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Deformation Studies of Polymers by Time-Resolved Infrared Spectroscopy IV: A Modified Approach

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Recent studies have demonstrated how effective the time-resolved Fourier transform spectroscopic technique is in obtaining dynamic information about microstructural change in the millisecond time scale. In this current study, the time efficiency of the method has been improved by the development of a scheme implementing the use of a separate microprocessor to maintain synchronization between the interferometer movement and the external event. This method eliminates the need for

accurate external timing circuits and their interface to the FT-IR. Therefore, data collection software of the FT-IR system need not be modified as in previous cases.

Index Headings: Infrared spectroscopy, time-resolved; Polymer deformation

INTRODUCTION

The study of the dynamics of microstructural changes occurring with deformation is of great importance in un-

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derstanding the structure-property relationships of polymers. Previously, the motions of the various structural subunits had been characterized by a combination of dynamic x-ray, light scattering, and birefringence techniques.¹⁻³ Unlike the techniques mentioned above, vibrational spectroscopy possesses high selectivity, i.e., the ability to distinguish chain segments of various conformation and environment. Therefore, if sufficiently high temporal resolution can be achieved, vibrational spectroscopy can be a powerful characterization tool for following the deformation-induced conformation or orientation changes.

The dynamics of structural change occur in times as short as milliseconds. Until very recently, vibrational spectroscopy has generally been used to characterize stationary phenomena or events lasting much longer than the measurement time. The development of the time-resolved Fourier transform technique has greatly enhanced the usefulness of vibrational spectroscopy for following structural changes.⁴⁻⁸ The principles representing several different approaches to this type of time-resolved Fourier transform infrared spectroscopy have been presented in a number of publications.^{4,6,9,10} Each one of these approaches incorporates some form of ordered sampling technique, which generally results in the collection of a large amount of data that must later be sorted to obtain properly time-ordered interferograms. In all cases, spectroscopic data of high temporal resolution is only possible when a definite phase relationship can be established between the time domain of the external event, such as deformation, and the retardation of the interferometer. In our experiments, we employ the use of a commercial fast-scanning interferometer; therefore the phase relationship between the spectrometer and the external event can be established in two ways. We have used the Take Data signal as the initiation trigger¹⁰ for the external event or, alternatively, we have correlated the timing of the spectrometer and the external event to an external clock.¹¹ Details of the experiments are described in the references given. The first scheme has the advantage that accurate phase relationships can be obtained with minimal hardware modification. But stepwise deformation gives rise to transient effects in polymers and therefore cannot be correlated to other mechanical information obtained from techniques such as rheovibron. The second scheme is a more useful technique which allows the deformation event to run continuously, but the initiation of the external event and the interferogram scan are uncorrelated. Therefore, for experiments requiring high time-resolution, significant signal averaging can only be achieved at long experimental times. In order to overcome this disadvantage, we incorporated a separate microprocessor, in addition to the one associated with the FT-IR in our time-resolved spectroscopy experiment, to control and monitor the deformation event. Since the cycle time of the interferometer is accessible through the Take Data signal, this microprocessor can measure and adjust the relative phase between the two events. Thus the spectroscopic signal corresponding to the same segment of time can be accumulated very efficiently. Since all the programs are written in Pascal, this newly developed scheme eliminates the need to construct specialized

electronic timing circuitry or to write program patches in assembler language for control purposes. A detailed description of the newly developed scheme and its applications is reported here.

EXPERIMENTAL

Three major components are needed for this time-resolved Fourier transform infrared technique: (1) FT-IR, (2) a microprocessor, and (3) a mechanical stretcher. The FT-IR used in our study is an International Business Machine model IR-98. It has a vacuum bench and is capable of both mid- and far-infrared analysis. In general, all infrared data are of 1 cm^{-1} resolution. Full or partial spectra are stored on a magnetic disk system for further analysis. It has multitasking capability and can be programmed with higher level languages such as Pascal or FORTRAN. The 8-bit microprocessor was purchased from H-Square, Palo Alto, CA. Its configuration includes 64 K random access memory, two serial ports, two eight-line parallel ports, and two eight-inch floppy disk drives.

