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Corresponding Author: Dr. ANGEL MARCOS,

Corresponding Author's Institution: Instituto de Ciencia y Tecnologia de Polimeros CSIC

First Author: ANGEL MARCOS

Order of Authors: ANGEL MARCOS; Alberto Tena; Angel E Lozano; Jose G de la Campa; Javier de Abajo; Laura Palacio; Pedro Prádanos; Antonio Hernández

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***Graphical Abstract**

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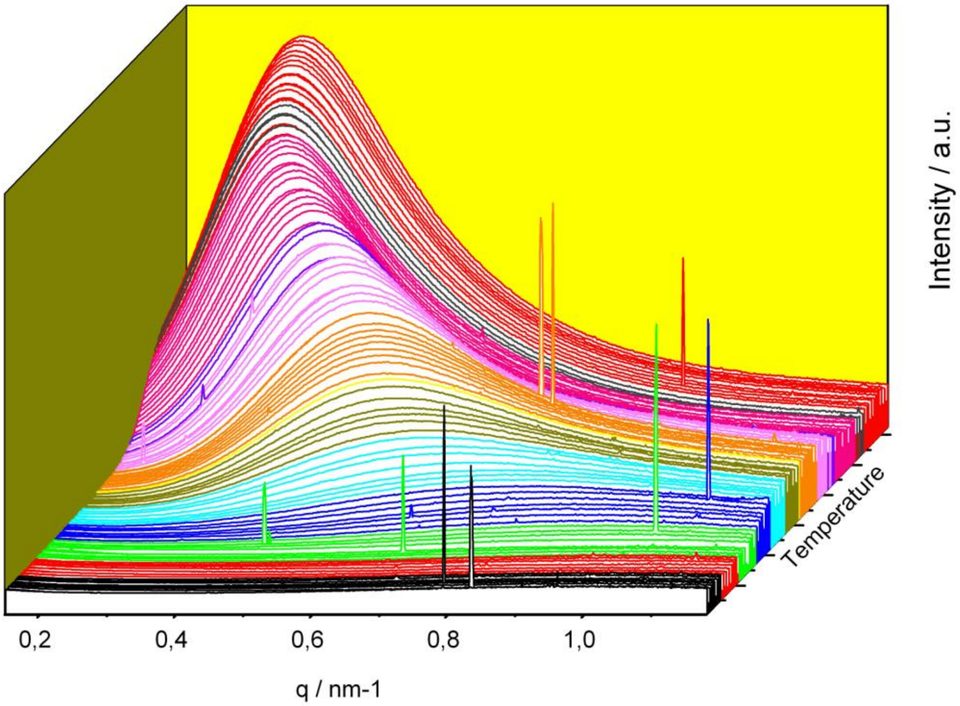

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[1]*Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.*
[2]*Dpto. Física Aplicada, Universidad de Valladolid, Facultad de Ciencias, Real de Burgos s/n, 47071 Valladolid, Spain*
** Corresponding author. Tel.: +34-912-587-555; fax: +34-915-644-853. E-mail address: amarcos@ictp.csic.es (Angel Marcos-Fernández)*

Abstract

Polyimides having long poly(ethylene oxide), PEO, moieties in the main chain have been synthesized by a classical two-steps polycondensation method with good yield and high molecular weight. In contrast with previous works on this topic, essentially full conversion of the polyamic acid to polyimide was attained by heating at relatively low temperatures (around 160 ºC).

These copolyimides undergo an increase of phase separation between the PEO part and the polyimide one after a thermal annealing. This phase separation increases gas separation properties of membranes made up of these copolymers. An exhaustive study of polymer properties as a function of the thermal treatment has been carried out in order to figure out the origin of this behavior. The analysis performed included TGA, DSC, SAXS and mechanical testing.

The polymers studied in this paper have medium thermal stability. In fact, degradation of the polyether chain under nitrogen takes place at temperatures above 300 ºC. However, their thermal stabilities were much lower under oxidant atmosphere.

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INTRODUCTION

Attending to new social and economical necessities such as energy efficiency, global warming and use of currently non-economical resources, the recovery of CO_2 from mixtures is an important industrial objective in view of several aspects such as natural gas reforming, biomedical applications, synthesis gas processes and clean and efficient coal burning. In particular, some gas purifications to be accomplished using new technologies in the near future are: CO_2/N_2 CO_2/H_2 and CO_2/CH_4.

Polymeric membranes have been used in many gas separation processes for mixtures including CO_2 as those mentioned above, because they offer low energy cost, simplicity of operation, and also they present good thermal and mechanical properties. However, for polymeric membranes it has been shown that there is a trade-off between selectivity and permeability, which means that membranes with high gas permeabilities have low selectivities and viceversa [1].

Diverse polyimides having high permeability to CO_2 (P_{CO2}), have been reported [2], but they use to exhibit low CO_2/N_2 selectivity due to the small difference in the effective molecular size of both gases [3,4]. However, recently reported modified polyimides able to undergo thermal rearrangement processes (TR polymers), exhibited extraordinary gas separation properties, including CO2, due to microcavity evolution after thermal treatment [5-7]. The introduction of polar groups that can interact favorably with CO_2, such as amine [8] or carboxyl [9] groups has also proved to be a very efficient method to increase the CO_2/N_2 or CO_2/CH_4 selectivity.

In this regard, poly(ethylene oxide), PEO, is a very attractive polymer due to the strong affinity of CO_2 towards the oxygen of the oxyethylenic units [10], and there have been many recent studies of polymeric membranes containing PEO or similar polar ether segments in carbon dioxide separations [11–26]. Since PEO does not have the mechanical and thermal resistance required for the preparation of thin membranes, research efforts have been carried to incorporate PEO segments into polyurethanes, polyesters, polyamides and polyimides (PI) [14–26]. Block copolymers containing PEO segments are interesting membrane materials since they exhibit high CO_2 permeability and high polar/non polar gas selectivity. In these materials, CO_2 permeation occurs through the PEO-domains (soft segments) whereas the other domains (the polyimide hard segments) contribute to the mechanical strength [14–26].

Okamoto et al. reported for the first time data of PEO-copolyimides for gas separation [19]. The short, rigid aromatic polyimide segments and the flexible polyalkylene oxide segments were phase-separated into two major domains, which increased the selectivity for CO_2/N_2 gas separation [14,20]. These authors explored the effect of the hard segment of PEO-copolyimides on gas separation properties, and they found that copolyimides containing similar PEO weight percent and different chemical structure of the hard segments exhibited similar CO_2/N_2 selectivity (49–53), but different P_{CO2} (117–238 Barrer) [20].

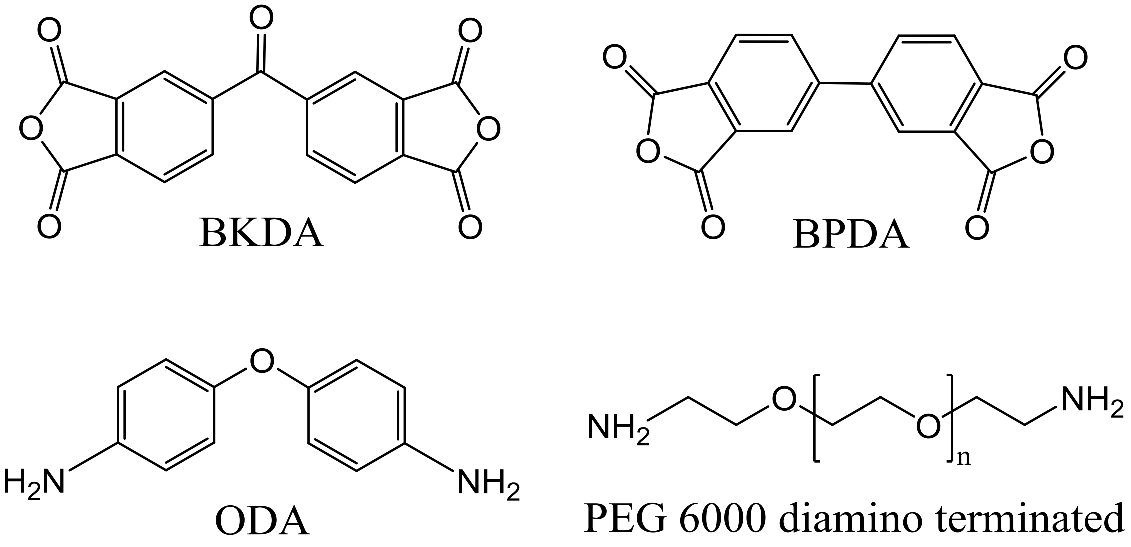
We previously reported preliminary results concerning the promising CO_2/N_2 separation properties of some thermally treated copolyimide membranes containing different PEO content (28–68 wt.%) [27,28]. It was found that, after a programmed thermal treatment, the studied membranes improved their permeability to CO_2 while the CO_2/N_2 selectivity just suffered a small drop.

In this work, we present the details on the physical characterization, including phase separated morphology, of the previously reported copolyimides [28] and some other related results. The study consists of a systematic evaluation of the physical properties of the synthesized copolyimides after different thermal treatments and its relationship with the evolution of the phase separated structure.

EXPERIMENTAL

Chemicals

3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BKDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) were purchased to Aldrich. These products were purified by sublimation at high vacuum just before being used. Polyoxyethylene bis(amine) with nominal molecular weight of 6000 g/mol was kindly donated by Kawaken Fine Chemicals Co., Ltd. (Tokyo, Japan), (PEG-6000 from here on). This polyether was dried at 70ºC 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. Scheme 1 shows the chemical structure of the monomers.



Scheme 1. Chemical structure of the monomers

Synthesis of copoly(ether-imide)s

The procedure for the synthesis of all the polymers in this study was as follows:

- A mixture of polyethyleneoxide bis(amine) 6000 (*x* mmol), PEG-6000, and ODA (*y* mmol) in weight ratios 1:1, 2:1, 4:1 or 6:1 was dissolved in anhydrous NMP (5 mmol (x+y)/10 mL) in a 100 mL three-necked flask blanketed with nitrogen.

- The reaction mixture was cooled down to 0ºC, and under mechanical stirring, a stoichiometric amount of BKDA or BPDA dianhydride (*x*+*y* mmol) was added all at once and the mixture was stirred overnight at room temperature. During this time the dianhydride completely dissolved and the solution reached high viscosity.

