

Abstract Submitted
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Local Heterogeneity in a Polymer Melt Demonstrated by Polarized Two-Dimensional Spectroscopy¹ HAORUI WU, MARK BERG, Univ of South Carolina — The rotation of a solute in a small-molecule solvent is exponential, but it becomes nonexponential in a polymer melt. This nonexponential behavior may be explained by either variations in the local viscosity of the polymer—a heterogeneous model—or local anisotropy of the polymer structure—a homogeneous model. Two-dimensional spectroscopies using six optical pulses called MUPPETS (multiple population-period transient spectroscopy) can distinguish homogeneous and heterogeneous causes of nonexponential decay, but have never been applied to molecular rotation. We developed a new, polarized version of MUPPETS and measured the anisotropy decay of Pyrromethene 597 in poly(dimethylsiloxane) (PDMS). The results show strong molecule-to-molecule variation in the rotation rate. They are consistent with local, short-length scale variations in viscosity within the polymer. No evidence for local anisotropy is found.

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