Journal of Membrane Science 434 (2013) 26–34

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

On the influence of the proportion of PEO in thermally controlled phase segregation of copoly(ether-imide)s for gas separation

Alberto Tena [a], Angel Marcos-Fernández [a,b], Laura Palacio [a], Pedro Prádanos [a], Angel E. Lozano [a,b], Javier de Abajo [a,b], Antonio 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 2 July 2012
Received in revised form
24 January 2013
Accepted 24 January 2013
Available online 31 January 2013

Keywords:
Copoly(ether-imide) membrane
SAXS
Phase segregation
Thermal treatment
Gas separation
Maxwell equation
Proportion
PEO
BPDA–ODA
Carbon dioxide (CO_2)

ABSTRACT

A complete series of aliphatic aromatic copoly(etherimide)s, based on an aromatic dianhydride (BPDA), an aromatic diamine (ODA) and a diamino terminated poly(ethylene oxide) (PEO2000) of 2000 g/mol molecular weight, using different PEO contents, has been synthesized. Cast films of these copolymers have been thermally treated and characterized by FTIR-ATR, DSC, TGA and SAXS. It has been found that there is a direct relationship between phase segregation and permeability for increasing treatment temperatures.

Results show that permeability is higher when PEO content increases in the copolymer. Selectivity for O_2/N_2 and CO_2/CH_4 gas pairs follows the same tendency, while those for CO_2/N_2, and CH_4/N_2 give higher selectivities for intermediate (30–40%) PEO contents. Especially promising are the results for these two pairs of gases because materials with high permeability with high selectivity can be obtained.

The Maxwell model has been applied to predict permeability (for CO_2, CH_4, O_2 and N_2) from known data for pure BPDA–ODA and neat PEO and it has been found that assuming PEO as the dispersed phase, the use of this equation is adequate for percentages up to approximately a 40% over which we should assume that it is the aromatic part of the copolymer which plays the role of dispersed phase.

1. Introduction

In order to decrease the world's dependence on oil, natural gas appears as an attractive alternative due to its lower carbon footprint as compared with gasoline or coal. Despite the increasing demand of natural gas, the gas reserves have remained reasonably stable because producers have been able to replace most of the drained reserves with new resources [1,2]. Nevertheless, a high percentage of natural gas reserves cannot be used because they are contaminated by nitrogen and thus they do not fit the required specifications for its transport and exploitation [3–5]. Moreover, it is obvious that separations where CO_2 is involved are of increasing interest nowadays due to its inconvenient climatic effects.

Nowadays, the role of polymeric membranes applied to gas separation is more and more important. In all cases, in order to guarantee a real application of a new polymeric material in gas separation, an adequate balance of high permeability and good selectivity must be achieved [6,7].

In order to be useful in such gas separation applications, a polymer film should show a preferential affinity for condensable gases such as CO_2 or CH_4 as compared with a mostly ideal gas such as N_2. Moreover, in addition to the criteria of permeability and selectivity, membranes to be used in this type of separations, must give high flow and have good mechanical and thermal resistance.

Glassy polymers and in particular polyimides are well known by 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 [6,8,9].

Typically these materials have a high selectivity but with a not always sufficiently high permeability [10,11]. It is therefore necessary to increase the affinity of the compounds for condensable gases such as CO_2, or CH_4 and one of the most common approaches to meet these requirements is the use of block-copolymers.

Aromatic–aliphatic block-copolymers usually combine hard and soft blocks. The hard block can be formed by a polymer with well-packed and highly rigid structures; as a result it forms the

---

[*] Corresponding author. Tel.: +34983 423134; fax: +34 983 423013.
E-mail addresses: membrana@termo.uva.es,
tonhg@termo.uva.es (A. Hernández).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.01.036

glassy segment of the polymer chain with usually low free volume. In contrast, the soft block can consist in a polymer with more flexible, low T_g, chains, which can form rubbery segments in the polymer chain normally with high free volume. Also, when aromatic–aliphatic block copolymers are phase-separated, their glassy polymer segments would provide mechanical support. The rubbery segments, due to the nature of the flexible chain structure, allow an efficient transport of gas, giving a good permeability to the copolymer [12,13].

It is known that poly(ethylene oxide) (PEO) compounds give excellent results for the CO_2 separation from other light gases [14,15]. In the same way, this category of compounds having oxyethylene groups in the structure showed good permeability for the couple CH_4/N_2 [16]. In view of this, block-copolymers combining aromatic and PEO polyimides, appears to be a successful route [17–19]. These compounds have also good permselectivity for the couples CO_2/N_2 and CH_4/N_2. This was attributed mainly to the high solubility–selectivity [16], which could be due to the existence of strong interactions of CO_2 with the oxyethylene group in PEO. The interaction between CO_2 and PEO has been discussed and used for the development of CO_2 selective membranes previously [20–22].