We have constructed several types of hydraulic or gear-driven mechanical stretchers in our laboratory. In this case the stretcher is driven by a Slo-Syn $\frac{1}{4}$ horsepower stepping motor. At a constant rate of rotation, a sinusoidal deformation is applied to the sample through a camming mechanism. The stepping motor is microprocessor-controlled through a digital stepper driver interface card purchased from Advanced Micro Systems. Four 12 V d.c. power leads supply the current from the stepper driver card to the motor. Internal logic of the driver card switches these power leads in a specific sequence causing the motor to rotate one full or one half step. The number of steps required for one revolution is 200 in the full-step mode and 400 in the half-step mode. The half-step mode has been used exclusively in our experiments in order to maintain a smoother deformation cycle.

Technique Development. Because of its multiplex advantage and high throughput, FT-IR has a higher speed of spectral acquisition than do dispersive instruments. Even so, when a short time phenomena is observed, it is necessary to reduce the signal-to-noise ratio (by decreasing the number of scans coadded and the time to collect each scan) and/or spectral resolution (shorter mirror travel) for better time resolution. The limit of an FT-IR is reached when the time period required for one scan of the moving mirror is longer than the time resolution required to describe the physical phenomenon. This deficiency led to the development of time-resolved Fourier transform spectroscopy.

The principles representing several approaches to TRS have been described in detail previously. In all cases, a normal interferogram, $I(\delta_j)$, is composed of points from $j=1$ to the maximum number, NDP , each taken at equal intervals of retardation (δ_j). TRS observes time-varying phenomena (polymer stretching, laser-induced chemical events, etc.), which are referred to as the sample event. Each of the TRS techniques divides the sample event into discrete elements of time, t_i . The time elements are normally of the same width Δt . Therefore, the time associated with each element t_i is $i \times \Delta t$ as i goes from 0

SCHEMATIC OF TIME RESOLVE COMPONENTS

FIG. 1. The schematic diagram of a time-resolved experiment.

to n , the number of Δt intervals per sample event. During a TRS experiment, the interferogram points, $I(\delta_j, t_i)$ are functions of both time and retardation. Several schemes employing either step scanning or continuous scanning interferometers exist to collect spectroscopic data for all j and i . When the collection is finished, the points are sorted to reconstruct interferograms at constant time. Each resulting interferogram then contains data points numbered from 1 to the maximum number, NDP , all collected during a particular t_i . In our laboratory, we use only fast-scanning interferometers; therefore special hardware and software were designed and constructed for time-resolved spectroscopy work.¹¹

Continuous External Events. The mechanical properties of polymers are most often analyzed by the application of a continuous periodic strain function. In our past experiments, we developed highly specialized time circuits to oversee both the interferometer movements and the initiation and timing of such external events.¹¹ Furthermore, a considerable amount of software was written to enable the minicomputer of the FT-IR system to access information from the external event and relate it to the spectroscopic data obtained. Although a time-resolved spectroscopy package of this type is quite flexible and can be applied to a large number of experiments, with different time resolutions achievable, the investment in time and effort was substantial and not easily transferred to other spectrometer systems. For many of our experiments the external event period is on the order of 0.1 to a few seconds. This type of experiment cannot be conveniently handled in the usual time-resolved experiments developed earlier, nor can these be

FIG. 2. Flow diagram of computer control program for continuous deformation experiment.

studied with the use of the "rapid scan" option. In that case, a sufficient signal-to-noise ratio simply cannot be achieved with desired spectral resolution. To overcome some of these disadvantages, we have incorporated a microprocessor into the time-resolved experiment. Its function is to control the external event and adjust its relative phase to the interferometer movements. When such a scheme is used, the FT-IR is essentially decoupled from the external event. Its only function is to collect the interferograms and store them on the magnetic disk system. All the interferograms may be coadded with the use of the standard signal-averaging technique common to all commercial instruments. All the timing and

FIG. 3. Scheme showing the phase relationship between the interferometer movement and the external event for a continuous deformation cycle. A separate interferogram file is collected for each of n clock values, where n = event period/time resolution.

control functions of the microprocessor need not be programmed with assembler language and instead can be written with higher level languages such as Pascal.

