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Polymer 42 (2001) 7933–7941

polymer

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# Novel aromatic polyamides with 1,3-benzoazole groups in the main chain. 1. Polymers derived from 2-(4-carboxyphenyl) benzoxazole-5- and 6-carboxylic acids. Synthesis and characterization

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Received 10 February 2001; received in revised form 20 April 2001; accepted 27 April 2001

**Abstract**

Two series of aromatic poly(amide-benzoxazole)s have been obtained from 5-chlorocarbonyl-2-(4-chlorocarbonylphenyl)benzoxazole (NBOC) and 6-chlorocarbonyl-2-(4-chlorocarbonylphenyl)benzoxazole (OBOC). NBOC and OBOC were synthesized by a three-step process with high yields, and they were reacted with aromatic diamines by using the in situ silylation method which yielded polymers of high inherent viscosities. The solubility of these polymers was similar to that of aromatic polyamides, being soluble in aprotic polar solvents. All polymers could be processed to tough, creasable amorphous films with good mechanical properties, the values of tensile strength ranging from 92 to 113 MPa with moduli above 2 GPa. The glass transition temperatures were above 300°C, whilst the onset of thermal degradation ranged from 455 to 515°C. A theoretical study was also done, by means of computational chemistry methods, to relate the orientation of the benzoxazole ring in both series with monomer reactivity and polymer properties. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Aromatic polyamides; Polybenzoxazoles; In situ silylation

## 1. Introduction

Aromatic polyamides are a class of polymeric materials which present a combination of outstanding properties [1–3]. They are highly stable polymers with excellent mechanical properties and good processability on several solvents. Owing to this balanced combination of properties, they have found a place in many industrial applications as aerospace materials, high strength-high modulus fibers, protective coatings or as gas separation membranes [4–7]. On the other hand, aromatic polybenzoxazoles have even better thermal stability, excellent mechanical properties and good hydrolitical and oxidative stability [5,8–10]. Yet, they present poor solubility and tractability which limits their application in many fields [1,11]. In fact the only commercial polybenzoxazole fiber (ZYLON®) is processed from strong acid solutions [12]. Attempts have been made to combine benzoxazole units with other stable linkages along the backbone of aromatic polymers, in order to get more tractable macromolecular structures; in this way, poly(amide-benzoxazole)s, poly(imide-benzoxazole)s and poly(ester-benzoxazole)s have been previously reported [13–16]. Kricheldorf et al have also reported on the properties of poly(amide-benzoxazole)s that show lyotropic characteristics [17]. These authors claimed that polymers with benzoxazole units, and particularly poly(amide-benzoxazole)s, seem to offer an interesting approach to special polymer materials.

In this paper, the preparation of polyamides containing benzoxazole groups from two monomers is reported, along with their combination with aromatic diamines to render two families of poly(amide-benzoxazole)s which differ from each other in the orientation of the benzoxazole rings.

The combination of both amide and benzoxazole groups on the polymer chain was expected to bring about a better tractability without any drawback on the thermal resistance.

## 2. Experimental part

### 2.1. Reagents and solvents

Solvents and reagents were commercially available and used as received, unless otherwise indicated. *N*,*N*-dimethylacetamide (DMA) was twice distilled at reduced pressure, the first time over phosphorus pentoxide and the second time over calcium hydride. DMA was then stored in a

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PII: S0032-3861(01)00316-0

dark sealed flask over molecular sieves (4 Å). Lithium chloride was dried at 325°C for 12 h. Commercial aromatic diamines were purified by sublimation just before use.

### 2.2. Synthesis of intermediates and monomers

#### 2.2.1. Dimethyl benzoxazoles

Dimethyl benzoxazoles were prepared by the reaction of equimolar amounts of 4-methylbenzoic acid and 4 or 5-methyl-2-aminophenol in a mixture of phosphorus pentoxide and methanesulfonic acid (1:5) (PMPA) at 120°C, blanketed by dry nitrogen, for 24 h. The dark red solution was poured into water, and the resulting precipitate was filtered off, washed with water and treated with a 0.1 M solution of NaOH down to a pH of 3. The solid was filtered by suction, thoroughly washed with water and dried. The product was used without further purification in the following step of the synthetic procedure. For identification purposes, one analytical sample was obtained by sublimation (twice).

*2.2.1.1. 2-(4-methylphenyl)-6-methyl-benzoxazole.* Yield = 85%, mp = 104°C (DSC).

$^1$H NMR ($CDCl_3$; ppm): 2.39 (s, 3H), 2.46 (s, 3H), 7.12 (dd, $J = 8.2$, 0.8 Hz, 1H), 7.28 (d, $J = 8.1$ Hz, 2H) 7.32 (s, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 8.09 (d, $J = 8.1$ Hz, 2H).

$^1$H NMR (DMSO-$d_6$; ppm): 2.39 (s, 3H), 2.45 (s, 3H), 7.20 (dd, $J = 8.1$ Hz, $J = 0.4$ Hz, 1H), 7.44 (d, $J = 8.1$ Hz, 2H) 7.56 (d, $J = 0.4$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 1H), 8.05 (d, $J = 8.1$ Hz, 2H).

$^{13}$C NMR ($CDCl_3$; ppm,): 21.5, 21.7, 110.6, 119.1, 124.6, 125.6, 127.4, 129.5, 135.2, 139.9, 141.7, 150.9, 162.7

*2.2.1.2. 2-(4-methylphenyl)-5-methyl-benzoxazole.* Yield = 80%, mp = 130°C (DSC).

