509e Crosslinking of High Free Volume Polymers for the Separation of Organic Vapors from Permanent Gases

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High free volume polymer membranes are often very weakly size-sieving and, consequently, can remove large gas or vapor molecules from a gas mixture with smaller molecules. This capability finds application in reverse-selective gas separations such as VOC removal from permanent gas streams and monomer recovery from the exhaust of polymerization reactors. Poly(1-trimethysilyl-1-propyne) (PTMSP) is a stiff chain, high free volume glassy polymer well known for its very high gas permeability [1]. PTMSP also has outstanding vapor/gas selectivity. For example, the n-C4H10/CH4 mixed gas selectivity at 25oC is 35, which is the highest value ever reported for this gas pair [2]. Such properties make PTMSP an interesting material for vapor/gas separations.

However, gas permeabilities in PTMSP are sensitive to processing history and time [3]. PTMSP undergoes significant physical aging, which is the gradual relaxation of non-equilibrium excess free volume in glassy polymers. PTMSP is also soluble in many organic compounds, leading to potential dissolution of the membrane in process streams where its separation properties are of greatest interest. These phenomena compromise the practical utility of PTMSP.

This study investigates the effect of crosslinking PTMSP on transport properties and physical aging. PTMSP films are crosslinked using bis azides, which have been shown to crosslink PTMSP [4]. The crosslinking chemistry is discussed, and the extent of crosslinking is correlated with the transport properties of this polymer. When PTMSP is crosslinked, it becomes insoluble in common PTMSP solvents such as toluene, cyclohexane and tetrahydrafuran. Thus, there is a significant increase in the chemical stability due to crosslinking. The initial permeability of PTMSP decreased with increasing crosslinking due to the loss in fractional free volume (FFV) upon crosslinking. The O2/N2 selectivity increased as the FFV decreased, showing that crosslinked PTMSP is more size selective than uncrosslinked PTMSP. A strong correlation between permeability and 1/FFV was found. The sorption properties of PTMSP were unaffected by crosslinking, so the decrease in permeability was due to a decrease in diffusion coefficients.

Nanoparticles such as fumed silica and titanium oxide were added to crosslinked PTMSP films and permeability of these films increased by up to 200% compared to crosslinked films with no nanoparticles. A systematic study of the effect of type, shape and amount of nanoparticles added to crosslinked PTMSP has been conducted.

The crosslinked PTMSP N2, O2 and CH4 permeability stability is improved and films have been tested for up to 250 days. The increased stability may be due to the crosslinks constraining the PTMSP chains and not allowing them to relax the excess, non-equilibrium FFV that is inherent in PTMSP. Over the same time scale, n-Butane permeability increased by 20%. This result is interesting and could be due to n-butane conditioning the membrane. Further research is required to fully understand the time dependence of permeation properties of crosslinked PTMSP.

Mixed gas experiments data show that crosslinked PTMSP displays enhanced mixed gas selectivities, similar to those in uncrosslinked PTMSP. The effect of vapor/gas composition, temperature and pressure on mixed gas permeation properties of crosslinked PTMSP has been studied, and the results from this study will be presented.

[1] K. Nagai, T. Masuda, T. Nakagawa, B. D. Freeman and I. Pinnau, Poly[1-(trimethylsilyl)-1-propyne] and Related Polymers: Synthesis, Properties and Functions, Progress in Polymer Science, 26 (2001) 721-798.

[2] T. C. Merkel, Z. He, I. Pinnau, B. D. Freeman, P. Meakin and A. J. Hill, Effect of Nanoparticles on Gas Sorption and Transport in Poly(1-trimethylsilyl-1-propyne), Macromolecules, 36 (2003) 6844-6855.

[3] T. Nakagawa, S. Fujisaki, H. Nakano and A. Higuchi, Physical Modification of Poly[1-(trimethylsilyl)-1-propyne] Membranes for Gas Separation, Journal of Membrane Science, 94 (1994) 183-93.

[4] J. Jia and G. L. Baker, Crosslinking of Poly[1-(trimethylsilyl)-1-propyne] Membranes Using Bis(Aryl Azides), Journal of Polymer Science, Part B: Polymer Physics, 36 (1998) 959-968.