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

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Summary

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 ºC.

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.

Keywords: Membranes**;** PEO; BKDA-ODA; carbon dioxide (CO_2); thermal treatment; permeation temperature; measurement temperature

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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, 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, 2005). Among these methods, *Postcombustion* 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, 1987; Ghosh, 1996; Wilson, 1990).

Typically these materials have a high selectivity but they sometimes do not exhibit sufficiently high permeability (Ayala et al., 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; Okamoto, 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 diamine polyethylene oxide, PEO-6000), are common to all structures.

2. Experimental

2.1 Chemicals

3,3′,4,4′- Benzophenonetetracarboxylic dianhydride (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 ºC in vacuum for 5 hours 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. Figure 1 shows the chemical structure of the monomers.

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

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 ratios 1:1, 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.

Then, the reaction mixture was cooled down to 0 ºC, 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.

Table 1. Polymers synthesized in this work.

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 levelled a glass plate. The resulting film was covered with a conical funnel to avoid fast evaporation of the solvent, dried at 80 ºC overnight, and finally thermally treated under inert atmosphere at different temperatures (see Figure 2 for a description of the different thermal treatments). Films of the copolymers of 80-100 μm in thickness were obtained.

Figure 2. Sketch of the thermal treatment protocol.

2.4 *Physical Characterization*

Some of the physical characteristics of these copolymers have been shown in a previous paper(Marcos-Fernández et al., 2010).

For example, Attenuated total internal reflectance-Fourier transform infrared analysis (ATR-FTIR) has been used to verify the complete removal of solvent as well as imidization process, verifying that all the treated samples were completely imidized (Marcos-Fernández et al., 2010). Thermomechanical analysis (TMA) was used to attain the T_g of the aromatic part of the sample, showing that for all the copolymers, the T_g of the aromatic polyimide is well above ambient temperature(Marcos-Fernández et al., 2010).

Small Angle X-ray Scattering (SAXS) proved that the systems suffer intense phase segregation after being thermally treated which increase for increasing percentage of PEO (Marcos-Fernández et al., 2010). Moreover, mechanical properties of these membranes have been found to be good enough to allow their application to gas separation, although their mechanical resistance decreases slightly as the percentage of PEO increases (Marcos-Fernández et al., 2010).

On the other hand, from the standpoint of polymeric characterization, the use of thermogravimetric analysis (TGA) determined the thermal stability of the samples, and differential scanning calorimetry (DSC) was employed to determine the T_g and T_m of the aliphatic part of the sample and to determine the percentage of crystalline PEO in the sample.

Some results obtained by these techniques will be summarized below in order to correlate them with the gas transport and separation properties of such membranes.

2.5 Gas permeation

The permeability, P, for He, O_2, N_2, CO_2 and CH_4 were determined by using a barometric permeator using a constant volume technique which uses the *time-lag* operation method. The measurements were carried out at 30 ºC and 50 ºC and the applied pressure was 3 bar. A sketch of the device used has been shown elsewhere, (Marchese et al., 2006). The strategy known as *time-lag* method, attributed to Daynes et al. (Daynes, 1920), is very appropriate to determine permeability, diffusivity and solubility of a sample by a simple, rapid and accurate method working under transitory regime. The method has been successfully applied to determine polymer gas permeation by many authors (Crank, 1975; Paul, 1965). Its theoretical framework along with as the practical possibilities and limits of the technique have been abundantly documented, (Rutherford and Do, 1997). This system is nowadays an accepted method to assess the permeability and diffusion coefficients of gases through a polymer film.

3. RESULTS AND DISCUSSION

3.1 Thermal Stability

Dynamic thermogravimetric runs in high-resolution mode have been performed in a nitrogen atmosphere for fully imidized copolymers (annealed at 220 ºC for 0,5 hours).

TGA graphs showed a weight loss pattern consisting of three consecutive steps (see figure 3); an initial loss from ambient temperature to 300-350 ºC; a second loss from 300-350 ºC to 460-470 ºC; and a third loss from 460-470 ºC to 700 ºC.

Figure 3. TGA curves in dynamic conditions for PEO based copolymers.

The first loss can be attributed to the absorbed water plus the solvent trapped in the film. This weight change is in range from 2 to 2.5 % (Hedrick et al., 1995). The second loss step, after correcting for the previous weight decrease step, agrees with the theoretical contribution of α,ω-diamine-poly(ethylene oxide) in the copolymer composition (Marcos-Fernández et al., 2010), within a 3% error (see Table 2) and it is therefore assigned to the weight loss due to the degradation of polyether block sequences. The differences between the weight losses should be due to the different mass percentages of PEO in the copolymers. The third and final stage of weight loss is due to the thermal decomposition of the remaining aromatic polyimide segments.

