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The effects of chemical structure on gas transport properties of poly(aryl ether ketone) random copolymers

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Abstract

The physical properties and gas permeation behavior of a series of homo/random copolymers of 4,4′-difluorobenzophenone (DFBP)−2,2-bis(4-hydroxy-phenyl)propane (BPA)/2,2-bis(4-hydroxy-3,5-dimethyl-phenyl)propane (TMBPA) have been investigated by systematically varying the diol ratios. The tetramethyl substitution group on the phenyl rings simultaneously increases polymer free volume and chain stiffness. These were confirmed by experimental and simulated methods. With the increase in TMBPA content, the gas permeation coefficients, diffusion and solubility coefficients of H_2, O_2, N_2, CO_2 and CH_4 were found to increase. The gas transport coefficients of the copolymers predicted from the additional rule were compared with the experimental results and the results obtained were within the expectations. In addition, the logarithm of gas permeation coefficients and the reciprocal of fractional free volume (1/FFV) also exhibited a good correlation. However, with the incorporation of TMBPA moiety, the permselectivity of gas pairs such as H_2/N_2, O_2/N_2 and CO_2/CH_4 remains reasonably high. As a result, the gas separation performance of TMBPA modified poly(aryl ether ketone) approaches the upper bound of the corresponding gas pairs. After comparing this work with gas separation performance of other methyl substituted polymers, one may conclude there is a general phenomenon that methyl substitution increases the gas permeability of the modified polymer with a small loss in gas selectivity for small gas pairs.

Keywords: Gas permeation; Poly(aryl ether ketone); Random copolymer

1. Introduction

Polymeric materials are utilized extensively for gas separation. Various membrane materials have been synthesized and investigated in the last two decades for their good gas separation and mechanical properties [1−3]. However, there still exists a tradeoff relationship between gas permeability and permselectivity for polymeric membranes [4,5]. To overcome the membranes' limitations, synthesizing new materials and modifying the existing membrane materials for better separation performance creates new market opportunities. It is now well documented that the gas permeability of polymeric materials can be improved by restricting the motion of polymer chains. Reducing the concentration of flexible linkages in the backbone, attaching bulky side groups, and cross-linking polymer chains have been widely studied to prepare new materials with high gas separation performance [6−8]. Among the above methods, attaching bulky side groups not only improve the gas diffusivity selectivity but also give a more open structure leading to higher gas permeabilities.

Synthesizing entirely new materials often involves high cost and lengthy period of time. In addition, the blending of different polymers also involves complicated phase behavior during membrane fabrication as most polymers are immiscible. Therefore copolymerization may be a more attractive option due to its simplicity, reproducibility, processibility and low development cost. Copolymerization of polymers is a simpler method which may synergistically combine the advantages of different material properties and eliminate the deficiencies of individual components [9−13].

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Poly(aryl ether ketone), PAEK, is a glassy polymer widely used due to its high thermal stability, good mechanical properties and chemical resistance. Although a few studies have already shown the relationship between gas transport properties and the chemical structure of PAEK [14–16], improving PAEK gas separation performance by copolymerization is still not available. In order to have a more in-depth understanding of the relationship between the gas permeation behavior and the ratio of bulky side groups on the ether–ether phenyl ring, a series of homo/random copolymers PAEK from 4,4-difluorobenzophenone (DFBP), 2,2-bis(4-hydroxy-phenyl)propane (BPA), and 2,2-bis(4-hydroxy-3,5-dimethyl-phenyl)propane (TMBPA) in varying ratios were synthesized and their gas permeation properties were characterized. In addition, the previous works on the effects of methyl substitution on gas transport properties will also be reviewed and compared with this work.

2. Experimental

2.1. Materials

The PAEK copolymers used in this study were provided by Mitsui Chemical, Inc. 2,2-Bis(4-hydroxy-phenyl)propane (BPA), 2,2-bis(4-hydroxy-3,5-dimethyl-phenyl)propane (TMBPA), and 4,4′-difluorobenzophenone (DFBP) were used as received from Tokyo Kasei Kogyo Co. Ltd. Solvents and anhydrous potassium carbonate were obtained commercially and were used as received. The chemical structures of DFBP–BPA/TMBPA copolymers are shown in Fig. 1. Dichloromethane was employed as the solvent to prepare the dense membranes. Gases O_2, N_2, CH_4 and CO_2 with specified purities better than 99.9% were obtained from Soxal (except CH_4 from Linde).

