Design of nanoporous polymer networks using a reactive encapsulation of solvent (RES) technique

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Potential applications of nanoporous polymer networks (NPNs) include polyelectrolytes in fuel cells, separation membranes, and substrates for nanocomposites. Designing NPNs for these applications involves controlling the network and pore structures and the resulting properties by tailoring the pore size, structure and pore interface activity/functionality. NPNs are often synthesized via free radical mechanisms and by using solvents that phase separate during polymerization. In this work, a novel technique for synthesizing NPNs was developed based on reactive encapsulation of a solvent (RES) using step-growth polymerization without micro/macroscopic phase separation. This technique compared to the techniques based on phase separation could potentially provide a facile and straightforward way of controlling the nanoporosity. The objective is to develop a new class of NPNs based on the RES technique in which structural attributes such as pore size and porosity and chemical attributes of the pore interface can be tailored. Goals include (i) synthesis of NPNs with controlled pore structure (ii) characterization of network and pore structures (iii) characterization of transport properties as related to structural attributes and (iv) tailoring of pore interface chemistry/activity. A stepgrowth system of epoxy-amine (diglycidyl ether of bisphenol A - EPON 828 and 4,4'methylenebiscyclohexanamine) and tetrahyrdofuran (THF) as the solvent satisfied the established criteria required for reactive encapsulation to occur and was used to study the RES technique. The cure kinetics of epoxy-amine reactions and the influence of THF were studied in order to understand the network and pore structures forming mechanisms. The network structures were analyzed using the equilibrium swelling (v2s) and glass transition (Tg) behaviors. The transport properties such as permeability (P), diffusivity (D) and partition coefficient (K) were experimentally determined using permeation and equilibrium sorption studies. In order to investigate the pore structures, the epoxy-amine-THF gels were supercritically dried using carbon-dioxide. The pore structures and sizes of the resulting materials called polymer aerogels (PAs) were analyzed using SEM, SAXS, BET and mercury pycnometer techniques. Polymer aerogels with average pore size between 1-50 nm, porosity between 0-80% and specific surface area $\sim 200 \text{ m}2/\text{g}$ were obtained. The pore interface hydrophilicity was tailored by chemically grafting acrylamide and sulfonic acid groups. Future work would involve designing functional nanostructured materials using the RES and chemical grafting techniques for applications such as separation membranes and polymer-polymer nanocomposites.