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Polymer Deformation Studies by Time Resolved Fourier Transform Infrared Spectroscopy

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SUMMARY

We have applied a newly developed time resolved Fourier transform infrared spectroscopy to follow microstructural changes in two semicrystalline polymers with time resolution in the order of milliseconds. This is the first demonstration of a spectroscopic technique which is capable of measuring structural changes at the segmental level and relating them to macroscopic changes measured by dynamical mechanical spectroscopy.

INTRODUCTION

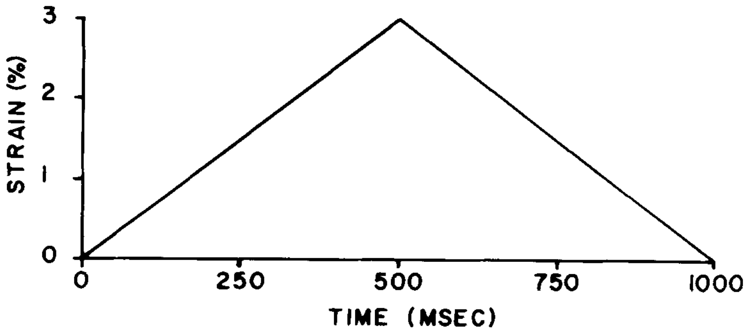
When polymers are deformed the structural changes at the micro level may consist of molecular slippage, reorientation of the crystallites and elongation of the amorphous segments. Depending on sample morphology, these molecular processes such as crystallite orientation have been estimated to occur at a time scale ranging from milliseconds to seconds (1). Normally, mechanical tests are carried out as a function of frequency and temperature to assess the macroscopic behavior. In addition, dynamical x-ray, birefringence, and light scattering studies are often used in combination to probe the dynamics of microstructural changes. If the bands are properly assigned, vibrational spectroscopy can provide the selectivity needed to directly measure the response of individual chain segments, but usually lacks the time resolution required to obtain dynamic information. Even with the use of the rapid scan option of the Fourier transform infrared spectrometer, which can yield spectra of acceptable signal to noise ratio and spectral resolution as close as seconds apart, most of the structural changes at short time intervals are still inaccessible. To achieve better time resolution and S/N ratios, we have developed a combination of mechanical and time resolved vibrational spectroscopic techniques to follow structural changes with millisecond time resolution (2,3). Information at the macroscopic level, in terms of stress or strain values, can be collected along with microstructural information in terms of infrared data. Those and other attempts (4,5) have demonstrated the potential usefulness of the technique in understanding dynamical structural changes of polymer solids. However, up to now the interfaces between the stretcher used to deform the sample and FTIR were somewhat inflexible and the information obtained could not directly be related to the continuous cyclic strain functions which are used in polymer deformation studies. We have developed a new time resolved spectroscopy to overcome this limitation (6); and have applied such a technique to characterize structural changes in semicrystalline polymers such as polyethylene and poly(butylene terephthalate). In this note we presented the type of information that is currently available with this technique.

EXPERIMENTAL

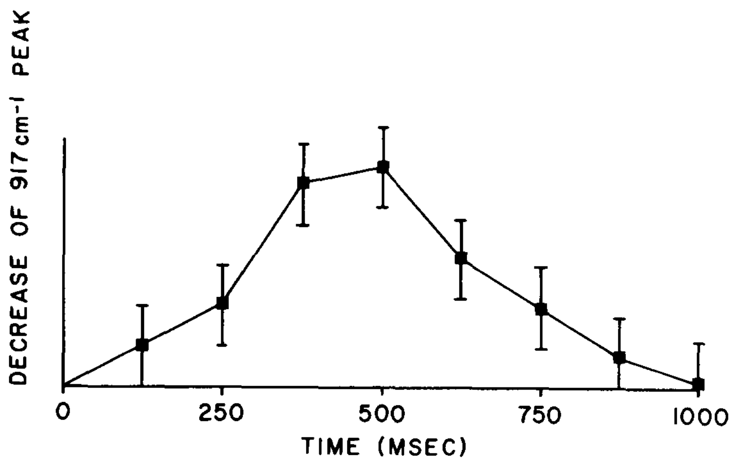
Associated with the deformation experiments, we have developed a closed-loop hydraulic stretcher to uniaxially deform polymer films. The details of this stretcher and its interface to a Nicolet FTIR have been presented elsewhere (2,3,6). Our spectrometer employs the standard Nicolet optical bench. However, modifications in the parallel input/output interface and developments of new computer programs written in assembly or FORTRAN allow the time ordered stress and strain values to be stored along with appropriate infrared spectra on magnetic disks for analysis.

