Available online at www.sciencedirect.com

ScienceDirect

Journal of Membrane Science 291 (2007) 199–209

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Reversible diamine cross-linking of polyimide membranes

Clem E. Powell, Xavier J. Duthie, Sandra E. Kentish,
Greg G. Qiao*, Geoff W. Stevens

Cooperative Research Centre for Greenhouse Gas Technologies, Department of Chemical and Biomolecular Engineering,
The University of Melbourne, Parkville, Victoria 3010, Australia

Received 2 October 2006; received in revised form 11 January 2007; accepted 17 January 2007

Abstract

The reversible chemical cross-linking of polyimide membranes with diamines has been investigated. This investigation has been carried out on model compounds, polymers and flat sheet polymeric membranes. Reaction between an imide containing model compound and an amine causes each imide ring to be converted into two amide functional groups. Upon heating under vacuum, this reaction can be reversed. The reaction between an amine and the polyimide 6FDA–durene and the subsequent thermal reversal has been investigated. Upon thermal reconversion of the amide linkages back to imide rings, the molecular weight of the polymer is significantly reduced. It is proposed that the polymer undergoes backbone scission with incorporation of the amine as an end group. Polymeric gas separation membranes were formed incorporating the cross-linker in the casting process. The process in which these membranes were constructed ensured that there was a low degree of cross-linking. While significant changes in the physical properties of these membranes are observed upon cross-linking, no insoluble gels are formed. These membranes show a decrease in carbon dioxide permeability and an increase in plasticization resistance and selectivity upon reaction with a diamine. Compared with some literature examples of diamine cross-linked membranes, the reduction in permeability in the membranes presented here is considerably lower but the plasticization resistance is less extensive.

Keywords: Polyimides; Cross-linking; Amines; Membranes; Gas separation

1. Introduction

Over the last 20 years polymeric gas separation membranes have grown from a research laboratory subject into a significant industry [1]. In particular, polyimide membranes have been commercialized for the separation of a range of gases and considerable quantities of research has been published on the gas transport properties of these materials [2–12]. Potential future uses of polyimide membranes includes the separation of carbon dioxide from flue gases for geosequestration; however, for this to become economical, significant advances in the efficiency and lifetimes of polymeric membranes will be required [13].

Cross-linking has been proposed as a strategy to improve gas separation membranes by improving the permselectivity while maintaining a high permeability and increasing resistance towards aggressive gases [14]. In particular, cross-linking is seen as a mechanism to resist the swelling of a membrane material that occurs upon exposure to a condensable gas such as carbon dioxide. This phenomenon, known as plasticization, causes an overall increase in membrane permeability, a loss in selectivity and leads to time-dependent membrane performance.

Three different techniques have been used in the chemical cross-linking of polyimides: synthesis of branched polyimides [15,16], synthesis of polyimides which incorporate cross-linkable functional groups [17–20] and the use of diamines to cross-link via reaction with carbonyl groups [21–31]. It is this third approach that is the focus of the present paper. Hayes has suggested that in this case, the amine group reacts with a carbonyl group on the imide ring yielding two amide linkages [21]. The reaction between a polyimide membrane and a monoamine has also been described by Chung and co-workers [32]. Diamine cross-linking has been shown to reduce the effects of aging on thin films [33].

Chung and co-workers reported that when either 1,2-diaminoethane or 1,3-cyclohexanebis(methylamine) is used as the cross-linking agent, heating the cross-linked sample under

---

* Corresponding author. Tel.: +61 3 8344 8665; fax: +61 3 8344 4153.
E-mail address: gregghq@unimelb.edu.au (G.G. Qiao).

0376-7388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2007.01.016

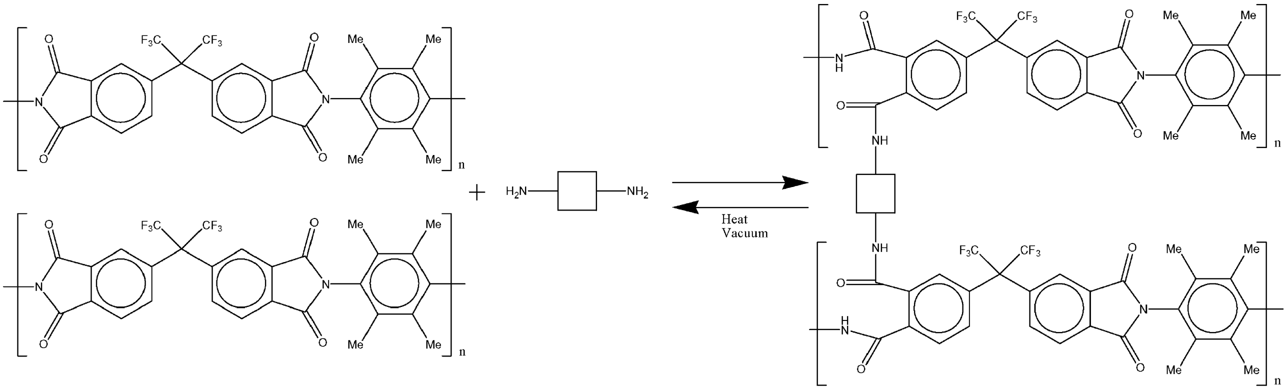

Fig. 1. Diamine cross-linking reaction. The reverse reaction which has been observed for some diamines is also displayed.