- The resultant viscous copolyamic acid solution was diluted with NMP to the appropriate viscosity for casting, filtered through a nominal number 2 fritted glass funnel, degassed, and cast onto leveled glass plates. The resulting films were covered with a conical funnel to avoid fast evaporation of the solvent, dried at 80ºC overnight, and finally treated at 120ºC for 6 hours in a vacuum oven.

Films of the copolymers of 85-150 μm in thickness were obtained. After that, thermal treatments under inert atmosphere were carried out at different temperatures.

In addition to the copoly(ether-imide)s, two pure aromatic polyimides, BKDA-ODA and BPDA-ODA were prepared as references using the same procedure. The films from the pure polyimides were thermally treated to produce imidization with a final step at 285ºC for 1 hour.

In table 1, the complete list of the synthesized polymers, and its denomination throughout this paper, can be found.

Table 1. Polymers synthesized in this work

Dianhydride	**DP* Imide segment**	**Mol ratio PEG-6000/ODA**	**Weight ratio PEG-6000/ODA**	**Denomination**
BKDA	∞	0/100	0/100	BKDA-ODA
BKDA	60.9	30/1	1/1	BKDA 1/1
BKDA	31.0	15/1	2/1	BKDA 2/1
BKDA	16.0	7.5/1	4/1	BKDA 4/1
BKDA	11.0	5.0/1	6/1	BKDA 6/1
BPDA	∞	0/100	0/100	BPDA-ODA
BPDA	60.9	30/1	1/1	BPDA 1/1
BPDA	31.0	15/1	2/1	BPDA 2/1
BPDA	16.0	7.5/1	4/1	BPDA 4/1
BPDA	11.0	5.0/1	6/1	BPDA 6/1

* Theoretical degree of polymerization calculated from the feed ratio

Experimental 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 Thermal Analysis Q500 instrument was used for thermogravimetric analysis (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 10ºC/min under a flux of nitrogen (in some cases with air, as detailed in the corresponding section).

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 5–15mg 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 25ºC, the sample was heated at 10ºC/min to a target temperature; once reached, the sample was cooled at the maximum cooling rate accessible for the instrument to -90ºC, held at this temperature for 15 min and reheated at 10ºC/min to the next target temperature. The procedure was followed until the last treatment temperature was reached and a final run from -90ºC to 80ºC 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.

SAXS measurements were performed at the beamline BM16 at the European Synchrotron Radiation Facility (Grenoble, France). Wave length of the X-ray beam was 0.980 Å. Detector calibration was done with silver behenate ($AgC_{22}H_{43}O_2$), and 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 10ºC/min while the SAXS spectra were recorded. Calibration of temperature gave a difference of approximately 7ºC between the temperature reading at the hot stage display and the real temperature at the sample.

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 10ºC/min with a static stress of 3 MPa.

Tensile properties were measured in a MTS Synergie 200 testing machine equipped with a 100 N load cell. Rectangular test pieces of 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 polymer. Tests were conducted at room temperature and in some cases, when PEO was crystalline at ambient temperature, also at approximately 50ºC, as noted in the corresponding table. The samples were heated in situ by blowing hot air transversally to the cross-section side of the specimen in order to avoid stress on the sample. In this case, temperature was measured with a thermometer close to the specimen.

RESULTS AND DISCUSSION

Copoly(ether-imide)s imidization

Polyethyleneoxide chains are prone to oxidation [29], and therefore, a great care was taken to carry out the imidization. After the films were dried overnight, they were heated at 120ºC for 6 h to almost completely remove the solvent, and infrared spectra were recorded to check for the progress of imidization. Once treated at 120ºC, the polymer films became insoluble in any organic solvent.

Under the commented protocol, membranes with polyether ratios 4/1 and 6/1 were completely imidized according to their FTIR spectrum, but the films with polyether ratios 2/1 and 1/1 did not undergo a full imidization. These latter films were totally imidized (within the detection limits of the FTIR technique) after a further heating at 160ºC during two additional hours. In figure 1, the FTIR spectra of copolyimide BPDA 1/1 and its corresponding poly(amic acid) precursor are shown.

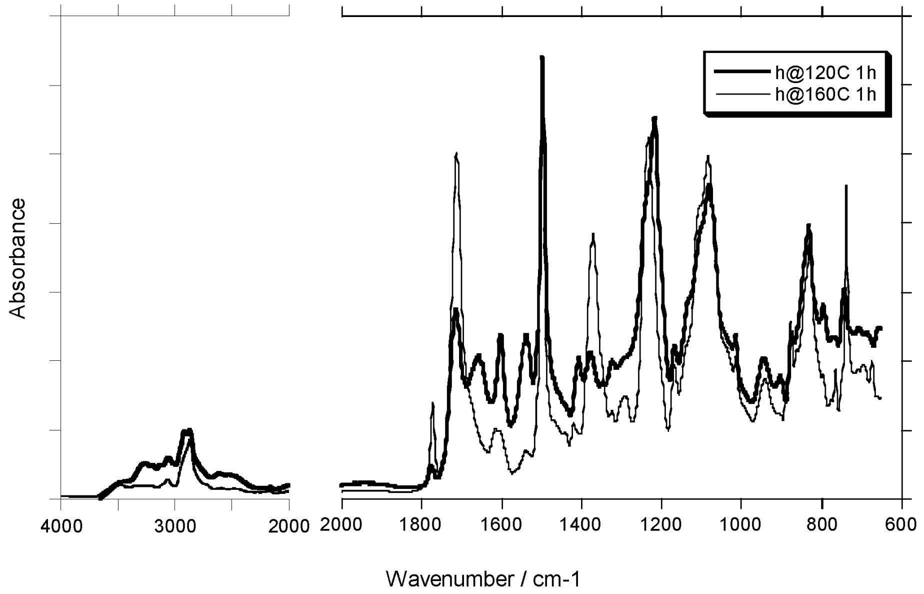


Figure 1. FTIR spectra of copolymer BPDA 1/1 before imidization (thick line) and after the thermal treatment at 160ºC for 2h (thin line).

In this figure, the bands centered around 3257, 2500, 1657, 1603 and 1538 cm^{-1} strongly decrease or disappear, and the bands at 1774, 1713, 1372 and 738 cm^{-1} increase or appear with imidization. The band at approximately 738 cm^{-1} is identificative of BPDA derived imides, and can be found in between 738-742 cm^{-1} in all copolyimides based on BPDA dianhydride [30]. For the BKDA series, a band appears in the FTIR spectrum at 720 cm-1 due to imidization. This band is actually broader than that appearing at 738 cm-1 due to the BPDA derived imides. The rest of the infrared spectra are almost identical for both series except for the peak at 1667 cm-1 that appears in the BKDA series, due to the ketone group linking the aromatic rings in the dianhydride.

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, showed a weight loss pattern consisting of four consecutive steps (see figure 2): an initial loss of up to 2% weight from ambient temperature to 100ºC; a second loss from 100 to 250ºC; a third loss from 250 to approximately 450ºC; and a fourth loss from 450 to 800ºC.

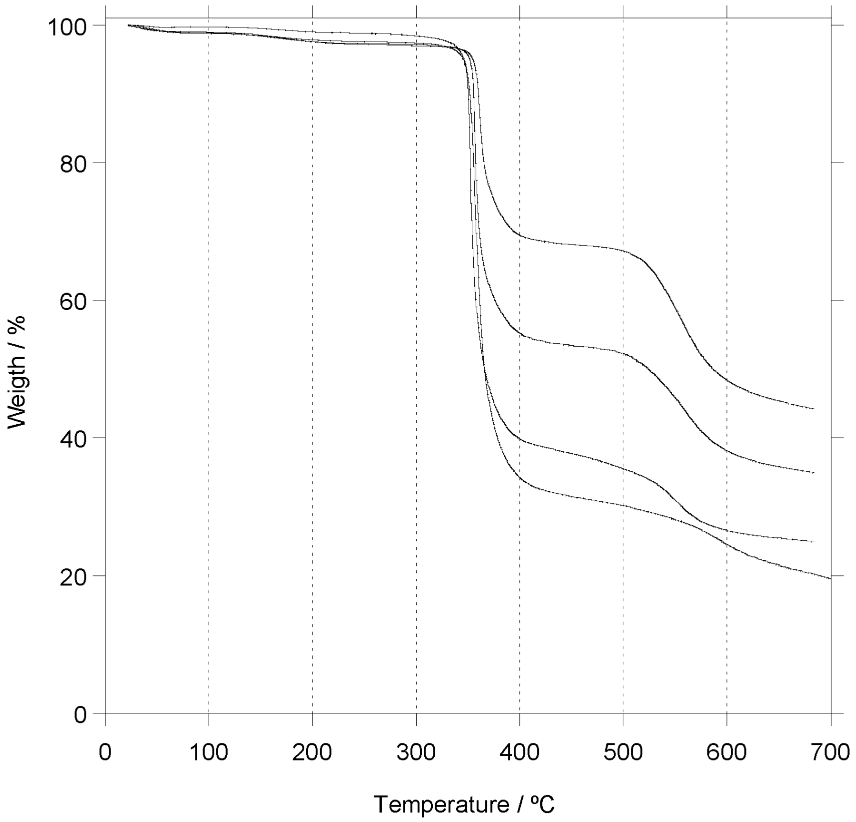


Figure 2. TGA curves in dynamic conditions for copolymers of series BPDA. From top to bottom: 1/1 (treated at 160ºC); 2/1 (treated at 120ºC); 4/1 (treated at 120ºC); 6/1 (treated at 120ºC).

The first loss can be attributed to the adsorbed water in the sample. The second step is thought to be due to both the water from imidization and the solvent trapped in the film. This weight change is very large (4 to 6 % weight) for the 1/1 copolymers, which were partially imidized as exhibited by FTIR. This weight loss step is substantially reduced (to less than 2%) for these copolymers after 2 h treatment at 160ºC. For the rest of the copolymers, this weight loss is also low. If incomplete imidization was the only source for this second weight loss, simple calculations would give a percentage of imidization for the samples treated at 120ºC of 39 to 74%, which is not true based on the FTIR results, that clearly showed that all these samples were virtually fully imidized. The third loss step, after correcting for the two previous weight decrease steps, agrees with the theoretical contribution of polyethyleneoxide bis(amine) 6000 entering the copolymer composition, within a 2% error (see Table 2) and it is therefore assigned to the loss of polyether block sequences. The fourth and final stage of weight loss is due to the thermal decomposition of the remaining aromatic polyimide segments.

