

Glass transition of atactic polystyrene probed at the submolecular level by dynamic infrared linear dichroism (DIRLD) spectroscopy

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ABSTRACT

Dynamic infrared linear dichroism (DIRLD) spectroscopy is a rheo-optical characterization technique developed specifically to probe the submolecular dynamics of polymer segments. The technique combines the measurement of submolecular orientation based on the directionally selective absorption of polarized IR light with a small-amplitude oscillatory tensile deformation used in dynamic mechanical analysis. A DIRLD spectroscopic study of atactic polystyrene reveals that a dramatic change in the reorientation behavior of aromatic side groups is observed around the glass transition temperature of 100 °C. The transition point for the main chain backbone, on the other hand, is observed at a much higher temperature around 125 °C. Thus, the macroscopically observable glass transition of polystyrene seems to be dominated by the dynamics of side groups rather than that of the coordinated motions of polymer segments along the backbone. This result suggests a fundamental similarity between the glass transition phenomena of polymers and those of small-molecule inorganic glasses.

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1. Introduction

The glass-to-rubber transition plays an important role in determining various properties of amorphous component of polymers [1–4]. Typically, the glass transition temperature of a polymer is characterized by probing the changes in macroscopic properties. Thermal and mechanical techniques, such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), are often used for the detection of glass transition temperatures [3,4]. Although such techniques are recognized to be very useful, there is also a need to provide the fundamental molecular level understanding of the glass transition phenomena of polymers.

The nature of polymeric glass at the molecular scale is an interesting subject of discussion. Amorphous polymers go through the transition from a viscous or rubbery condition to a hard and relatively brittle one in a manner similar to the solidification of liquid to glass [1]. Polymeric glass, therefore, seems to obey the same basic physics of matter observed for small molecules, such as

inorganic glassy materials. One the other hand, the glass-to-rubber transition of polymers is often said to involve some sort of cooperative motions of much longer segments of macromolecules unhampered by the interactions between neighboring chains [2]. Such segmental chain structure with finite molecular connectivity of building units is unique to polymers and not seen in the systems of small molecules. Thus, how similar or different polymeric glass is compared to glassy materials made of small molecules, especially at the molecular level, becomes an intriguing question.

Rheo-optics [5] is a branch of analytical science where optical signals, like those detected in a spectroscopic or scattering experiment, are measured simultaneously in conjunction with macroscopic rheological phenomena, such as flow, deformation, and relaxation processes. The characterization of polymer samples under various deformation modes using an infrared probe has been recognized as one of the very powerful areas of rheo-optical studies. Siesler [6–10] pioneered the extensive use of IR and NIR in rheo-optical measurements to establish the correlation between macroscopic and molecular level dynamics. These techniques are extensively used in the study of polymers [11,12]. It seems promising to utilize IR-based rheo-optical techniques to probe the nature of polymeric glass at the molecular level.

Dynamic infrared linear dichroism (DIRLD) spectroscopy [13–16] is a type of IR rheo-optical characterization technique developed specifically to probe the time-dependent submolecular dynamics of polymer segments. This technique specifically aims at

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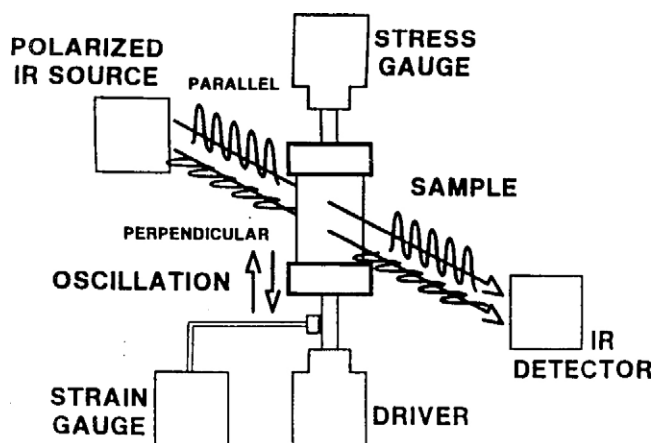


Fig. 1. Schematic representation of a DIRLD spectrometer. Reproduced with permission from [14], copyright (1988) Society for Applied Spectroscopy.

the measurement of time-dependent submolecular or segmental orientations by using the directionally selective absorption of polarized IR light combined with a small-amplitude oscillatory tensile deformation used in dynamic mechanical analysis. A schematic diagram of the DIRLD spectrometry is shown in Fig. 1. We have been using DIRLD spectroscopy to elucidate the molecular level dynamics of polystyrene around the glass transition temperature for some time [14,17–19]. An interesting insight has recently emerged from DIRLD experiment on the glass transition phenomenon of certain polymers. In this study, the glass transition phenomenon of atactic polystyrene is examined in terms of the dynamics of polymer chain backbone and of phenyl side groups.

