

Advances in the design of co-poly(ether-imide) membranes for CO₂ separations. Influence of aromatic rigidity on crystallinity, phase segregation and gas transport.

Alberto Tena^{1,3}, Ángel Marcos-Fernández^{1,3}, Mónica de la Viuda¹, Laura Palacio^{1,2}, Pedro Prádanos^{1,2}, Ángel E. Lozano^{1,3}, Javier de Abajo^{1,3} and Antonio Hernández^{1,2}

¹Smep UA-UVA-CSIC, Parque Científico Universidad de Valladolid, Paseo de Belén, s/n, 47011 Valladolid, Spain.

²Dept. Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain

³Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.

Summary

In our previous works, it was observed a clear relationship between the structure and the properties for different copoly(ether-imide)s, besides a good relation was found between SAXS characterization and permeability results. Here, a series of aliphatic aromatic copoly(ether-imide)s, based on an aromatic diamine (ODA), a diamine terminated poly(ethylene oxide) (PEO2000) of a molecular weight of 2000 g/mol and different aromatic dianhydrides (BPDA, BKDA (or BTDA) and PMDA) has been synthesized and characterized.

The permeability for O₂, N₂, CO₂ and CH₄, increased with the rigidity of the monomers (BKDA < BPDA < PMDA), with the amount of PEO2000 in the copolymers, as well as with the increase in the temperature of treatment of the films. In this case, it was observed that when the proportion of PEO in the copolymer exceeded 50%, the permeability was similar for all samples, and the aromatic portion had no significant influence.

Attending to glass transition temperature, T_g, of the aliphatic part, to its melting temperature, T_m, and to its crystallinity, segregation was better for more rigid dianhydrides at lower temperatures of treatment. Higher dianhydride rigidity produced better mechanical properties that were good but decreased a little bit when the percentage of PEO in the samples increased.

Good permselectivity compromises were attained for the CO₂/N₂ separation. This work gives light to design advanced materials for this separation with the increasing possibilities of controlled structure and properties.

Keywords: Copoly(ether-imide) membrane; Phase segregation; Thermal treatment; Gas separation; Structure; PEO (poly(ethylene oxide)); BPDA; BKDA ; PMDA; carbon dioxide (CO₂); CO₂/N₂;

*membrana@termo.uva.es

1. Introduction

Nowadays, the role of polymeric membranes applied to gas separation is more and more important. Although some of them have already an application in industrial separations [1], research is still necessary to discover new materials and/or to improve the properties of existing polymers to assure them an actual applicability at an industrial level. 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 [2, 3].

There are several sources (power plants, steel, cement production plants or the chemical industry) where important amounts of CO₂ are generated, and it is therefore necessary to develop new technologies to curb, as far as possible, the greenhouse effect. Specifically, one of the most demanding applications is the CO₂/N₂ separation [3, 4].

In order to be useful in such gas separation applications, a polymer film should show a preferential affinity for condensable gases such as CO₂ or CH₄ as compared with a mostly ideal gas such as N₂. 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 resistances.

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 [2, 5, 6]. Typically these materials present a high selectivity but with a not always sufficiently high permeability [7, 8]. Therefore, it would be convenient to increase permeability without losing selectivity. One of the most common approaches to meet these requirements is the use of block-copolymers including aliphatic chains showing a certain affinity for condensable gases such as CO₂, or CH₄.

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 glassy segments within the polymer chain with usually low free volume. In contrast, the soft block can consist in a polymer with more flexible, low glass transition temperature (T_g) chains, which can form rubbery segments within the

polymer chain normally with high free volume. When aromatic-aliphatic block copolymers are phase-separated, their glassy polymer segments would also 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 [9, 10].

It is known that poly(ethylene oxide) (PEO) compounds give excellent results for the CO₂ separation from other light gases due to the existence of favorable electronic interactions with the ether moiety [11-13]. In consequence, block-copolymers combining aromatic and PEO polyimides appear to be a successful route [14, 15]. These compounds have also good permselectivity for the couple CO₂/N₂, and usually this is attributed mainly to the high solubility-selectivity [16], which is due to the commented strong interactions of CO₂ with the oxyethylene group in PEO. The interaction between CO₂ and PEO has been discussed and used previously for the development of CO₂ selective membranes [17-19]. For these reasons it is necessary to carry on studies for a better understanding of this type of PEO copolymers, in order to reach optimal structures for specific applications. In particular, here we will focus on the influence of the rigidity of the dianhydride on segregation, crystallinity and permselectivity.

2. Experimental

2.1. Chemicals

The dianhydrides: pyromellitic dianhydride (PMDA); 3,3',4,4'- biphenyltetracarboxylic dianhydride (BPDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA or BKDA) and the diamine 4,4'-oxydianiline (ODA) were purchased from Aldrich. These chemicals were purified by sublimation at high vacuum just before use. Poly oxyethylene bis(amine) (JeffamineED-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 hours and stored in a desiccator at vacuum until use. Anhydrous N-methyl pyrrolidinone (NMP), to be used as polymerization solvent, was purchased from Sigma-Aldrich Co. Figure 1 shows the chemical structure of the monomers.

Figure 1.- Chemical structure of the monomers used in this work.

2.2. Synthesis of copoly(ether-imide)s

The samples were synthesized by combination of the aliphatic diamine (PEO) with the aromatic diamine (ODA), and different dianhydrides (BPDA, BKDA and PMDA). The corresponding copoly(ether-imide) will be nominated by adding the dianhydride abbreviation and the w/w ratio between the aliphatic/aromatic diamines. Thus, BKDA_1/1 refers to the sample BKDA-PEO2000-ODA with a 1:1 weight ratio of the aliphatic diamine to the aromatic one, which corresponds to a mass proportion of PEO in the final copolymer of around 28%.

Diamine-terminated poly(oxyethylene oxide) (PEO2000) (x mmol), and 4,4'-oxydianiline (ODA) (y mmol) in weight ratios 1:1, 2:1, and 4:1 were dissolved in anhydrous NMP ($5 \text{ mmol } (x+y)/10 \text{ mL}$) 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 the corresponding dianhydride (BPDA, BKDA or PMDA) ($x+y$ mmol) was added and the mixture was stirred overnight at room temperature. During this time the dianhydride completely dissolved and the solution reached high viscosity. Table 1 records the proportions of PEO and the acronym for each of the polymers synthesized in this work.

Table 1. Polymers synthesized in this work.

2.3. Preparation of the copolyimide dense films.

The resultant viscous polyamic 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 hours in a vacuum oven, in order to get a complete imidization. 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 Perkin Elmer Spectrum One infrared spectrometer equipped with an ATR accessory. 16 scans were performed at a resolution of 4 cm^{-1} and were averaged to get the FTIR spectra.

A Thermal Analysis Q500 instrument was used for thermogravimetric study of the copolymers (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, with an initial heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under a flux of nitrogen, where the heating rate is automatically adjusted in response to changes in the rate of weight loss, which results in improved resolution.

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 aluminum pans. Samples were heated with the following cyclic method in order to monitor the changes in thermal properties with thermal treatment: from $25\text{ }^{\circ}\text{C}$, the sample was heated at $10\text{ }^{\circ}\text{C}/\text{min}$ to a target temperature; once reached, the sample was cooled at the maximum cooling rate accessible for the instrument to $-90\text{ }^{\circ}\text{C}$, held at this temperature for 15 min and reheated at $10\text{ }^{\circ}\text{C}/\text{min}$ to the next target temperature. The procedure was followed until the last treatment temperature was reached and a final run from $-90\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$ 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.

Thermomechanical (TMA) tests were performed in a Rheometric Scientific instrument model DMTA V. Rectangular test pieces of 3 mm width and 20 mm length were cut

from films. A distance of 10 mm was set between fixation clamps. Runs were carried out from ambient temperature at 2 °C/min with a static stress of 0.5, 1.5 and 3 MPa for copolymers with weight ratios 4:1, 2:1, and 1:1 respectively. With these stresses, the samples had an initial strain of less than 1% at 50°C.

Tensile properties were measured in a MTS Synergie 200 testing machine equipped with a 100 N load cell. Rectangular test pieces of 3.5 mm width and 25 mm length were cut from films. A crosshead speed of 5 mm/min was used. Strain was measured from crosshead separation and referred to 10 mm initial length. At least six samples were tested for each copolymer at room temperature.

The permeability, P, for CO₂ and N₂ was determined by using a permeator with constant volume which uses the *time-lag* operation method. The measurements were carried out at 3 bar and 30 °C. A sketch of the device and the analyzed method used has been described in previous studies [20].

3. RESULTS AND DISCUSSION

3.1. Copoly(ether-imide)s imidization

After the films were dried overnight, they were annealed at different temperatures (160, 200 and 250 °C) to almost complete removal of the solvent, and infrared spectra (shown in Figure 2) were recorded to check for the progress of imidization. After this process, the polymer films resulted to be insoluble in dimethyl acetamide (DMAc), NMP, Hexane, Toluene, tetrahydrofuran (THF) and dichloromethane.

Figure 2.- FTIR spectra for the copolymer with a 1:1 proportion of a diamines, treated at 160 °C.

