$ thick iPP film prestretched to a draw ratio of ~ 4 and roughened with a fine polishing paper in order to eliminate the interference fringes. Sinusoidal deformation was applied to the sample at room temperature using a PM-100 Polymer ModulatorTM microrheometer from Manning Applied Technology (Troy, ID) driven by a Wavetek function generator (Model 171, San Diego, CA). Deformation amplitudes between 0.021 and 0.14% were used, well within the linear range for iPP.¹⁷ Deformation frequencies of approximately 14.36 and 7.18 Hz were used because they were exact fractions of the frame rate of the FPA and thus allowed recording exactly 8 and 16 spectra, respectively, during the course of each deformation cycle.

By precisely controlling the FPA triggering, it was possible to acquire spectra at specific phases in the deformation cycle, including at the minimum and maximum, as well as the rising and falling inflection points of the strain vs. time curve. The strain output of the microrheometer was fed into a lock-in amplifier (Stanford Research Systems Model 850, Sunnyvale, CA) to generate a transistor-transistor logic (TTL) signal synchronized with the deformation. This TTL signal was used to trigger a 0.08795 Hz square wave on a DS345 arbitrary waveform generator (Stanford Research Systems, Sunnyvale, CA), which, in turn, triggered the camera head sync of the FPA to initiate the 600-frame acquisition. This procedure permitted nearly perfect reproducibility of the measurements.

The raw spectral images were obtained using WinIR 3.6.0.5 (Santa Barbara Focalplane, Goleta, CA) and were processed using custom programs in MatLab 5.3 (MathWorks, Natick, MA). The in-phase (A') and quadrature (A'') spectra were calculated as:

$$A' = -\log_{10} \left(\frac{I_s - I_{\text{dbk}}}{I_u - I_{\text{dbk}}} \right)$$

$$A'' = -\log_{10} \left(\frac{I_{\text{fi}} - I_{\text{dbk}}}{I_{\text{ri}} - I_{\text{dbk}}} \right) \quad (1)$$

where I_s , I_u , I_{fi} , and I_{ri} are the single beam spectra recorded at the maximum and minimum strain and at the falling and rising inflection points, respectively, and I_{dbk} is the spectrum recorded when the slit was closed. Pixel binning and pixel-to-wavenumber conversion were performed as described elsewhere.³⁰

The step-scan measurements were performed using a Bio-Rad FTS 6000 spectrometer equipped with a liquid-nitrogen-cooled MCT detector. A single scan of 1021 points (undersampling ratio of 4) was collected at 8 cm^{-1} resolution with a step frequency of 0.5 Hz, for a total acquisition time of 34 min. The DSP2 mode was used to demodulate the experimental signal into the static and dynamic in-phase and quadrature spectra. The polymer stretching frequency and strain were 10 Hz and 0.14%,

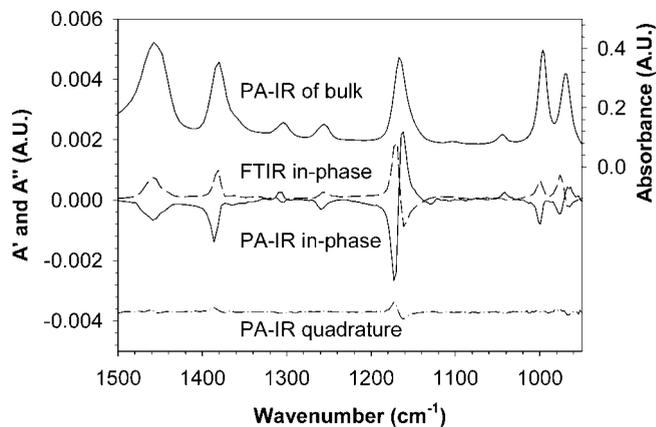


FIG. 1. Dynamic in-phase and quadrature spectra of the isotactic polypropylene sample recorded in 20 s with the PA-IR spectrograph (14.36 Hz) and dynamic in-phase spectrum (10 Hz) measured in 34 min using a step-scan FT-IR spectrometer. The FT-IR spectrum has been inverted for clarity. All spectra were acquired with a polarizer oriented parallel to the stretching direction. The static PA-IR spectrum of the bulk sample is shown for reference.

respectively. A KRS-5 wire-grid polarizer with its transmitting axis parallel to the stretching direction was used.