Table 2. Results obtained by TGA for the prepared copolymers.

TGA analysis confirmed that the polyether thermal stability is much lower than the thermal stability of the aromatic polyimide segments, as already found for other copoly(ether-imide)s based on poly(ethylene oxide), and therefore a selective degradation of the polyether moiety could be performed in these copolymers. Other authors have also found that poly(propylene oxide) segments can be selectively degraded in: triblock (Hedrick et al., 1996a; Hedrick et al., 1996b), linear (Philip Gnanarajan et al., 2002) and grafted (Do et al., 2004) copolyimides to produce nanofoams.

The temperature of maximum weight loss rate was between 355-365 ºC for all copolymers. Of course, the char residue at 700 ºC is higher for the copolymers with more proportion of aromatic diamines, which leaves a higher residual content.

3.2 *Calorimetric analysis*

The samples were heated in a DSC instrument with a cyclic method in order to monitor the changes in thermal properties with the temperature of treatment (Tena et al., 2012). All copolymers showed only the T_g and T_m corresponding to the poly(ethylene oxide) segments, and no transition for the aromatic polyimide segments could be detected. However, it was possible to obtain the T_g of the aromatic block by TMA. No significant changes in polyether T_g with thermal treatment took place, and thus T_g, for all the poly(ether-imide)s, was between -55 and -52 ºC.

T_g of the polymers is known to depend mainly on composition and length (Hu et al., 2003), although here composition seems to play a limited role on T_g. However, there were changes in the T_m of the copolymers. The T_m in the polymer is related with its crystallinity, and correlated with the purity of the PEO domains, because only pure PEO could crystallize. A clear correlation appears between the percentage of poly(ethylene oxide) in the sample and the T_m of the polymer. It is known that in dispersed materials, the melting point is strongly influenced by the size of the domains (and correspondingly of the crystals); thus, higher melting point for cPI-69 copolymer means that the size of the PEO domains is bigger than those for the rest of the copolymers. Figure 4 shows the changes in the Tm and the percentage of maximal crystallinity for PEO chains as a function of the treatment temperature (the temperature instantaneously reached by the DSC) for the copolymers studied.

Figure 4. T_m (a) and maximal crystallinity (b) for the PEO portion of the copolymers as a function of the treatment temperature.

If a value of 8.67 kJ/mol is taken for the melting enthalpy of PEO (Van Krevelen, 1990), the amount of crystallized PEO, in the samples studied in this paper can be calculated as shown in Table 3. Note that the amount of crystallized PEO increases when its percentage does.

The amount of PEO-6000 crystallized in each sample for each heat treatment is relevant in what refers to gas permeability because the crystals act as obstacles to the passage of gas through the polymer. Under this assumption, it can be seen that if the sample is kept at 50 °C the percentage of crystallized poly(ethylene oxide) would be zero. At 30 ºC the amount of crystallized PEO for the samples cPI-29 and cPI-44 should be very low or negligible, while for the samples cPI-60 and cPI-69 the percentage of crystallized polyether is relatively important (see Table 3).

Table 3. Percentage of crystallized PEO at 30 ºC calculated by DSC.

3.3 Gas transport properties

3.3.1 Behaviour with the temperature of measurement

The behavior of the polymers is strongly influenced by the percentage of amorphous or crystalline PEO in the sample. By DSC it was determined that samples contain a high percentage of crystalline PEO-6000 and that this crystallinity augments when the PEO content increases (higher phase segregation).

It is therefore very important to check the permeation performance as a function of the measurement temperature because high temperatures would lower the presence of such microcrystals in the segregated domains that could act as barriers hampering the passage of gases through the film.

Arrhenius' representation can help us to understand the behavior of the samples as a function of temperature. In effect, the dependence of gas diffusion on temperature can be expressed in terms of an Arrhenius type relationship that considers the movement of the gas molecules through a membrane as a thermally activated process (Kesting, 1993). Mathematically, the temperature dependence of diffusion is given as:

$$D = D_0 \, exp\left(\frac{E_D}{RT}\right) \tag{1}$$

where D_0 is the pre exponential factor and E_D is the activation energy of diffusion. The activation energy term depends on the size of the penetrant and not on its mass (Crank, 1975). Taking into account the temperature dependence for the diffusion and sorption coefficients, the temperature effect on gas permeability is given as (Kesting, 1993):

$$P = P_0 \, exp\left(\frac{E_P}{RT}\right) \tag{2}$$

where E_P is the activation energy of permeation , which is the algebraic sum of E_D and ΔH_S. In general, permeability increases when temperature does. The results, for cPI-60, are shown in a plot of the natural logarithm of Permeability versus 1000/T in Figure 5. In this Figure it can be seen that there is a change in the trend when the measurement temperature is above 50 °C (1000/T=3.09). This demonstrates that samples must be in the same state at these high temperatures and that all PEO chains should be already in amorphous state.