$^1$H NMR ($CDCl_3$; ppm): 2.40 (s, 3H), 2.46 (s, 3H), 7.10 (ddd, $J = 8.4$, 1.4, 0.6 Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H) 7.40 (s, 1H), 7.52 (dd, $J = 1.4$, 0.6 Hz, 1H), 8.10 (d, $J = 8.2$ Hz, 2H).

$^1$H NMR (DMSO-$d_6$; ppm): 2.39 (s, 3H), 2.43 (s, 3H), 7.20 (ddd, $J = 8.1$, 1.5, 0.6 Hz, 1H), 7.40 (d, $J = 7.8$ Hz, 2H) 7.56 (dd, $J = 1.5$, 0.6 Hz, 1H), 7.61 (d, $J = 8.1$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 2H).

$^{13}$C NMR ($CDCl_3$; ppm,): 21.4, 21.5, 109.7, 119.7, 124.5, 125.9, 127.4, 129.5, 134.1, 141.8, 142.3, 148.8, 163.3

#### 2.2.2. Benzoxazole dicarboxylic acids

Benzoxazole dicarboxylic acids were synthesized by oxidizing the corresponding dimethyl intermediates with $KMnO_4$ in a mixture of pyridine and water (1:1 by volume). A 10-fold molar excess of $KMnO_4$ was used to achieve full oxidation, and the reaction was carried out at 90°C for 24 h. By-product $MnO_2$ (black powder) was eliminated by filtration, and extracted with 2 × 200 ml of a 1 M solution of NaOH. The extracts were joined with the filtrated solution and treated with 2 M HCl to a pH of approximately 3. The resultant precipitate was dissolved in 1 M NaOH and reprecipitated by acidification with a 0.1 M solution of HCl to a pH of 3. The white precipitate was filtered off, washed with water until a neutral reaction was obtained and dried in a vacuum oven overnight.

*2.2.2.1. 2-(4-carboxyphenyl)benzoxazole-6-carboxylic acid.* Yield = 71%, mp = 375°C (DSC).

$^1$H NMR (DMSO-$d_6$; ppm): 7.88 (dd, $J = 8.4$, 0.6 Hz, 1H), 7.99 (dd, $J = 8.4$, 1.5 Hz, 1H) 8.12 (d, $J = 8.7$ Hz, 2H), 8.25 (dd, $J = 1.5$, 0.6 Hz, 1H), 8.28 (d, $J = 8.7$ Hz, 2H), 10.6 (s, br.).

$^{13}$C NMR (DMSO-$d_6$; ppm,): 111.2, 119.9, 126.4, 127.8, 128.5, 129.5, 130.2, 133.9, 145.0, 150.1, 163.6, 166.5, 166.8.

Elemental analysis ($C_{15}H_9NO_5$) (283.24) Calc. C: 63.61, H: 3.20, N: 4.95; Found C: 63.21, H: 3.45, N: 4.63.

*2.2.2.2. 2-(4-carboxyphenyl)benzoxazole-5-carboxylic acid.* Yield = 78%, mp = 345°C (DSC).

$^1$H NMR (DMSO-$d_6$; ppm): 7.91 (dd, $J = 8.6$, 0.6 Hz, 1H), 8.06 (dd, $J = 8.6$, 1.6 Hz, 1H) 8.15 (d, $J = 8.6$ Hz, 1H), 8.32 (d, $J = 8.6$ Hz, 2H), 8.33 (dd, $J = 1.6$, 0.6 Hz, 2H), 10.7 (s, br.).

$^{13}$C NMR (DMSO-$d_6$; ppm,): 111.2, 121.3, 127.4, 127.6, 128.1, 129.5, 130.1, 133.8, 141.5, 153.1, 162.8, 166.5, 166.8.

Elemental analysis ($C_{15}H_9NO_5$) (283.24) Calc. C: 63.61, H: 3.20, N: 4.95; Found C: 63.26, H: 3.53, N: 4.71.

#### 2.2.3. Benzoxazole diacid dichlorides

Benzoxazole diacid dichlorides were prepared by refluxing the dicarboxylic compounds with a five-fold excess of thionyl chloride and some drops of *N*,*N*-dimethylformamide (DMF) for 5 h. The excess of thionyl chloride was distilled off and toluene was added to dissolve the solid residue. The solution was filtrated and poured over hexane. The resulting white precipitate was filtrated, washed with hexane and dried, followed by vacuum sublimation.

*2.2.3.1. 2-(4-chlorocarbonylphenyl)-6-chlorocarbonyl-benzoxazole (OBOC).* Yield = 82%, mp = 166°C (DSC).

$^1$H NMR ($CDCl_3$; ppm): 7.89 (d, $J = 8.5$ Hz, 1H), 8.20 (dd, $J = 8.5$, 1.7 Hz, 1H), 8.29 (d, $J = 8.5$ Hz, 2H), 8.41 (d, $J = 8.5$ Hz, 2H), 8.42 (d, $J = 1.7$ Hz, 1H).

$^{13}$C NMR ($CDCl_3$; ppm,): 114.5, 120.6, 128.4, 130.7, 131.7, 136.0, 147.5, 150.4, 164.8, 167.3, 167.5.

*2.2.3.2. 2-(4-chlorocarbonylphenyl)-5-chlorocarbonyl-benzoxazole (NBOC).* Yield = 77%, mp = 186°C (DSC).

