International Journal of Greenhouse Gas Control 12 (2013) 146–154

Contents lists available at SciVerse ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Gas separation properties of systems with different amounts of long poly(ethylene oxide) segments for mixtures including carbon dioxide

A. Tena[a], A.E. Lozano[a,b], L. Palacio[a], A. Marcos-Fernández[a,b], P. Prádanos[a], J. de Abajo[a,b], A. Hernández[a,*]

[a] Smap UA-UVA_CSIC, Universidad de Valladolid, Facultad de Ciencias, Real de Burgos s/n, 47071 Valladolid, Spain
[b] Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

ARTICLE INFO

Article history:
Received 11 February 2012
Received in revised form 10 October 2012
Accepted 17 October 2012
Available online 20 December 2012

Keywords:
Membranes
PEO
BKDA-ODA
Carbon dioxide (CO_2)
Thermal treatment
Permeation temperature
Measurement temperature

ABSTRACT

A complete series of aliphatic aromatic copolyimides has been synthesized. In this case all the samples had the same structure, BKDA-PEO6000-ODA, but different percentage of PEO in the final polymer. These copolymers have been thermally treated and characterized by several techniques. A direct relationship between temperature of treatment and both phase segregation and permeability improvement has been demonstrated.

Results show that the permeability is higher when higher the PEO content is, but otherwise the selectivity does not follow the same trend. Notable is the case of the CO_2/N_2 couple of gases that show selectivity-versus-permeability very near the upper bound of Robeson especially when permeation is done at 50 °C.

The Maxwell model has been applied to carry out the prediction of permeability (for CO_2, CH_4, O_2 and N_2) and it has been found that depending on the percentage of amorphous PEO in the polymer, the model reproduces well the experimental tendency.

1. Introduction

The augment of carbon dioxide concentration in atmosphere due to the use of fossil fuels has caused a global warming that due to its potential dangerous effects requires resolved actions (Houghton et al., 2001). The 60% of total CO_2 emissions are produced by power generation facilities and industrial factories. Of course research should focus on the optimization of clean energy sources and on the more efficient use of energy. However, it is also necessary to reduce CO_2 levels, so carbon capture and storage (CCS) must be considered as an urgent issue (Davidson, 2005). CO_2 can be captured by a variety of methods, which can be classified as post-combustion, pre-combustion and oxy-combustion ones (Figueroa et al., 2008; Metz et al., 2005). Among these methods, *Post combustion* appears as one of the most attractive alternatives (Davison and Thambimuthu, 2004). This process can be applied to different sources: power, steel, cement or petrochemical plants, etc. (Steeneveldt et al., 2006). In this process the flue gas after the combustion step must be concentrated and purified to meet the transport and storage specifications (de Visser et al., 2008).

The role of polymeric membranes applied to gas separation is increasingly gaining importance (Baker, 2002). Currently they are presented as a good alternative for this type of processes (Herzog, 2001; Koros, 2004) when compared with the processes that have been used up to now (Gibbins and Chalmers, 2008; Krumbeck, 2007; Programme, 2007/4).

The amount of CO_2 in the flue gas ranges from low (4%) to high (30%) concentrations and therefore the applied technology should consider these differences (Davison and Thambimuthu, 2004; Favre, 2011). Other compounds in the flue are O_2, H_2, CO, NO_x or SO_x, although the most frequent is N_2, which appears in the coal power plants, where CO_2 concentrations are typically around 15% (Bounaceur et al., 2006; GCEP, 2005; Steeneveldt et al., 2006).

Polymers to be applied for this type of separation should have an adequate balance of permeability and selectivity (Favre, 2007). But, it is also necessary to have a high gas flow and good mechanical and thermal resistance.

Glassy polymers and in particular polyimides are well known for their excellent thermal oxidative stability, good organic solvent resistance and exceptional mechanical properties, along with an extraordinary ability to separate complex mixtures of gases in diverse applications (Bessonov et al., 1987; Ghosh, 1996; Wilson and Hergenrother, 1990).

Typically these materials have a high selectivity but they sometimes do not exhibit sufficiently high permeability (Ayala et al.,

* Corresponding author.
E-mail address: membrana@termo.uva.es (A. Hernández).

1750-5836/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijggc.2012.10.014

2003; Tanaka et al., 1989). In order to increase the selectivity to CO_2, it is convenient to increase the affinity of the material for this gas. One of the most common approaches to meet these requirements is the use of block-copolymers having moieties able to interact with a certain gas.

Block-copolymers can combine hard and soft blocks. The hard block can consist in a polymer with well-packed rigid structure; while the soft segments usually contain more flexible chains. The hard segments are glassy while the soft segments behave as rubbery polymers with relatively high free volume fractions. In this way the glassy polymer segments will provide the mechanical resistance. The rubbery segments generally form continuous nanodomains with high gas permeability (Barbari et al., 1988; Li et al., 1997).

It is widely known that$CO_2$is highly soluble in polyethylene oxide (PEO) and thus it has been used to separate carbon dioxide from other light gases (Hirayama et al., 1999; Kawakami et al., 1982). In view of this, the use of block-copolymers combining aromatic diamines with aliphatic ones based on PEO (Jeffamines), appears to be a promising route (Okamoto et al., 1995, 1993; Suzuki et al., 1998). These compounds have good permselectivity for the couple CO_2/N_2 (Okamoto et al., 1996), which was attributed mainly to the high solubility-selectivity due to the existence of strong interactions between the hydrophilic and rubbery domains of the oxyethylene groups in PEO and CO_2. The role of the interaction between CO_2 and ethylene oxide (EO) groups in CO_2 selectivity has been discussed and used for the development of new membranes (Car et al., 2008; Lin and Freeman, 2004; Reijerkerk et al., 2010).