Under the commented protocol, the films were almost completely imidized according to their FTIR spectra (within the detection limits of the FTIR technique) at 160 °C as it was shown in previous studies [21]. For the synthesized copolymers, few differences were observed. Common bands appeared in the spectra: 2880 cm⁻¹ (aliphatic C-H

stretching), 1774 cm^{-1} (symmetric stretching of C=O imide groups), 1712 cm^{-1} (asymmetric stretching of C=O imide groups), 1370 cm^{-1} (C-N stretching of imide groups), 1250 cm^{-1} (twisting CH_2), 1090 cm^{-1} (C-O stretching), 840 cm^{-1} (rocking CH_2) and $720\text{-}750\text{ cm}^{-1}$ (imide ring deformation different for each dianhydride). For the BKDA copolymers a new band appeared at 1660 cm^{-1} which is related to the stretching of the ketone group of BKDA.

3.2. Thermal Stability

Thermogravimetric analysis was performed to evaluate the thermal stability of the synthesized copolymers. Dynamic runs in High-Resolution mode, in a nitrogen atmosphere, for fully imidized copolymers (annealed at $160\text{ }^\circ\text{C}$ for 6 hours) showed a weight loss pattern consisting of three consecutive steps (see Figure 3): an initial loss from ambient temperature to $300\text{ }^\circ\text{C}$; a second loss from $300\text{ }^\circ\text{C}$ to $460\text{-}480\text{ }^\circ\text{C}$; and a third loss from $460\text{-}480\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$.

Figure 3.-TGA curves in dynamic conditions of copolymers having different aromatic dianhydride annealed at $160\text{ }^\circ\text{C}$ for 6 h.

The first loss can be attributed to the absorbed water plus the residual solvent trapped in the film. The weight change for this step was in the order of 2 to 2.5 % [22]. The second loss stage, after correcting for the first one, agreed with the theoretical contribution of poly(ethylene oxide) bis(amine) entering the copolymer composition [23], within a 2% error (see Table 1), and it was therefore assigned to the loss of polyether block sequences. The third and final stage of weight loss was due to the thermal decomposition of the remaining aromatic polyimide segments.

TGA analysis confirmed that the polyether chains are much less thermally stable than the aromatic segments, as already found for another copoly(ether-imide)s based on poly(ethylene oxide) [16] and therefore a selective degradation of the polyether moiety can be performed in these copolymers. The temperature of maximum weight loss rate took place between $360\text{-}380\text{ }^\circ\text{C}$ for all copolymers. This temperature increased when the amount of aliphatic diamine decreased. Similarly, the char residue at $800\text{ }^\circ\text{C}$ increased with the increase of the aromatic content in the copolymer.

3.3. Calorimetric Studies

The samples were heated in a DSC instrument with a cyclic method in order to monitor the changes in their thermal properties with thermal treatment [16]. All the copolymers showed only the T_g , and in some cases the melting temperature, T_m , for the poly(ethylene oxide) segments, and no transition for the aromatic polyimide segments could be detected.

Changes in the polyether T_g were observed with thermal treatment as a function of the dianhydride and the amount of PEO. In Figure 4, the change in T_g for the PMDA series is shown. The T_g value decreased always when the PEO content increased, as expected, and for copolymers PMDA_2/1 and PMDA_4/1 the value after treatment at high temperatures, above 250 °C, reached the expected value [24] for a PEO chain of 2000 g/mol with restricted movement at the chain ends. For copolymer PMDA_1/1 the final value was higher, indicating some degree of mixing of the segments. Similar behavior was found for the BPDA and BKDA series, but the minimum T_g value reached was higher than for the PMDA series, around -50 °C for 2:1 and 4:1 PEO content and between -45 to -50 °C for 1:1 PEO content. According to these results it seems clear that more rigid dianhydrides would lead to more independent or segregable phases especially at high PEO proportions.

Figure 4.- T_g for PEO in the copolymers of the PMDA series annealed at 160 °C, 6h, after “instantaneous” treatment at different temperatures

A clearer picture about the phase-separated structure of these copolymers can be deduced from the melting endotherm of the PEO segments. In Figure 5, the percentage of PEO crystallinity is represented. Copolymers with 1:1 PEO content did not show PEO crystallinity, and for the other PEO contents, the higher the treatment temperature, the higher the amount of crystallized PEO. As expected, series with higher PEO content (4:1) were more crystalline than series with lower PEO content (2:1), but dianhydride had a strong effect on crystallinity. Copolymers based on PMDA dianhydride were more crystalline than copolymers based on BPDA, and the latter were more crystalline than copolymers based on BKDA. Thus, the increase in the rigidity of the structure of

the dianhydride, results in a better phase-separated morphology. The sequence of increasing rigidity (and segregation and crystallinity) is (see Figure 1):

BKDA<BPDA<PMDA

Figure 5.- Percentage of PEO crystallinity for copolymers annealed at 160 °C, 6h, after “instantaneous” treatment and different temperatures

The temperature of the maximum of the endotherm is shown in Figure 6. It seems clear that the melting point did not follow the same tendency as shown by crystallinity (see Figure 5). It also worth to note that the temperature of disappearance of crystalline phase was always below ambient temperature and therefore PEO segments were amorphous at room temperature. Copolymers based on BPDA melted at higher temperature than copolymers based on BKDA and copolymers based on PMDA melted at lower temperature than the other ones. This result can be explained in terms of the size of the crystals that strongly influence the melting point. It has already been found for similar copolymers, based on diamines of different rigidity, that diamines with higher rigidity had lower T_g values and lower melting points for the PEO segments [16]. SAXS analysis demonstrated that for these diamines the phase-segregated morphology was better than for a less rigid diamine, and that the lower melting point was due to a lower size of the segregated aliphatic phase. Thus, for these copolymers based on different dianhydrides, the PMDA (the most rigid dianhydride) copolymers are expected to have the phase-separated structure with the lowest characteristic length (lowest T_m), and the BKDA copolymers to show the highest spacing characteristic lengths (highest T_m). Thus, from the DSC results it can be deduced that PEO segments are in a separated phase of relatively high purity at any PEO content in the copolymer [23].

Figure 6.- Temperature on the maximum of the melting endotherm for copolymers annealed at 160 °C, 6h, after “instantaneous” treatment and different temperatures

3.4. Thermomechanical Analysis

Thermomechanical analysis was carried out in order to detect the glass transition temperature of the aromatic polyimide hard segments, which was not detected by DSC. Several criteria can be chosen to determine the transition temperature. For example, it could be taken as the minimum in the first derivative of the strain vs. temperature curve, or the zero value in the second derivative. With the former criteria, the values were not clearly resolved, so that we decided to choose a different criterion, the temperature when strain is 10 times that of the sample at 100 °C, which gives lower transition values than the other two mentioned criteria [23]. This criterion can be accepted at least for comparative purposes.

For all the copolymers, the T_g of the aromatic polyimide part was well above ambient temperature (from 193°C for BKDA_4/1 to 293°C for PMDA_1/1), although lower than the corresponding T_g for the corresponding pure aromatic polyimide homopolymer, BPDA-ODA, BKDA-ODA and PMDA-ODA. This is due to the lower polymerization degree of the polyimide moiety in the copolymers and, consequently, to the lower length of the aromatic polyimide segments as compared to the corresponding homopolymer and to the possible inclusion of some polyether segments in the polyimide domains (Marcos-Fernández et al., 2010). The T_g of the aromatic portion of the copolymer clearly increased when the PEO content decreased (e.g. 213 °C for PMDA_4/1, 249 °C for PMDA_2/1 and 293 °C for PMDA_1/1). All samples have the same aliphatic polyether, thus the differences can only be due to the differences in the aromatic polyimide segments. The order of the aromatic T_g obtained for the copolymers in this work were:

Proportion 1:1 > Proportion 2:1 > Proportion 4:1

PMDA copolymers > BPDA copolymers > BKDA copolymers

The aromatic T_g increased with the rigidity of the dianhydride, so the more rigid PMDA copolymers had higher T_g for the aromatic segments than for the rest of the copolymers.

3.5. Mechanical Properties

In general, the mechanical properties were good for copolymers 1:1 and 2:1, and reasonable for copolymers 4:1. As expected, the maximum stress and the modulus

decreased when the PEO content increased (see Table 2). The strain was reasonably high for all copolymers except for BPDA_4/1. For this copolymer, the prepared film was the thinnest of all series and therefore, the material was more sensitive to defects that could produce a premature failure. No trend in the mechanical properties with respect to the dianhydride was found.

Table 2. Mechanical properties of the copolymers synthesized in this work.
--

For this type of copolymers, it has been shown that decreasing the PEO content in the copolymer increases the mechanical properties, approaching that of the pure aromatic polyimide homopolymer [23].

3.6. Gas transport properties

In agreement with our previous results for other similar aliphatic-aromatic copoly(ether-imide)s [25, 26], the copolymers prepared and studied here showed an improvement in permeation properties with the increase of the temperature of annealing. Results showed a direct correlation between annealing temperature and permeation properties due to the improvement on the phase segregation.