$^1$H NMR ($CDCl_3$; ppm): 7.72 (d, $J = 8.7$ Hz, 1H), 8.22 (dd, $J = 8.7$, 1.9 Hz, 1H) 8.29 (d, $J = 8.8$ Hz, 2H), 8.41 (d, $J = 8.8$ Hz, 2H), 8.63 (d, $J = 1.9$ Hz, 1H).

$^{13}$C NMR ($CDCl_3$; ppm,): 111.3, 124.9, 128.2, 129.4, 130.6, 131.8, 131.9, 135.8, 142.3, 155.0, 163.2, 167.6, 167.7.

### 2.3. Polymers syntheses

The general procedure consisted of adding portionwise, 20.0 mmol of the acid dichloride to a stirred, cooled (0°C), solution of 20.0 mmol of diamine and 30.0 mmol of trimethylsilyl chloride in 40 ml of DMA with 5% (w/v) of LiCl. The mixture was allowed to react under a blanket of nitrogen for 2 h, then the temperature was raised to room temperature and the reaction was allowed to proceed for 4 h more. The viscous polymer solution was poured into distilled water and the polymer filtered off and washed with water several times until a neutral reaction was obtained. The polymer was extracted with acetone for 24 h and finally dried in a vacuum oven at 100°C overnight. Yields over 95% were obtained.

### 2.4. Measurements

Melting points were determined by the capillary method, except for high melting point compounds, for which DSC was used.

Microanalyses were carried out in an analyzer Heraeus model CHN-Rapid.

$^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Unity-500 spectrometer tuned at 499.84 and 125.71 MHz, respectively, at room temperature, using deuterated chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-$d_6$) as solvent, and tetramethylsilane (TMS) as internal reference. Some heteronuclear 2D shift correlated spectra were performed to help signals assignation.

Viscosities were measured on 0.5% *N*-methyl-2-pyrrolidinone (NMP) solutions at 30 ± 0.1°C in an automatic Ubbelohde viscosimeter.

Differential scanning calorimetry (DSC) measurements and thermogravimetric analysis (TGA) were performed on Perkin–Elmer models DSC-7 and TGA-7, respectively. All samples were tested under nitrogen at a heating rate of 10°C/min.

Wide angle X-ray diffraction (WAXD) patterns were obtained for polymer films at room temperature by using a Philips Geiger X-ray diffractometer, operating in the $2\theta$ range between 5 and 35° at a rate of 2°/min and using Ni-filtered CuK$\alpha$ radiation.

Water uptake measurements were carried out by placing polymer samples, previously dried over phosphorus pentoxide at 120°C in a vacuum oven for 24 h, in a chamber where 65% RH was maintained by means of an over-saturated solution of sodium nitrite at 20°C. The samples were periodically reweighed until they reached equilibrium.

For the measurements of mechanical properties, strips 5 mm wide and 30 mm long were cut from polymer films (40–60 $\mu$m thick) and tested on an MTS Synergie 200 tensile tester at 20°C. Mechanical clamps were used, and an extension rate of 10 mm/min was applied, with a gauge length of 10 mm.

Gel permeation chromatography (GPC) analyses were carried out using PLgel columns (Polymer Laboratories) of nominal pore sizes 500, $10^4$ and $10^5$ Å. *N*,*N*-dimethylformamide with 0.1% of LiBr was used as solvent and the measurements were done at 70°C with a flow rate of 1.0 ml/min and using an UV detector. The columns were calibrated with narrow standards of a suitable aromatic polyamide poly(*m*-phenylenisophthalamide).

Semiempirical quantum-mechanical calculations were performed using the original parameters of the program AM1 [18] based on the restricted Hartree–Fock (RHF) methodology. This method is included in MOPAC version 6.0 [19], using as graphics interface and data analysis the Cerius2 program [20]. This semiempirical method is commonly accepted to allow a better description of the lone-pair/lone-pair repulsion in several heterocyclic compounds [21]. The MOPAC program ran on a Silicon Graphics Octane R12000 workstation.

Geometries were optimized in internal coordinates. The optimization was stopped when Herbert or Peter tests were satisfied in the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [22]. The PRECISE option was applied for semiempirical calculations during the optimization process with the gradient norm set to 0.01. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles) without any assumption of symmetry.

Mulliken population analyses [23] were used to discuss the electron distributions. The charges obtained by this method are adequate for present purposes since they reflect the trend in populations and electronic densities which seem to be important, rather than their actual values, regarding differential reactivity [24].

## 3. Results and discussion

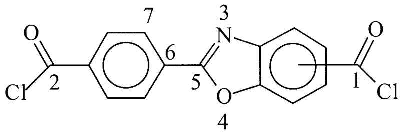
### 3.1. Theoretical calculations and molecular simulation study

In addition to the synthesis and characterization of the two condensation monomers, a theoretical estimation of their structural and electronic features has been carried out, and the results are presented in Table 1.

The dihedral angle N3–C5–C6–C7 is the same for both monomers with a value very close to 0°. More interesting is the angle formed between the C1–$C_{Ar}$ and the C2–$C_{Ar}$ bonds because this angle gives an indication of macromolecular chain linearity. The obtained values are quite similar for both monomers (138 and 149° for OBOC and NBOC), reflecting that these monomers should give more *rod-like* macromolecular chains than those of 1,3-substituted monomers like isophthaloyl chloride or even 1,4-substituted monomers with a kink between two aromatic rings like bis(chlorocarbonylphenyl)ether, which have angles of 120°.

