



~~~~ Polymer Physics Seminar ~~~~

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301 Steidle Bldg.

Study of Vibrational Relaxation and Dynamic Transitions in Polymer Systems by Infrared Spectroscopy

The shapes and widths of infrared bands are an importance source of information on interactions and molecular dynamics. They have been used to study vibrational and rotational relaxation processes in the picoseconds time range. However, most of the previous work in this area has focused on small molecules, our work focuses on the vibrational spectroscopy of polymers, specifically in these areas:

1. Vibrational relaxation and dynamic transitions in Atactic polystyrene

We explored the temperature dependent FTIR absorption of atactic polystyrene in order to elucidate the relationship of band shapes to relaxation phenomenon on the picosecond time-scale. After curve resolving, we found the time correlation functions of the modes near 1601cm^{-1} and 1583cm^{-1} and their variation with temperature can be fit into a modified two-process Kubo model. The model includes a fast relaxation process characterized by a single relaxation time that is inhomogeneously broadened by a slower process, which is also characterized by a single relaxation time. The fundamental mode near 1583cm^{-1} is sensitive to temperature as a result of a coupling to overtone bands mediated by a lattice vibration, which enables us to determine the vibrational energy relaxation behavior and its sensitivity to dynamical transitions.

2. Application to deuterated Poly(methyl methacrylate)-d₃ ester

As with the atactic polystyrene, a similar study was done on deuterated poly(methyl methacrylate)-d₃ ester. There are three reasons why deuterated poly(methyl methacrylate) was chosen for this study. First, C-H stretching vibrations are conformationally insensitive. Second, we can obtain samples that are selectively deuterated. Third, we have preliminary evidence that the C-D stretching modes of PMMA are sensitive to dynamical transitions.

The study on d₃-PMMA shows some similarities to that of *a*-PS in terms of the model used to fit the experimental data and the sensitivities to dynamic transition temperatures; yet because of some unique properties of PMMA, like the merging of the α and β relaxation, we get more complex results