Available online at www.sciencedirect.com
SCIENCE DIRECT®
European Polymer Journal 42 (2006) 140–148
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Gas separation properties of aromatic poly(amide-imide) membranes

Shu-Hsien Huang [a], Chien-Chieh Hu [b], Kueir-Rarn Lee [b,*], Der-Jang Liaw [c], Juin-Yih Lai [a]

[a] *R&D Center for Membr. Technol. and Department of Chemical Engineering, Chung Yuan University, Chung-Li 32023, Taiwan*
[b] *Department of Chemical Engineering, Nanya Institute of Technology, Chung Li, 32034, Taiwan*
[c] *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 10772, Taiwan*

Received 3 May 2005; received in revised form 14 June 2005; accepted 25 June 2005
Available online 18 August 2005

Abstract

Aromatic poly(amide-imide)s were synthesized using direct 2,2-bis[*N*-(4-carboxyphenyl)-phthalimidyl] hexafluoropropane (6FDIA) polycondensation with various diamines containing flexible ether groups and bulky substituents. The oxygen and nitrogen gas transport in the poly(amide-imide) membranes was investigate at 35 °C with the pressure between the interval at 2–10 atm. The proposed method is expected to promote the gas permeability of the poly(amide-imide) membrane and maintain the gas selectivity. It was found that both gas permeability and selectivity of poly(amide-imide) membranes increased with increasing fractional free volume and *d*-spacing. The gas permeability had good correlation with the γ-transition temperature. The bulky pendent group introduced into diamine moiety of poly(amide-imide) could efficiently promote the gas permeability. For the behaviors of gas separation, the gas diffusivity coefficient and solubility selectivity controlled the gas permeability and selectivity, respectively. The sorption behavior of the aromatic poly(amide-imide) membranes can be well explained using the dual mode sorption model. The Langmuir capacity constant and Henry's law constant increase with FFV increasing. 6F-TBAPS has the best O_2/N_2 separation performance among the poly(amide-imide) membranes.

Keywords: Poly(amide-imide)s; Gas-separation; Oxygen enrichment

1. Introduction

Membrane-based gas separation has emerged as a commercially important technology for replacing, or used in combination with traditional gas separation methods such as pressure swing adsorption, cryogenic distillation and amine absorption. Therefore, gas separation membrane systems have received a lot of attention. Various membrane materials have been synthesized for gas separation applications in the last two decades. A great deal of interest exists in the field of gas separation for the development of new high performance polymeric membranes combining high selectivity with high permeability. To achieve such materials it is essential to investigate systematically the relationships between chemical

---

* Corresponding author.
E-mail address: krlee@nanya.edu.tw (K.-R. Lee).

0014-3057/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2005.06.032

and physical structures of the polymers and their gas transport properties.

Numerous studies on the relationship between the molecular structure of polymers and gas transport properties have been reported in an attempt to gain a better understanding of the transport mechanism [1]. The motivation is to improve transport properties by overcoming the "trade-off" trend between gas permeability and permselectivity of polymers, i.e., to increase gas permeability and selectivity simultaneously. The major physicochemical factors influencing polymer gas permeability and permselectivity control are (1) the mobility of the polymer chains, as reflected in many cases by the glass or sub-glass transition temperature of the polymer, (2) the intersegmental spacing, used to measure the mean free polymer volume, and (3) the penetrant-polymer interactions, as reflected by the solubility of the penetrant gases in polymers. It is well known that there are few specific polymer interactions with permanent gases such as oxygen and nitrogen at relatively low gas pressures (below 10 atm). The exception is carrier-mediated transport. Thus, for a given permanent gas, the permeation properties depend primarily on the packing density and the polymeric chain mobility. The former has been frequently interpreted in terms of the free volume, specific volume and *d*-spacing. The latter can be examined through dynamic mechanical analysis (DMA) [2–5].