RESULTS AND DISCUSSION

Figure 1 shows the static spectrum and the dynamic in-phase and quadrature spectra of the iPP sample recorded using the PA-IR spectrograph, along with the in-phase spectrum (inverted for clarity) of the same sample obtained using the step-scan FT-IR spectrometer, as described in the Experimental section. All spectra were acquired with a polarizer oriented parallel to the stretching direction. The in-phase dynamic spectrum measured using the PA-IR spectrograph is in good agreement with that obtained with the FT-IR spectrometer and with previously published spectra.^{12–15} The signal-to-noise ratio also appears similar for both techniques, although the acquisition time was only 20 s for the PA-IR experiment as compared to 34 min for the step-scan FT-IR measurement. It will be shown below that the measurement time for the PA-IR experiment can be significantly reduced while preserving good signal-to-noise ratios. In comparing the spectra of Fig. 1, it should be emphasized that series of PA-IR experiments performed under the same conditions have given identical data within the noise limit, while consecutive step-scan FT-IR experiments provided much less repeatable results.

As expected, the quadrature spectrum in Fig. 1 is much weaker than the in-phase spectrum because the experiments were performed at room temperature, well above the glass transition temperature (T_g) of iPP. It is well known that a large signal in the loss modulus (in DMA) or in the quadrature spectrum (in infrared rheo-optics) only appears at the onset of a new dissipation mechanism, for example, at the sample T_g .^{1,2,23}

The most prominent feature in the dynamic spectra of iPP is the bisignate band at 1167 cm^{-1} that is due to C–C backbone stretching and to CH_3 rocking. The shape of this band has been attributed to a spectral shift caused by a stress-induced change in the C–C bond length along the main chain of the polymer.¹³ Indeed, this slight shift can

be directly observed by comparing the static spectra (not shown) recorded at the fully extended and relaxed extremes of the deformation cycle. The simultaneous measurement of such static spectra can thus improve our understanding of the dynamic changes associated with the deformation. In contrast with step-scan FT-IR, for which truly static spectra at the fully extended and relaxed extremes of the deformation cycle must be recorded (in the rapid-scan mode) independently from the dynamic experiment, the PA-IR acquisition scheme simply requires the collection of a background single beam in order to extract pseudo-static spectra from the dynamic set at any phase along the deformation cycle. This strongly limits the risk of artifacts associated with sample relaxation during the static acquisition of the stretched spectrum and thus constitutes a clear advantage of PA-IR over the usual approach.

The dynamic spectra recorded in an infrared rheo-optical experiment can provide useful information about molecular reorientation and changes in the molecular environment of the dipoles, but they also contain a contribution that results from sample thinning. Since the thickness of the sample is reduced in the elongated state, this appears as negative bands in the dynamic spectra. However, this effect has usually been considered to be small as compared to the overall signal in the dynamic spectra.^{13,31} Chase and Ikeda have shown that it is possible to avoid sample thinning by performing a shear deformation instead of a tensile deformation.⁴ For the spectra of Fig. 1, it can be calculated that, assuming that the sample is incompressible and that the deformation is isotropic, sample thinning contributes about 7% of the dynamic in-phase signal for the 1167 cm^{-1} band, while it is 11% for the band at 1377 cm^{-1} . This effect is thus small for these spectra, but this is not necessarily always true. In particular, the relative effect of sample thinning on the iPP dynamic spectra recorded with light polarized perpendicular to the stretching direction (not shown) was considerably larger, and thus needs to be accounted for when considering band intensities and even sign.

Although there is a good agreement between the step-scan FT-IR and PA-IR dynamic spectra in Fig. 1, a significant intensity difference can be observed for the 1167 cm^{-1} band. This discrepancy is most probably due to a difference in initial static strain for the two measurements. The deformation frequency, 14.36 Hz for the former and 10 Hz for the latter, does not account for the difference since superimposable spectra (not shown) have been obtained at 7.18 and 14.36 Hz using the PA-IR spectrograph. This observation is in marked contrast with the results of Budevskaya et al., who have observed a significant intensity increase for the in-phase spectrum when reducing the deformation frequency from 23 to 13 Hz.¹³ They did not explain this non-intuitive behavior, as the storage modulus would be expected to slightly decrease when reducing the deformation frequency.