Table 2. Total polyether weight loss obtained by TGA for the prepared copolymers.

Copolymer	Theoretical polyether weight in the copolymer (%)	Experimental polyether weight loss (%)
BPDA 1/1	30.0	29.8
BPDA 2/1	45.7	45.2
BPDA 4/1	61.9	61.2
BPDA 6/1	70.2	68.5
BKDA 1/1	28.8	28.3
BKDA 2/1	44.2	43.8
BKDA 4/1	60.4	60.3
BKDA 6/1	68.9	69.1

Thus, TGA analysis confirmed that the polyether thermal stability is much lower than the thermal stability of the aromatic polyimide segments, and therefore a selective degradation of the polyether moiety could be performed in these copolymers. Isothermal experiments in nitrogen showed that at temperatures above 325ºC, the PEO chains completely broke down, and that the evolution proceeded faster at higher temperatures. For copolymer BPDA 2/1 for example, heating at 375ºC for 2 h was enough to reach the plateau; at 325ºC, at least 24 h were necessary; and at 300ºC, PEO rests were not completely removed after 60 h. When the plateau was reached, at least 97% of the initial polyether had been removed. The absence of the bands at 2925 and 2854 cm^{-1} in the FTIR spectra of the samples degraded isothermally until the plateau was reached, confirmed the loss of polyether segments.

As mentioned, the copolymers were stable below 300ºC for long times in a nitrogen atmosphere, however, this is totally different in an atmosphere containing oxygen. Actually, a high degree of degradation was observed in air well below this temperature. It is known that polyethers are prone to oxidation [29,31], and these copolymers showed the expected sensitivity to oxygen, not only at high temperatures, but also when undergoing relatively moderate temperatures for long times. In Figure 3, the isothermal experiment at 160ºC for copolymer BPDA 2/1 is presented. As it can be seen, after an induction period of approximately 17 h, a sharp decay in weight takes place. In a simple experiment, samples of copolymers BKDA 1/1 and BKDA 2/1 were heated for 2 h at several temperatures in nitrogen and in air atmosphere. In Figure 4, the results for the BKDA sample with the 1/1 composition are displayed. It is clear that in nitrogen, temperatures above 300ºC are necessary for a significant breakdown of the PEO chains, whereas in air, a high degree of degradation takes place well below this temperature. The same behavior was observed for copolymer 2/1 when it was subjected to the same thermal treatments in air and in nitrogen.

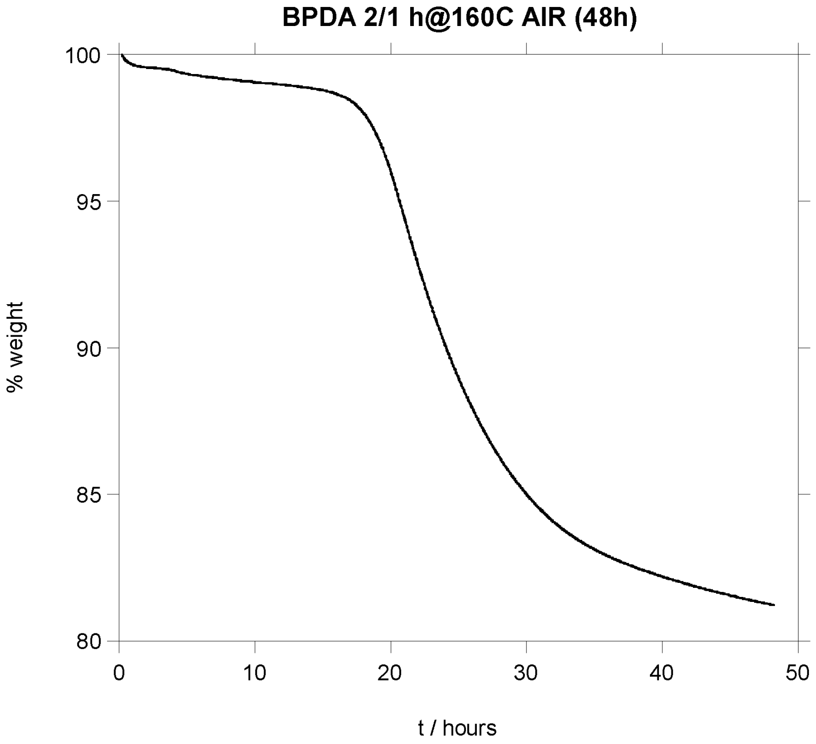


Figure 3. TGA isothermal curve of copolymer BPDA 2/1 at 160ºC in air.

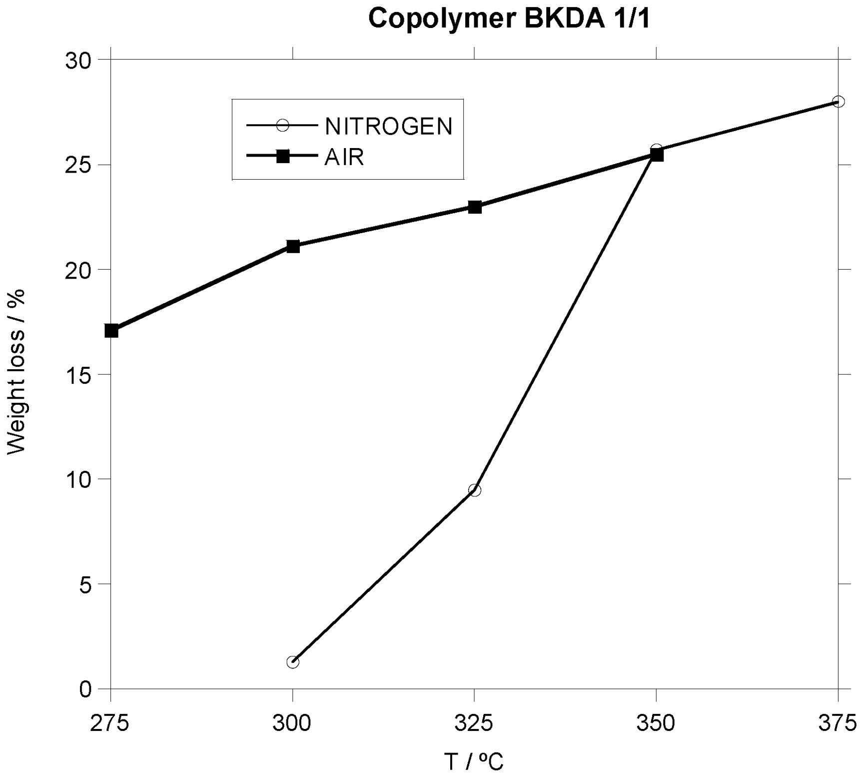


Figure 4. Weight loss for copolymer BKDA 1/1 after thermal treatment at several temperatures for 2 h in air and in nitrogen atmosphere.

Calorimetric Studies

The samples were heated in a DSC instrument with a cyclic method in order to monitor the changes in thermal properties with thermal treatment. In figure 5, the DSC traces show the increase in the PEO melting endotherm after several "instantaneous" treatments for copolymer BPDA 2/1. Eventually, step by step, a curve with the developed crystallinity for PEO vs. "instantaneous" thermal treatment could be built for all copolymers. The melting enthalpy of PEO was taken from literature as 8.67 KJ/mol [32]. In Figures 6 and 7 the results are shown for both the BKDA and BPDA series.

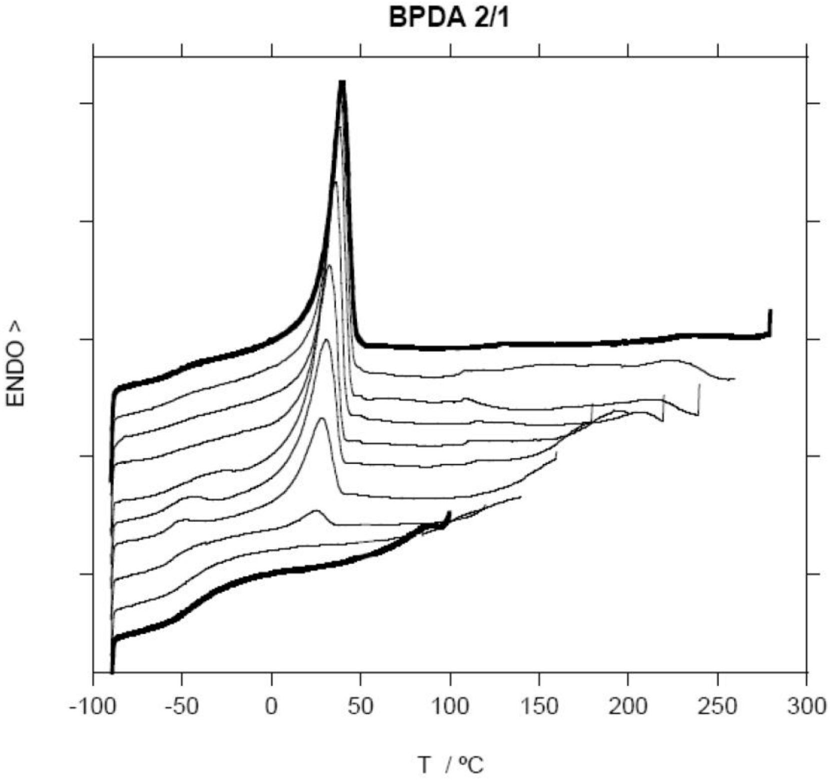


Figure 5. DSC curves for copolymer BPDA 2/1 after "instantaneous" treatment at (from bottom to top): 80, 100, 120, 140, 160, 180, 200, 220, 240 and 260ºC.