The experimental parameters which need to be defined are:

NSS = number of scans of the same phase to be coadded.

T = cycle time or event time.

$\Delta T_1 = T/400$ = time interval between each step.

ΔT_2 = time resolution desired.

$N = T/\Delta T_2$ number of files into which the external event or interferogram must be divided.

The overall flow diagram of the time-resolved experiment is shown schematically in Figs. 1 to 3.

Unlike in our previous experiments, the period of the event must be exactly synchronous to the period of the interferometer scan (including the back sweep). Of course this scheme will limit the flexibility of the time-resolved experiment since the event time is then determined by the available mirror velocities and the number of data points. Practically speaking, this has not been a problem since there are a sufficiently large number of mirror velocities available, and the resolution needed in our experiments is not critical.

Initially, once the event time period and the time resolution needed to follow the kinetics are determined, all other experimental parameters and the execution of the

experiment are supervised by the microprocessor. Since the Take Data pulse (TKDA) from the interferometer is available to the microprocessor, the period of the sweep time or, in our experiment, the event time, T , can be easily calculated and stored in memory. The computer then calculates ΔT_1 . Since the number of steps to complete a revolution is fixed at 400, it is then a simple matter to send pulses of $10 \mu s$ duration every ΔT_1 to the stretcher driver card. For the first file, NSS number of interferograms are stored in the memory. During the writing operation to the disk, which can take as long as 8 s, the microprocessor advances the external event in order to introduce a net time difference, ΔT_2 , between the initiation of the next set of NSS scans and the external event. This process is repeated until N files, each containing NSS scans, are collected. Since the time relationship between each file is clearly defined, separate interferograms may be constructed for each time element t_i within a time resolution of ΔT of the sample event. In Figs. 4A and 4B the interferograms are shown as being divided into blocks and reconstructed to generate new interferograms corresponding to a particular time in the event. The program to carry out this process is written in Pascal and can be used in a large number of processors.

Periodic Stepwise Event. In our laboratory we have been quite interested in characterizing the dynamics of electric field-induced microstructural changes of a piezoelectric polymer, poly(vinylidene fluoride) (PVF₂). In this application of time-resolved spectroscopy, it is desirable to apply a periodic squarewave field lasting several seconds across the PVF₂ film. This type of external event can be handled conveniently only by the present technique. Similar to the previously described scheme, the technique in this case has the microprocessor send an output pulse consisting of an array of N elements, each consisting of eight bits individually addressable by the microprocessor. In the present case only one bit per element of this output array is used. It turns on the high voltage transistor when the bit is set to 1 or turns off the voltage when the bit is set to 0. The signal at the port will stay high or low until the next time this port is addressed. The phase relationship between the interferometer movement and the stepwise periodic external event is shown in Fig. 5. Each file is collected by the coadding of the interferogram NSS times. The external event occurs in synchronization with the interferometer movement and is controlled by the external event array. Even though each element of the output array is represented as one bit in the high or low state, it is possible to use all eight bits to generate a more complex external event such as a segment of the sine function. This digital signal could then be converted to an analog sine wave by use of digital-to-analog converter. The collection and file sorting are executed as described previously.

RESULTS AND DISCUSSION

It is most important to test the accuracy of the phase relationship between the interferogram and the associated external event. We designed a time-resolved experiment with the transient event being the continuous rotation of a highly oriented polymer film in front of a

FIG. 4. During the data collection the phase relationship between the interferogram and the external event is varied in a systematic manner. A, Here the interferogram is shown segmented to depict how it is divided for the sorting procedure. B, After sorting, each interferogram corresponds to a specific segment of the time.