The Mulliken charges on the chlorocarbonyl carbons ($Q_{C(COCl)}$) are very similar for both monomers, not only on

Table 1
Electronic parameters of OBOC and NBOC monomers and some reference diacid chlorides (IPC: isophthaloylchloride; ODC: bis(4-chlorocarbonylphenyl)ether; SDC: bis(4-chlorocarbonylphenyl)sulfone)



| Monomer | $E_{\mathrm{LUMO}}$ (eV) | $E_{\mathrm{LUMO+1}}$ (eV) | $Q_{\mathrm{C1(COCl)}}$[a] (e.u) | $Q_{\mathrm{C2(COCl)}}$[b] (e.u) |
|---|---|---|---|---|
| OBOC | −1.81 | – | 0.285 | 0.281 |
| NBOC | −1.67[c] | − 1.06[d] | 0.287 | 0.282 |
| IPC | −1.34 | – | 0.284 | 0.284 |
| ODC | −1.23 | – | 0.289 | 0.289 |
| SDC | −1.71 | – | 0.273 | 0.273 |

[a] Net charge on carbon Cl.

[b] Net charge on carbon C2.

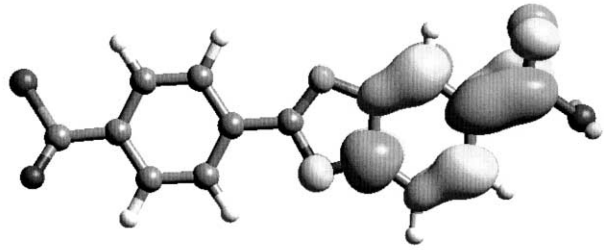
[c] The highest coefficient for this orbital is located on carbon C2.

[d] The highest coefficient for this orbital is located on carbon Cl.

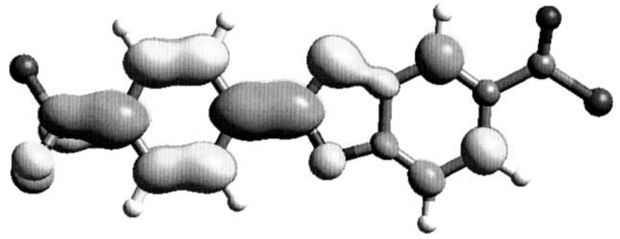
the phenyl moiety (0.281 and 0.282 e.u. for OBOC and NBOC, respectively) but also on the benzoxazole moiety (0.285 and 0.287 e.u.) in spite of the isomeric differences on this moiety. Therefore, by charge considerations, both monomers should have a very similar reactivity on polycondensation reactions, and this can also be said for the differential reactivity between the two chlorocarbonyl groups in each monomer [25–28].

Orbitalic energies are best fitted to explain the reactivity of these monomers [25]. It is well known that, in reactions between an electrophilic and a nucleophilic monomer, as it is the case for acid chlorides and amines, the reactivity of the electrophilic monomer is controlled by the energy of the unoccupied molecular orbitals (UMO's) and mainly of the lowest unoccupied molecular orbital (LUMO) [25,29–33]. As it can be seen in Scheme 1 (LUMO of NBOC and OBOC and LUMO + 1 of OBOC), in the case of OBOC only the LUMO should be considered because the LUMO + 1 is very similar and has a higher energy. However, in NBOC, both LUMO and LUMO + 1 orbitals have to be considered because the highest orbital coefficient of the LUMO is located on carbon C2 (no LUMO coefficient located on C1), while the highest UMO coefficient for carbon C1 corresponds to the orbital LUMO + 1.

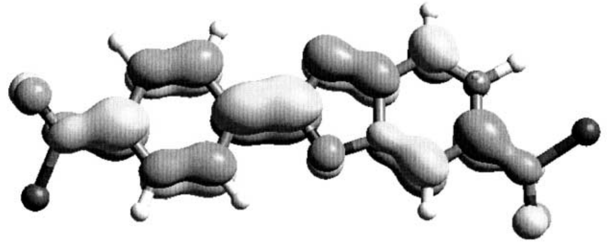
The energy values of the orbitals are summarized also in Table 1 from which two conclusions can be drawn out: First, the reactivity of the chlorocarbonyl carbons attached to the phenyl moiety, which is controlled by the LUMO orbital, is quite similar in both cases (slightly higher reactivity for OBOC). Second, the reactivity of the second chlorocarbonyl group, which is controlled by the LUMO orbital in OBOC and by the LUMO + 1 orbital in NBOC, is significantly higher for OBOC. Actually, the reactivity of this second group is similar to that of the first one in OBOC, and lower than that of the first one in NBOC.



NBOC (LUMO+1)



NBOC (LUMO)

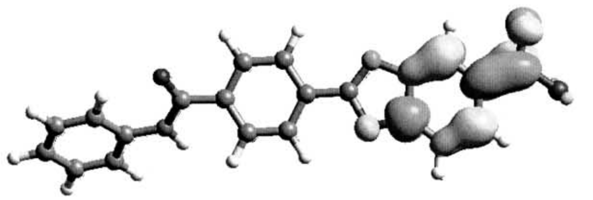


OBOC (LUMO)

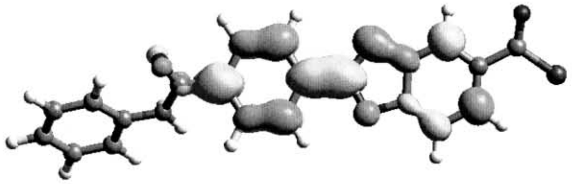
Scheme 1.