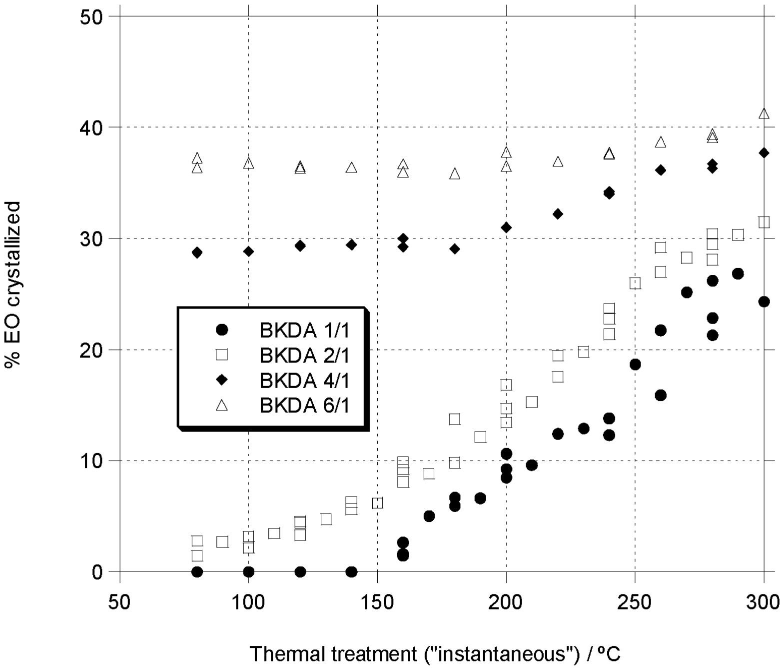


Figure 6. Crystallinity of the PEO segments for the BKDA series as a function of temperature.

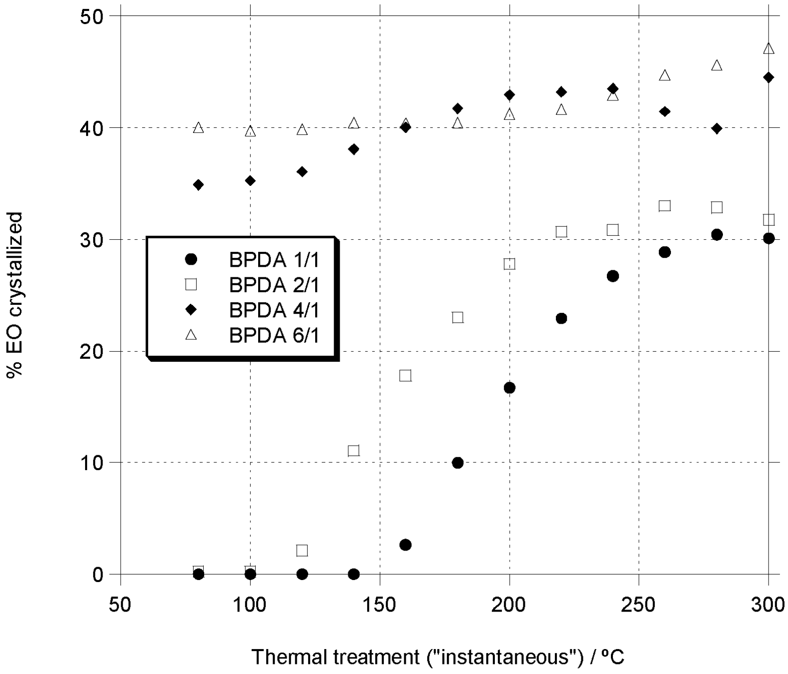


Figure 7. Crystallinity of the PEO segments for the BPDA series as a function of temperature.

From these figures it is apparent, within each series, that for 4/1 and 6/1 copolymers the PEO content is high enough to segregate in a pure phase and to achieve a relatively high crystallinity degree from the beginning. It can be also observed that the higher the PEO content, the higher the crystallinity developed in the BKDA series. The copolymers 1/1 and 2/1, initially with no crystallinity (or only a very small one for BKDA 2/1) after film preparation at 120ºC, started to develop a noticeable crystallinity above approximately 120ºC for 2/1 copolymers and 150ºC for 1/1 copolymers. For copolymers of higher PEO content, a slight increase of crystallinity was also observed at higher temperatures.

When comparing both series, the crystallinity obtained for the copolymers of the same PEO content was slightly higher for the BPDA series. In the copolymers with lower PEO content, those with compositions 1/1 and 2/1, the crystallinity built up more rapidly for the BPDA series. This result can be interpreted as due to a higher thermodynamic incompatibility between the aromatic polyimide segments and the PEO segments for the BPDA series.

For all copolymers, the crystallinity development was simultaneous to the second weight loss found in the TGA experiments, which was presumed to be due to the splitting off of both water caused by the completion of the imidization and residual solvent trapped in the film.

For the lower PEO content copolymers, 1/1 and 2/1, the calorimetric results were consistent with a system of partially mixed PEO and aromatic polyimide segments that, when heated, was driven by the release of residual solvent and completion of imidization towards a more perfectly phase separated system, where part of the PEO segments segregated in a completely pure domain which was able to crystallize. For the higher PEO content copolymers, 4/1 and 6/1, the pure PEO domains were obtained just from the beginning in a relatively high extent, but higher temperatures were needed to improve phase separation on these systems.

The values for the maximum of the melting peak and the percentage of crystalline PEO, after “instantaneous” treatment at 300ºC, are listed in Table 3.

Table 3. Maximum of the endotherm and % of crystalline PEO after heating at 300ºC

Copolymer	Polyether content (%)	Maximum (ºC)	Crystalline PEO (%)
BPDA 1/1	30.0	37	30
BPDA 2/1	45.7	42	32
BPDA 4/1	61.9	48	44
BPDA 6/1	70.2	51	47
BKDA 1/1	28.8	34	24
BKDA 2/1	44.2	38	31
BKDA 4/1	60.4	45	38
BKDA 6/1	68.9	49	41

Within each series, on increasing the PEO content the maximum of the melting endotherm and the percentage of crystalline PEO increased. This is most probably due to the restrictions imposed by the rigid polyimide segments, which are more important when its content in the copolymers increases. This fact brings about a more confined environment which disturbs PEO crystallization, resulting in a lower amount of PEO chains free to crystallize and a smaller size of the crystals.

When compared with data reported in the literature, it could be confirmed that, as expected, the melting maxima and the percentage of crystalline PEO were higher for the current copolymers than for PEO-containing block copolymers with a shorter PEO length of approximately 2000 g/mol [14,18,20,22,33-35]. For other systems, when the length of the PEO chain rose to 3400 g/mol or more, the values approach the results we have obtained only when the PEO content in the copolyester [22] and copolyamides [35] were higher than 75%. For PEO-containing copolyimides, in networks treated at 250ºC for 1 hour and PEO chains of 3400 g/mol, the maximum percentage of crystalline PEO reached a 30% for a 80% PEO content [36], and in the case of linear BPDA and ODA based copoly(ether-imide) treated at 170ºC for 20 hours with PEO sequences of approximately 9000 g/mol and a 62% of PEO, endotherm maximum was found at 25ºC [37], well below our values.

Taking into account these antecedents, it appears evident that the current copolymers, after appropriate thermal treatment, achieve better phase separation than the block copolymers reported in literature so far. Although the existence of a pure PEO phase is clearly proved by these results, it is impossible to establish anything on the composition of the rest of the system by calorimetric studies. It could consist of a homogeneous phase of mixed aromatic polyimide segments and the PEO segments not involved in the formation of PEO crystalline domains, or it could comprise polyimide rich domains with a broader or sharper interface in between both domains. No transition was found for the possible aromatic polyimide segments by DSC, and nothing can be concluded at this point about the nature of the phases other than the pure segregated PEO domains.

Small Angle X-ray Scattering

X-ray scattering experiments were performed at a synchrotron radiation source in order to follow, in real-time conditions, the development of the phase separated structure in these copolymers. In figure 8, the evolution of the scattering (Iq^2 vs. q) with increasing temperature for copolymer BPDA 2/1 is shown as an example. Samples used for SAXS analysis were taken from the films treated at 120ºC for 6 hours. A single broad peak was obtained when the sample showed scattering. Two parameters were calculated over the scattering curve: the relative invariant, Q’, as the integral below the curve Iq^2 vs. q in between the detector limits, related to the extent of the phase separation; and the maximum on the scattering curve, q_{max}, related to the size scale of the separated phases, calculated also from the curve Iq^2 vs. q. It is known that for lamellar systems the length scale (L) of the phase separation can be calculated directly from the curve Iq^2 vs. q, while for other morphologies a calculation of L from the I vs. q curve gives more realistic results [38]. For the current copolymers, we do not investigated if a lamellar morphology is present, but we are more interested on the changes with temperature than on the absolute values, and the representation Iq^2 vs. q highlights the maximum and makes it easier to detect, especially when using automated macros for the processing of the huge amount of data generated in a synchrotron experiment. Therefore this will be the criterion used here to get information on the L value.

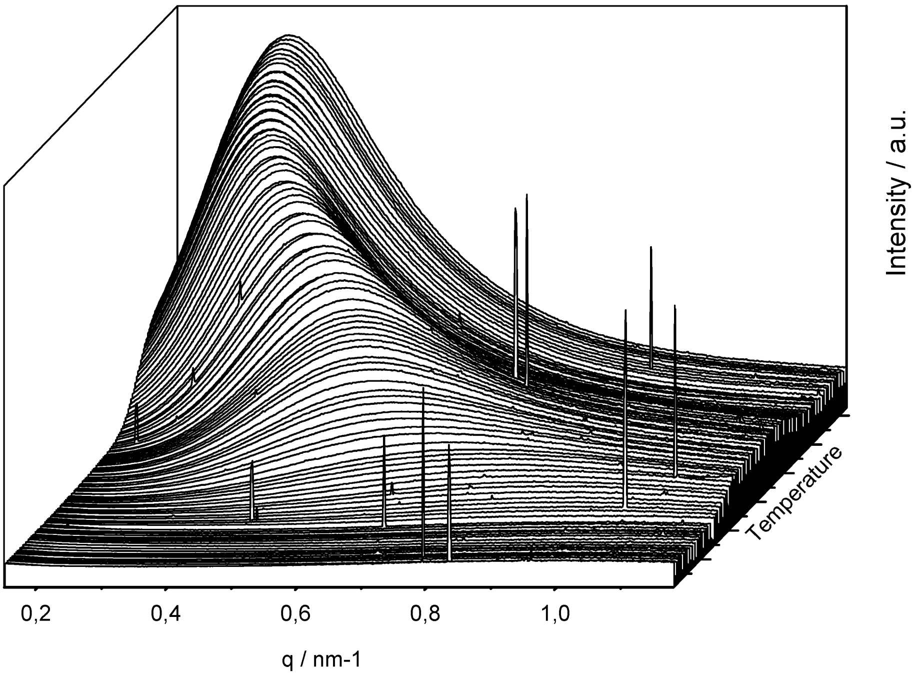


Figure 8. Evolution of the Iq^2-q curves with temperature for copolymer BPDA 2/1.

