Deformation studies of polymers by time resolved Fourier transform infra-red spectroscopy:
1. Development of the technique

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We have constructed a miniature closed-loop servo-controlled hydraulic tensile tester interfaced to our fast scanning Fourier transform infra-red spectrometer. Macroscopic information in the form of stress–strain curves can be collected along with the microstructural changes in the form of infra-red data. This technique in conjunction with our newly developed time resolved Fourier transform spectroscopy package has been used to follow structural changes in macromolecules.

Keywords Infra-red spectroscopy; time resolved; polymer deformation studies; stress–strain curves

INTRODUCTION

Traditionally, external stress or strain induced microstructural changes in polymers such as chain segment orientation rate or unit cell distortion have been measured by a combination of dynamic X-ray, light scattering and birefringence techniques[1–6]. However, a more direct and profitable approach to studying the response of individual chain segments is by vibrational spectroscopy. In many polymers the infra-red spectra exhibit absorption bands that are characteristic of the details of local conformation or environment. If band assignments are established and, additionally, if the directions of the transition moments with respect to the chain axis are known, vibrational spectroscopy offers the advantage that stress induced changes in orientation, conformation, packing, and degradation effects can all be measured. In fact, recent studies have clearly shown the sensitivity of the spectroscopic technique in detecting structural changes associated with polymers deformed by external stress[7–12]. Changes in frequency and intensity have been related to molecular stress, chain axis orientation, viscoelastic behaviour, and conformational changes.

Most of the experiments in vibrational spectroscopic studies, however, suffer in that the short time-dependent phenomena cannot be measured conveniently. Fourier transform infra-red spectroscopy (*FT*i.r.) has proven to be a powerful tool in polymer characterization. Until recently, however, it has been applied to observation of events that are stationary in time, or at least stationary with respect to the measurement time. The multiplex characteristic (the ability to measure all spectral elements) of the interferometer together with the high energy throughput provide *FT*i.r. with a substantial gain in signal to noise ratio for a given measurement time when compared to a dispersive instrument. Therefore, it is feasible to use a rapid scanning *FT*i.r. to study time dependent phenomena. Simultaneous measurements of band position, shape, and relative intensity can be retained for a wide spectral region. With recent advances made in interferometers and their associated electronics, collection of infra-red spectra with time resolution as fast as 1 s can be achieved. Nevertheless, it is impractical, if not impossible, for the interferometer to mechanically follow the rapid structural changes which can occur in the time scale shorter than 1 s. Furthermore, fast microstructural changes in polymers can be masked due to co-adding scans to improve signal to noise ratio. Therefore, we have developed a time resolved Fourier transform infra-red spectroscopy in order to follow the rapid structural changes. Our experimental apparatus and preliminary results are reported here.

EXPERIMENTAL

Hydraulic stretcher

In previous deformation experiments, stretching apparatus which generally employ a combination of gear-spindle drives have been used with great success[7–12]. In general, however, this type of device cannot be operated at high deformation frequency or amplitude with sufficient reproducible accuracy necessary in cyclic experiments. Therefore, in our laboratory we have developed a hydraulic stretching device which can be used for stress relaxation, creep, or harmonic deformation experiments in conjunction with a rapid scanning *FT*i.r.

This hydraulic system is schematically outlined in *Figure 1*. This tester incorporates a closed-loop servo-controller, which drives a hydraulic servo-valve attached to a hydraulic piston. Input to the controller is driven by a function generator, enabling a predefined strain function to be applied to a sample (0.5 cm × 3.0 cm) film in the infra-red beam. In the feedback loop for accurate control, actual instantaneous sample displacement and load

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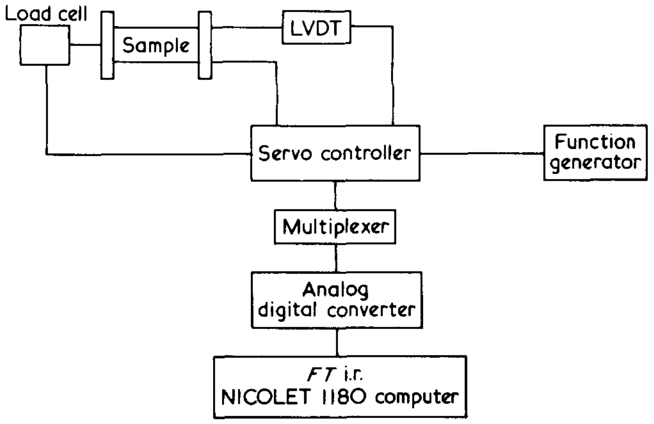