2.1.1. Synthesis of PAEK copolymer (in case of BPA/TMBPA = 50/50)

A mixture of 11.3 g (0.0495 mol) of BPA, 14.1 g (0.0495 mol) of TMBPA, 21.8 g (0.1000 mol) of DFBP, and 17.1 g (0.1238 mol) of anhydrous potassium carbonate in 142 g of *N*-methyl-2-pyrrolidinone was stirred at 200 °C for 8 h under nitrogen atmosphere. It was then cooled down to 120 °C and poured into the mixture of methanol and water (1:1, 600 ml). The polymer was collected and first washed with 1500 ml of water, followed by washing with 1500 ml of methanol. The polymer was collected by filtration and dried at 180 °C for 4 h under nitrogen atmosphere. The yield was 39.5 g (92%). The inherent viscosity of the polymer was 0.64 dl/g, measured using an Ubbelohde viscometer in a solvent (NMP), at a concentration of 0.5 g/dl at 35 °C. The molecular weight distributions of the polymers were characterized using a Shodex GPC system-21H by means of a RI detector and a KF-803L*2 column with a flow rate of 1 ml/min. Tetrahydrofuran was used as the solvent and the testing temperature is maintained at 40 °C.

2.2. Preparation of dense membranes

A 2% (w/w) polymer solution was prepared by dissolving PAEK in dichloromethane (used as received). The polymer solution was then filtered through a Whatman filter (1 μm) to remove undissolved materials or dust particles and cast onto a stainless steel ring mounted on a leveled silicon wafer at ambient temperature. The casting ring was covered with a piece of glass and a small gap was kept for slow solvent evaporation. After slow solvent evaporation for about four days, the membrane was dried at 60 °C in a vacuum oven for one day to remove the residual solvent. The membrane was then heated at a rate of 12 °C/20 min to 20 °C above the T_g of the polymer and hold for 20 min before air quenching to room temperature. After the drying procedure, all membranes were cut into circles of 38 mm diameter and their thicknesses were measured by a Mitutoyo digital micrometer with a resolution of 1 μm. Only the membranes with about 60 ± 5 μm thickness were used in the following studies.

2.3. Physical properties characterization

The thermal stability of the dense films was evaluated using Shimadzu 50 type thermogravimetric analyser (TGA) to analyse their thermal stability. Under air atmosphere, the polymers were heated at a rate of 10 °C/min. All the PAEKs exhibit good thermal stability and the 5% decomposition temperatures were above 400 °C. The glass transition temperatures were

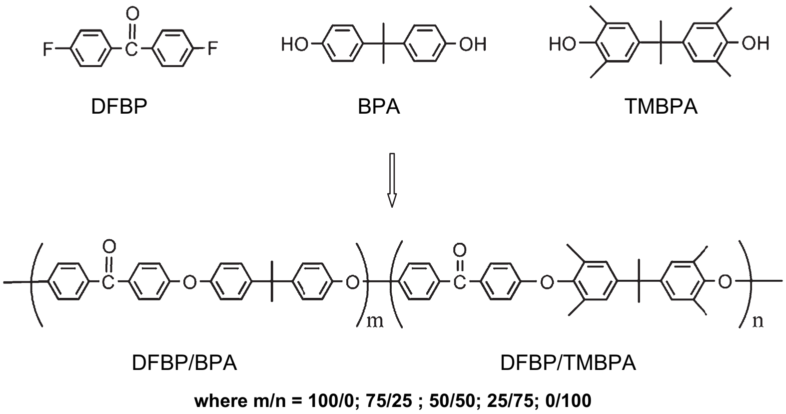

Fig. 1. Chemical structure of DFBP–BPA/TMBPA copolymers.