2. Background

The infrared dichroic difference $\Delta A(\nu)$ measured at wavenumber ν is defined as the difference in the absorption of polarized IR light oriented parallel and perpendicular to a reference axis. For a uniaxial rheo-optical measurement in DIRLD spectroscopy, the reference axis is defined as the direction of the dynamic tensile strain. It is well established that IR dichroism is proportional to the average orientation, or the second moment of the orientation distribution function, of the electric dipole-transition moment associated with a specific molecular constituent [20,21]. When a small-amplitude sinusoidal deformation $\tilde{\epsilon}(t) = \tilde{\epsilon} \sin \omega t$ is applied to a sample film, the dynamic reorientation of molecular constituents induced by the deformation will result in the sinusoidal fluctuation of dichroic difference.

$$\Delta \tilde{A}(\nu, t) = \Delta \hat{A}(\nu) \sin[\omega t + \beta(\nu)] \quad (1)$$

Because of the time-dependent nature of molecular reorientation processes, a phase difference $\beta(\nu)$ is usually observed between the applied strain and dichroism signal measured at a particular wavenumber ν . The dynamic dichroism can be further separated into two orthogonal components, which are in-phase with and quadrature to the applied strain [13,14].

$$\Delta \tilde{A}(\nu, t) = \Delta A'(\nu) \sin \omega t + \Delta A''(\nu) \cos \omega t \quad (2)$$

These quantities, $\Delta A'$ and $\Delta A''$, are referred to, respectively, as the in-phase spectrum and quadrature spectrum of dynamic dichroism. In essence, they represent the *storage* and *loss* components of dynamic reorientation responses of molecular segments under the applied deformation. The successful rheo-optical measurement of

in-phase and quadrature spectra laid the foundation for the development of dynamic 2D IR spectroscopy [21,22], which later evolved to the generalized 2D correlation spectroscopy technique applicable to a much broader scope of analytical problems [23–25].

3. Experimental

3.1. Sample

A film of atactic polystyrene (Aldrich, M_w 300,000) was cast from 1% toluene solution on a Teflon[®] sheet, which is transparent in the IR spectral region of current interest. The sample was annealed at 120 °C for 9 days, quenched, and then stored at –10 °C until being used.

3.2. DIRLD measurement

DIRLD spectra were collected with a home-built dispersive spectrometer equipped with a ZnSe photo-elastic modulator operated at 37 kHz to switch the IR polarization between parallel and perpendicular direction with respect to the stretching direction of the film. The details of this instrumentation and its operation are fully discussed elsewhere [14]. A 23 Hz dynamic strain was applied to the sample with an amplitude of 0.1%. A 2 mm × 2 mm narrow-band MCT detector with a 24-h hold liquid N₂ dewar was used. The temperature chamber holding the sample was controlled within 0.1 °C during the measurement.

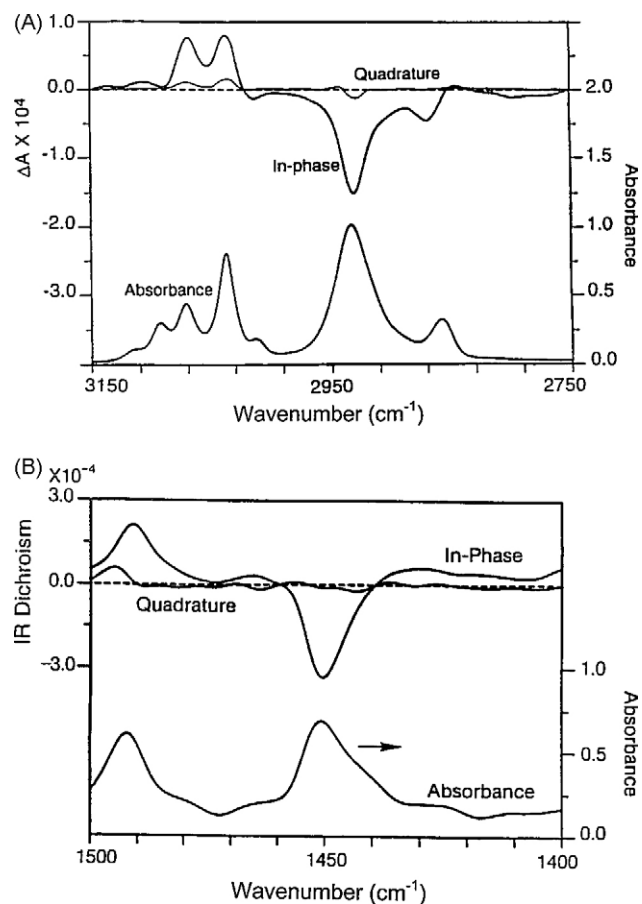


Fig. 2. DIRLD spectra of atactic polystyrene at room temperature in (A) CH-stretching region and (B) ring semicircle-stretching vibrations region. Reproduced with permission from [22], copyright (1994) American Chemical Spectroscopy and from [14], copyright (1988) Society for Applied Spectroscopy.

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