Figure 1 Schematic drawing of the stretching apparatus

applied are available from a solid state displacement transducer and a load cell. Through this feedback loop to the controller, both the stroke and load are programmable. In addition, both the load and displacement values applied to the sample are available in digitized form and accessible by our minicomputer associated with the *FT*i.r. This accurate macroscopic mechanical information in the form of stress–strain data is collected along with microscopic information in the form of infra-red spectra.

Time resolved Fourier transform spectroscopy

We have also developed a time resolved Fourier transform infra-red spectroscopy package in order to follow structural changes. In these experiments, repetitive oscillatory strains are applied to preloaded polymers. Many cycles of data can be collected and sorted in time space. The interferogram for any particular segment of time can be reconstructed and transformed into the frequency space. The principles representing several different approaches to this type of time resolved Fourier transform infra-red spectroscopy have been presented in a number of publications[13–17]. Each one of these approaches incorporates some form of ordered sampling technique which generally results in the collection of a large amount of data which must later be sorted to obtain properly time ordered interferograms.

Our interferometer is a continuous scanning type, which uses a HeNe laser to determine accurately the changing position of a moving mirror relative to the fixed mirror. The transform of a monochromatic source (6328 Å of the HeNe laser) is sinusoidal in nature. The zero crossings of this curve defines the coordinates in the retardation space, x. The mirror moving at constant velocity therefore intercepts these zero crossings at well defined time intervals, Δt, which can be calculated as

$$\Delta t = \frac{\lambda_{\text{laser}}}{2v} \tag{1}$$

where λ_{laser} is the laser wavelength and v is the velocity. For a time evolving event, a single scan of the interferometer would represent a collection of interferogram elements, $I(x,t_n)$, where x is the optical path difference and t_n is the time at nth data point. x and t_n are related as shown in equation (2).

$$t_n = t_0 + \frac{x}{v} \tag{2}$$

A constant time interval, t_0, is measured relative to a white light centre burst, which is approximately 900 data points before the i.r. central burst.

The first event is triggered by the white light centre burst, all subsequent event triggers are delayed by multiples of Δt. This is continued until N events have been collected. This provides a definite relationship between the retardation of the moving mirror and the time into the event. Thus the set of the initial interferogram elements of each of these N spectra represents the interferogram of the sample at time t_0 (strain or stress equals zero). The interferogram corresponding to the structure of the sample at a time of $n\Delta t$ into the deformation are the set of interferogram elements which correspond to the nth data point of each of the N time averaged interferograms. The entire scheme is shown in *Figure 2.* With our instrumentation, the theoretical maximum time resolution achievable is 15 μs (time/data point). Since the velocity of mirror travel is adjustable in our experiments, the time period associated with the full interferometer stroke is matched to the one cycle of the oscillatory strain to shorten the measurement time.

RESULTS

We are currently using this mechanical–spectroscopic technique to understand the stress induced changes in

