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Single molecule study of heterogeneous dynamics in polymers

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Polymers are very heterogeneous close to glass transition temperature (T_g) and a complex dynamics with a non-exponential relaxation is observed by bulk techniques as well as by single molecule (SM) techniques. We have performed measurements of rotational diffusion of single perylene dimide (PDI) dye molecules in poly (methyl acrylate) (PMA) and poly (vinyl acetate) (PVAc) close to their T_g . We have found that the dynamics of a single molecule is temporally heterogeneous and the heterogeneity changes with change in temperature. SM results are compared to results from dielectric measurements and to shear viscosity data. Average rotational times from single molecule measurements follow similar temperature dependences as predicted from Debye–Stokes–Einstein (DSE) law for polymer viscosity whereas dielectric spectroscopy reveals the decoupling of segmental motions from probe rotational motions.

Single dye (Alexa 488 & Cy3) labeled polymers are synthesized. Single molecule (SM) lifetime measurements of free PDI dye molecules and single dye (Alexa 488 & Cy3) labeled polymers in PMA are performed. A broad distribution of lifetimes is observed for single dye labeled polymers in PMA. This also signifies the heterogeneity in polymer systems.

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References

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