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Publisher's version / Version de l'éditeur:

Polymeric materials, 86, 110, 2002

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Gas Transport Properties of Tetramethyl Polysulfones and Other Polymers Containing Bulky Side Group Substituents.

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INTRODUCTION

Polysulfone was the first polymeric material to be used as the basis for commercial gas separation membranes because of its combination of relatively high permselectivities and adequate permeabilities to various gases. The polymer also has good mechanical properties and excellent fiber spinning qualities. Several studies have shown that an improvement in gas transport properties could be obtained by modifying the polymer structure. Most relevant to the present work is a noteworthy study by the group of Koros and Paul.¹ Symmetrical substitution of methyl groups on the bisphenol or biphenol segment of polysulfone (PSf) or polyphenylsulfone (PPSf) respectively, resulted in a large increase in permeability without too great a loss in permselectivity. In the present work, the effect of incorporating various amounts and types of functional groups on gas transport properties was studied.

RESULTS AND DISCUSSION

For the initial phase of our work, we prepared PSfs and PPSfs containing different types of silyl side groups substituted on the bisphenol ring or the phenylsulfone ring and determined the effect of substitution on gas transport properties.²⁻⁴ Polymers containing trimethylsilyl (TMS) side groups showed one of the most favorable improvements in gas transport properties. Permeability coefficients for oxygen increased with increasing amounts of substitution, with minimal loss in O₂/N₂ ideal permselectivity. The site of substitution was also important: TMS groups ortho- to ether on bisphenol resulted in the greatest permeability increase (almost seven-fold), which was approximately twice as high as on the ortho-sulfone site. In addition to silyl substituents, a number of other functionalities were incorporated onto the polymer chain, and their effects on gas transport properties observed.

Following the initial phase, selected performance-enhancing functional groups (e.g. TMS) were incorporated onto polymer backbones having better gas transport properties. Tetramethyl-polysulfone (TM-PSf) and tetramethyl-polyphenylsulfone (TM-PPSf) were modified to incorporate TMS groups. Permeability coefficients for all gases increased with the introduction of TMS and the increases were especially large with higher substitution. Overall increases in performance were observed for the O₂/N₂ pair, characterized by large increases in oxygen permeability but with decreases in permselectivity. The data for CO₂/N₂ show a different trend than those for O₂/N₂. When compared with either TM-PSf or TM-PPSf, the silyl derivatives show a lesser decrease in permselectivity while having significantly large gains in permeability. In all cases, the TM-polymers modified with TMS had improved performance over the TM-polymer starting materials. TM-polymers having a degree of substitution (DS) of ~1.5 TMS groups per repeat unit had d-spacing values of ~5.3 Å, only slightly higher than the TM-polymer starting materials. Above DS 2, the d-spacing increased rapidly. TM-polymers with the highest DS of ~2.6 had d-spacing values above 6.0 Å. The highly silylated TM-polymers were around the

'upper-bound' limit⁵ for P(CO₂) versus P(CO₂)/P(N₂). Other modified polysulfones containing hexafluoroisopropylidene (6F-PSf) were also studied. In addition to TMS, other performance-enhancing functional groups were identified.

ACKNOWLEDGEMENT

The authors gratefully acknowledge partial financial support from the international collaboration project between the National Research Council of Canada and the Korea Institute of Science and Technology.

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