It should be mentioned that an intrinsic difference between PA-IR and FT-IR dynamic spectra is the fact that the resolution of a dispersive instrument is constant in wavelength and not in frequency, as for FT-IR spectrometers.³⁰ In the present case, the spectral resolution varies gradually from about 6 to 13 cm^{-1} from 950 to 1500 cm^{-1} . This reduced spectral resolution explains the broad-

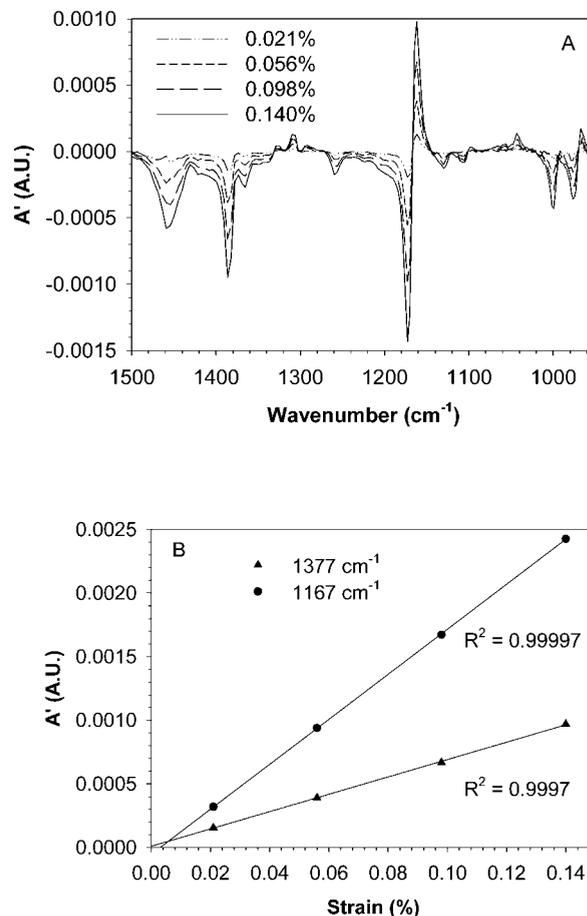


FIG. 2. (A) In-phase PA-IR spectra of isotactic polypropylene obtained for different dynamic strains at a 7.18 Hz deformation frequency, and (B) plot of the absolute intensity of the dynamic infrared signal for the 1377 and 1167 cm^{-1} bands as a function of dynamic strain.

er shape of the 1458 cm^{-1} band in the PA-IR spectrum as compared to the FT-IR spectrum measured with 8 cm^{-1} resolution.

To further assess the value of the PA-IR spectrograph for rheo-optical studies, the deformation of iPP has been followed for dynamic strains ranging from 0.021% to 0.14%, at a 7.18 Hz deformation frequency and with unpolarized light. Figure 2A clearly shows that all the spectral features are highly reproducible and that only their intensity varies with strain within this range. The intensity (absolute value) of the symmetric C-H bending¹² at 1377 cm^{-1} and the difference between the positive and negative peaks of the 1167 cm^{-1} band have been plotted as a function of the applied strain in Fig. 2B. A linear relation between dynamic intensity and strain holds for both bands, with correlation coefficients larger than 0.9997. This result constitutes a very nice validation of the reproducibility and quantitative nature of the PA-IR spectrograph for rheo-optical studies.

When using a lock-in amplifier or a digital signal processor to demodulate the dynamic signal of a modulated phenomenon into the in-phase and quadrature signals, as with the step-scan FT-IR approach, it is implicitly assumed that the forward and reverse processes possess the same phase lag with respect to the external stimuli.³² In the case of dynamic polymer deformation, this detection