In general, the highest increase in permeability was found for the highest annealing temperature, when most of the residual solvent was released and the improvement in the phase separation was greater. For samples containing the dianhydride BKDA, the evolution was smaller, resulting probably from a poorer ability to produce phase segregation. Always, at low PEO contents in the copolymer, the effect of the segregation was very significant, see Figure 7. In this Figure and in Figures 8, 9, and 10, the values of permeability and selectivity for the homopolymers BPDA-ODA, BKDA-ODA, PMDA-ODA and for pure PEO are shown in order to obtain a clear comparison. The permeability and selectivity of pure homopolymers were taken from literature [8, 27, 28]. Higher phase segregations produced an increase of the permeability to different gases. According to permeability, the ability of segregation follows this order: BKDA<BPDA<PMDA, in agreement with DSC results.

Figure 7.- Evolution of the CO₂ permeability as a function of the temperature of annealing for the copolymers with a weight ratio 1:1 between diamines.

In the case of the samples annealed at 250 °C, the sample containing the PMDA dianhydride showed a carbon dioxide permeability three times higher than that of the sample containing the BKDA dianhydride. Therefore, for low PEO content, the contribution of the aromatic part is quite important to determine the thermal and thermomechanical properties, but also for the contribution to the segregation and permeability.

Figure 8 shows the evolution of CO₂ permeability as a function of the proportion of PEO in the copolymers. In this case, the data have been represented for samples annealed at 250 °C, when the phase segregation for these polymers is almost complete. As already reported in other copoly(ether-imide)s, the permeability increases when the PEO content in the copolymer is higher. When the aliphatic to aromatic diamine weight ratio was 1:1 and 2:1, the highest permeability was obtained for the samples containing PMDA, and the lowest value was obtained for samples derived from BKDA. This must be due to their different ability to segregate. As mentioned, the BKDA dianhydride is the less rigid, and for this reason the packing between the chains is poorer, leading to a less efficient segregation. The PMDA dianhydride, by contrast, is more rigid and consequently the phase segregation is more efficient. For the dianhydride BPDA intermediate results between PMDA and BKDA were found.

Figure 8.- Evolution of the CO₂ permeability as a function of the PEO content.

Moreover when the PEO content was high, 4:1, the copolymers showed similar behavior. In this case, the permeability was practically the same (assuming that the PEO content is not exactly the same) regardless of the type of dianhydride used. This can probably be explained by assuming that the aliphatic phase forms an almost-continuous phase in the polymer with no significant influence of the aromatic phase on the permeability of the copolymer.

For gas selectivity, the observed trend was analogous to the tendency shown by permeability. Figure 9 describes the evolution of CO_2/N_2 selectivity as a function of PEO content in the copolymer for the samples annealed at 250°C . Differences were observed for the 1:1 and 2:1 samples whereas for 4:1 samples, selectivity values were similar for all the dianhydrides.

Figure 9. Evolution of the CO_2/N_2 selectivity as a function of the PEO content.

To facilitate the evaluation of the permeation properties of the copolymers, the most significant and comprehensible way of showing the level of gas separation performance is the Robeson's plot [29]. In this representation, see Figure 10, the distance to the upper bound can give an idea of the compromise between permeation and selectivity of the samples.

Figure 10.- CO_2 permeability vs CO_2/N_2 for the copolymers synthesized in this work annealed at 250°C , and for the homopolymers (BPDA-ODA, BKDA-ODA, PMDA-ODA and PEO). Arrows correspond to increasing the PEO content. PIs refer to the corresponding polyimides.

For these copolymers it can be seen that regardless of the starting aromatic homopolymer, the values obtained for samples with a 4:1 ratio are practically the same, with only the aliphatic portion affecting the permeation properties. Thus, as long as the copolymer is able to undergo complete phase segregation, the behavior will be similar.

A good material should give permeability values as close as possible to the values of PEO, especially when CO_2 is involved due to the favorable interactions between PEO and carbon dioxide. The permeability increased always with the percentage of PEO in the sample, and at higher percentages of PEO, these copolymers gave both high permeability and selectivity that placed them very close to the corresponding upper bound.

4. Conclusions

A set of new copoly(ether-imide)s were prepared by the reaction between an aromatic diamine (ODA), an poly(ethylene oxide) diamine (PEO-2000) and different aromatic dianhydrides (BPDA, BKDA and PMDA) of different rigidity. While the aromatic phase contributed to the mechanical and thermal stability of the polymer, the aliphatic phase contributed to high CO₂ permeability.

Compared to pure aromatic polyimides, a relatively low temperature, 160°C, was enough to produce a whole imidization. The thermal stability in inert atmosphere was above 300°C, showing a two-step decomposition, being the PEO segments the less stable units.

These copolymers presented a phase separated structure. The occurrence in DSC of PEO related transitions, and the T_g values obtained, demonstrated the existence of a relatively pure PEO phase with increasing purity at higher treatment temperature, increasing PEO content and increasing rigidity of the dianhydride. PEO segments were amorphous at room temperature, and their melting point depended mainly on the size of the separated phases. TMA measurements proved the existence of an aromatic polyimide phase, with T_g values above 190°C that increased with the increase in the rigidity of the dianhydride and the decrease in PEO content. In summary, an improvement of the segregation produced a purer PEO phase, which was reflected in a lower aliphatic T_g, and a purer aromatic phase, which showed a higher aromatic T_g.

Regardless of the PEO proportion, the mechanical and thermal properties of the copolymers were dependent on the rigidity of the used dianhydride. Thus, higher dianhydride rigidity produced better mechanical properties and better segregation in phases at lower temperatures. The overall mechanical properties hinged mainly on PEO content and ranged from good at lower PEO contents to fair at high PEO content.

Permeabilities and CO₂/N₂ selectivity increased with the increase in the temperature of annealing due to the improvement on the phase separation, which (in agreement with DSC results) depended on the PEO content and the rigidity of the dianhydride. For high PEO content, permeability and selectivity values approached quite closely the values for pure PEO, and placed these copolymers close to the Robeson upper bound. For PEO contents below 50%, the more rigid dianhydride, PMDA, produces better segregation,

and in turn higher permeability values. For PEO proportions over 50 %, the permeability obtained were similar regardless of what dianhydride was used. In this case, the permeability only depends on the PEO percentage in the polymer.

These results show that it is possible to obtain PEO copolymers with controlled structures. Thus, the properties can be tuned to some extent by simply varying the aromatic composition in the copolymer. Besides, it is possible to control several parameters: cost, processability, solubility and other factors in order to adapt these copolymers to any specific application and process.

There are different strategies to improve the permselective properties in this kind of PEO copolymers. The first one is to increase the PEO content in the copolymer (keeping good enough mechanical properties for a specific application). The second way would be the formation of copolymers from homopolymers with optimal permeabilities and selectivities for each targeted couple of gases that could segregate at relatively low temperatures.

5. Acknowledgements

We are indebted to the Spanish Junta de Castilla y León for financing this work through the GR-18 Excellence Group Action and to the Ministry of Science and Innovation in Spain for their economic support of this work (MAT2008-00619/MAT, MAT2010-20668/MAT, MAT2011-25513/MAT and CIT-420000-2009-32). We also acknowledge financial support from the program Consolider Ingenio 2010 (project CSD-0050-MULTICAT). The help provided by Sara Rodriguez in measuring gas permeability and selectivity is greatly appreciated. Alberto Tena thanks CSIC for a predoctoral JAE fellowship.

6. References

- [1] Baker RW. Future Directions of Membrane Gas Separation Technology. *Industrial & Engineering Chemistry Research*. 2002;41(6):1393-1411.
- [2] Bessonov MT, Koton MM, Kudryavtsev VV, Laius LA. *Polyimides: Thermally Stable Polymers*. New York: Consultants Bureau; 1987.