The obtained results for Q' and q_{max}, after data treatment, are represented in figures 9 to 16. For the BPDA copolymers with compositions 4/1 and 6/1 (figures 13 and 14), the cooling ramp has also been depicted to show the effect of temperature on Q' and q_{max} when no changes on the morphology are taking place. It is evident that the increase in temperature, when there were no changes in the morphology of the system, produced a linear increase in Q’ and a linear decrease in q_{max} (increase in L). The difference between the values on the heating ramp and on the cooling ramp gives the real change on the parameter for each temperature.

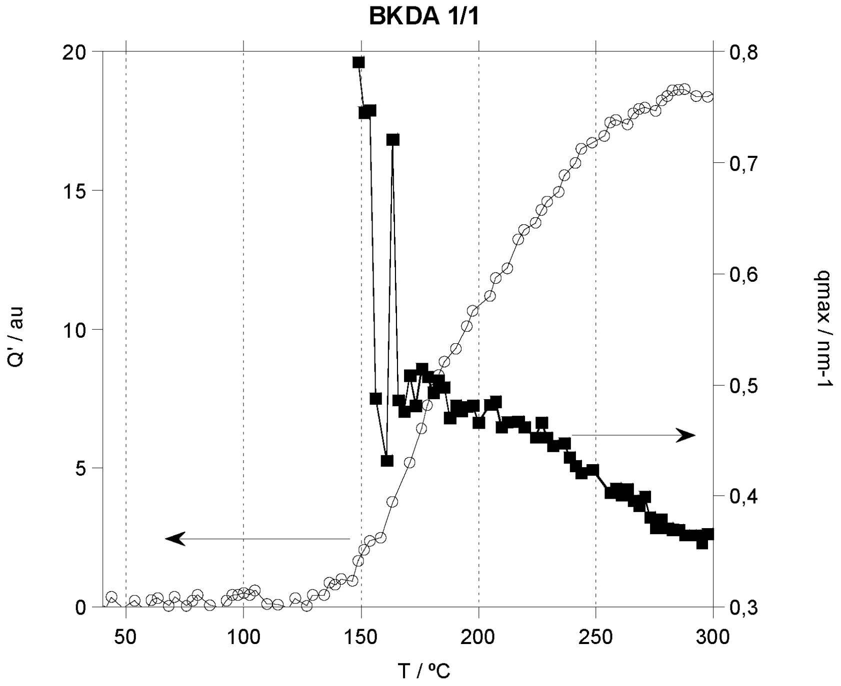


Figure 9. Changes in Q’ and q_{max} with temperature for copolymer BKDA 1/1 when heated at 10°C/min.

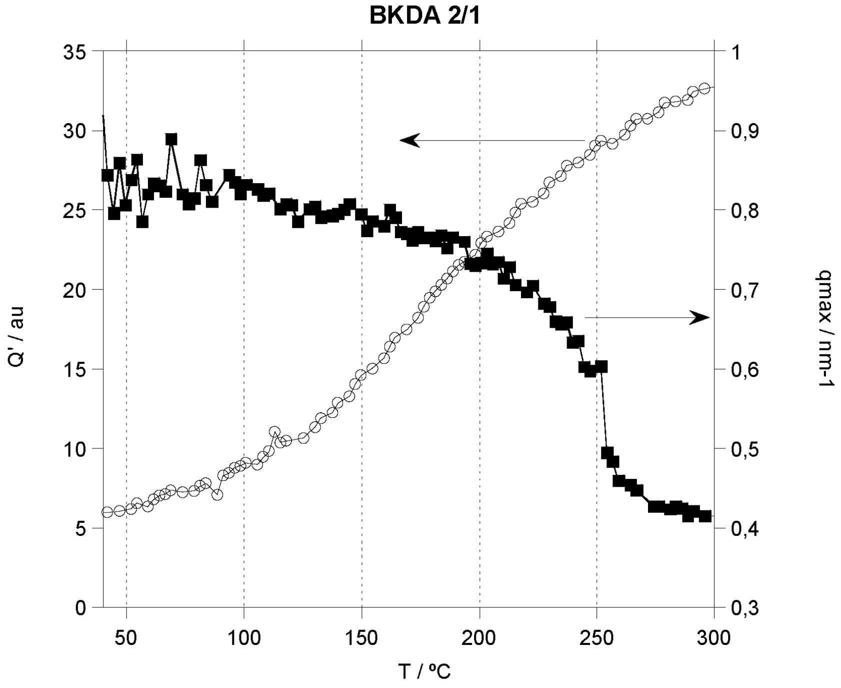


Figure 10. Changes in Q' and q_{max} with temperature for copolymer BKDA 2/1 when heated at 10ºC/min.

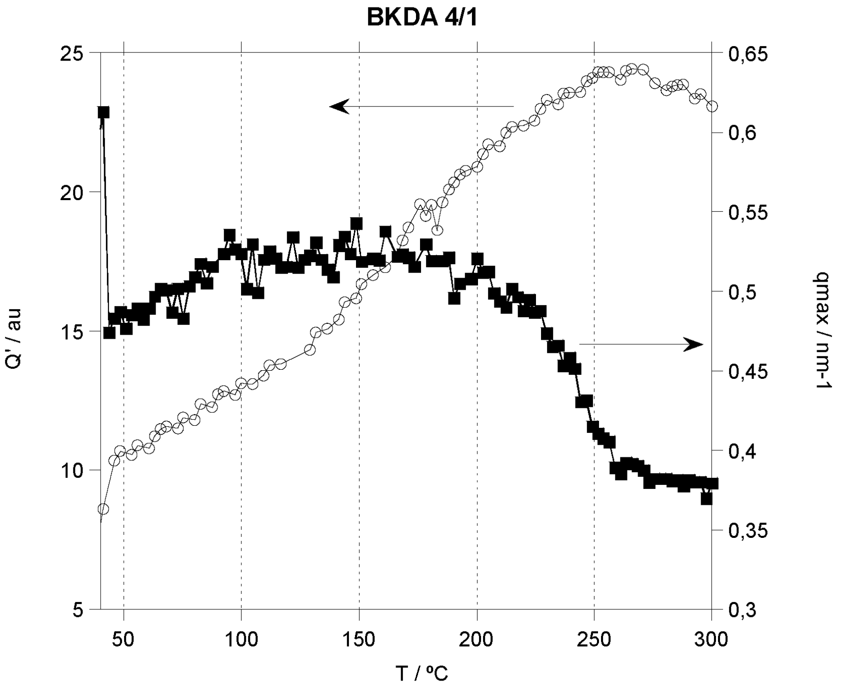


Figure 11. Changes in Q' and q_{max} with temperature for copolymer BKDA 4/1 when heated at 10ºC/min.

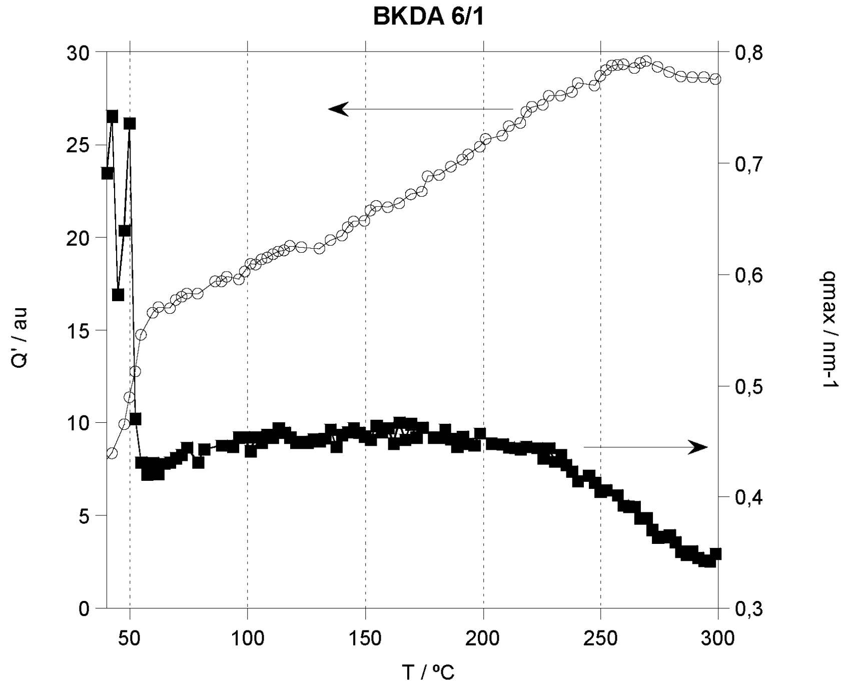


Figure 12. Changes in Q' and q_{max} with temperature for copolymer BKDA 6/1 when heated at 10ºC/min.

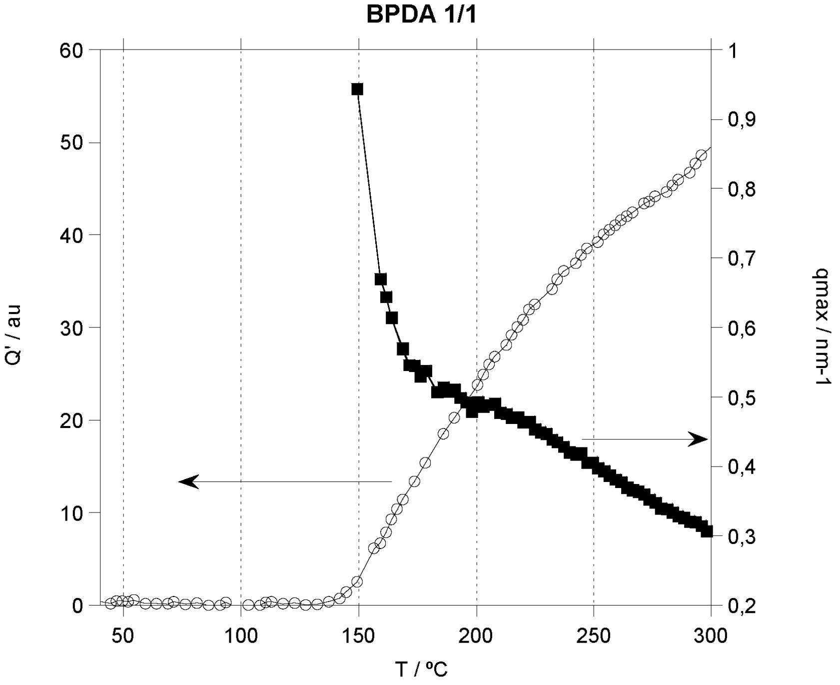


Figure 13. Changes in Q' and q_{max} with temperature for copolymer BPDA 1/1 when heated at 10ºC/min.