In addition, it is necessary to reach a good balance between the hard and soft block segments in order to provide good gas separation balance without loss of permeability. For this reason, it is proposed here a complete study of the influence of composition on the properties of separation for a system where both the hard part, in this case the aromatic polyimide (ODA rich phase), and the soft section, the aliphatic (rich in the diaminepolyethylene oxide, PEO-6000), are common to all structures.

2. Experimental

2.1. Chemicals

3,3′,4,4′-Benzophenonetetracarboxylicdianhydride (BKDA), and 4,4′-oxydianiline (ODA) were purchased from Aldrich. These products were purified by sublimation at high vacuum just before being used. α,ω-Diamine-poly(ethylene oxide) with nominal molecular weight of 6000 g/mol, were kindly donated by Kawaken Fine Chemicals Co., Ltd. (Tokyo, Japan), (PEO-6000 from here on). This polyether was dried at 70 °C in vacuum for 5 h and stored in a desiccator at vacuum until use. Anhydrous N-methylpyrrolidinone (NMP), to be used as polymerization solvent, was purchased from Sigma–Aldrich Co. Fig. 1 shows the chemical structure of the monomers.

2.2. Synthesis of copoly(ether-imide)s

The samples were synthesized by combination of the dianhydride (BKDA) with an aromatic amine (ODA), and changing the proportion of the aliphatic amine (PEO-6000). The corresponding copoly(ether-imide) will be designated by adding cPI before the figures corresponding to the weight proportion of PEO. cPI-69 should be an example for the sample BKDA PEO-6000 ODA with a 6:1 (w/w) relation between the aliphatic and aromatic diamines, that correspond to a (w/w) PEO proportion of a 69%.

The first step for the synthesis of all the polymers here was to make a mixture of poly(ethylene oxide) (PEO-6000)(x mmol), and 4,4′-oxydianiline (ODA) (y mmol), in weight ratios1:1,2:1, 4:1, and 6:1, dissolved in anhydrous NMP (5 mmol $(x+y)$/10 mL) in a 100 mL three-necked flask blanketed with nitrogen.

Table 1
Polymers synthesized in this work.

Sample	Weight ratio PEO/ODA	Theoretical polyether weight in the copolymer (%)	Acronym
BKDA PEO-6000 ODA 6_1	6:1	68.9	cPI-69
BKDA PEO-6000 ODA 4_1	4:1	60.4	cPI-60
BKDA PEO-6000 ODA 2_1	2:1	44.2	cPI-44
BKDA PEO-6000 ODA 1_1	1:1	28.8	cPI-29

Then, the reaction mixture was cooled down to 0 °C, and under mechanical stirring, a stoichiometric amount of BKDA dianhydride ($x+y$ mmol) was added and the mixture was stirred overnight at room temperature (see final resulting amounts of PEO-6000 in the samples in Table 1). During this time the dianhydride completely dissolved and the solution reached high viscosity.

2.3. Preparation of the copolyimide dense films

The resultant viscous copolyamic acid solution was diluted with NMP to the appropriate viscosity for casting, filtered through a nominal #1 fritted glass funnel, degassed, and cast onto leveled a glass plate. The resulting film was covered with a conical funnel to avoid fast evaporation of the solvent, dried at 80 °C overnight, and finally thermally treated under inert atmosphere at different temperatures (see Fig. 2 for a description of the different thermal

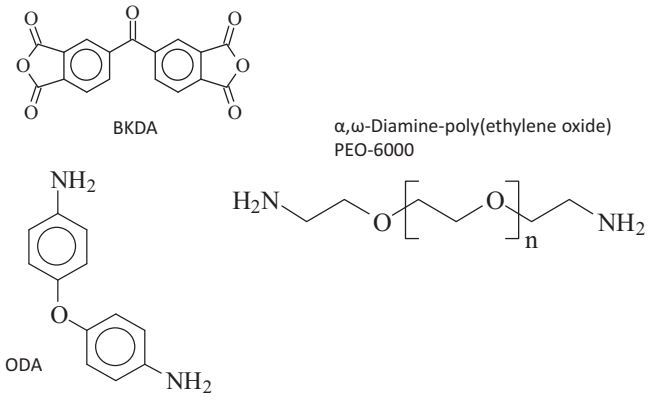

Fig. 1. Structure of the monomers used to build up the poly(ether-imide)s.

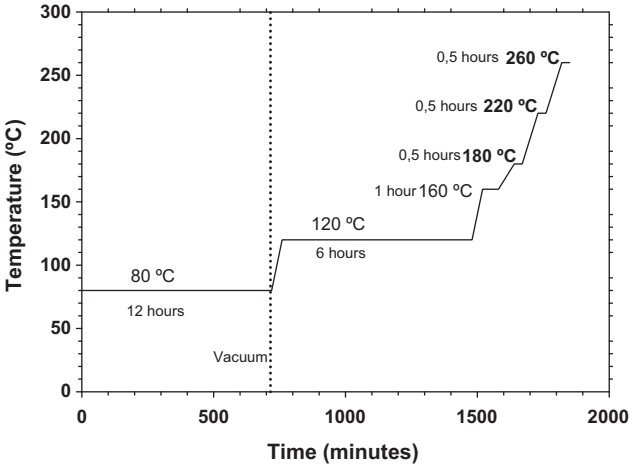

Fig. 2. Sketch of the thermal treatment protocol.