vacuum can reverse the cross-linking reaction liberating the diamine [28,29]. Upon heating, the two amide functional groups are said to reconvert back into the imide ring with loss of the diamine (Fig. 1). These reactions have been characterized by IR spectroscopy and XPS, both of which do not give definitive data on exact molecular structures.

The aim of this research is to investigate this cross-linking reaction and in particular, the reversible nature of the reaction. We have chosen three related means of studying this reaction. The first is a model compound study to investigate the chemistry of the cross-linking reaction, while the second is a study of the change in the molecular weight of polymers with a low cross-link density. Finally, a study on the effect of cross-linking and heating on the carbon dioxide permeabilities has been undertaken.

2. Experimental

2.1. Model compound synthesis

4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) (Lancaster), 1,4-diaminodurene (TCI), benzylamine (Merck), 4-methylbenzylamine (Aldrich), 1,3-diaminobenzene (Fluka), acetic anhydride (BDH), triethylamine (LR grade, Ajax Finechem), diethyl ether (Anhydrous, Merck), methanol (AR grade, Merck) and dichloromethane (AR grade, BDH) was used as received. *N*-Methylpyyrolidone (99.5%, Aldrich) was distilled before use and stored over molecular sieves.

A number of model compounds (**1**, **2** and **3**) were prepared from these chemicals as follows:

- *5,5′-(Perfluoropropane-2,2-diyl)bis(2-benzylisoindoline-1,3-dione) (**1**).* To a solution of 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) (3.18 g, 7.16 mmol) in *N*-methylpyyrolidone (15 mL) was added benzylamine (1.6 mL, 14.6 mmol) and the solution stirred at room temperature for 23 h. Acetic anhydride (2.7 mL, 28.6 mmol) and triethylamine (0.9 mL, 6.5 mmol) were added to remove water and the solution was stirred at room temperature for a further 20 h. Water (50 mL) was added to the reaction mixture and a white solid was collected by filtration. The precipitate was washed with water and diethyl ether to yield a white solid **1** (3.42 g, 77%). For full characterization data see supporting information.
- *5,5′-(Perfluoropropane-2,2-diyl)bis(N^1,N^2-dibenzylphthalamide) (**2**).* To a solution of **1** (690 mg, 1.11 mmol) in dichloromethane (15 mL) was added benzylamine (0.24 mL, 2.2 mmol) and the solution stirred for 2 h at room temperature. The solvent was removed under reduced pressure and a solid collected. This was washed with water and diethyl ether to yield a faint yellow solid **2** (725 mg, 78%). For full characterization data see supporting information.
- *5,5′-(Perfluoropropane-2,2-diyl)bis(N^1,N^2-benzyl-4-tolylmethylphthalamide) (**3**).* To a solution of **1** (200 mg, 0.32 mmol) in dichloromethane (10 mL) was added 4-methylbenzylamine (0.08 mL, 80 mg, 0.66 mmol) and the solution stirred for 17 h. The solvent was removed under reduced pressure and a solid collected. This was washed with water and diethyl ether to yield a faint yellow solid **3** (178 mg, 64%). For full characterization data see supporting information.

The structure of these model compounds was confirmed using ^{1}H and ^{13}C NMR on a Varian Unity + 400 in d_6-DMSO at 400 and 100 MHz, respectively, and referenced against residue solvent. ^{13}C NMR assignments were made using ^{13}C Attached Proton Test (APT) spectroscopy, ChemDraw ^{13}C NMR prediction software [34] and literature values of structurally similar compounds as a guide [35,36]. Fourier Transform Infrared Spectroscopy was carried out with KBr disks on a Bio-Rad FTS-165 FTIR spectrophotometer. High resolution mass spectroscopy was carried out on a Bruker BioApex 47e FT-ICR. Low resolution ESI and LC/MS measurements were performed on a Micromass Platform II with a Waters Alliance 2690 HPLC system.

2.2. Polymer synthesis

The polymer, 6FDA–durene (Fig. 2) was synthesized by reaction between 6FDA and 1,4-diaminodurene in *N*-methylpyyrolidone to give a polyamic acid, which was subsequently imidized *in situ* with triethylamine and acetic anhydride to yield the desired polymer. The polymer was