Furthermore, because of the very low values of $E_{\mathrm{LUMO}}$ in both cases, much lower than for commercial diacid chlorides as isophthaloyl (IPC) chloride, and even lower than that of acid chlorides with very strong electronwithdrawing groups, as bis-(4-chlorocarbonylphenyl)-sulfone (SDC) (see Table 1), the reactivity of the carbonyl groups controlled by this orbital (both groups in OBOC and the group joined to the phenyl group in NBOC) should be very high. The reactivity of the second carbonyl group in NBOC, ($E_{\mathrm{LUMO+1}}$: −1.06 eV) is placed between the values of benzoyl chloride and sophthaloyl chloride ($E_{\mathrm{LUMO}}$: −0.76 and −1.32 eV, respectively). Therefore, this reactivity should be high enough to permit the synthesis of polymers, mainly if high reactivity diamines are used.

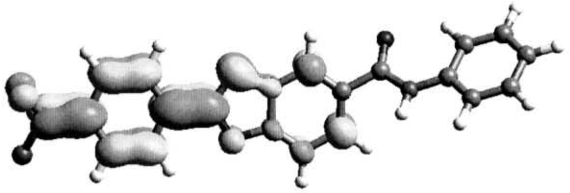
In order to get a deeper insight on the polycondensation reaction for these monomers, a theoretical study of the possible stages of the polycondensation process has been



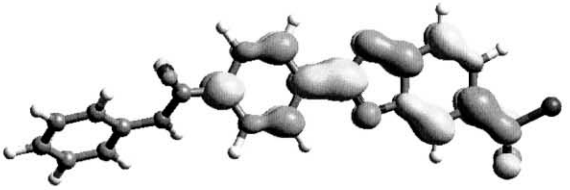
NBO-A (LUMO+1)



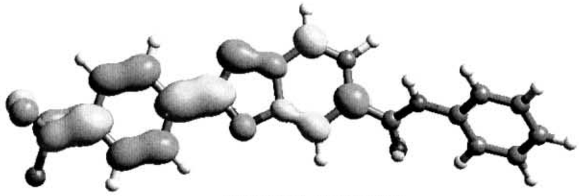
NBO-A (LUMO)



NBO-B (LUMO)



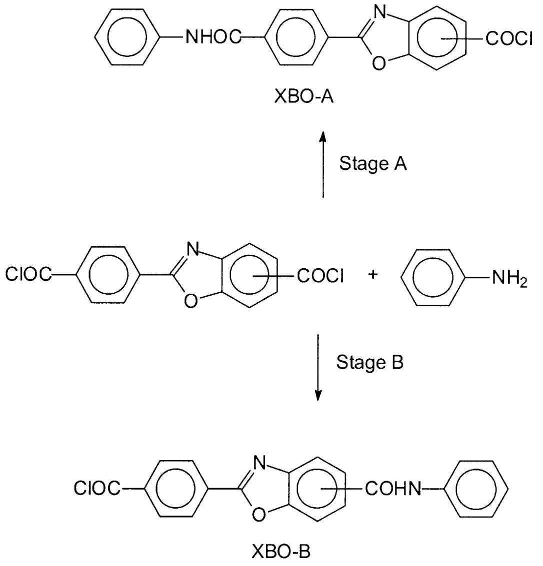
OBO-A (LUMO)



OBO-B (LUMO)

Scheme 2.

Table 2
Electronic characteristics for the first condensation of OBOC and NBOC with aniline



| Structure | $E_{\mathrm{LUMO}}$ (eV)[a] | $E_{\mathrm{LUMO+1}}$ (eV)[a] | $Q_{\mathrm{C(COCl)}}$ (e.u.)[b] |
|---|---|---|---|
| OBO-A | −1.62 (−1.81) | | 0.281 (0.285) |
| OBO-B | −1.64 (−1.81) | | 0.283 (0.281) |
| NBO-A | | −1.00 (−1.06) | 0.282 (0.287) |
| NBO-B | −1.43 (−1.67) | | 0.285 (0.282) |
| IP-S[c] | −1.10 (−1.35) | | 0.285 (0.284) |
| OD-S[c] | −1.01 (−1.23) | | 0.288 (0.289) |
| SD-S[c] | −1.14 (−1.71) | | 0.273 (0.273) |

[a] The energy value of the initial UMO orbital, either LUMO or LUMO + 1, centered on the same chlorocarbonyl group of the initial monomer is given in parenthesis.

[b] The net charge of the same chlorocarbonyl groups of the initial monomer is given in parenthesis.

[c] IP-S, OD-S and SD-S stand for the acronymous of the monoreacted compounds of aniline with IPC, ODC and SDC, respectively.

carried out. In this way, the LUMO energies for the products of the reaction of both monomers, NBOC and OBOC, with one molecule of aniline were calculated, and the results are presented in Scheme 2 (LUMO of the products of the first condensation of OBOC and NBOC with aniline and LUMO + 1 of the product of the first condensation of NBOC with aniline through the phenyl side) and Table 2. It was found that the reactivity of the carbonyl groups is controlled by the LUMO orbital in the case of OBO molecules and this is also the case for NBO when the cholorocarbonyl group joined to the heterocycle reacts in a first stage with aniline. However, when aniline reacts with the chlorocarbonyl group attached to the phenyl group, the reactivity of the second carbonyl group is controlled by the LUMO + 1 orbital, as it happened with NBOC.