- [3] Favre E. Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? *Journal of Membrane Science*. 2007;294(1–2):50-59.
- [4] Bounaceur R, Lape N, Roizard D, Vallieres C, Favre E. Membrane processes for post-combustion carbon dioxide capture: A parametric study. *Energy*. 2006;31(14):2556-2570.
- [5] Ghosh MK, Mittal KL. *Polyimides: Fundamentals and Applications*. New York: Marcel Dekker; 1996.
- [6] Wilson D, Stenzenberger HD, Hergenrother PM. *Polyimides*. Glasgow: Blackie; 1990.
- [7] Ayala D, Lozano AE, de Abajo J, García-Perez C, de la Campa JG, Peinemann KV, et al. Gas separation properties of aromatic polyimides. *Journal of Membrane Science*. 2003;215(1–2):61-73.
- [8] Tanaka K, Kita H, Okamoto K, Nakamura A, Kusuki Y. Gas permeability and permselectivity in polyimides based on 3,3',4,4'-biphenyltetracarboxylic dianhydride. *Journal of Membrane Science*. 1989;47(1–2):203-215.
- [9] Barbari TA, Koros WJ, Paul DR. Polymeric membranes based on bisphenol-A for gas separations. *Journal of Membrane Science*. 1989;42(1–2):69-86.
- [10] Tena A, Lozano AE, Palacio L, Marcos-Fernández A, Prádanos P, de Abajo J, et al. Gas separation properties of systems with different amounts of long poly(ethylene oxide) segments for mixtures including carbon dioxide. *International Journal of Greenhouse Gas Control*. 2013;12(0):146-154.
- [11] Chen HZ, Xiao YC, Chung T-S. Multi-layer composite hollow fiber membranes derived from poly(ethylene glycol) (PEG) containing hybrid materials for CO₂/N₂ separation. *Journal of Membrane Science*. 2011;381(1–2):211-220.
- [12] Hirayama Y, Kase Y, Tanihara N, Sumiyama Y, Kusuki Y, Haraya K. Permeation properties to CO₂ and N₂ of poly(ethylene oxide)-containing and crosslinked polymer films. *Journal of Membrane Science*. 1999;160(1):87-99.
- [13] Minelli M, Giacinti Baschetti M, Hallinan Jr DT, Balsara NP. Study of gas permeabilities through polystyrene-block-poly(ethylene oxide) copolymers. *Journal of Membrane Science*. 2013;432(0):83-89.
- [14] Okamoto K-i, Fujii M, Okamoto S, Suzuki H, Tanaka K, Kita H. Gas permeation properties of poly(ether imide) segmented copolymers. *Macromolecules*. 1995;28(20):6950-6956.
- [15] Suzuki H, Tanaka K, Kita H, Okamoto K, Hoshino H, Yoshinaga T, et al. Preparation of composite hollow fiber membranes of poly(ethylene oxide)-containing polyimide and their CO₂/N₂ separation properties. *Journal of Membrane Science*. 1998;146(1):31-37.
- [16] Tena A, Marcos-Fernández A, Lozano AE, de la Campa JG, de Abajo J, Palacio L, et al. Thermally treated copoly(ether-imide)s made from bpda and alifatic plus aromatic diamines. Gas separation properties with different aromatic diamines. *Journal of Membrane Science*. 2012;387–388(0):54-65.
- [17] Car A, Stropnik C, Yave W, Peinemann KV. Pebax®/polyethylene glycol blend thin film composite membranes for CO₂ separation: Performance with mixed gases. *Separation and Purification Technology*. 2008;62(1):110-117.
- [18] Lin H, Freeman BD. Gas solubility, diffusivity and permeability in poly(ethylene oxide). *Journal of Membrane Science*. 2004;239(1):105-117.
- [19] Reijerkerk SR, Knoef MH, Nijmeijer K, Wessling M. Poly(ethylene glycol) and poly(dimethyl siloxane): Combining their advantages into efficient CO₂ gas separation membranes. *Journal of Membrane Science*. 2010;352(1–2):126-135.

- [20] Tena A, Fernández L, Sánchez M, Palacio L, Lozano AE, Hernández A, et al. Mixed matrix membranes of 6FDA-6FpDA with surface functionalized γ -alumina particles. An analysis of the improvement of permselectivity for several gas pairs. *Chemical Engineering Science*. 2010;65(6):2227-2235.
- [21] Tena A, Marcos-Fernandez A, Palacio L, Cuadrado P, Pradanos P, De Abajo J, et al. Phase Segregation and Gas Separation Properties of Thermally Treated Copoly(ether-imide) from an Aromatic Dianhydride, an Aromatic Diamine and Various Aliphatic Diamines. *Industrial & Engineering Chemistry Research*. 2012.
- [22] Hedrick JL, Carter KR, Cha HJ, Hawker CJ, DiPietro RA, Labadie JW, et al. High-temperature polyimide nanofoams for microelectronic applications. *Reactive and Functional Polymers*. 1996;30(1-3):43-53.
- [23] Marcos-Fernández A, Tena A, Lozano AE, De La Campa JG, De Abajo J, Palacio L, et al. Physical properties of films made of copoly(ether-imide)s with long poly(ethylene oxide) segments. *European Polymer Journal*. 2010;46(12):2352-2364.
- [24] Krellen DW. *Properties of polymers: their correlation with chemical structure, their numerical estimation and prediction from additive group contributions*: Elsevier; 1990.
- [25] Tena A, Marcos-Fernández A, Lozano AE, De La Campa JG, De Abajo J, Palacio L, et al. Thermally segregated copolymers with PPO blocks for nitrogen removal from natural gas. *Industrial and Engineering Chemistry Research*. 2013;52(11):4312-4322.
- [26] Tena A, Marcos-Fernández A, Palacio L, Prádanos P, Lozano AE, de Abajo J, et al. On the influence of the proportion of PEO in thermally controlled phase segregation of copoly(ether-imide)s for gas separation. *Journal of Membrane Science*. 2013;434:26-34.
- [27] Kim TH, Koros WJ, Husk GR, O'Brien KC. Relationship between gas separation properties and chemical structure in a series of aromatic polyimides. *Journal of Membrane Science*. 1988;37(1):45-62.
- [28] Xu Z-K, Xiao L, Wang J-L, Springer J. Gas separation properties of PMDA/ODA polyimide membranes filling with polymeric nanoparticles. *Journal of Membrane Science*. 2002;202(1-2):27-34.
- [29] Robeson LM. The upper bound revisited. *Journal of Membrane Science*. 2008;320(1-2):390-400.

Table 1. Polymers synthesized in this work.

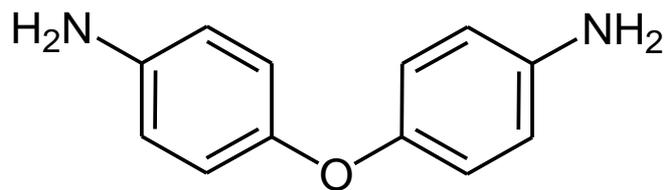
<i>Polymer</i>	<i>PEO/ODA*</i>	<i>Acronym</i>	<i>PEO content (%w)</i>	<i>PEO content (%w)**</i>
BPDA/PEO2000/ODA	1:1	BPDA_1/1	29.2	28,2
	2:1	BPDA_2/1	43.7	43,6
	4:1	BPDA_4/1	58,5	58,2
BKDA/PEO2000/ODA	1:1	BKDA_1/1	28,0	27,5
	2:1	BKDA_2/1	42,4	42,2
	4:1	BKDA_4/1	57,0	56,9
PMDA/PEO2000/ODA	1:1	PMDA_1/1	33,3	31,2
	2:1	PMDA_2/1	48,8	46,4
	4:1	PMDA_4/1	63,6	63,1

* w/w ratio between the diamines aliphatic / aromatic

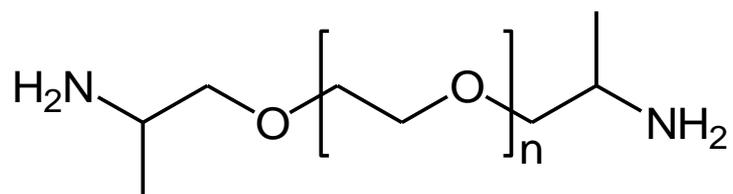
** Calculated by TGA analysis

Table 2. Mechanical properties of the copolymers synthesized in this work.

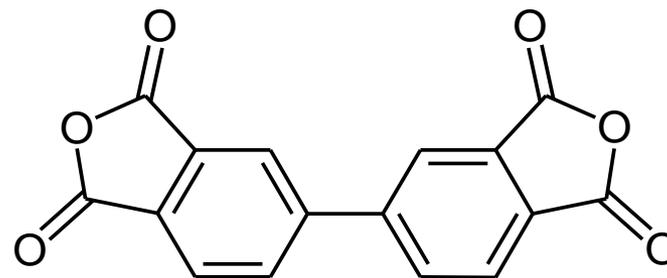
Samples		Strain / %	Modulus / GPa	Stress / MPa
<i>Pis-BPDA</i>	BPDA_1/1	8.4±1.3	1.03±0.16	53±14
	BPDA_2/1	115±15	0.38±0.04	22.1±1.7
	BPDA_4/1	9±2	0.089±0.01	3.2±0.5
<i>Pis-BKDA</i>	BKDA_1/1	56 ± 10	0.89 ± 0.11	66.3 ± 1.0
	BKDA_2/1	270 ± 90	0.59 ± 0.06	36.0 ± 1.1
	BKDA_4/1	390 ± 130	0.127 ± 0.016	19.3 ± 1.8
<i>Pis-PMDA</i>	PMDA_1/1	206 ± 8	0.77 ± 0.07	59 ± 3
	PMDA_2/1	300 ± 60	0.41 ± 0.03	27.1 ± 1.4
	PMDA_4/1	360 ± 80	0.111 ± 0.006	12.0 ± 1.0



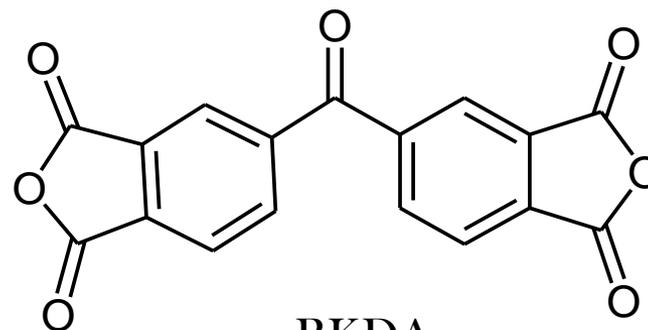
ODA



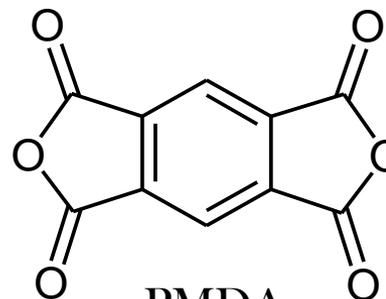
PEO-2000



BPDA



BKDA



PMDA

Figure 1.- Chemical structure of the monomers used in this work.