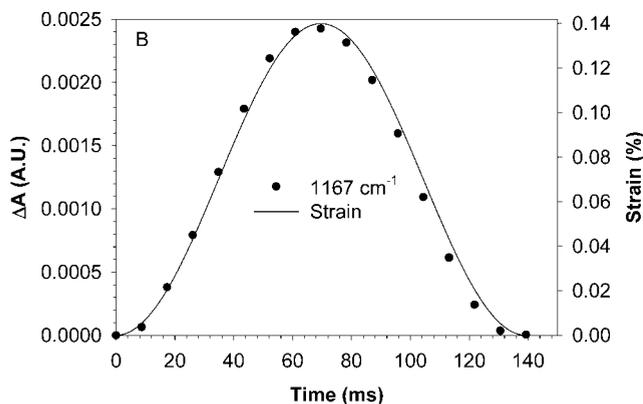
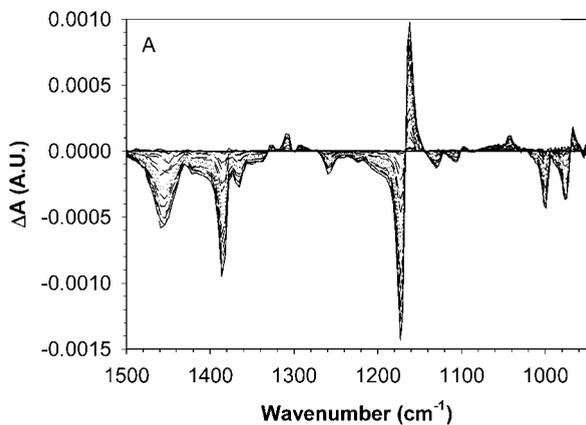


FIG. 3. (A) Series of dynamic PA-IR spectra recorded along the deformation cycle in a single experiment at a deformation frequency of 7.18 Hz, and (B) evolution of the dynamic signal for the 1167 cm^{-1} band with the applied dynamic strain as a function of time during the deformation cycle.

scheme will only provide an average phase lag for the overall process, although the sample might, for instance, deform in phase with the applied strain but relax with a delayed kinetics. The PA-IR spectrograph can overcome this limitation because it generates a series of single-beam spectra along the deformation cycle and not only the dynamic in-phase and quadrature signals. It is thus possible, using a reformulated Eq. 1, to retrieve difference spectra from any pair of points along the deformation cycle with a time resolution of 8.7 ms.

Figure 3A shows a series of 16 spectra recorded in a single experiment at a deformation frequency of 7.18 Hz. Figure 3B demonstrates that a sinusoidal function is obtained when plotting the intensity of any spectral band as a function of time. The frequency of this sine function is the same as that of the applied strain, but a slight phase lag exists between them because of the partly viscous response of the material. For a perfectly elastic material, superimposed strain and dynamic infrared intensity curves (or dynamic stress) would have been obtained. Although no significant difference in the phase lag for the stretching and relaxing parts of the deformation cycle is evident in Fig. 3B for this almost perfectly elastic sample, the possibility of using PA-IR to follow independently these two processes in a time-resolved fashion should prove useful in the future.

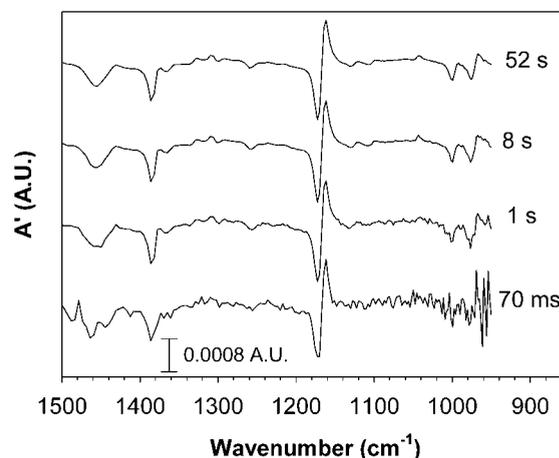


FIG. 4. In-phase PA-IR spectra of the isotactic polypropylene sample deformed at 14.36 Hz recorded in a total acquisition time of 52 s, 8 s, 1 s, and 70 ms.

As introduced above, one of the main limitations to the more extensive use of infrared spectroscopy for the rheo-optical study of polymers is the relatively long time necessary to perform the experiments. This has many practical consequences, the first being a requirement of very high stability for the spectrometer during the measurement process. From the sample standpoint, many polymers cannot be strained for several minutes without showing relaxation or plastic deformation. Any modification of the sample during the acquisition of an interferogram will create artifacts in the spectra. In many cases, films of the sample of interest have been deposited on a Teflon or polypropylene substrate to avoid such effects,^{4,14,16,21} but this procedure could potentially alter the viscoelastic properties of the sample. Finally, the time scale of the FT-IR experiments limits, both from the instrumental and sample standpoints, the possibility of performing complete temperature sweeps. To measure a full mechanical relaxation spectrum, as is often realized in conventional DMA experiments, such a complete temperature or frequency sweep is necessary. Up to now, studies of the temperature dependence of the dynamic infrared spectra have generally been limited to a few discrete temperatures.^{8,11,23,27}