Figure 5. Arrhenius plot for the permeability of the gases studied.

In the same way, it is possible to make a representation of the ideal selectivity (the ratio of pure gas permeabilities), presented in Figure 6. There, we can clearly see that the change in tendency for temperatures over 50 ºC appears clearly. This is especially obvious for the CO_2/He couple probably because helium, due to its small size, is less affected by the PEO crystals.

Figure 6. Natural logarithm of selectivity as a function of 1000/T.

3.3.2 Behaviour with the thermal treatment

Results show an improvement in permeability when the temperature of treatment is high. Therefore a correlation appears between high segregation and high permeability because both terms are caused by the thermal treatment of the copolymers. This correlation was already shown by us for other aliphatic-aromatic copoly(ether imide)s (Tena et al., 2012).

Figure 7 presents the permeability of different gases for the copolymer cPI-29 as a function of thermal treatment for two measurement temperatures: 30 (black symbols) and 50 ºC (white symbols).

Figure 7. Permeability versus treatment temperature for the copolymer cPI-29 (1Barrer= 3.348×10^{-19} kmol m / (m^2 s Pa)).

The figure shows that when the samples are measured at 50 °C higher permeabilities are obtained because then we can assume that most of the PEO in the copolymer is in amorphous state. In general, permeability increases for high treatment temperatures, when most of the remaining solvent is released and the improvement in phase separation is higher. The same trend was observed for all the copolymers.

3.3.3 Permeation properties as a function of the PEO percentage

Figure 8 shows the CO_2 permeability obtained for copolymers with different percentages of PEO for different samples thermally treated at the maximum temperature of 260 °C. When permeability is measured at 30 ºC there is a maximum permeability at approximately a 40 % of PEO followed by a steep decrease in permeability. This behavior fully disappears when permeation is measured at 50 ºC and a monotonous increase in permeability is obtained.

This is due to the hindering role of the increasing proportion of crystalline PEO appearing in the segregated domains for the copolymers containing high percentages of polyether chains.

Figure 8. CO_2 permeability for samples treated at 260 ºC containing different percentages of PEO.

It has been already mentioned that PEO crystals are practically impermeable to the passage of gases, so that if the total percentage of PEO in the sample is substituted by the percentage in the amorphous state (represented by white squared symbols in Figure 8), It can be observed that there is indeed a clear direct trend also at 30 °C between the permeability and the percentage of polyethylene oxide in the sample.

The representation also shows the values of the BKDA-ODA homopolymer (Tanaka et al., 1992) and pure PEO (Lin and Freeman, 2004) at 35 °C (0 and 100% of PEO in the sample, respectively). It is clearly evident that the permeability values obtained for the samples are between them.

Recent works suggest that it should be a maximal length of PEO in the samples

(Hangzheng et al., 2010; Yave et al., 2010). Our results suggest that that the apparent presence of such a maximum could be due to the presence of high crystallinity for long PEO chains. Thus, the correct strategy should be to increase the temperature of the permeation experiment to avoid the presence of these PEO crystals.

Similarly, Figure 9 shows the selectivity for several gas pairs as a function of the percentage of PEO. Particularly noteworthy is the behavior for the couple CO_2/N_2, where the selectivity values are over those exhibited for both the BKDA-ODA and PEO homopolymers. As expected, when the measurement temperature is higher, the selectivity decreases a little.

Figure 9. Selectivity for some gas pairs at 30 ºC (black squares) and 50 ºC (white symbols).

3.3.4 *Robeson's plots*

A visual way of illustrate and compare the permeability versus selectivity performances of a membrane for different gases are the corresponding Robeson's plots (Robeson, 1991, 2008). In these diagrams, in which the selectivity is shown as a function of the permeability of the most permeable gas in the couple, there is an upper bound which is called Robeson trade-off limit. The distance to this limit gives us an idea of the permeation properties of the samples. It has been shown in this paper that by measuring the samples at 50 °C permeability increases substantially with a very moderate decrease in selectivity due to the elimination of most or all the crystals of PEO from the copolymer. In order to present permselectivity at 50 ºC it is necessary to take into account that the corresponding Robeson limit depends also on the temperature of measurement (Rowe et al., 2010). These charts are shown for some couples of gases in Figures 10-12. In this case in addition to our results the values of permeability and selectivity for PEO (Lin and Freeman, 2004) and BKDA-ODA (Tanaka et al., 1992) at 35 ºC have been represented. In this way, assuming that our samples are *mixtures* of both the homopolymers BKDA-ODA and BKDA-PEO, the obtained gas separation properties should be intermediate between the values for these two polymers. It is worth noting that BKDA-PEO has very poor mechanical properties thus PEO data can be used assuming that BKDA-PEO should have permselectivities quite similar to that of pure PEO.