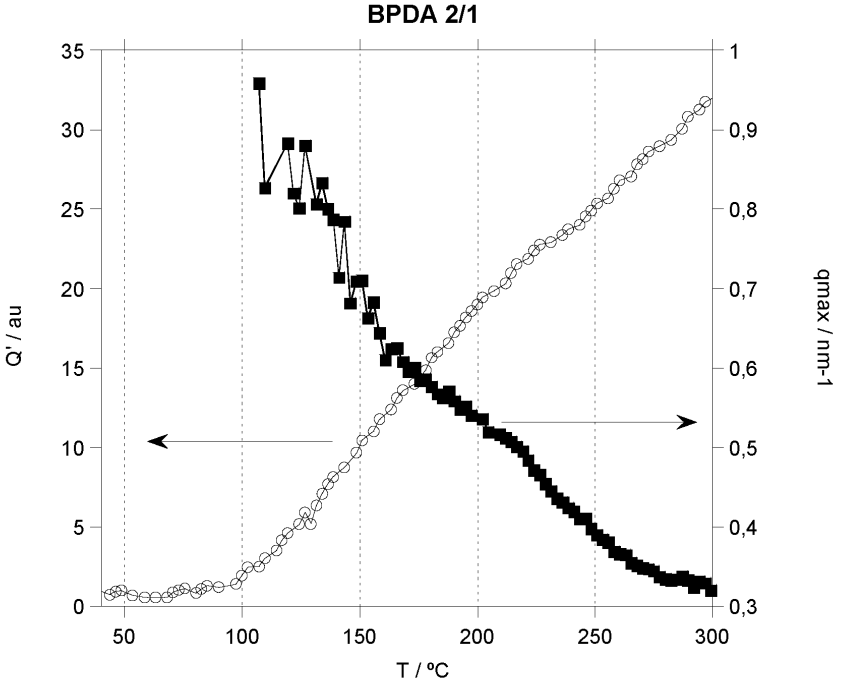


Figure 14. Changes in Q' and q_{max} with temperature for copolymer BPDA 2/1 when heated at 10ºC/min.

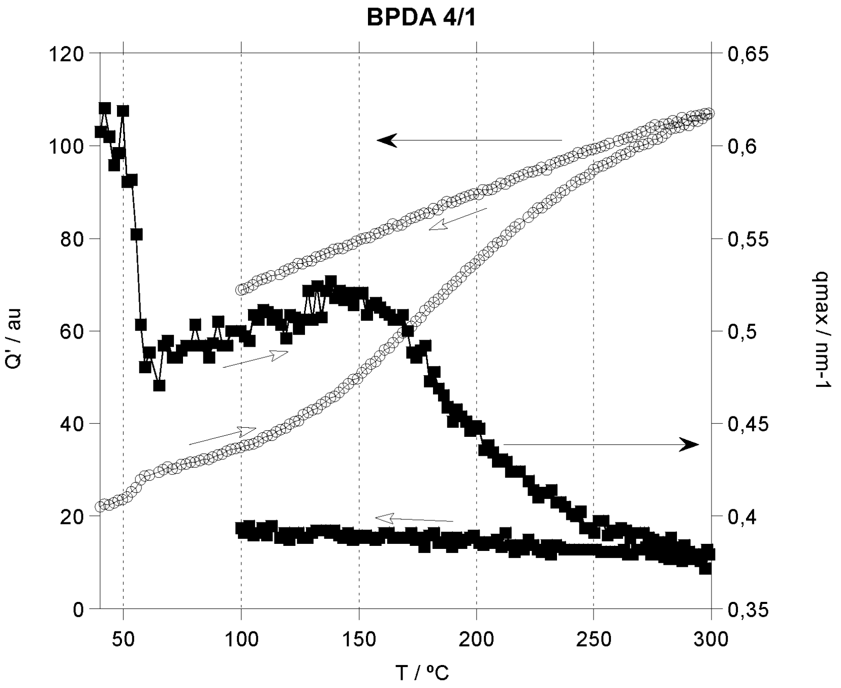


Figure 15. Changes in Q' and qmax with temperature for copolymer BPDA 4/1 when heated at 10ºC/min.

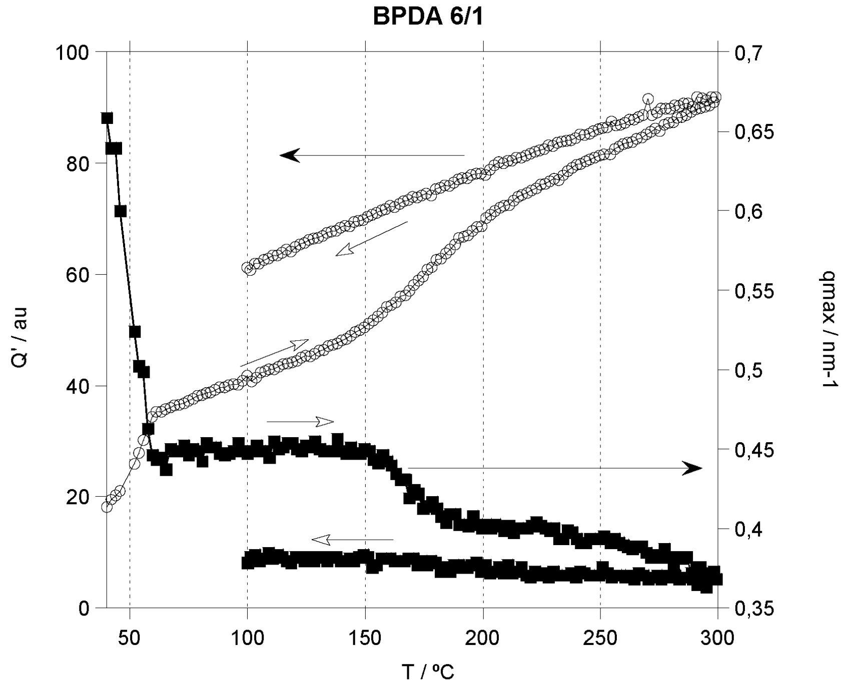


Figure 16. Changes in Q' and qmax with temperature for copolymer BPDA 6/1 when heated at 10ºC/min.

For 1/1 copolymers (figures 9 and 13), a defined maximum in the scattering did not appear until reaching a temperature of approximately 150ºC. At the same time that the maximum appeared, the relative invariant, Q' started to grow, and this growth was continuous until practically the maximum temperature of the test is reached, 300ºC. So, once the imidization had been completed and the residual solvent released, a process of phase separation started in the system and the extension and length scale of such separation increased with temperature.

For copolymers 2/1 (figures 10 and 14), above 150ºC, the behavior was similar, with a steady growth of Q' and a decay of the scattering vector value in the maximum, q_{max}, above 200ºC and up to approximately 270ºC, when it practically leveled. For these samples, different to 1/1 samples, the imidization was practically completed, as tested by FTIR at 150ºC, but as for the 1/1 samples, once the phase separation started at relatively low temperatures, the release of residual solvent was completed while the phase separation proceeds, and it progressed with increasing temperature.

The copolymers 4/1 (figures 11 and 15) and 6/1 (figures 12 and 16) showed an initial phase separated morphology. At low temperatures, around 50ºC, an initial jump on Q' was detected due to the melting of the PEO crystals. Afterwards, the increase was linear due to the effect of the increase in temperature until approximately 130ºC for copolymers 4/1 or 140ºC for copolymers 6/1 and afterwards Q' grew more quickly. At higher temperatures, above 250ºC, the Q' value decayed for BKDA samples as a consequence of the sample falling out of the holder; but BPDA samples were retained and showed that the growth in Q' was steady until 300ºC. A significant difference in the response of the two series was that for the BPDA samples, the decay in q_{max} (increase in L) appeared at lower temperatures (above 150ºC) than for the BKDA samples (above 200ºC). This result can be interpreted as caused by a higher incompatibility of BPDA with PEO, which leads to an increase in the length scale of the segregated phase at lower temperatures than for the BKDA samples. This incompatibility was also assumed when analyzing the DSC results.

Once the phase separation appears, with the simultaneous increase on Q' and appearance of a maximum in the scattering curve, the changes in Q' and q_{max} do not necessarily follow the same trend. Q', and therefore phase separation, steadily improved with temperature. However, q_{max} showed inflection points at temperatures when Q' did not show any relevant change. Although tentatively, the changes in q_{max} could be related to the glass transition of the aromatic polyimide segments. However, it should be note out that at this point of the discussion that there is not enough information to entirely explain the changes in q_{max}.

On comparing the SAXS and DSC results, a parallelism between PEO crystallinity and Q' behavior could be found. When crystallinity appeared, Q' started to grow, and when crystallinity increased, Q' increased. Only for copolymers BPDA 1/1 and 2/1, when high treatment temperatures were reached, above 240ºC for BPDA 1/1 and above 220ºC for BPDA 2/1, the crystallinity had almost leveled at a plateau whereas the relative invariant still grew. In figures 17 and 18, the PEO crystallinity is compared with the changes in Q' and L for the BKDA 2/1 sample to illustrate this statement.

