TITLE: Synthesis of highly crosslinked poly(butyl acrylate) networks to study the effect of mesh size, Tg, and segmental dynamics on probe diffusion

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ABSTRACT:

To understand the effect of permanent crosslinks in polymer networks on probe diffusion, extremely dense poly(n-butyl acrylate) networks were synthesized with varying degrees of crosslinking. The degree of polymerization between crosslink junctions in these this system was varied from 2-100 repeat units, controlling the distance between crosslinks in this manner as it approaches the size of the probe molecule. As the degree of polymerization between crosslink junctions decreased, both the glass transition temperature (Tg) and Tg-breadth were seen to significantly increase using both calorimetric and dielectric methods. Fluorescence Recovery After Photobleaching (FRAP) was used to determine the translational diffusion as a function of Tg-normalized temperature (Tg/T) and the size ratio between the dye and average distance between crosslink junctions (d/l). The probe diffusion was found to exhibit a single exponential decay dependence on both Tg/T and d/l, decreasing two orders of magnitude over the range of repeat units between crosslink junctions. To compare the probe diffusivity with segmental relaxation times determined by dielectric spectroscopy, these probe diffusion coefficients were converted to an “effective” diffusion timescale. Both the segmental relaxation times and “effective” diffusion time scale exhibited single exponential relationships as a function of Tg/T and d/l at three different experimental temperatures. While they both exhibit exponential relationships, the segmental relaxation times exhibited a stronger dependence on both Tg/T and d/l than the “effective” diffusion times, indicating that probe diffusion is partially decoupled from segmental mobility. These results provide new insights into how covalent crosslinking affects probe diffusion and provide necessary insight for the design and development of separation membranes.