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Vibrational Relaxation and Dynamical Transitions in Atactic Polystyrene HANQING ZHAO, YUNG PARK, PAUL PAINTER — Infrared bands and Raman lines recorded in the frequency domain have a counterpart in the time domain in the form of time-correlation functions, which are sensitive to molecular dynamics on the picosecond time scale. This is explored by calculating time correlation functions and their variation with temperature for the conformationally insensitive modes observed near 1601 cm-1 and 1583 cm-1 in the infrared spectrum of atactic polystyrene. The correlation functions were modeled by assuming that there is a fast relaxation process characterized by a single relaxation time that is inhomogeneously broadened by a slower process, also characterized by a single relaxation time. The fundamental mode, near 1583 cm-1, is inhomogeneously broadened, but the relaxation time calculated for this mode is sensitive to temperature as a result of anharmonic coupling to a combination mode. A change in the modulation of the 1583 cm-1 band becomes apparent about 10–20 degrees below the thermally measured Tg. Relaxation times at first increase then decrease and becomes negligible at temperatures near 180 degrees. These results are consistent with theories of the glass transition.

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