Rotational-Rate Heterogeneity in Polymers on the Picosecond and Second Timescales through 2D Kinetics[1] MARK BERG, SACHIN DEV VERMA, Dept of Chemistry and Biochemistry, University of South Carolina, DAVID VANDEN BOUT, Dept of Chemistry and Biochemistry, University of Texas — In a polymer, the anisotropy decay of a small solute is nonexponential, i.e. it has rate dispersion. This dispersion could reflect heterogeneity in the local structure and dynamics of the polymer. On the other hand, homogeneous mechanisms are also possible: anisotropic local structure, multiple, independent rotational processes, or a relaxation hierarchy. Two-dimensional (2D) kinetics separate heterogeneous and homogeneous relaxation by monitoring dynamics over two time periods before ensemble averaging. Far from the glass transition, subnanosecond rotation in PDMS has been measured by MUPPETS (multiple population-period transient spectroscopy), a nonequilibrium technique. These experiments are the first to use polarization in MUPPETS to make 2D anisotropy measurements. Near the glass transition, rotation on the seconds timescales in poly(cyclohexyl acrylate) has been analyzed with 2D correlation functions calculated from single-molecule trajectories [*J. Phys. Chem. B*, **113** 2253 (2009)]. This method is an equilibrium approach to 2D kinetics. By averaging over the entire ensemble, the known problems of subensemble averaging are avoided. Both measurements indicate that rotational-rate dispersion in polymers is primarily due to heterogeneous local environments.

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