Figure 10. Robeson’s plot for the O_2/N_2 gas pair.

Figure 11. Robeson’s plot for the CO_2/CH_4 gas pair.

Figure 12. Robeson’s plot for the CO_2/N_2 gas pair.

Our aim with these copolymers is, as mentioned, to combine aliphatic blocks to provide high permeability plus aromatic blocks that should supply excellent mechanical strength. Thus, a good result would approach as far as possible to the PEO permeability. For separations where similarly condensable gases (O_2/N_2 or CO_2/CH_4) selectivity of the copolymers should not change too much because then the selectivity is mainly determined by the aromatic portion of the copolymer. For gas mixtures with very different condensability (CO_2/N_2 for example) the selectivity is even improved by the presence of PEO due to their easy condensability in the PEO moieties.

For both O_2/N_2 and CO_2/CH_4 separations, as expected, the performances of the membranes made out of the BKDA-ODA-PEO-6000 are between the two values corresponding to the homopolymers. In the CO_2/CH_4 case, the selectivity doesn’t change substantially (it is actually determined by solubility which is similar for these gases). On the other hand, for the O_2/N_2 couple, selectivity even decreases with higher content of polyethylene oxide. In both cases permeability increases clearly when the content of polyethylene oxide increases. This increase in permeability is stronger for permeation experiments performed at 50 ºC although the distance to the corresponding upper bound is quite similar. Note that, for the gas pairs, results are below those for the pure homopolymers.

In any case, it is worth noting the particularly good permselectivity for the CO_2/N_2 gas couple. For this pair of gases, the selectivity is even over that of pure BKDA-ODA homopolymer. The corresponding permeabilities increase with the percentage of PEO in the sample, in such a way that for the samples with large proportions of polyether, selectivity versus permeability approaches the Robeson’s upper bound at 30 ºC. The theoretical limit proposed by Rowe et al, (Rowe et al., 2010) at 50 ºC is even more closely approached by the copolymers with high content of PEO as can be seen in Figure 12. The selectivity found for CO_2/N_2 substantially enhances that found for other polymers (Powell and Qiao, 2006).

Thus, it has been proved that it is possible to modulate the permeability and the selectivity of block copolymers having PEO chains by controlling the amount of their soft and hard constituents. The presence of PEO blocks enhances permeability while a high selectivity for gas pairs containing CO_2 (principally for CO_2/N_2) is retained. Also, the presence of the aromatic polyimide part ensures good mechanical properties.

3.3.5 Permeability modeling

For this type of copolyimides consisting of an aromatic polyimide (hard part) and an aliphatic polyimide (soft PEO part), the permeability for the sample BKDA-ODA-PEO with different PEO percentages in the polymer may be predicted by the Maxwell equation as exposed below (Maxwell, 1954):

$$P_{eff} = P_C \left[\frac{P_D + 2P_C - 2\phi_D \left(P_C - P_D \right)}{P_D + 2P_C + 2\phi_D \left(P_C - P_D \right)} \right] \tag{3}$$

where P_{eff} is the effective permeability, P_C and P_D are the permeability of the continuous and the dispersed phase respectively and ϕ_D is the volume fraction of the dispersed phase in the block copolymer. In this type of polymers, we should consider that the continuous phase could be the aromatic or the aliphatic one. We will consider PEO phase to be the continuous phase when the amount of PEO is higher than 20% because it has been established that for these PEO contents the consideration of the aromatic part as the continuous phase would make the model deviate from experimental results (Hangzheng et al., 2010). It is worth to note that the Maxwell model assumes that there is a mixture without interaction of impenetrable domains (disperse phase) within a continuous phase. Of course the role should be interchanged for some proportions near the 50 % proportion. Moreover within the range of compositions when the roles are reversing it is not at all a question of pure distinguishable and separated disperse and continuous phases and obviously the equation doesn’t fit the results.

The permeability of pure PEO in the amorphous state is used as the permeability of the soft segments (Lin and Freeman, 2004) and the permeability of the aromatic homopolymer BKDA-ODA as that for the hard segments (Tanaka et al., 1992).