RESULTS AND DISCUSSION

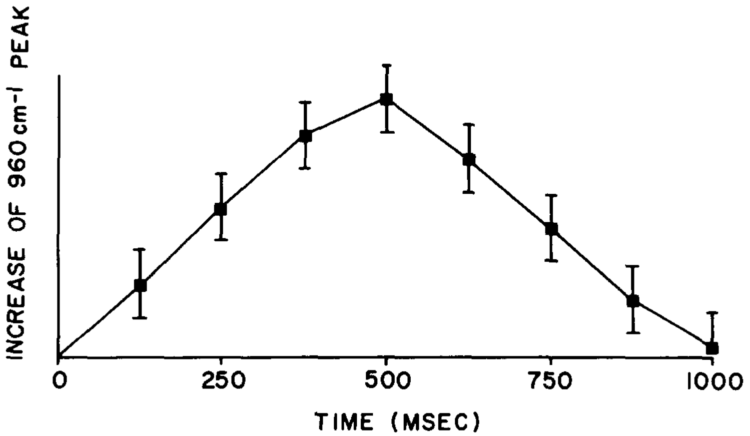
In our laboratory we have a particular interest in characterizing the deformation behavior of copolymers of poly(butylene terephthalate) and polyesters. The relative motion of the chains at the segmental level is of high interest. Previous x-ray and spectroscopic studies have established that stress can induce a reversible phase transformation in PBT (7-13). This phase transformation involves both a chain conformation change as well as substantial changes in the crystalline unit cell parameters. The extent and rate of structural change may depend on sample morphology and composition and is the current subject of study. In this preliminary experiment to demonstrate the utility of the time resolved spectroscopy, a film was hot drawn to a draw ratio of 2.5 in order to align the crystals in the stretch direction, giving more effective coupling of the applied forces onto the chains in the crystal. This film was then mounted and prestretched in our stretcher to prevent slackening during the deformation experiment. We then applied a periodic triangular strain function with a maximum amplitude of 3% to the PBT film. Spectra of high quality were obtained with the time resolved technique. The bands most sensitive to the strain applied are the CH_2 rocking vibration in the 900 cm^{-1} region. A band at 917 cm^{-1}, characteristic of the α phase, decreased in intensity when the film was elongated. Conversely, a band at 960 cm^{-1}, characteristic of the β phase, increased in intensity with increasing strain. As can be seen in Figure 1,



The strain function applied.



The decrease in the α phase.

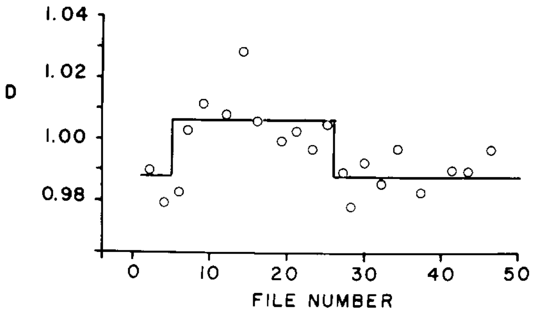


The increase in the β phase.

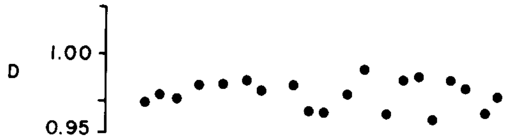
FIGURE 1: A measure of the α-β phase transformation in poly(butylene terephthalate).

the increase in the β phase with the corresponding decrease in the α phase follows the applied strain function accurately with a time resolution of 125 msec. Even though a great deal of static and dynamic measurements in the order of 30 seconds have suggested that conformation conversion is directly related to stress applied, our study is the first evidence of this type.

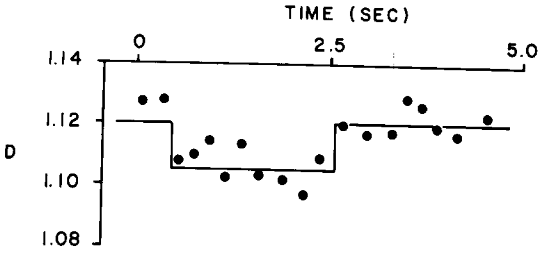
The results of a time resolved experiment on low density polyethylene film is shown in Figure 2. In that experiment, we intended to follow the



crystalline 720 cm^{-1} band, transition dipole along the A direction



730 cm^{-1} band, transition dipole along the B direction



1300 cm^{-1} amorphous band

FIGURE 2: The dichroic ratios measured for various bands in polyethylene.

segmental orientation as a function of temperature and frequency in order to explain the unexpected relative contribution of amorphous and crystalline chains in dynamic birefingence measurements (14). We applied a periodic square function (period of 5 seconds) with 2% amplitude to a prestretched film. The orientational rate measured for the CH_2 crystalline units are consistent with previous dynamic x-ray results (15). Even more interesting are the rate dependencies of vibrations with transition moments along the a or b axis of the unit cell.

The CH_2 rocking vibrations of polyethylene usually are observed as a doublet at 720 and 731 cm^{-1} as a result of interchain crystalline field splitting (16-18). The 720 cm^{-1} and 731 cm^{-1} components have transition moments along the b and a axis, respectively. The dichroic ratios measured with our technique for these bands are quite different. The 720 cm^{-1} component follows the applied strain function. In contrast, the dichroic ratio measured as a function of strain for the other component band at 731 cm^{-1} exhibits no such strain dependence.

In this note we have shown the applicability of such a time resolved spectroscopic technique in providing high quality infrared spectra with sufficient time resolution to characterize the dynamics of polymer structural changes. Details of these studies will be published in the near future.

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