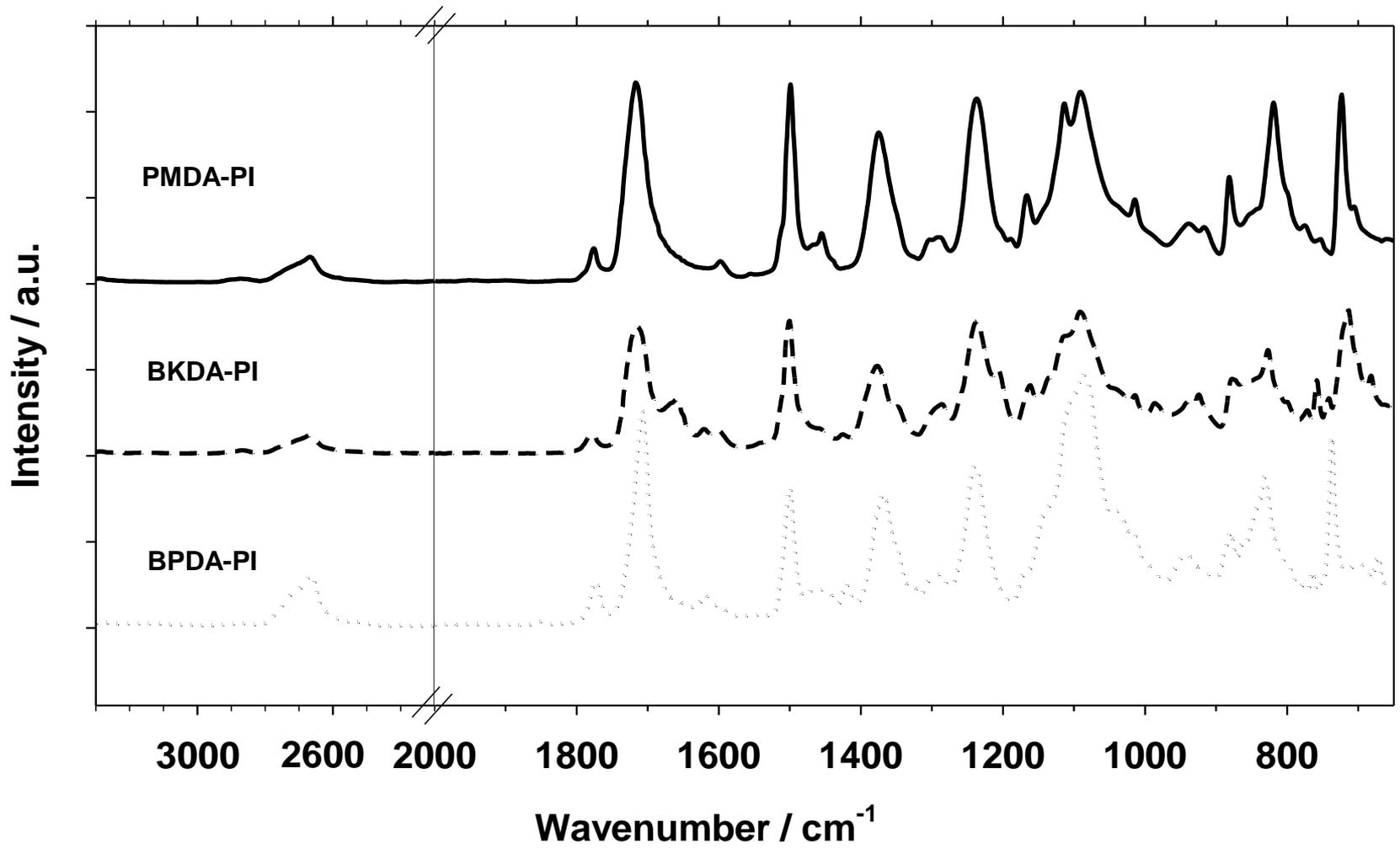


Figure 2.- FTIR spectra for the copolymer having a 1:1 diamines proportion, annealed at 160 °C.

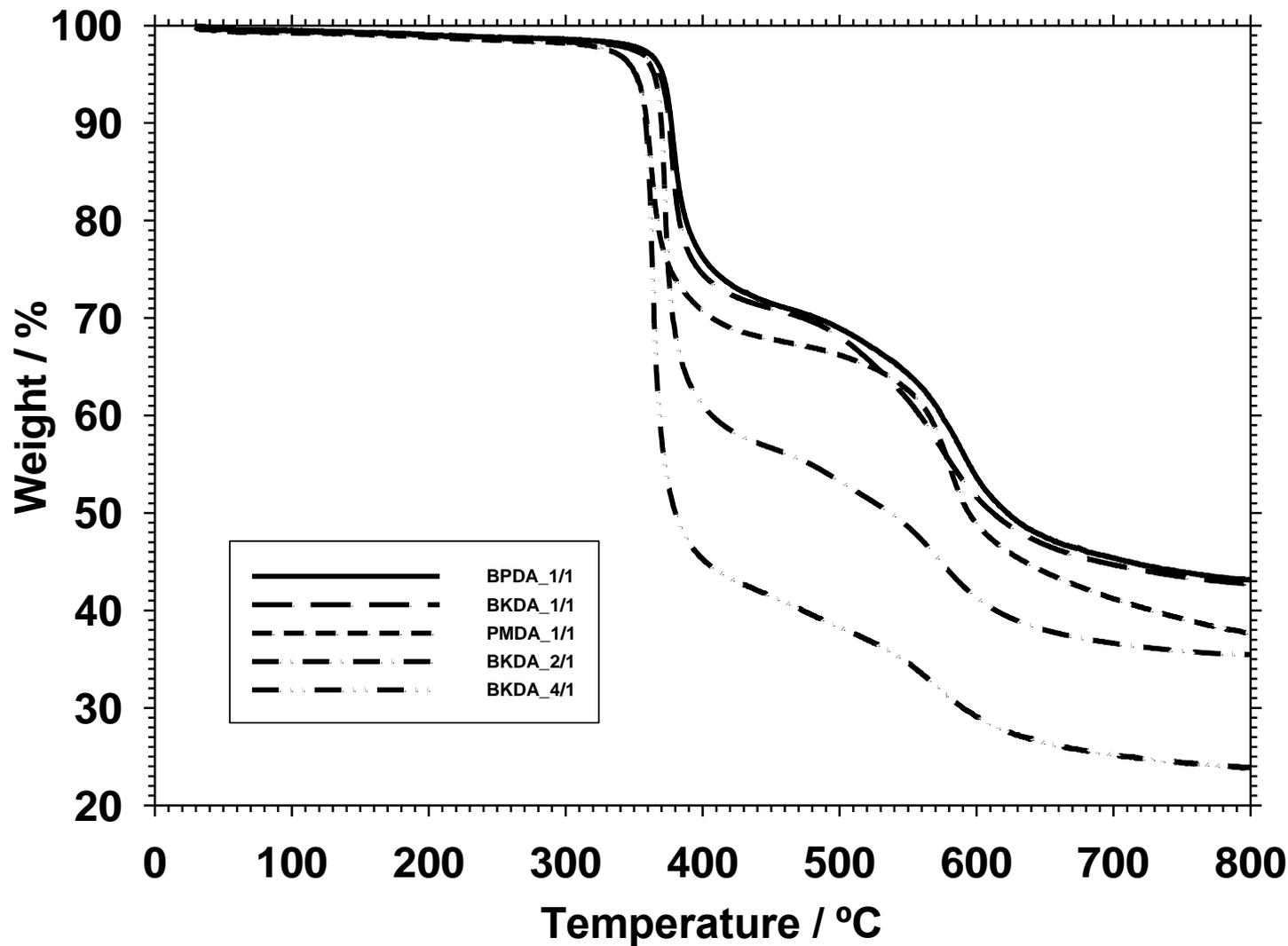


Figure 3.- TGA curves in dynamic conditions of copolymers having different aromatic dianhydride, annealed at 160 °C for 6 h.