Therefore, as the energy of this LUMO + 1 orbital is significantly higher than those of all the LUMO orbitals, the reactivity of the carbonyl group attached to the heterocyclic moiety in NBO is again lower than that of the other carbonyl groups. Consequently, the capacity of NBOC to give high molecular weight polymers is significantly impaired compared to that of OBOC.

In conclusion, OBOC is as very reactive acid chloride and hence it is a feasible polycondensation monomer. However, NBOC, although very reactive through one of the carbonylic carbons, has a much lower reactivity through the other carbon, and consequently, its ability to give high molecular weight is lower. As a matter of fact, this behavior could be experimentally confirmed as can be seen in Table 3.

Table 3
Viscosity and thermal properties of polymers from OBOC and NBOC

| Polymer | $\eta_{inh}$ (dl/g) | $T_g$ (°C) | $T_d$ (°C) | $T_{d_{5\%}}$ (°C) | $Y_c$ (%) |
|---|---|---|---|---|---|
| MPD-OBO | 2.5 | 325 | 460 | 480 | 63 |
| MPD-NBO | 0.9 | 345 (ex.)[a] | 455 | 485 | 64 |
| DDE-OBO | 3.8 | 310 | 505 | 510 | 51 |
| DDE-NBO | 1.8 | 295 | 515 | 520 | 49 |
| 6F-OBO | 2.7 | 350 | 460 | 485 | 57 |
| 6F-NBO | 1.1 | 340 | 465 | 490 | 56 |
| DDS-OBO | 2.1 | 365 | 470 | 475 | 50 |
| DDS-NBO | 0.8 | 350 | 470 | 480 | 47 |

[a] No $T_g$ could be seen. The only observed thermal transition was an exotherm at 345°C.

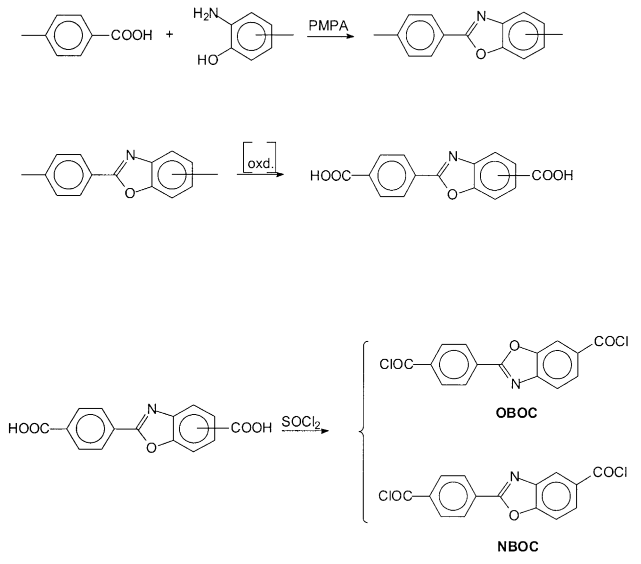
### 3.2. Monomers and polymers syntheses

The synthesis of the monomers OBOC and NBOC was achieved by a high yield three-step process as presented in Scheme 3 (syntheses of monomers OBOC and NBOC). The first step is the process where the benzoxazole ring is formed. Several methods are feasible to build this heterocycle structure. Among them, those based on the reaction of carboxylic acid derivatives, mainly acid chlorides, esters and cyano compounds, with 2-aminophenol stand out by simplicity and economy sake [34,35]. These reactions can be carried out by one or two step condensations. The two-step process consists of the formation of an *o*-hidroxyamide and subsequent chemical or thermal cyclodehydration to the corresponding benzoxazole [11,36]. This method uses to be very mild and permits to carry out the reaction in the presence of several groups. However, the one step method is the preferred one used in polymer chemistry to obtain high molecular weight polybenzoxazoles from aromatic diacids and bis-2-aminophenols. The cyclodehydration reagents commonly used in this one-step route are polyphosphoric acid [37–40], trifluoromethanesulfonic acid or Eaton's reagent (PMPA, a mixture 10/1 of methanesulfonic acid and phosphorus pentoxide) [41,42]. The cyclodehydration reaction of 4-methylbenzoic acid and 4 or 5-methyl-2-hydroxyaniline using a modification of the Eaton's reagent [43] (a mixture 5/1 of methanesulfonic acid and phosphorus pentoxide) proceeded with high yield, over 75% for the dimethyl intermediates.

