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Polymer Dynamics Effects on Solute Transport in Hairy Nanoparticle Membranes[1] EILEEN BUENNING, CONNOR BILCHAK, CHRISTOPHER DURNING, Columbia University, BRIAN BENICEWICZ, University of South Carolina, ALEXEI SOKOLOV, University of Tennessee/Oak Ridge National Laboratory, SANAT KUMAR, Columbia University — Molecular transport measurements in matrix-free grafted nanoparticle (MFGNP) films have shown remarkable enhancement of permeability and ideal selectivity of small condensable molecules and simple gases over the neat polymer melts and conventional, dispersed nanoparticle composites. Films comprised of covalently-attached poly(methyl acrylate) PMA chains to the surface of 14nm silica particles self-assemble into ordered arrays, and we postulate this structure plays an important role in regulating solute transport. This self-assembly creates interstitial spaces between the nanoparticle cores, which the polymer chains can only fill by stretching. Here we use small-angle neutron scattering (SANS), broadband dielectric spectroscopy (BDS), rheology and temperature-modulated differential scanning calorimetry (TMDSC) to probe polymer chain and segmental dynamics and investigate this hypothesis of chain stretching in MFGNP materials. We found that grafting slows both chain and segmental relaxation, and increases fragility, indicating that the chains are more "frustrated" in the grafted systems. We propose that the effects of the chain/surface interactions on chain dynamics leads to an increase in available free volume and thus enhances transport properties in MFGNP systems.

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