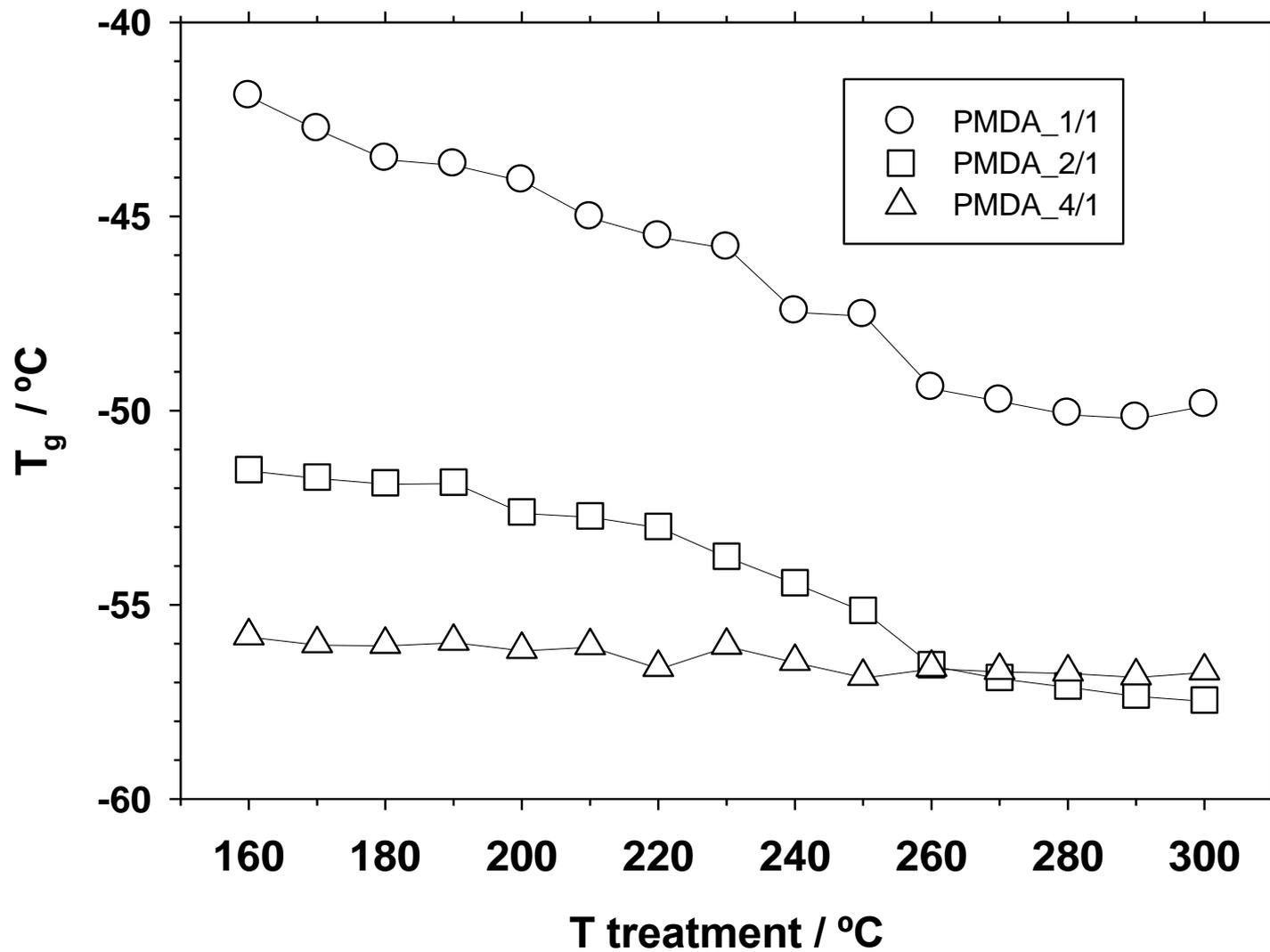


Figure 4.- T_g for PEO in copolymers derived from PMDA annealed at 160 °C, 6h, after “instantaneous” treatment at different temperatures

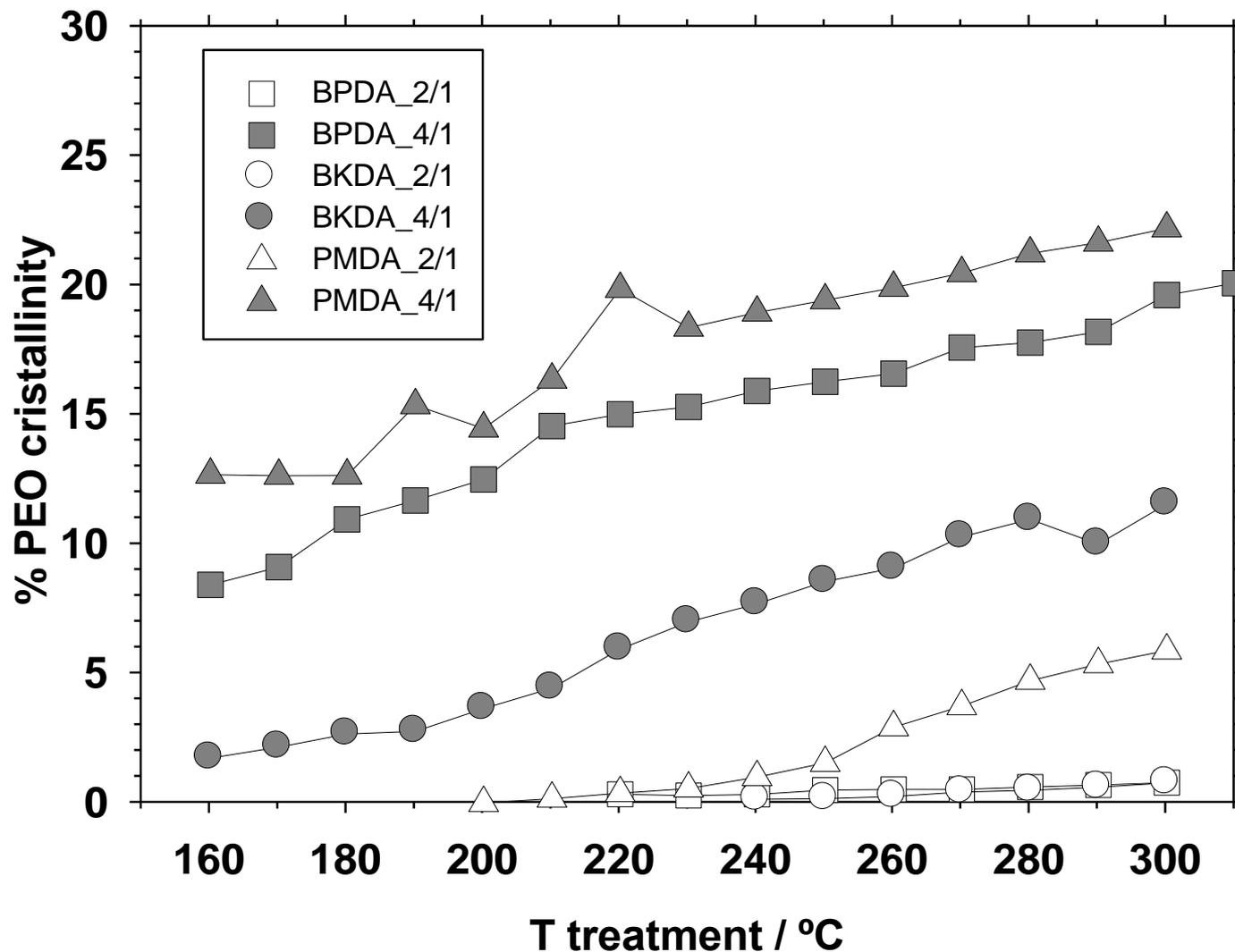


Figure 5.- Percentage of PEO crystallinity for copolymers annealed at 160 °C, 6h, after “instantaneous” treatment and different temperatures