To fully demonstrate the time advantage of the PA-IR spectrograph, Fig. 4 shows the in-phase spectra obtained for total acquisition times of 52 s, 8 s, 1 s, and 70 ms at a deformation frequency of 14.36 Hz with unpolarized light. Obviously, the signal-to-noise ratio is better for the longer experiments, but all the spectral features are easily observed in the 1 s spectrum, including the weak wagging and bending deformations between 1240 and 1350 cm^{-1} . The peak-to-peak noise for these spectra is 4.3×10^{-5} A.U. for the 1 s experiment and a remarkable 4.0×10^{-6} A.U. for the 52 s acquisition. As expected, the peak-to-peak noise in the polarized spectra increases by a factor similar to the reduction in transmitted intensity, compared to the unpolarized case. In addition, when the polymer deformation frequency is modified, for instance, on going from 14.36 to 7.18 Hz, a different number of deformation cycles can be averaged for a constant measurement time. In consequence, the noise level for a con-

stant acquisition time increases as the deformation frequency is reduced.

In contrast to the conventional methods, for which the minimum measurement time is largely determined by instrumental constraints, it is possible with the PA-IR spectrograph to adjust the measurement time to obtain the desired signal-to-noise ratio. The only limit is the necessity of measuring through a single deformation cycle, i.e., about 70 ms at a deformation frequency of 14.36 Hz. In that case, the peak-to-peak noise around the 1167 cm^{-1} band is 4.4×10^{-4} A.U., still small enough to clearly observe the bisignate band in Fig. 4. Considering that large storage and loss moduli changes occur when crossing the glass transition temperature of a sample, such noise levels strongly suggest that, using an appropriate temperature-controlled microrheometer, it should be possible to perform dynamic rheo-optical measurement during a temperature sweep at typical DMA rates between 5 and 20 K/min.

CONCLUSION

The results obtained in this work strongly suggest that the new PA-IR spectrograph has the potential to create a breakthrough in the rheo-optical study of polymers by infrared spectroscopy. Highly reproducible dynamic spectra of isotactic polypropylene with an excellent noise level of 4.4×10^{-6} A.U. have been recorded in 52 s, and spectra with acceptable signal-to-noise ratio have been recorded in as little as 70 ms, as compared to 5 min for the conventional FT-IR based measurement. Such measurement speed should expand the application of infrared rheo-optics to more samples and enable temperature sweep measurements. The drawbacks of PA-IR as compared to FT-IR are a reduction of spectral range, resolution, and frequency accuracy. The new approach has the additional advantage of providing the static absorbance spectra as well as multiple dynamic spectra along the deformation cycle. The simple no-moving-part design of the PA-IR instrument also reduces the sensitivity to mechanical vibrations introduced by the environment and by the microrheometer. Spectral data presented here were acquired in a time-resolved format, demonstrating the potential utility of this instrument for other types of time-resolved spectroscopic measurements.

ACKNOWLEDGMENTS

The authors acknowledge the NSF Division of Materials Research (NSF-DMR-0315461), the NSF Approaches to Combat Terrorism (NSF-CHE-0346454), and NIH for partial support during the course of this work. C.P. also thanks the NSERC of Canada for a post-doctoral fellowship and Dr. Richard Ikeda for useful discussions.