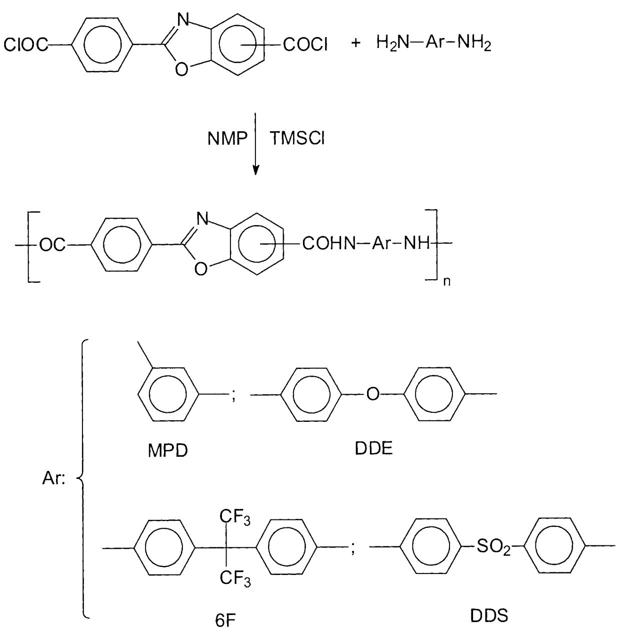
The second step, that is, the oxidation of methyl groups to their corresponding aromatic diacids, was accomplished by the classical oxidation with $KMnO_4$ in a mixture of pyridine-water with yields over 70%. Finally, the treatment of these diacids with thionyl chloride gave the corresponding acid dichlorides with excellent yields in the last step. It should be noted out that the monomer NBOC had been obtained by Kricheldorf et al. by using a four-step synthesis [44]. These authors prepared a series of aromatic polyamides [17] and polyesters [45,46], from this monomer. However, except for NBOC, all the intermediates, monomers and polymers synthesized in this work are new.

Both monomers, NBOC and OBOC, were fully characterized by elemental analysis and spectroscopic means, $^1H$ and $^{13}C$ NMR.

The polymers syntheses were carried out by reaction of several aromatic diamines and both acid dichlorides, OBOC and NBOC as depicted in Scheme 4 (synthesis of polymers from OBOC and NBOC). The in situ silylation method was used in order to obtain high molecular weight polymers because this method enhances the reactivity of aromatic amines allowing the use of weak nucleophilic diamines [47–49]. The obtained polymers were high molecular weight polyamides, as evidenced from their inherent viscosities ($\eta_{inh}$) values, in the range 2.1–3.8 dl/g and 0.8–1.8 dl/g for the polymers from OBOC and NBOC,



Scheme 3.



Scheme 4.

respectively (Table 3). It is worth pointing out the differences between the homologous polymers for each monomer. Thus, the polymers derived from OBOC had much higher inherent viscosities than those from NBOC. The explanation of this fact has been given above by theoretical considerations. Anyway, from the values of $\eta_{\mathrm{inh}}$ and the results of GPC measurements on selected soluble polymers (those from 6F and DDS), it could be demonstrated that the current poly(amide-benzoxazole)s are indeed high molecular weight polymers. The GPC data showed narrow polydispersity values, around 1.5, and weight average molecular weights ranging from 28,000 to 49,000 g/mol and from 87,000 to 121,000 g/mol for the polymers from NBOC and OBOC, respectively. All polymers gave transparent, tough and creasable films from polar aprotic solvent solutions, except the polymers from MPD that shrank during the drying.

### *3.3. Thermal characterization*

DSC, and TGA, were used to evaluate the thermal properties. The data depicted in Table 3 show that they are thermally stable polymers with glass transition temperatures ($T_g$'s) ranging from 310 to 365°C and from 295 to 350°C for the polymers arising from OBOC and NBOC, respectively. These values are very high, as correspond to aromatic polymers with amide and heterocyclic moieties in the main chain, and they can be explained by the polymer chain rigidity, the high density of hydrogen bonding, the existence of polar interchain interactions, and linearity of the monomers. None of the polymers showed crystallization exotherm or melting endotherm between 75°C and the temperature at which the polymers began to decompose, thus indicating that the polymers were essentially amorphous. This assumption was supported by WAXD analysis, where all the polymers showed the typical amorphous halo without any evidence of crystalline order.

Initial degradation temperatures ($T_{d_{\mathrm{onset}}}$) determined by dynamic TGA are in the range 460 to 505°C and 455 to 515°C for the polymers derived from OBOC and NBOC, respectively. These values, shown in Table 3, correspond to polymers with a high ratio of aromatic, hetereoaromatic and sp$^2$ atoms in their structure. These features are also responsible for the high values of char yield ($Y_C$) that ranged from 47 to 64% depending on the nature of the diamine moiety. The differential TGA curves showed two maxima, with the first maximum ranging from 500 to 515°C and from 525 to 560°C for the second one. As an exception, the polymer from DDE showed only a maximum at 530°C. In conclusion, these polymers present a thermal behavior much closer to polybenzoxazoles than to polyamides. This enhanced thermal stability along with the good hydrolytic stability associated to 1,3-benzoazoles, and the possibility of complexing transition metals permit these polymers to be serious candidates in specific gas separation processes at high temperature in the presence of water or acid gases [50,51]. Gas permeation properties for these polymers are being evaluated and they will be reported in a near future.

### *3.4. Solubility and water uptake*

The solubility of these polymers in several solvents is shown in Table 4. They were soluble in sulfuric acid and, contrarily to what happens with polybenzoxazoles, most of them dissolved in highly polar aprotic solvents at room temperature, except the polymers from MPD that had to be heated in order to dissolve them. The polymers from DDE were only soluble in DMA and NMP when the solvents included 5% of LiCl. In less polar solvents, e.g. pyridine (Py), and *m*-cresol (*m*-C), the solubility was much lower and greatly depended on the diamine.