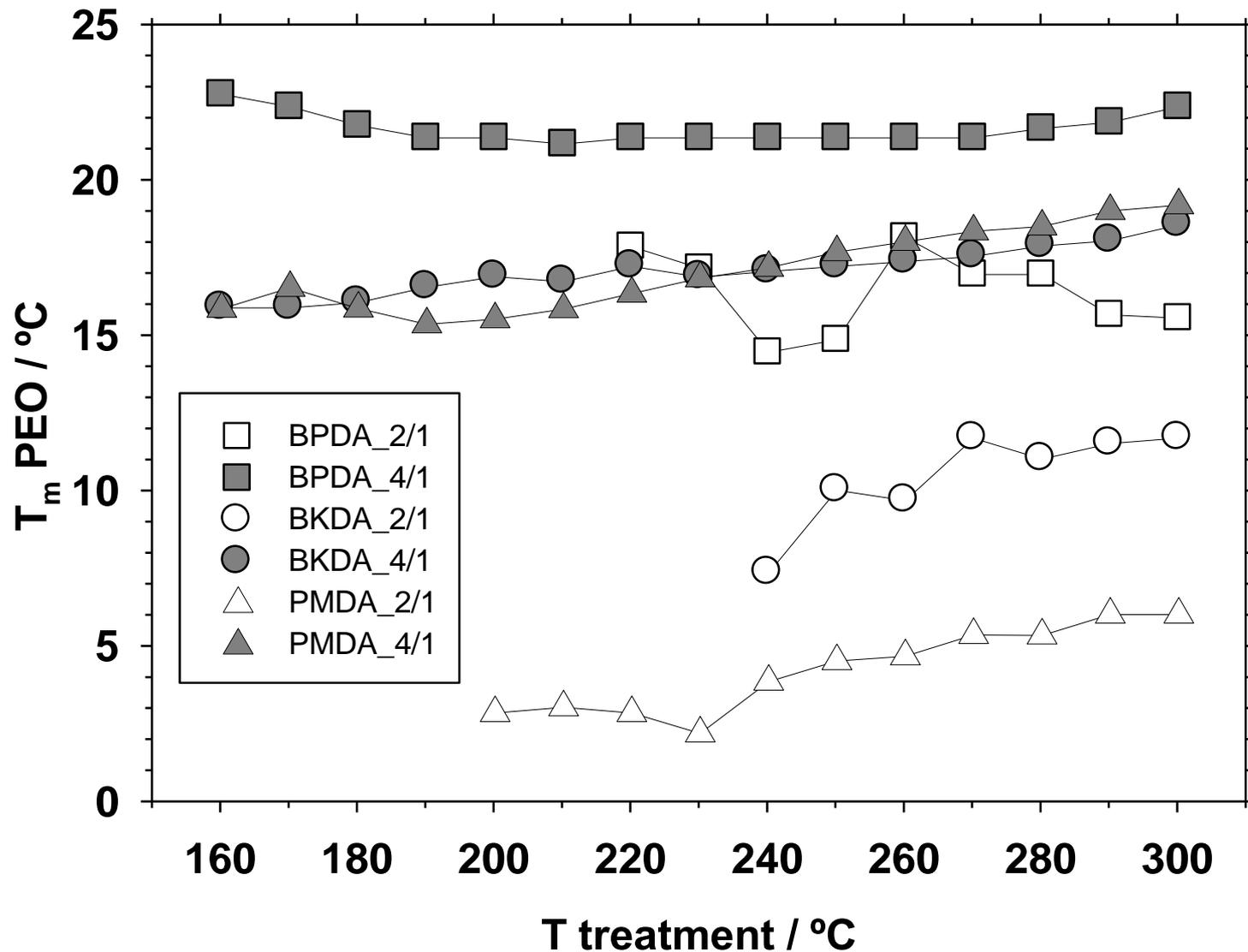


Figure 6.- Temperature on the maximum of the melting endotherm for copolymers annealed at 160 °C, 6h, after “instantaneous” treatment and different temperatures

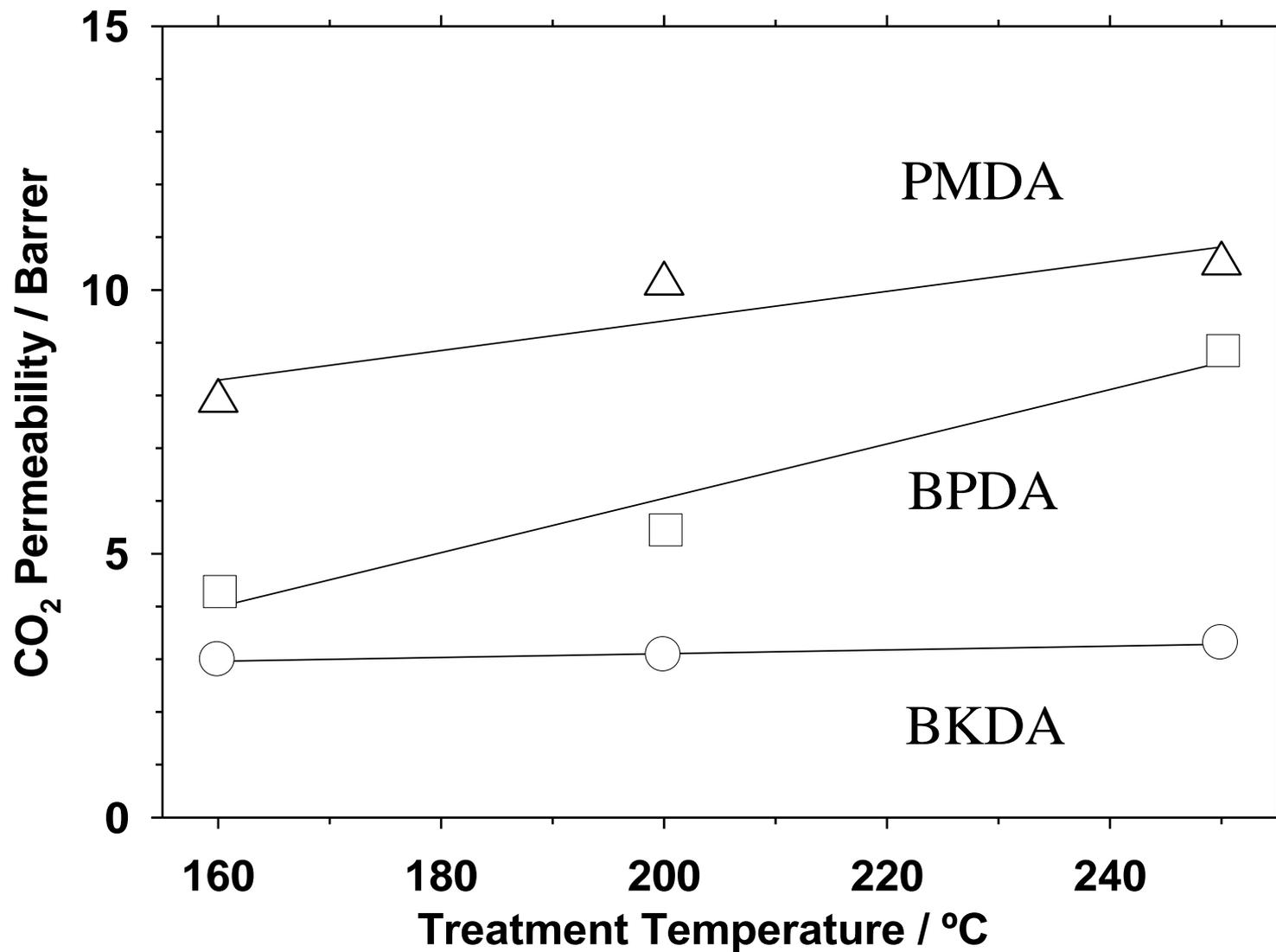


Figure 7.- Evolution of the CO₂ permeability as a function of the temperature of annealing for the copolymers with a 1:1 diamines ratio .

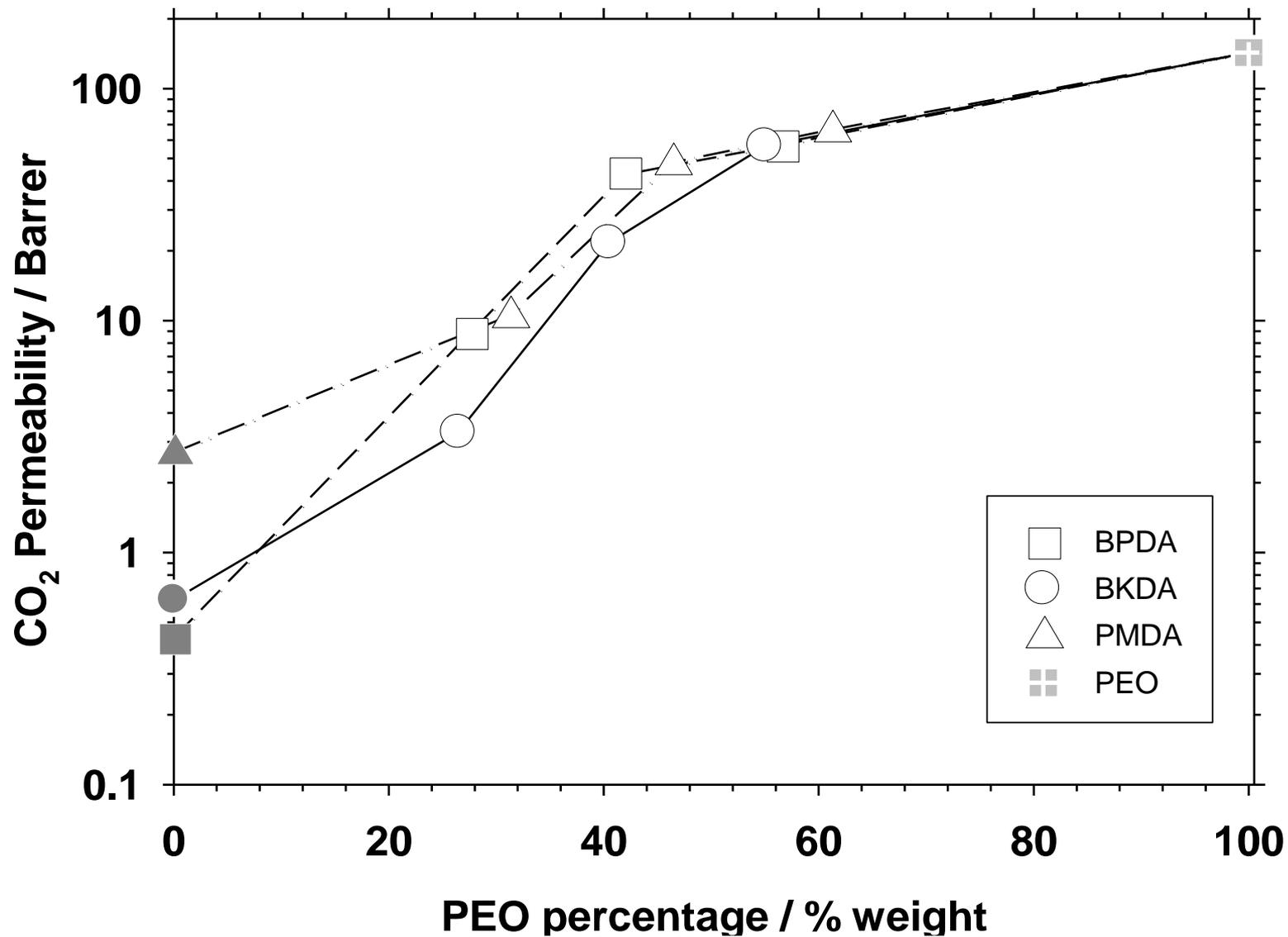


Figure 8.- Evolution of the CO₂ permeability as a function of the PEO content.