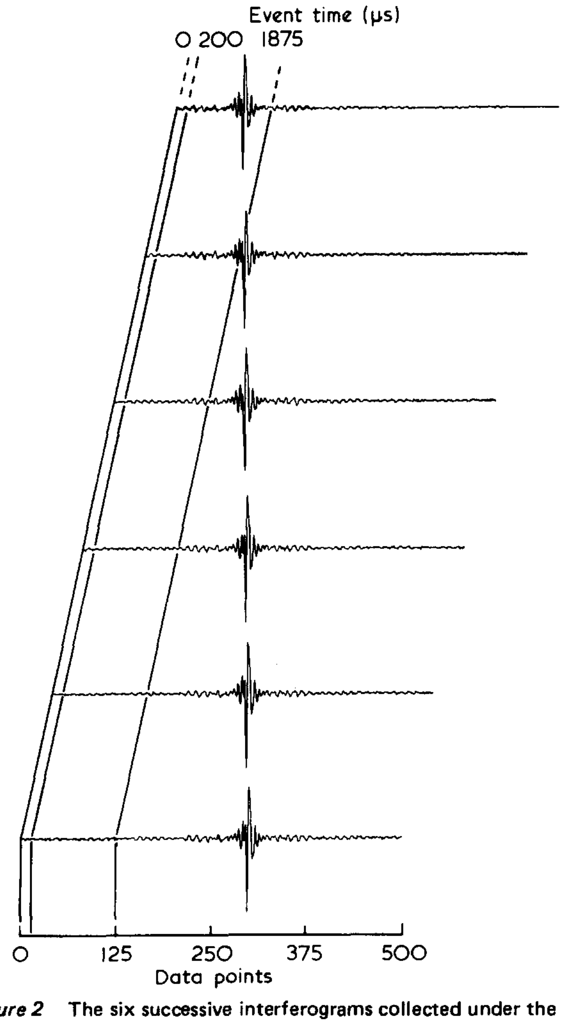

Figure 2 The six successive interferograms collected under the time resolved mode. The diagonal lines represent the interferogram elements at constant event time

Table 1 Experimental conditions for a time resolved Fourier transform spectroscopy experiment

Number of data points	4096
Time resolution	200 μs
Period of external stress	50 000 μs
Strain amplitude	2%
Velocity	1.43 cm s^{-1}
Measurement time	~40 min

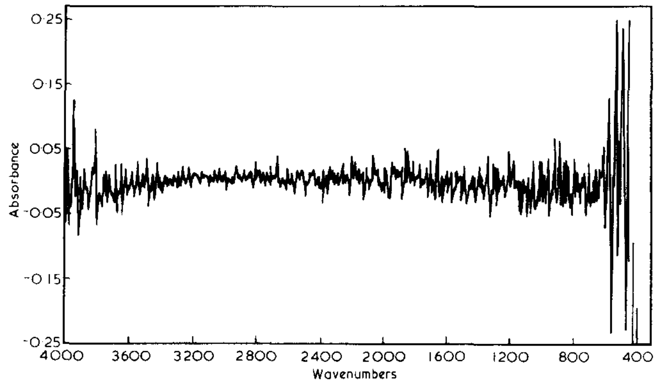

Figure 3 Signal to noise ratio obtained under the time resolved mode: number of data points = 4096; number of transform points = 4096; number of co-added scans = 4

various semicrystalline polymers, heterophase polymers (polyurethanes, polymer blends, ion containing polymers) and rigid rod polymers. In this note we are presenting the application of the time resolved spectroscopy to follow structural response rate of the subunits in the ion-containing ethylene–methacrylic acid copolymers. These polymers have crystalline and amorphous phases of polyethylene, and ion domains of submicroscopic dimensions (10 Å–1 μm). However, neither the aggregate structure nor size has been completely defined[18–21]. Although the enhancement of mechanical properties of these ionomers is well known, a number of fundamental problems still remain in the understanding of structure–property relationships.

As a first step, it is important to establish and 'calibrate' the changes in vibrational band shape, intensity, frequency and dichroism as a function of strain amplitude. In a previous publication[22] there are measurable changes in dichroic ratio or frequency for strain amplitude as small as 2% for the ethylene–methacrylic acid copolymer. The experimental conditions for most of our polymer work is shown in *Table 1*. Each spectrum obtained under the time resolved mode should be identical as a function of time. The ratio of any two spectra commonly refer to the 100% line can be used to estimate the expected signal to noise ratio. This is shown in *Figure 3*. However, when external strain is applied, the successive time resolved spectra exhibit features which follow the strain amplitude. One such region is shown in *Figure 4*. We observed the dichroic ratio of the 2674 cm^{-1} parallel band to change as a function of strain in times as short as 200 μs.