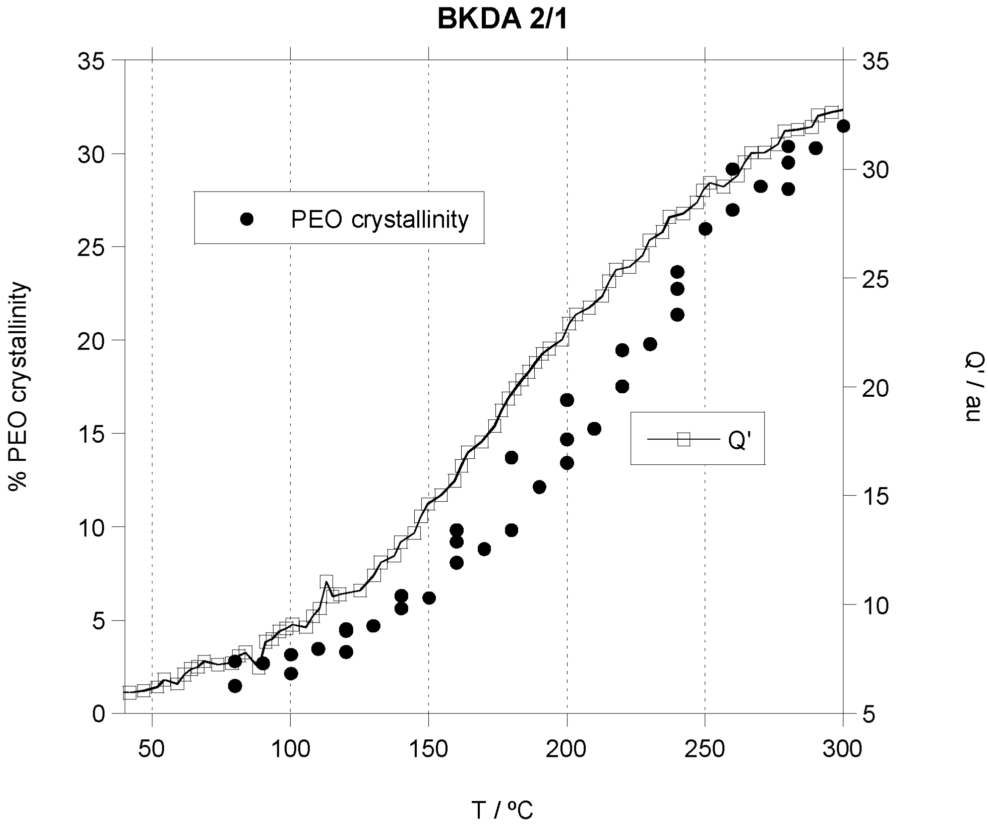


Figure 17. Development of PEO crystallinity compared with the changes in Q' with temperature for sample BKDA 2/1.

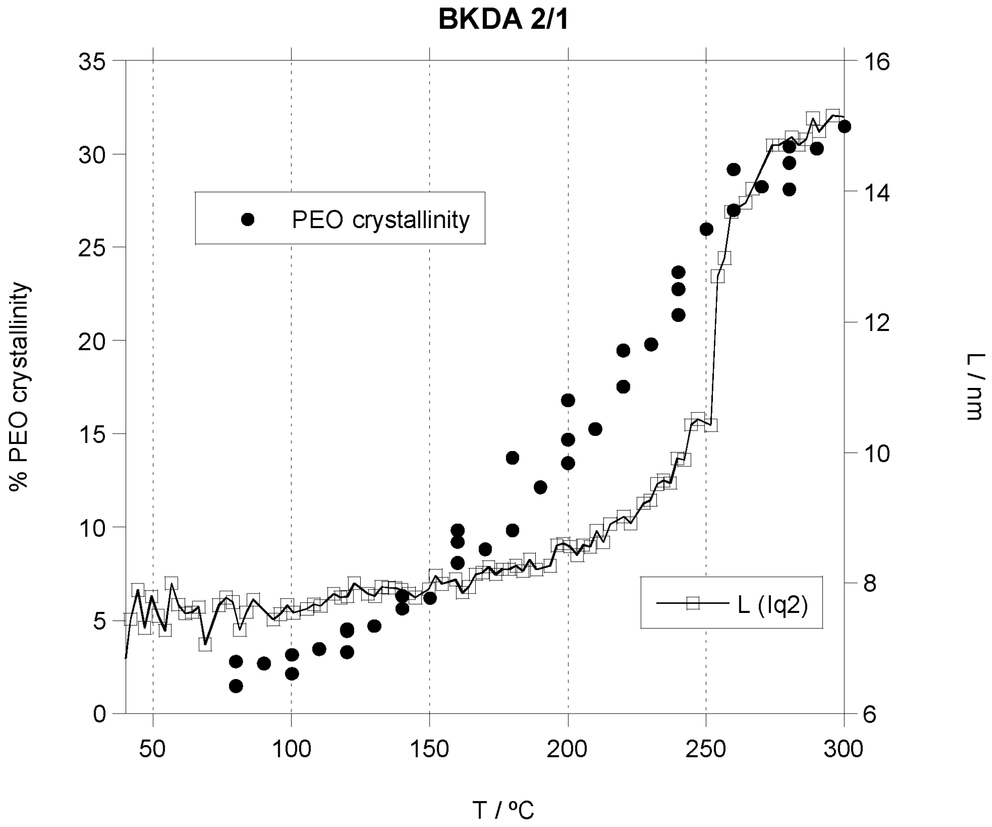


Figure 18. Development of PEO crystallinity compared with the changes in L with temperature for sample BKDA 2/1.

Therefore, for these copolymers, if temperature does not reach a value where degradation occurs, there is a direct relationship between the amount of developed PEO crystallinity and the extent of the phase separation in the system. When studying this type of copolymers, we can then use the amount of PEO crystallinity, at least up to relatively high temperatures, to semiquantitatively evaluate the phase separation achieved by the copolymer.

The size of the domains, L, after thermal heating at 300ºC was calculated at room temperature from the I vs. q and Iq^2 vs. q curves, and they are listed on table 4. The values span from 20 to 26 nm when calculated from I curve, and from 15 to 22 nm when calculated from Iq^2 curve. These values are comparable to the values found in literature for similar PEO-containing block copolymers with lamellar morphology (comparison with Iq^2 vs. q column). Thus, authors found a 13 nm long spacing value for branched polyimide-PEO (2000 g/mol) [39], and 12-15 nm for aliphatic polyamide-PEO [21].

Table 4. Long spacing values measured at ambient temperature after thermal treatment at 300ºC for the copolymers prepared

Copolymer	**L / nm (I vs. q)**	**L / nm (Iq^2 vs. q)**
BKDA 1/1	25.1[a]	16.8
BKDA 2/1	19.9	15.1
BKDA 4/1	22.5	16.3
BKDA 6/1	22.7	18.3
BPDA 1/1	25.1[a]	22.2
BPDA 2/1	23.3[a]	18.9
BPDA 4/1	26.3	17.6
BPDA 6/1	21.5	15.4

[a] For these samples, the maximum was not well defined in the scattered intensity and the error in the determination is quite high

Apart from the expected higher values when the calculation is done on the I plot, no trend was found on the data. Values were sometimes higher for BKDA copolymers and sometimes for BPDA copolymers when the counterparts were compared, and within a series, only for the BPDA series and for the values calculated from the Iq^2 curve a decay appeared in length spacing with the increase on PEO content.

Thermomechanical Analysis

Thermomechanical analysis has been also carried out in order to detect the glass transition temperature of the aromatic polyimide hard segments, which were not detected by DSC. Samples were heated at 180ºC, 220ºC and 260ºC for 30 minutes, and the changes on the strain with temperature were measured. As an example, in figure 19, the curves for the copolymer BKDA 1/1 treated at the three mentioned temperatures can be seen.

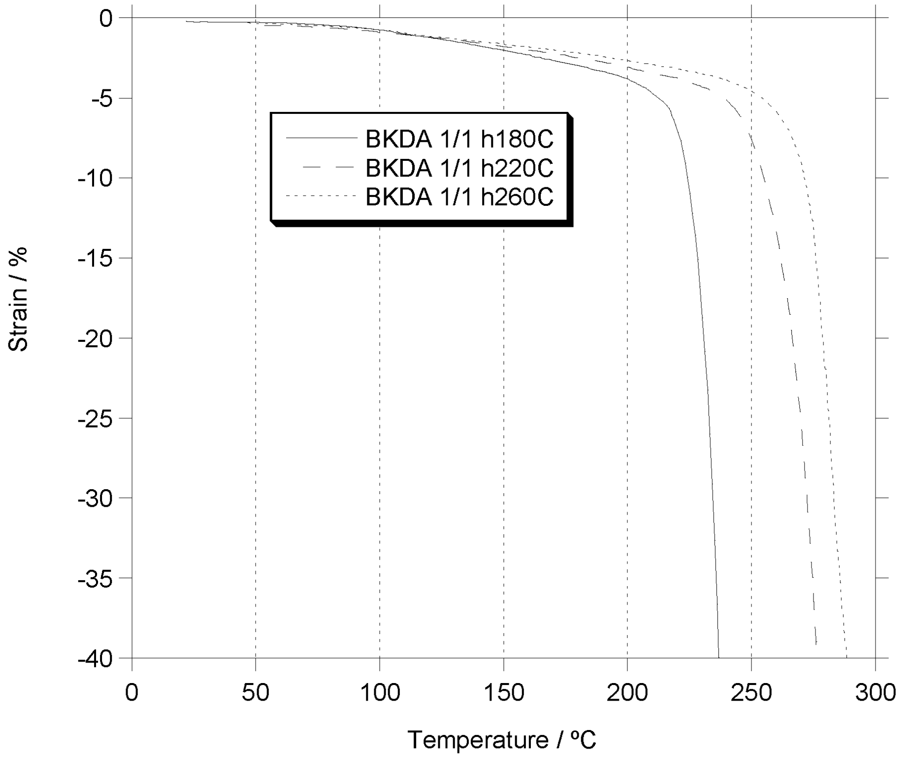


Figure 19. TMA curves for the copolymer BKDA 1/1 treated at several temperatures

Several criteria can be chosen to establish the seek transition temperature. For example, it could be taken as the minimum in the first derivative of the strain versus temperature curve, or the zero value in the second derivative. With the former criterion, the values are not clearly resolved, so that we decided to choose a different criterion, the temperature when strain is 10 times that of the sample at 100ºC, which gives lower transition values than the other two mentioned criteria. The so obtained results are listed on Table 5.

Table 5. Polyimide hard segment glass transition temperature at different treatment temperatures

Copolymer	**180ºC, 30 m**	**220ºC, 30m**	**260ºC, 30 m**
BKDA 1/1	221 ºC	253 ºC	267 ºC
BKDA 2/1	242 ºC	246 ºC	266 ºC
BKDA 4/1	189 ºC[a]	184 ºC[a]	219 ºC[a]
BKDA 6/1	183 ºC	181 ºC	204 ºC
BPDA 1/1	220 ºC	239 ºC	243 ºC
BPDA 2/1	205 ºC	228 ºC	262 ºC
BPDA 4/1	191 ºC	175 ºC[a]	214 ºC[a]
BPDA 6/1	153 ºC[a]	83 ºC[a]	153 ºC[a]

[a] Sample broke before reaching the established criterion for the strain

For the BPDA 6/1 film, the sample was too thin and broke very early in the test. For the rest, even if the sample breaks before the criterion chosen for the glass transition was accomplished, it is clear that aromatic polyimide hard segment has a transition at temperatures over 175ºC. The thermal treatment, as expected from the DSC and SAXS results, brought about an increase of the transition temperature. Although it was not possible to correlate directly the changes in q_{max} observed in SAXS with the glass transition of the polyimide segments, it seems clear that the transition temperatures followed the same trend as that observed for q_{max} with the temperature of treatment. This allowed to presume that there should be such a correlation.