Figure 13. Predicted values for CO_2 and CH_4 permeabilities by using Maxwell equation. Empty squares correspond to the content of amorphous PEO.

Figure 14. Predicted values for CO_2/CH_4 selectivity using Maxwell equation. Empty squares correspond to the content of amorphous PEO.

Figure 13 and Figure 14 show the permeability and selectivity prediction for the CO_2 and CH_4. The model is clearly more precise to predict permeabilities than selectivities and gives better results once the portion of crystallinity has been substracted. Of course both of them are only approximately fitted but at least the model reproduces the tendency. It is also clear that the corrected results for experiments done at 30 ºC fit better the model than those for 50 ºC because the permeabilities of the homopolymers used in Equation (3) have been taken at ambient temperature.

4. *Conclusions*

A series of copoly(ether-imide)s presenting good gas separation properties have been prepared. These copolymers have been synthesized by the reaction between an aromatic dianhydride (BKDA), an aromatic diamine (ODA) and a diamine terminated poly(ethylene oxide) having a molecular weight of 6000 g/mole (PEO-6000), in a different percentage of PEO in the final copolymer.

TGA analysis confirmed the exact amount of PEO present in the material and showed that it can be selectively eliminated from the rest of the sample. DSC proved that the T_g values for the aliphatic blocks are quite similar, which means that the structure of PEO in the copolymers is alike. Nevertheless, the melting temperature associated to the PEO chains is different decreasing when the segregated domains are smaller. The maximal crystallinity is higher for copolymers containing larger percentages of PEO while the real crystallinity can be relatively high at low temperatures of operation. The permeability increases with the percentage of PEO in amorphous state (i.e. for percentages corrected to take into account the crystallinity of the samples).

The thermal treatment of the samples improved phase segregation, which as well produced an increasing permeability. Permeability and selectivity are between those for the homopolymers except for the CO_2/N_2 pair of gases. Although permeability increases with increasing percentage of PEO, the selectivity for the CO_2/CH_4, remains almost constant while for O_2/N_2 it decreases slightly. For the CO_2/N_2 gas couple, results for high PEO percentages at 30 °C are quite close to the Robeson bound. In the case of the measurements at 50 °C, the permeability-selectivity values approach even more closely to the limit for this temperature. In conclusion, it seems clear that these copolymers are suitable for separations where CO_2 is involved and a non-condensable gas are involved, especially for the separation CO_2/N_2. These separations have a great importance in the remediation of greenhouse effect and make these membranes good candidates for their application at industrial level.

We have also compared the experimental results with those calculated by using the Maxwell's model. In this case, the percentage of amorphous PEO should be used and the crystallinity has to be taken into account for low permeation temperatures. If these corrections are made the model fits relatively well the permeability experimental results and it is also reasonably valid to be used to justify the found selectivities in spite of the clear simplifications assumed. The need to take into account the truly amorphous portion of PEO makes necessary to optimize both the amount of poly(ethylene oxide) in the sample and the operating temperature of these materials for a specific length and amount of PEO.

5. Aknowledgements

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FIGURE CAPTIONS

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

Figure 2. Sketch of the thermal treatment protocol.

Figure 3. TGA curves in dynamic conditions for PEO based copolymers.

Figure 4. T_m (a) and maximal crystallinity (b) for the PEO portion of the copolymers as a function of the treatment temperature.

Figure 5. Arrhenius plot for the permeability (in Barrers) of the gases studied (for the sample cPI-60 at 180 ºC).

Figure 6. Natural logarithm of selectivity as a function of 1000/T (for the sample cPI-60 at 180 ºC).

Figure 7. Permeability versus treatment temperature for the copolymer cPI-29 (1 Barrer = 3.348×10^{-19} kmol m / (m^2 s Pa)).

Figure 8. CO_2 permeability for samples treated at 260 ºC containing different percentages of PEO.

Figure 9. Selectivity for some gas pairs at 30 ºC (black squares) and 50 ºC (white symbols).

Figure 10. Robeson's plot for the O_2/N_2 gas pair.

Figure 11. Robeson's plot for the CO_2/CH_4 gas pair.

Figure 12. Robeson's plot for the CO_2/N_2 gas pair.

Figure 13. Predicted values for CO_2 and CH_4 permeabilities by using Maxwell equation. Empty squares correspond to the content of amorphous PEO.

Figure 14. Predicted values for CO_2/CH_4 selectivity using Maxwell equation. Empty squares correspond to the content of amorphous PEO.

TITLES OF THE TABLES

Table 1. Polymers synthesized in this work.

Table 2. Results obtained by TGA for the prepared copolymers.

Table 3. Percentage of crystallized PEO at 30 ºC calculated by DSC.