In addition, we have carried out similar experiments to follow the deformation of neutralized samples with Zn^{++} as counter ions. Both static (drawn material) and dynamic (time resolved spectroscopy) experiments were conducted. Some of the spectral changes are easily observable, others can only be established using difference spectra because small frequency shifts and intensity changes often cannot be identified easily. It should be noted that some of the changing sample thickness may introduce absolute intensity differences. However, these 'artifacts' are of

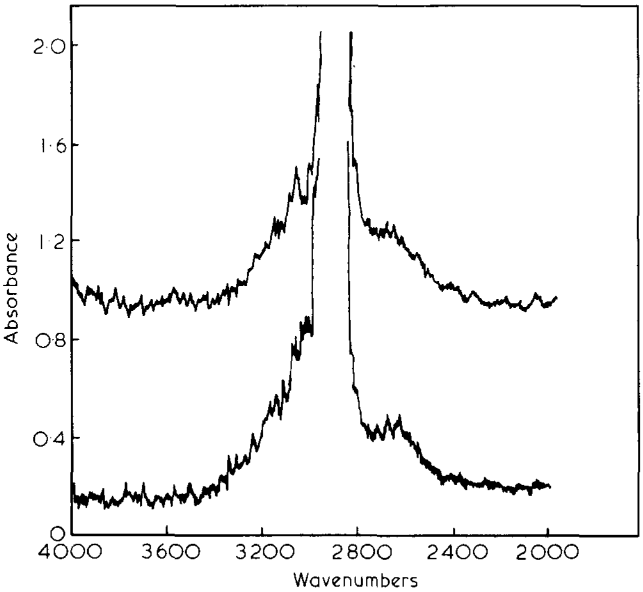

Figure 4 The intensity change associated with the 2673 cm^{-1} band. The lower curve is at $t = 0$; the upper curve is obtained 500 μs later

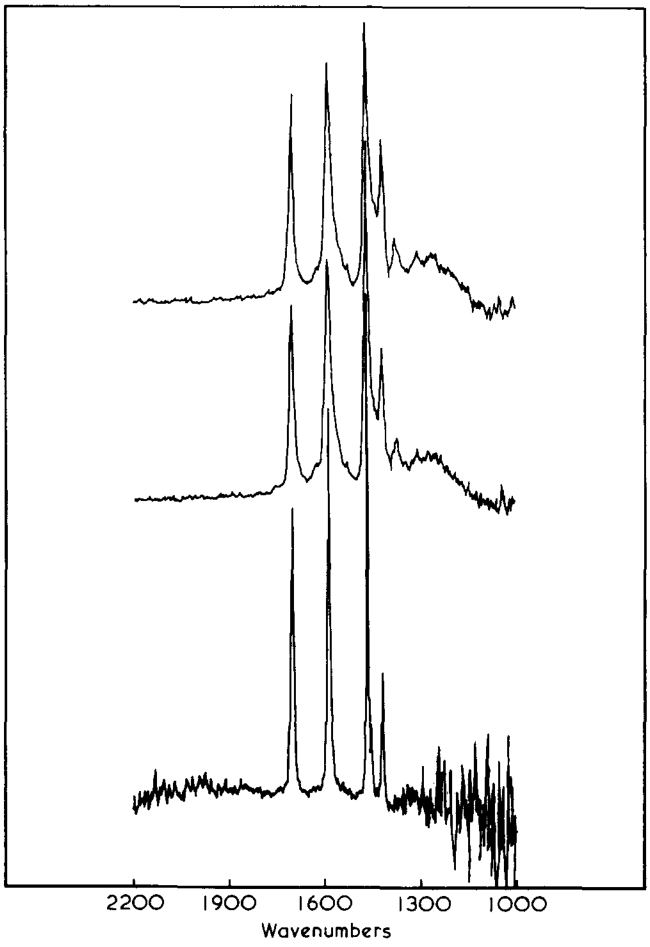

Figure 5 Intensity changes of infra-red bands (2200–1000 cm^{-1}) measured as a function of time: Top and middle spectra correspond to times 0 and 200 μs respectively. The bottom spectrum represents the difference

much smaller magnitude than the other results obtained under the time resolved mode. Bands at 1418, 1585, and 1700 cm^{-1} increased significantly with time up to 0.2 s (*Figure 5*). In contrast, bands such as that at $\sim 1440\,cm^{-1}$, also in the CH_2 bending region, do not. To our knowledge this is the first application of the time resolved technique applied to follow the structural changes of polymeric solids.

Despite considerable experimental difficulties encountered during the development of this new technique, we feel the time resolved Fourier transform technique can contribute to the study of molecular dynamics leading to a better understanding of the structure–property relationship.

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