Amorphous polymers with high glass transition temperature such as polyimides exhibit excellent thermal stability, good chemical resistance and mechanical strength. When they are used as a membrane material for gas separation, they have high gas selectivity, but low permeability, insolubility and infusibility restrict their full potential. To overcome this limit, many efforts have been performed to modify the physical and chemical properties of polyimides, aimed at obtaining tractability and good gas separation performance membrane materials [6–11]. Recent studies have demonstrated that both permeability and selectivity may be enhanced by incorporation of bulky pendent groups in glassy polymeric membranes that make the molecular structure rigid and simultaneously inhibit efficient chain packing and reduce local segmental mobility [12–14]. 6FDA-based polyimides usually have good solubility in common organic solvents and possess good mechanical and thermal properties, which are required for the fabrication of gas separation membranes [15–18]. The poly(amide-imide)s investigated in this study were synthesized by a completed imide structure. Thus, they remain soluble and possess excellent membrane forming properties.

In this study, we report on the effects of diamine moietie chemical structures on the gas permeability and permselectivity for poly(amide-imide)s membranes based on various diamines. Three kinds of poly(amide-imide) membranes was synthesized from diimide-dicarboxylic acid, 2,2-bis[*N*-(4-carboxyphenyl)-phthalimidyl] hexafluoropropane diimide-dicarboxylic acid (6FDIA) with various diamines. It was especially investigated in detail how the variation in polymer-structure would influence gas permeability and permselectivity.

2. Experimental

2.1. Synthesis of poly(amide-imide)s

The diamines, 4,4′-bis(4-aminophenoxy)biphenyl (BAPB), 2,2′-dimethyl-4,4′-bis(4-aminophenoxy)biphenyl (DBAPB) and 3,3′,5,5′-tetramethyl-bis[4-(4-aminophenoxy)phenyl]sulfone (TBAPS), were synthesized in two steps by the aromatic nucleophilic displacement reaction of diols and two mole equivalents of *p*-chloronitrobenzene, giving the dinitro compounds, followed by reduction with hydrazine monohydrate/Pd–C [19,20]. The diimide-dicarboxylic acid, 2,2-bis-[*N*-(4-carboxyphenyl)-phthalimidyl] hexafluoropropane (6FDIA), was obtained according to 4,4′-Hexafluoroisopropylidenediphthalic anhydride (6FDA) reacted with two mole equivalents of 4-aminobenzoic acid to form an amic acid in homogeneous solution. In a subsequent amic acid cyclodehydration reaction accomplished using dehydrating agents such as the mixture of acetic anhydride and pyridine, 6FDIA was afforded, which precipitated from the reaction mixture [21].

Poly(amide-imide)s were prepared by the direct polycondensation polymerization of the diimide-dicarboxylic acid, 2,2-bis[*N*-(4-carboxyphenyl)-phthalimidyl] hexafluoropropane (6FDIA), and various diamines. The route is illustrated in Fig. 1. A mixture of 0.9 mmol of diamine, 0.9 mmol of diimide-dicarboxylic acid monomer 6FDIA, 0.3 g of calcium chloride, 0.8 ml of triphenyl phosphite (TPP), 0.7 ml of pyridine and 2.5 ml of NMP was heated with stirring at 100 °C for 2 h under argon atmosphere. After cooling, the reaction mixture was poured into large amount of methanol with constant stirring. The precipitate was washed thoroughly with methanol and hot water. The polymer was then washed with hot acetone using a Soxhlet extractor for 3 h collected on a filter and dried at 100 °C under vacuum. The inherent viscosities of poly(amide-imide)s were in the range of 0.93–1.43 dl/g. The poly(amide-imide)s reaction pairs are shown in Table 1.

2.2. Membrane preparation

The dense poly(amide-imide)s membranes were prepared by casting a *N*,*N*-dimethylacetamide (DMAc) solution containing about 8 wt% polymer on glass plates. Membranes were then dried in an oven at 70 °C for 1 h. After drying, the membranes were removed from the glass plates by distilled water, placed in a vacuum dryer and dried for 24 h at 1 atm and room temperature.