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High-Tg Polynorbornene-Based Block and Random Copolymers for Butanol Pervaporation Membranes

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Vinyl addition polymers of substituted norbornene (NB) monomers possess desirably high glass transition temperatures (Tg); however, until very recently, the lack of an applicable living polymerization chemistry has precluded the synthesis of such polymers with controlled architecture, or copolymers with controlled sequence distribution. We have recently synthesized block and random copolymers of NB monomers bearing hydroxyhexafluoroisopropyl and n-butyl substituents (HFANB and BuNB) via living vinyl addition polymerization with Pd-based catalysts. Both series of polymers were cast into the selective skin layers of thin film composite (TFC) membranes, and these organophilic membranes investigated for the isolation of n-butanol from dilute aqueous solution (model fermentation broth) via pervaporation. The block copolymers show well-defined microphase-separated morphologies, both in bulk and as the selective skin layers on TFC membranes, while the random copolymers are homogeneous. Both block and random vinyl addition copolymers are effective as n-butanol pervaporation membranes, with the block copolymers showing a better flux-selectivity balance. While polyHFANB has much higher permeability and n-butanol selectivity than polyBuNB, incorporating BuNB units into the polymer (in either a block or random sequence) limits the swelling of the polyHFANB and thereby improves the n-butanol pervaporation selectivity.

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