stationary silver bromide polarizer. The sample used is an ethylene-vinyl acetate copolymer which has been uniaxially oriented by drawing to a draw ratio of 3.5 at 110°C. It is mounted on a retaining ring rotated by the stepping motor used in the stretcher. The experimental

parameters are listed in Table I. Each rotation is matched to the cycle time (1.22 s) of the interferometer. The difference between the sample period and the interferometer cycle period is no more than 0.75 millisecc per cycle. This deviation is not cumulative since our timing scheme

FIG. 5. Scheme showing phase relationship between the interferometer movement and the external event for a squarewave event cycle. The computer output array contains the waveform of the external event.

automatically corrects for any difference once each cycle. In this manner the interferometer and sample rotation remained in phase as each interferogram was coadded to the file. A series of 20 interferogram files was collected with each being the average of 50 scans.

The shape of the unsorted interferograms shows the expected interferometric modulation but also has a low frequency modulation in the baseline (Fig. 6). The low frequency component is the result of large changes in the total absorbance of the sample as a function of the angle between the polarizer and the orientation direction. Since the sample is thick ($25 \mu\text{m}$) and highly polarized, its total absorbance change, when rotated with respect to the fixed polarizer, can be large enough to cause the baseline modulation. After the interferograms are sorted this baseline modulation manifests itself as a sawtooth function (Fig. 7). Each time block in the interferogram corresponds to the same phase in the cycle; thus a similar slope is repeated throughout the interferogram. When these sorted interferograms were Fourier transformed, the resulting time-resolved spectra contained periodic spikes. This is shown in Fig. 8.

Although this example, showing such large absor-

TABLE I. The experimental conditions used to test the operation of the time-resolved infrared spectroscopic equipment.

Event period	1.22
Time clocks per event	20
Clock period (time resolution)	61 milliseconds
NDP points per interferogram	16,384
Spectral resolution	1 cm^{-1}

FIG. 6. The interferogram obtained which shows a low frequency modulation related to absorbance change as a function of the external event.

bance change, is an extreme case, a similar effect must exist in other time-resolved experiments as well. Since many of the spectral changes associated with time-resolved experiments are small, an evaluation of such spectral artifacts should be interesting and relevant. In order to simulate such intensity modulation, a periodic sawtooth perturbation was added to a normal background interferogram. The form of this sawtooth function is

$$y_i = y_i^0 + a[\text{Rem}(i/N) - N/2]$$

y_i = resulting interferogram intensity.

y_i^0 = normal interferogram intensity.

i = data point index of interferogram.

N = number of data points per sawtooth.

a = sawtooth amplitude.

Rem = retain the remainder of the quotient. (1)

Figure 9 shows the interferogram before and after modification. When the modified interferogram is Fourier transformed the resulting energy curve has the same type of spectral artifact as is observed in the time-resolved data. The ratio of this energy curve against the unperturbed one shows the artifact more clearly (Fig. 10). The

FIG. 7. The modulation manifests itself as a sawtooth pattern in the sorted interferogram.

FIG. 8. The Fourier transformed spectrum of the interferograms containing low frequency modulation can show an artifact in the form of evenly spaced spikes.

periodicity of this artifact is 10.6 cm^{-1} , which corresponds to $1/[\delta_{\text{max}}(N/NDP)]$, where N is the number of data points per block, NDP is the total number of data points in the interferogram, and δ_{max} is the spectral retardation of the last data point of the interferogram. We found the intensity of the spikes to be proportional to the magnitude of the discontinuity in the sawtooth. In actual time-resolved spectroscopic experiments this would correspond to the change in transmitted energy (for example, from sample thickness change) during one clock period, ΔT_2 . In the rotating film test, this change in transmission is of sufficiently large magnitude to cause spectral artifacts in the spectra obtained, making interpretation of the time-resolved data difficult. For this reason a method was developed to correct for the discontinuities before the interferogram is transformed. A computer program using a function similar to Eq. 1 matches the last data point in each block with the first data point in the next block. This eliminates the discontinuity by leveling out the slope in each block. This correction was applied to the time-resolve data of the ethylene-vinyl acetate copolymer. From the analysis of the simulation data and the ethylene-vinyl acetate copolymer spectra we feel confident that this artifact is gen-

FIG. 10. When the modified interferogram is transformed the resulting ratioed spectrum exhibits a distinct derivative-like artifact.

erally negligible. If it does exist, the correction can be carried out.