Simple theoretical calculations of the polymerization process demonstrated that the length of the polyimide segments decreased when polyether content increased (see table 1). Therefore, in the case of completely phase separated systems, glass transition temperature of the polyimide segments should decrease when polyether content increases. This trend was clearly confirmed for BKDA treated at 220ºC and at 260ºC, and for BPDA treated at 180ºC and at 220ºC. Nevertheless, such a tendency is only approximately accomplished for BKDA treated at 180ºC, and for BPDA treated at 260ºC

Pure aromatic polyimides BKDA-ODA and BPDA-ODA were synthesized in a similar manner to copolyimides, and thermally imidized at 285ºC for 1 hour. The thermomechanical analysis of this polyimides gave values for the glass transition temperature of 289ºC and 305ºC respectively (the corresponding values found in literature, measured by DSC, are 266ºC [37] and 270ºC [20] respectively). As expected, theses values are quite higher than those found here for the aromatic polyimide segments in the copolymers. This is very clearly associated to the much lower length of the aromatic polyimide segments in the copolymers, which does not reach the minimum value above which the transition temperature is independent of the length, and also because some polyether segments are mixed with the polyimide segments in the polyimide domains.

Mechanical Properties

The commented SAXS, DSC and thermomechanical studies have shown the changes produced in the morphology of the copolymers during thermal treatment and the changes in thermal properties. To complete the study on the physical properties of these copolyimides, mechanical properties were measured in tensile for the copolymers treated at various temperatures.

In table 6, the values for the imidized copolymers at 160ºC for 1/1 and 120ºC for 2/1, 4/1 and 6/1, are listed. For the sake of comparison, the results for the fully aromatic polyimides imidized at 285ºC, are also included.

Table 6. Mechanical properties of the imidized copolymers and reference fully aromatic polyimides determined at room temperature.

Polymer	**BKDA-ODA**	**BKDA 1/1**	**BKDA 2/1**	**BKDA 4/1**	**BKDA 6/1**
Max.Stress (MPa)	134 ± 7	69 ± 2	21 ± 3	6.4 ± 1.5 *8.0 ± 0.7*[a]	2.0 ± 0.4 *3.1 ± 0.3*[a]
Strain (%)	62 ± 3	131 ± 17	4.5 ± 1.0	3.9 ± 1.2 *19 ± 4*[a]	1.3 ± 0.4 *20 ± 7*[a]
Modulus (GPa)	1.87 ± 0.09	1.24 ± 0.09	0.67 ± 0.04	0.31 ± 0.02 *0.154 ± 0.007*[a]	0.59 ± 0.06 *0.055 ± 0.003*[a]
Polymer	**BPDA-ODA**	**BPDA 1/1**	**BPDA 2/1**	**BPDA 4/1**	**BPDA 6/1**
Max.Stress (MPa)	1.40 ± 30	77 ± 10	31 ± 2	12.6 ± 1.3 *6 ± 2*[a]	1.6 ± 0.7 *3.8 ± 0.2*[a]
Strain (%)	34 ± 20	210 ± 110	10 ± 3	12 ± 3 *37 ± 16*[a]	0.61 ± 0.3 *25 ± 5*[a]
Modulus (GPa)	2.5 ± 0.4	1.13 ± 0.10	0.71 ± 0.05	0.37 ± 0.05 *0.150 ± 0.012*[a]	0.51 ± 0.18 *0.068 ± 0.006*[a]

[a] Properties measured at approximately 50ºC

In general, the mechanical properties are good for copolymers 1/1 and 2/1, fair for copolymers 4/1 and poor for copolymers 6/1. As expected, the maximum stress decreased when PEO content increased.

Referring to the strain, except for the reference fully aromatic polyimides and the copolymers with ratio 1/1, where the curve showed a yielding point followed by a quasi-plateau, for the rest of the copolymers the strain value was small and the sample broke at the value of maximum stress. Strain value was especially small for the 6/1 copolymers, where the high crystallinity of the polyether chains and the low content of aromatic polyimide produced a very brittle copolymer.

The values of the modulus followed the same trend as the maximum stress except for the 6/1 copolymers. In this case, the high crystallinity of PEO chains increased the value of the modulus above the value for 4/1 copolymers. If the tensile tests are carried out at approximately 50ºC for 4/1 y 6/1 copolymers, all polyether chains have melted and are amorphous (it must be remarked that for gas separation, PEO chains have to be amorphous because crystalline PEO is known to present a very low permeability [24,25]), and the elastic moduli will be comparable to the rest of the copolymers, where PEO chains are not crystallized. In this way, and as presumed, when polyether chains are melted, the modulus follows the expected trend, decreasing when polyether content increases. Copolymers 4/1 and 6/1 became soft when PEO chains melted and the strain was increased and the modulus reduced, very strongly for copolymers 6/1.

Mechanical properties were also measured for copolymers 1/1 and 2/1 treated at 180ºC, 220ºC and 260ºC for 30 minutes in nitrogen atmosphere and the corresponding results are shown in table 7. For copolymers 4/1 and 6/1, with reduced mechanical properties, we only measured mechanical properties for different thermal treatments for the series for BKDA and the samples were tested at approximately 50ºC to avoid the effect of PEO crystallinity.

Table 7. Properties of copolymers treated at three different temperatures for 30 minutes.

Copolymer	**BKDA 1/1**			**BKDA 2/1**		
Treatment temperature (ºC)	**180**	**220**	**260**	**180**	**220**	**260**
Stress max. (MPa)	69 ± 3	69 ± 4	69 ± 5	36 ± 7	36 ± 3	39 ± 6
Strain (%)	160 ± 50	150 ± 40	130 ± 20	290 ± 60	80 ± 20	280 ± 40
Modulus (GPa)	1.18 ± 0.08	1.21 ±0.07	1.17 ± 0.06	0.64 ± 0.03	0.66 ± 0.01	0.63 ± 0.04
Copolymer	**BPDA 1/1**			**BPDA 2/1**		
Treatment temperature (ºC)	**180**	**220**	**260**	**180**	**220**	**260**
Stress max. / (MPa)	75 ± 4	76 ± 8	77 ± 14	47 ± 4	44 ± 3	55 ± 6
Strain	97 ± 30	110 ± 30	110 ± 16	197 ± 15	70 ± 20	206 ± 15

(%)						
Modulus (GPa)	1.16 ± 0.08	1.16 ± 0.05	1.10 ± 0.10	0.73 ± 0.09	0.87 ± 0.13	0.70 ± 0.13
Copolymer	**BKDA 4/1**[a]			**BKDA 6/1**[a]		
Treatment temperature (ºC)	**180**	**220**	**260**	**180**	**220**	**260**
Stress max. (MPa)	14 ± 4	12 ± 2	18 ± 4	11 ± 2	10 ± 3	13 ± 2
Strain (%)	640 ± 130	420 ± 110	500 ± 150	14 ± 2	420 ± 40	430 ± 30
Modulus (GPa)	0.161 ± 0.009	0.158 ± 0.010	0.042 ± 0.010	0.052 ± 0.014	0.052 ± 0.010	0.027 ± 0.06

[a] Properties measured at approximately 50ºC

Apart from some unexpected results, such us the low strain value for BKDA 2/1 and BPDA 2/1 treated at 220ºC and BKDA 6/1 treated at 180ºC, the mechanical properties did not change significantly with thermal treatment, probably because there are no significant differences in phase separation upon annealing. Thermal treatment at 180ºC for 30 minutes was probably enough to achieve a very high degree of phase separation, and a higher temperature did not improve it substantially.

CONCLUSIONS

A new series of copoly(ethylene oxide-imide)s with long poly(ethylene oxide) segments (6000 g/mol) have been synthesized and characterized in terms of morphology and physical properties.

Complete imidization was achieved at relatively low temperatures (120-160ºC). This is an evident processing advantage respect to fully aromatic polyimides, for which very high temperatures, generally above 300ºC, are necessary to achieve almost complete imidization.

These copolymers are stable in nitrogen up to high temperatures, whereas in an oxygen containing atmosphere, degradation takes place at relatively low temperature.

Phase separation, measured as the PEO segments crystallinity, increases with the increase of PEO content in the copolymer, and after treatment at high temperature below degradation temperature, the achieved phase separation increases.

SAXS experiments confirm DSC results and show evidence of phase separation with thermal treatment. For all copolymers, either with no initial phase separation (PEO content 30% and 45%) or initially phase separated (60% and 70%), domain segregation starts or improves when heated above 150ºC, which is coincident with the release of the trapped solvent, and the completion of the imidization in the case of the copolymers with the lowest PEO content. At certain temperature, that can be ascribed to the glass transition temperature of the hard polyimide segments, phase separation rate increases. Phase segregation appears slightly earlier for BPDA than for BKDA, and the annealed samples show a slightly better phase separation, due to the higher thermodynamic incompatibility of PEO and BPDA based polyimides. Phase separation scale is 15-20 nm, of the order of similar PEO-containing block copolymers found in literature.

The glass transition temperatures for the aromatic polyimide segments, detected by TMA, were above 150ºC for the copolymers with high PEO content and above 200ºC for those with lower PEO content. Thus, it seems clear that thermal treatment increases the transition temperature of the hard domains, which seems to demonstrate that phase separation process also changes the hard segment domains.

As expected, mechanical properties depend on the PEO content, with poorer properties for copolymers with increasing PEO content. The properties resulted good for copolymers with lower PEO content, 30% and 45%, fair for 60% PEO, and poor for 70% PEO. Thermal treatment at 180ºC for 30 minutes seems to be enough for a very good phase separation, and thermal treatments at higher temperatures do not have a significant effect on the mechanical properties.

The series of copoly(ether-imide)s prepared in this work have a phase separated morphology and physical properties able to be modulated by thermal treatments, that make them interesting candidates for membranes for CO_2 gas separation applications.

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30. This band is also found in BPDA copolyimides that we have synthesized with 6F diamine, and with poly(propylene oxide)s D4000, D2000, and poly(ethylene oxide)s ED2003, ED900 (Jeffamines).

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