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Dynamics of Polymerized Ionic Liquids and their Monomers

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Dielectric spectroscopy determines the static dielectric constants (ϵ_s) of polymers with imidazolium pendant structures containing a combination of alkylene and ethyleneoxy units as spacers between the backbone and the imidazolium cation. All monomers and their polymers exhibited two dipolar relaxations, assigned to the usual segmental motion (α) associated with the glass transition and a lower frequency stronger relaxation (α_2), attributed to ions rearranging. While ion pairs in conventional (smaller) ionic liquids prefer antiparallel alignment (Kirkwood $g \approx 0.1$ with $\epsilon_s \approx 15$), because their polarizability volumes strongly overlap, ion pair dipoles in the larger ionic liquid monomers display g of order unity and $50 \leq \epsilon_s \leq 110$. Longer spacers lead to higher static dielectric constant, owing to a significant increase of the relaxation strength of the α_2 process, which is directly reflected through an unanticipated increase of the static dielectric constant with ionic liquid molecular volume. The ionomers consistently exhibit 1.5 - 2.3 times higher static dielectric constants than the monomers from which they were synthesized, suggesting that polymerization encourages the observed synergistic dipole alignment ($g > 1$). Comparison of dielectric and linear viscoelastic responses reveals a strong connection between the time scales of polymer segmental motion (α), ion rearrangements (α_2) and the viscoelastic softening associated with the glass transition. For all polymers with imidazolium side chains and a wide variety of counter-anions, there is a strong correlation between glass transition temperature and repeat unit molecular volume. Large side chains have low $T_g \approx -50$ °C and their ionic conductivity increases as ethylene oxide repeats are incorporated into the side chains.