Synthesis and Gas Transport Properties of Polynorbornene Dicarboximides Bearing Trifluoromethyl Isomer Moieties

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Abstract: In industrial processes such as oil extraction and refining, products are handled or generated in the gas phase, which represents a challenge in terms of treatment and purification. During the past three decades, new scientific findings and technological advances in separation based on the use of membranes have led to simpler and more efficient gas separation processes, optimizing the use of energy and generating less pollution. This work reports the synthesis and ring-opening metathesis polymerization (ROMP) of new structural isomers based on norbornene dicarboximides bearing trifluoromethyl moieties, specifically N-2-trifluoromethylphenyl-exo, endo-norbornene-5,6-dicarboximide (2a) and N-3-trifluoromethylphenylexo,endo-norbornene-5,6-dicarboximide (2b), using tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5dihydroimidazol-2-ylidene][benzylidene] ruthenium dichloride (I), bis(tricyclohexylphosphine) benzylidene ruthenium (IV) dichloride (II), and bis(tricyclohexylphosphine) p-fluorophenylvinylidene ruthenium (II) dichloride (III). It was observed that the -CF3 moiety attached at the ortho position of the aromatic ring increases thermal and mechanical properties of the polymer, whereas meta substitution has the opposite effect. A comparative study of gas transportation in membranes, based on these fluorinated polynorbornenes, showed that -CF3 ortho substitution increases permeability of the polymer membrane as a consequence of the increase in both gas solubility and gas diffusion. In contrast, gas permeability coefficients of the metasubstituted polymer membrane are rather similar to those of that which is non-fluorinated; this can be attributed to a lower fractional free volume. The meta-substituted polymer membrane, besides showing the largest permselectivity coefficients of all the isomers studied here, was also found to have one of the largest permselectivity coefficients for separating H2/C3H6 into glassy polynorbornene dicarboximides.

Keywords: gas transport membranes, polynorbornene dicarboximide, ROMP, structural isomers

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