1. J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley and Sons, New York, 1980), 3rd ed.

2. C. Marcott and I. Noda, "Dynamic Infrared Linear Dichroism Spectroscopy", in *Handbook of Vibrational Spectroscopy*, P. R. Griffiths and J. M. Chalmers, Eds. (John Wiley and Sons, Chichester, 2002), vol. 4, p. 2576.
3. C. Marcott, A. E. Dowrey, and I. Noda, *Anal. Chem.* **66**, A1065 (1994).
4. D. B. Chase and R. M. Ikeda, *Appl. Spectrosc.* **53**, 17 (1999).
5. Y. X. Wang and S. Lehmann, *Macromol. Chem. Phys.* **199**, 2797 (1998).
6. Y. X. Wang and S. Lehmann, *Appl. Spectrosc.* **53**, 914 (1999).
7. S. Ekgasit, H. W. Siesler, and P. A. M. Steeman, *Appl. Spectrosc.* **53**, 1535 (1999).
8. I. Noda, A. E. Dowrey, and C. Marcott, *Appl. Spectrosc.* **42**, 203 (1988).
9. H. V. Shah, C. J. Manning, and G. A. Arbuckle, *Appl. Spectrosc.* **53**, 1542 (1999).
10. M. Sonoyama, K. Shoda, G. Katagiri, and H. Ishida, *Appl. Spectrosc.* **51**, 346 (1997).
11. M. Sonoyama, K. Shoda, G. Katagiri, H. Ishida, T. Nakano, S. Shimada, T. Yokoyama, and H. Toriumi, *Appl. Spectrosc.* **51**, 598 (1997).
12. G. Parthasarathy, M. Sevegney, and R. M. Kannan, *J. Polym. Sci. Part B: Polym. Phys.* **40**, 2539 (2002).
13. B. O. Budevskva, C. J. Manning, P. R. Griffiths, and R. T. Roginski, *Appl. Spectrosc.* **47**, 1843 (1993).
14. R. A. Palmer, C. J. Manning, J. L. Chao, I. Noda, A. E. Dowery, and C. Marcott, *Appl. Spectrosc.* **45**, 12 (1991).
15. M. Sonoyama and T. Nakano, *Appl. Spectrosc.* **54**, 968 (2000).
16. C. Marcott, A. E. Dowrey, and I. Noda, *Appl. Spectrosc.* **47**, 1324 (1993).
17. I. Noda, A. E. Dowery, and C. Marcott, "Characterization of Polymers using Polarization-Modulation Infrared Techniques: Dynamic Infrared Linear Dichroism (DIRLD) Spectroscopy", in *Fourier Transform Infrared Characterization of Polymers*, H. Ishida, Ed. (Plenum Press, New York, 1987), p. 33.
18. V. G. Gregoriou, I. Noda, A. E. Dowrey, C. Marcott, J. L. Chao, and R. A. Palmer, *J. Polym. Sci. Part B: Polym. Phys.* **31**, 1769 (1993).
19. C. Marcott, I. Noda, and A. E. Dowrey, *Anal. Chim. Acta* **250**, 131 (1991).
20. D. K. Graff, H. C. Wang, R. A. Palmer, and J. R. Schoonover, *Macromolecules* **32**, 7147 (1999).
21. V. G. Gregoriou, S. E. Rodman, B. R. Nair, and P. T. Hammond, *J. Phys. Chem. B* **106**, 11108 (2002).
22. S. Nomura, R. Ashitani, H. Matsuda, and L. Banda, *Polymer* **42**, 9045 (2001).
23. P. A. M. Steeman, R. J. Meier, A. Simon, and J. Gast, *Polymer* **38**, 5455 (1997).
24. P. A. M. Steeman, *Appl. Spectrosc.* **51**, 1668 (1997).
25. H. C. Wang, R. A. Palmer, and C. J. Manning, *Appl. Spectrosc.* **51**, 1245 (1997).
26. H. C. Wang, D. K. Graff, J. R. Schoonover, and R. A. Palmer, *Appl. Spectrosc.* **53**, 687 (1999).
27. H. C. Wang, S. R. Aubuchon, D. G. Thompson, J. C. Osborn, A. L. Marsh, W. R. Nichols, J. R. Schoonover, and R. A. Palmer, *Macromolecules* **35**, 8794 (2002).
28. M. Sonoyama, M. Miyazawa, G. Katagiri, and H. Ishida, *Appl. Spectrosc.* **51**, 545 (1997).
29. I. Noda, A. E. Dowrey, and C. Marcott, *J. Polym. Sci. Part C: Polym. Lett.* **21**, 99 (1983).
30. C. Pellerin, C. M. Snively, D. B. Chase, and J. F. Rabolt, *Appl. Spectrosc.* **58**, (2004).
31. B. R. Nair, V. G. Gregoriou, and P. T. Hammond, *J. Phys. Chem. B* **104**, 7874 (2000).
32. P. R. Griffiths, B. L. Hirsche, and C. J. Manning, *Vib. Spectrosc.* **19**, 165 (1999).