The water uptake of polymers and, particularly aromatic polyamides, can be directly related to their utility as membranes in processes of reverse osmosis. Even though the main target of this work was to obtain new materials for their evaluation in gas separation processes at high temperature, it was considered interesting to evaluate their water uptake. As can be seen in Table 4, the water uptake is not

Table 4
Solubility and water uptake of polymers from OBOC and NBOC (+ +, soluble at room temperature; +, soluble in hot; ±, partially soluble or swollen; −, insoluble)

| Polymer | Solubility | | | | | Water absorption % (w/w) | Mol $H_2O$/repeat unit |
|---|---|---|---|---|---|---|---|
| | $H_2SO_4$ | NMP | DMA | *m*-C | Py | | |
| MPD-OBO | ++ | + | + | − | − | 7.6 (9.3)[a] | 1.50 (1.23)[a] |
| MPD-NBO | ++ | + | + | − | − | 7.7 | 1.52 |
| DDE-OBO | ++ | − [b] | − [b] | − | − | 4.7 | 1.18 |
| DDE-NBO | ++ | + [b] | − [b] | − | − | 4.3 | 1.06 |
| 6F-OBO | ++ | ++ | ++ | + | ± | 3.8 | 1.21 |
| 6F-NBO | ++ | ++ | ++ | ± | − | 4.0 | 1.28 |
| DDS-OBO | ++ | ++ | ++ | + | ± | 6.8 | 1.87 |
| DDS-NBO | ++ | ++ | ++ | + | + | 6.7 | 1.85 |

[a] In parenthesis, the water uptake of poly-*m*-phenyleneisophthalamide with $\eta_{\mathrm{inh}} = 1.12$ dl/g is shown.

[b] Soluble in cold when the solvent has 5% of LiCl.

Table 5
Mechanical properties of polymers from OBOC and NBOC

| Polymer | Tensile strength (MPa) | Young modulus (GPa) | Elongation at break (%) |
|---|---|---|---|
| MPD-OBO | 107 | 2.6 | 62 |
| MPD-NBO | 92 | 2.0 | 8 |
| DDE-OBO | 110 | 2.3 | 38 |
| DDE-NBO | 97 | 2.0 | 36 |
| 6F-OBO | 113 | 2.0 | 38 |
| 6F-NBO | 102 | 2.0 | 13 |
| DDS-OBO | 106 | 2.3 | 45 |
| DDS-NBO | 99 | 2.4 | 14 |

very high, slightly lower than for similar aromatic polyamides. However, the water uptake expressed as mol of water by repeat unit is similar to that of related structures. It is widely accepted that water uptake in aromatic polyamides is generally proportional to the number of amide groups, and specifically to those *free* amide groups not involved in hydrogen bonds, so that, the nitrogen of 1,3-azole compounds should be also able to form hydrogen bonds, and the expected water absorption of these polymers should be higher than that experimentally measured. Therefore, and taking into account the high viscosities, it seems plausible to consider that the nitrogens of the benzoxazole moiety interact with the hydrogens of the amide group forming a very dense network of hydrogen bonds which decreases the water uptake.

### *3.5. Mechanical properties*

Films of both series of polymers were tested to evaluate their mechanical properties. As commented before, the polymers from MPD shrank during their casting but they gave good and creasable films. All polymers presented excellent mechanical properties, with tensile strengths around 100 MPa for all polymers (Table 5). The elastic moduli were typical for this class of polymers with values about 2 GPa. Elongations were high for the polymers from OBOC, with values ranging from 38 to 62%, and much lower for the polymers from NBOC with values in the range 8–36%. Thus, these aromatic polymers have good mechanical properties with values of tensile strength and elastic modulus, which compare well with aromatic polyamides and polybenzoxazoles. It is interesting to point out that the mechanical properties are not very dependent on the diamine moiety, in contrast with related polymers. This fact could again be explained by the structure of these polymers where the hydrogen bonds between amide groups and heterocyclic nitrogen help for a dense packing, with a high value of cohesive energy.

## 4. Conclusions

Two polycondensation aromatic diacid monomers with a benzoxazole moiety, 2-(4-carboxyphenyl)benzoxazole-5-carboxylic acid and 2-(4-carboxyphenyl)benzoxazole-6-carboxylic acid, were obtained by a straightforward three-step method with high yield where the limiting step of this synthesis is the oxidation of the aromatic methyl groups. By using the in situ silylation of aromatic diamines, the low temperature polyamidation method has been a convenient process to obtain high molecular weight polymers.

The electronic differences between both monomers, NBOC and OBOC, as calculated by semiempirical quantum-mechanical methods showed the reactivity of NBOC to be lower than that of OBOC because of orbital considerations. Thus, OBOC and NBOC have a very low LUMO energy, lower than those of very reactive acid chlorides. However, in NBOC, the reactivity of the chlorocarbonyl moiety anchored to the benzoxazole groups is controlled by the LUMO + 1 which has a much higher energy value. Due to this difference between both reactive groups, the global reactivity of NBOC on polycondensation processes is much lower.

The values of glass transition temperatures are higher than 300°C because of polymer chain rigidity, high density of hydrogen bonding, strong polar interactions and linearity of the macromolecular chain. Also, owing to the presence of benzoxazole groups in the macromolecular chain, the thermal stability and the char yield of these polymers are very high.

The dense network of hydrogen bonds, among the amide groups and also among the nitrogen of the benzoxazole groups and the hydrogens of the amide ones, causes a decrease of the water uptake of these polymers. Also, the commented dense network of hydrogen bonds combined with the existence of electronic interactions among $\pi$-rich aromatic moieties and $\pi$-deficient heterocyclic ones are responsible of the excellent mechanical properties, elastic moduli and tensile strengths, obtained in this work.

## Acknowledgements

This research was supported by the Comisión Interministerial de Ciencia y Tecnologia, CICYT, (Programs MAT98-0942 and MAT98-0905).

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