Measurement of Ultraslow Rotational Dynamics of Probes in Imidazolium-Based Ionic Liquids Near and Below the Glass Transition Temperature: Studying the Role of Structural Heterogeneity on Dynamic Heterogeneity

KAYLA MENDOZA, RAKHITHA UDUGAMA-ARACHCHILAGE, FEHMI BARDAK, GEORGE TAMAS, EDWARD QUITEVIS, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409 — The dynamics of imidazolium-based ionic liquids were probed in the supercooled liquid regime by observing the fluorescence recovery after photobleaching of directionally oriented tetracene molecules. Spatial heterogeneity arises in ionic liquids containing a 1-alkyl-3-methylimidazolium cation for alkyl chain lengths equal to and exceeding four carbons; aggregation of the alkyl tails leads to the formation of non-polar domains, which increase in size with increasing alkyl chain length. Near the glass transition, supercooled liquids relax non-exponentially, and this non-exponentiality has been attributed to dynamic heterogeneity. The purpose of this study was to observe the role of structural heterogeneity on dynamic heterogeneity. The rotational dynamics of tetracene in 1-butyl-3-methylimidazolium bistri fluoride, 1, 3-dibutylimidazolium bistri fluoride, and 1-heptyl-3-methylimidazolium bistri fluoride were observed in the vicinity of their glass transition temperatures. From the weak dependence of the degree of non-exponentiality exhibited by the relaxation function on alkyl chain length and cation symmetry, it was concluded that structural heterogeneity does not play a strong role in determining dynamic heterogeneity.

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