A series of the corrected spectra obtained by the time-resolved technique for the CH_2 rocking vibration is shown in Fig. 11. It is evident that the $720\text{--}730 \text{ cm}^{-1}$ doublet due to crystal-field splitting is perpendicularly polarized in this highly oriented film. As expected, the absorption reaches a maximum twice during each cycle. This occurs when the film orientation is perpendicular to the infrared polarization vector. This series of spectra clearly demonstrates the applicability of our newly modified technique to the collection and computation of time-resolved infrared spectral data.

Finally, we want to evaluate and compare the sensitivity of this modified technique in characterizing deformation-induced microstructural changes in an actual polymer sample undergoing deformation. The sample chosen for this study is poly(butylene terephthalate) which has a first-order crystal phase transition.^{12,14} Since this phase transition is strain-dependent and reversible^{13,14} it can be suitably followed by the time-resolved spectroscopic technique. The vibrational spectra of PBT has been well characterized.¹⁵ Several infrared active vibrations are highly sensitive to the conformation of the tetramethylene sequence existing in the various crystal-

FIG. 9. Interferogram containing computer simulated sawtooth function: A, as collected; B, after computer modification.

FIG. 11. Change in CH rocking intensity as a function of angle between polarizer and film orientation direction.

line phases. For example, the 917 cm^{-1} and 960 cm^{-1} bands are assignable to the CH_2 rocking of the α and β phases, respectively.¹⁵ The infrared spectrum of this region obtained for PBT is shown in Fig. 12. For our mechanical-vibrational spectroscopy experiment, the strain amplitude of the deformation used was 4%. Previously, a static strain test demonstrated that this was sufficient for observation of an increase in the amount of β phase. A complete list of parameters used in this experiment is

FIG. 12. Characteristic CH_2 rocking vibration in PBT associated with the α , β , and amorphous phase.

FIG. 13. A measure of the α - β phase transformation in poly(butylene terephthalate). Integrated absorbance change as a function of strain amplitude: ■, α form (917 cm^{-1}); ●, β form (970 cm^{-1}).

given in Table II. Ten time-resolved spectra corresponding to a time resolution of 122 millisecc were collected. For such small strain amplitude we found that the total absorbance change due to changing sample thickness during deformation was not enough to cause a baseline modulation in the interferogram. Therefore, no correction in the sorted interferograms was necessary and, in fact, no spectral artifacts were observed. Spectral subtraction has been used to monitor the change in intensity as a function of strain of the vibrations in the 900 cm^{-1} region. The relationship between the integrated absorbance change for these two bands and the applied strain function is shown in Fig. 13. The maxima of the change for both the 917 cm^{-1} and 970 cm^{-1} bands correspond to the maximum of the strain value, showing no time lag for the microstructural response, thus indicating that the transition occurs at a rate faster than the temporal resolution of the experiment, which is 122 millisecc. Even though a great number of static and dynamic

TABLE II. The experimental conditions used for the poly(butylene terephthalate) deformation experiment.

Event period	1.22
Time clocks per event	10
Clock period (time resolution)	122 milliseconds
NDP points per interferogram	16,384
Clock periods per interferogram	5.2
Spectral resolution	1 cm^{-1}

measurements on the order of 30 s have suggested that conformation conversion is directly related to strain applied, our study is the first evidence of this.

In both of the time-resolved spectroscopy experiments, infrared data has been obtained for cyclic events with a period of 1.22 s. Time-evolving events in this time domain have been particularly difficult to characterize in the past. Commercial schemes only apply for much shorter events, and the rapid scan method is better suited to longer event periods. This newly developed time-resolved method, incorporating a microprocessor to control the external event, offers high flexibility for studying a variety of cyclic events in polymers with periods of 0.5 to 5 s.

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