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TIME-DOMAIN DYNAMIC OPTO-RHEOLOGY STUDY OF POLYMER FILMS USING STEP-SCAN FTIR TIME-RESOLVED SPECTROSCOPY (S²FTIR TRS)

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Step-scan Fourier transform infrared spectroscopy in conjunction with impulse stress on polymer films has been used to monitor dynamic rheological responses in "real time". A novel piezo-electrically-driven polymer microrheometer was employed to apply repetitive impulses to the polymer sample while time-domain spectra were recorded. Recent results include the study of both semi-crystalline polymers such as isotactic polypropylene (iPP) and elastomers such as Estane polyester/polyurethane copolymer and Kraton tri-block copolymer. The spectral changes of iPP are consistent with frequency-domain results. For iPP at room temperature, large differences in the response times of different absorption bands are not seen. However, the orientation response of the CH_3 rocking mode is slightly slower than the responses of the backbone modes. To our knowledge, this is the first reported successful step-scan FTIR time-domain dynamic polymer opto-rheology experiment. The advantages of the time-domain experiment over the frequency-domain experiment are also discussed briefly. This technique appears to be applicable to a variety of polymer samples, and examples from additional results are illustrated.

INTRODUCTION

In recent years, there has been a steadily increasing interest in the effect of mechanical stress on the IR spectra of polymers (1). This is the so-called IR opto-rheology or IR rheo-optics.

Since IR spectroscopy is sensitive to the orientation of transition dipoles, and since each functional group within a molecule generally has a different IR absorption frequency, the use of infrared spectra (particularly the dynamic infrared spectra) allows the responses to mechanical strain, of specific functional groups and of specific components of polymer blends, copolymers and composites to be determined and to be distinguished. This provides information on the molecular and submolecular origins of macroscopic rheological properties (2, 3).

The well-known advantages of interferometric (Fourier transform, or FT) methods for infrared spectroscopy make FTIR the choice for virtually all broad band infrared spectral measurements, compared with dispersive spectroscopic method (4). Application of time-resolved FTIR on dynamic rheo-optical study started with the rapid-scan FTIR methods more than a decade ago (5, 6). However, this approach was complicated by the difficulty of separating the time dependence of the sample response from that of the spectral multiplexing. Later, Noda *et al.* demonstrated mid-infrared dynamic opto-rheology measurements of isotactic polypropylene (iPP) using a monochromator (7). Although this work was very successful, the dispersive IR method required long measurement times, particularly for the study of broad spectral ranges.

In the last ten years, step-scan FTIR spectroscopy (S²FTIR) has developed considerably. In a step-scan FTIR measurement, interferogram data are time-averaged retardation-by-retardation. The essential characteristic is that data are collected while the

The first 75 time slices, corresponding to the 1.5 ms period before pulse-on, while the polymer remains in the more stretched state, were averaged, and the result was used as the reference spectrum ($I_{reference}$). Every 10 slices (corresponding to 0.2 ms time periods) of the iPP data and every 25 slices (corresponding to 0.5 ms time periods) of the Estane data were then averaged and used as the sample spectra at time t ($I_{sampled\ at\ time\ t}$). Equation 1 was then used to calculate the absorbance difference spectra at time t ($\Delta A_{at\ time\ t} = A_{sampled\ at\ time\ t} - A_{reference}$) during the pulse-on and pulse-off phases. Finally, the response curves of the selected absorption bands in the absorbance difference spectra were plotted.

$$\Delta A_{at\ time\ t} = \log (I_{reference} / I_{sampled\ at\ time\ t}) \qquad (1)$$

RESULTS AND DISCUSSION

iPP:

The static absorbance spectrum of the iPP sample is shown in Figure 1. The spectral range 1250 cm^{-1} ~ 800 cm^{-1} was analyzed. This is the region where most of the backbone stretching and deformation vibrations absorb, which are known to be most affected by external deformation (17).
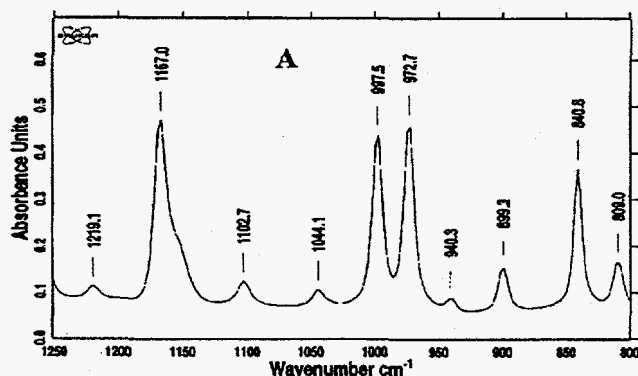

FIGURE 1. Absorption spectrum (between 1250 cm^{-1} and 800 cm^{-1}) of static iPP film in stretched state, obtained in the continuous-scan mode.

Figure 2 is the 3-D plot of the time-resolved absorbance difference spectrum. In this dynamic ΔA spectrum, between the 2 ms and 11 ms, only the 1167 cm^{-1}, 998 cm^{-1}, 973 cm^{-1}, and 841 cm^{-1} bands appear, indicating that in the 800 cm^{-1} ~ 1250 cm^{-1} range only these four vibrational modes have measurable spectral changes in response to the change in stress. This is consistent with previous results. The 1167 cm^{-1}, 973 cm^{-1}, and 841 cm^{-1} bands are bisignate (derivative-like), with their negative components to higher energy. This indicates that these

three absorbance bands shift to lower wavenumber when the polymer is more stretched. However, the 998 cm^{-1} absorbance band shows only an increase of intensity; it does not exhibit a frequency shift.

Theoretical calculation of the effect of strain on iPP has already been carried out and elaborated in detail by Tashiro *et al* (18). The absorption bands at 1167 cm^{-1}, 973 cm^{-1}, and 841 cm^{-1} are mostly associated with the skeletal backbone modes. When a tensile strain is applied along the polymer chain, this tensile strain will cause force field changes in the backbone modes, resulting in frequency shifts in these bands. Simultaneously, reorientation of the backbone chain occurs. Complete interpretation of the dynamic spectral change is not possible without a satisfactory separation of these two effects. On the other hand, the absorption band at 998 cm^{-1} consisting mostly of the rocking of the methyl side-group, exhibits almost no frequency shift, which can reasonably be attributed only to the orientation effect of the side chain.
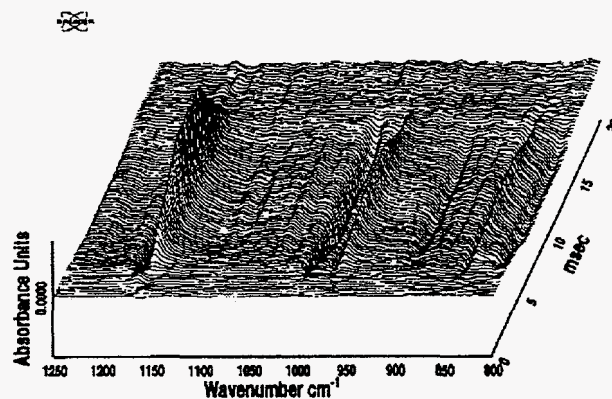

FIGURE 2. Time resolved absorption difference spectrum of iPP, obtained in the step-scan mode.

Considering the fact that the piezo element also has a response time on the millisecond time scale, prior to the dynamic measurements of polymers, a partial beam block is run to determine the instrument response curve, in effect, zero time. The partial beam block is clamped in the moving jaw of the stretcher, so as to chop the IR intensity with exactly the same speed as the jaw motion. To guard against the possibility that the additional load imposed by the polymer film might cause different delays, the polymer film is clamped in the stretcher jaws when the beam block measurement is made. The dynamic absorption difference spectra of the partial beam block experiment is analyzed in the same way as the polymer data.

The peak values of all the negative bands in the iPP stretching experiment (at 1170.3 cm^{-1}, 999.4 cm^{-1}, 975.3 cm^{-1}, and 843.1 cm^{-1}) are plotted as a function

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