It is also necessary for the development of new materials to find a good balance between the hard and soft block segments in order to provide good separation without loss of permeability. For this reason, we propose here a complete study of the influence of composition on the properties of separation for a system composed of hard aromatic polyimide segments (BPDA–ODA), and soft aliphatic polyether segments (PEO).

The properties of such material have been analyzed by standard techniques of characterization (DSC, TGA, TMA, mechanical properties and density). Also, SAXS experiments were performed to study the segregation in the different phases of poly(ether-imide)s. Finally, we have modeled the copoly(ether-imide)s in order to predict their permeability to different gases by applying the Maxwell's equation.

2. Experimental

2.1. Chemicals

3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), and 4,4′-oxydianiline (ODA) were purchased from Aldrich. These products were purified by sublimation at high vacuum just before being used. Polyoxyethylene bis(amine) (Jeffamine ED-2003, $n=41$) with nominal molecular weight of 2000 g/mol, was kindly donated by Huntsman® (Holland). 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 (BPDA) with the aromatic diamine (ODA), and different proportions of the aliphatic diamine (PEO) [20]. The corresponding copoly(ether-imide) will be nominated by adding cPI to the w/w percentage of the aliphatic proportion. Thus, cPI-58 refer to the sample BPDA-PEO2000-ODA with a weight ratio between the aliphatic and aromatic diamines of 4:1 which corresponds to a mass proportion of PEO in the final copolymer of around 58%.

Diamine-terminated poly(oxyethylene oxide) (PEO2000) (x mmol), and 4,4′-oxydianiline (ODA) (y mmol) in weight ratios 1:4, 1:2, 1:1, 2:1, and 4:1 were dissolved in anhydrous NMP (5 mmol $(x+y)$/10 mL) in a 100 mL three-necked flask blanketed with nitrogen.

Then, the reaction mixture was cooled down to 0 °C, and under mechanical stirring, a stoichiometric amount of BPDA dianhydride ($x+y$ mmol) was added and the mixture was stirred overnight at room temperature (see final resulting amounts 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 a leveled 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 treated at different temperatures for 6 h in a vacuum oven, in order to get a complete imidization (Table 1). Films of the copolymers of 50–70 μm in thickness were obtained. After that, thermal treatments under inert atmosphere were carried out at different temperatures. All films showed good mechanical properties.

2.4. Characterization methods

Attenuated total internal reflectance-Fourier transform infrared analyses (ATR-FTIR) were performed at room temperature using a PerkinElmer Spectrum One infrared spectrometer equipped with an ATR accessory. A number of scans (16) taken directly from the films at a resolution of 4 cm^{-1} were averaged to get the FTIR spectra.

A Thermal Analysis Q500 instrument was used for thermogravimetric study of the membranes (TGA). Disc samples cut from films with weights between 5 and 15 mg were tested. When running dynamic scans, it was done in Hi-Resolution mode, where the heating rate is automatically adjusted in response to changes in the rate of weight loss, which results in improved resolution, with an initial heating rate of 10 °C/min under a flux of nitrogen.

Differential scanning calorimetry (DSC) analyses were carried out in a Mettler Toledo (DSC 822e) calorimeter equipped with a liquid nitrogen accessory. Disc samples cut from films weighting 5–15 mg were sealed in aluminium pans. Samples were heated with the following cyclic method in order to monitor the changes in thermal properties with thermal treatment: from 25 °C, the sample was heated at 10 °C/min to a target temperature; once reached, the sample was cooled at the maximum cooling rate accessible for the instrument to −90 °C, held at this temperature for 15 min and reheated at 10 °C/min to the next target temperature. The procedure was followed until the last treatment temperature was reached and a final run from −90 to 80 °C was performed. In this way, in each heating run, the thermal properties for the copolymers after treatment to the previously reached temperature were obtained, and a plot of thermal properties versus "instantaneous" thermal treatment could be built.

The densities (ρ) of the dense membrane films were determined using a CP225D Sartorius balance, provided with an immersion density kit.

SAXS measurements were performed at the beamline BM16 at the European Synchrotron Radiation Facility (Grenoble, France). Wavelength of the X-ray beam was 0.980 Å. Detector calibration was done with silver behenate ($AgC_{22}H_{43}O_2$), and the characteristic distance L was calculated from the scattering vector ($q=4\pi(\sin\theta)/\lambda$, λ=wave length, 2θ=scattering angle). Disc samples cut from films were placed in a Linkam hot stage and heated at 10 °C/min while the SAXS spectra were recorded. Calibration of