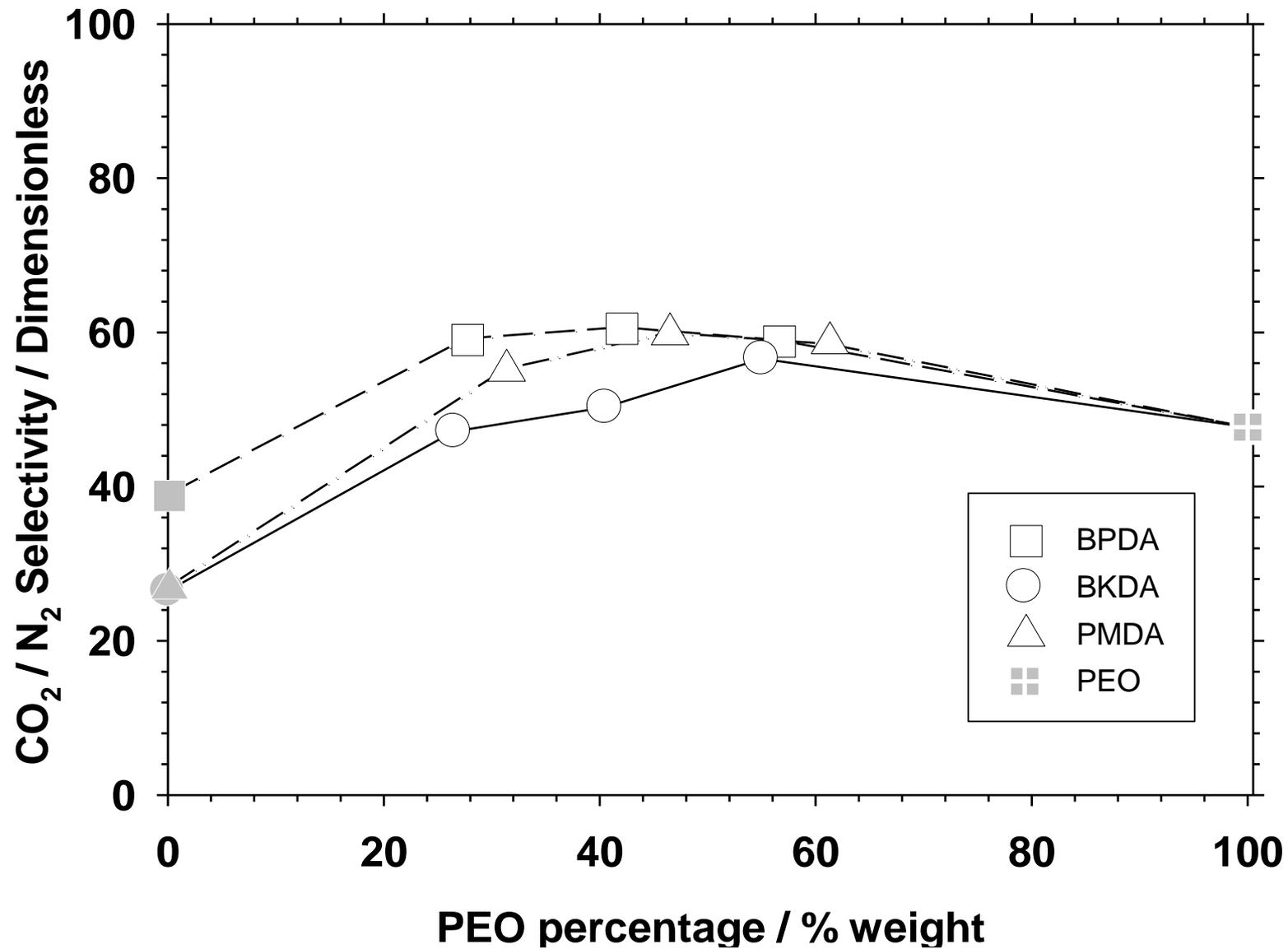


Figure 9.- Evolution of the CO₂/N₂ selectivity as a function of the PEO content.

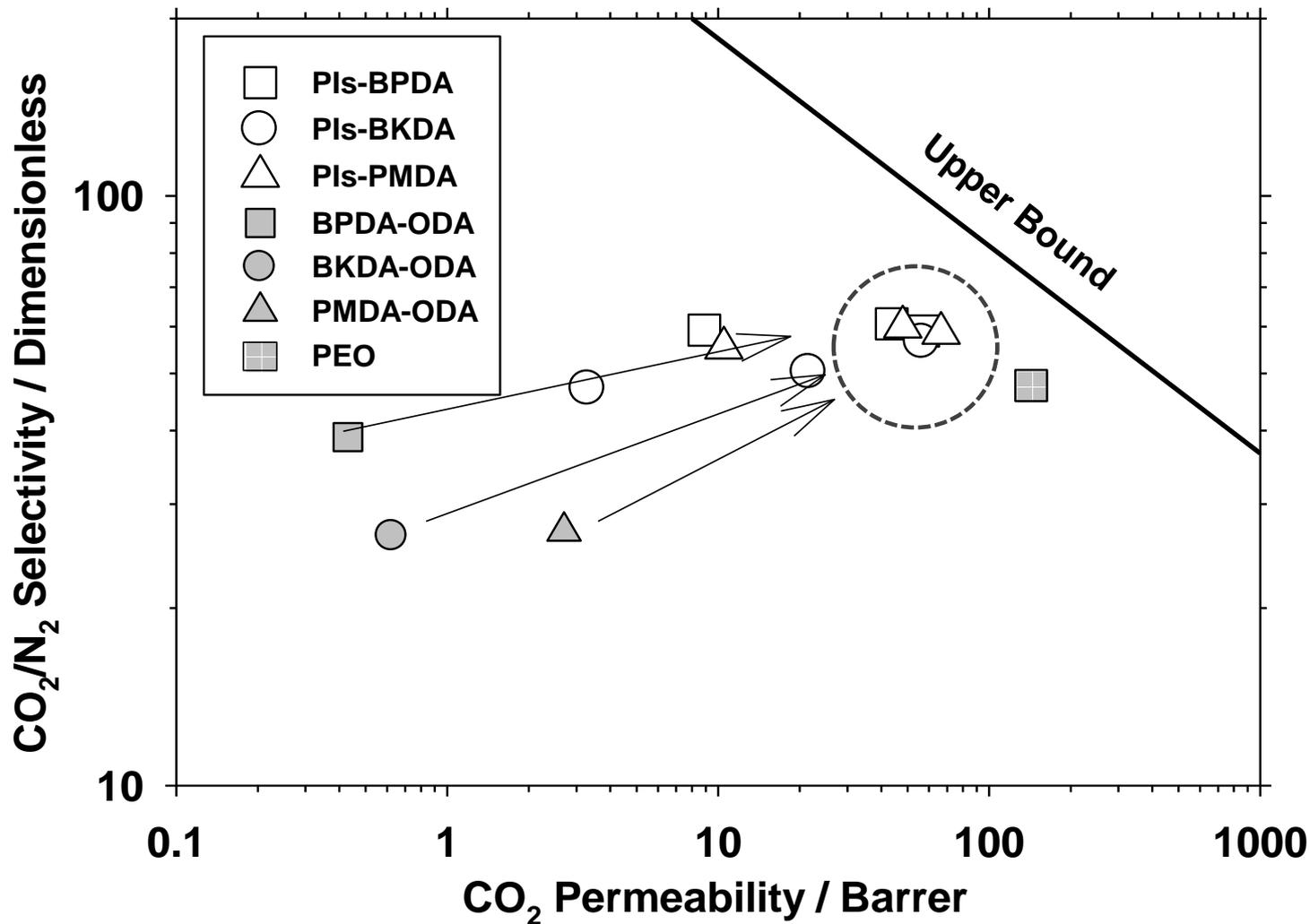


Figure 10.- CO_2 permeability vs CO_2/N_2 for the copolymers synthesized in this work annealed at 250 °C, and for the homopolymers (BPDA-ODA, BKDA-ODA, PMDA-ODA and PEO). Arrows correspond to the increase of the PEO content. Pls refer to the corresponding polyimides.