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Synthesis and properties evaluation of novel halogenated polyimides designed to prepare functional polymers

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Abstract

Three new aromatic polyimides containing one or two replaceable halogen atoms in the repeat unit have been prepared by one-pot polycondensation at high temperature from dianhydrides and diamines containing halogen atoms. The halogenated polyimides exhibited good thermal properties and great solubility in a wide range of organic solvents, which make them good candidates to prepare functional polymers. They also showed film-forming capabilities, good mechanical properties, and a very low ability to take water, with values of only around 1% water uptake. To show the usefulness of these polyimides as functional polymers, the halogen group of two of them was successfully replaced by 4-*tert*-butyl phenyl or 4-*tert*-butyl phenyl ethynyl groups by a Suzuki or a Sonogashira reaction, respectively.

Keywords: Polyimides; Halogen; Modification

1. Introduction

Aromatic polyimides have attracted considerable attention because of their outstanding thermal stability, good insulation properties, excellent mechanical resistance and other properties such as high chain rigidity and strong interchain interactions. These properties make them very useful in many applications such as electronics, coatings, composite materials or membranes [1].

To extend the scope of their applications, it is desirable that polyimides contain appropriate functional groups. For example, one approach to use polyimides as membranes for gas separation involves the incorporation of bulky pendant groups that disrupt chain packing efficiency, increasing the free volume and the permeability [2]. The general way to introduce most of bulky pendant groups into polyimides is by using monomers that bear those groups. Another approach consists on the introduction of groups with functionalities capable of interacting in an effective way with a certain permeant improving its solubility, and hence obtaining a membrane with enhanced gas separation properties. Thus, bulky groups such as phenyl [3] *tert*-butyl [4,5] or cardo [6] and functional groups such as crown-ethers [7] have been successfully introduced into polyimides through monomers containing those functionalities.

Hereafter, we report the synthesis and characterization of novel polyimides as targets to introduce other functional groups. The new polyimides contain one or two halogen atoms in the repeat unit, which are able to react with other compounds in order to attach new functionalities, which can give new polymers with attractive properties.

Two polyimides of the set here reported have one reactive bromine or iodine atom in the repeat unit, while the third member of the series is a bifunctional polyimide which contains both iodine and bromine. The halogen substituents can undergo a modification reaction for example with alkene derivatives using the Heck reaction conditions [8], with functionalised boronic compounds through the Suzuki cross-coupling reaction [9] or with ethynyl compounds through the Sonogashira procedure [10], which could provide a variety of new polyimides with tailor made properties.

However, to achieve good yields through all these modification reactions it is necessary to have highly soluble and processable polyimides. Wholly aromatic polyimides are rather insoluble, but their solubility can be usually improved by introducing flexible linkages [11,12], bulky pendant groups [2] or trifluoromethyl moieties [13–15]. In this work, we have incorporated trifluoromethyl groups as a hexafluoroisopropylidine moiety in the repeat unit of the mono-functionalized polyimides just to provide solubility. The polyimide containing

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Br and I was also a very soluble polymer despite of containing no extra group to impart solubility.

Due to the presence of halogen atoms, the polyimides of this study are themselves good candidates for several applications such as gas separation processes [16] or fire-resistant coatings and films [17]. The polymers have been characterized by general means, and their physical properties were measured, particularly their thermal resistance and their level of water uptake, and some of these results were compared with those of reference polyimides without halogen atoms in the repeat unit.

Finally, to demonstrate the usefulness of these polyimides as functional polymers, two examples of the replacement of the halogen by bulky groups have been also included in this work. After the obtained results, a new set of functional polyimides addressed to improved gas separation properties will be obtained in a near future.

2. Experimental part

2.1. Materials

1,3-Bis(3,4-dicarboxybenzoyl)-5-bromobenzene was synthesized according to the procedure previously reported [3].

5-Iodo-*m*-phenylenediamine (**ID**) was synthesized by diazotization [18] and subsequent iodation [19] of 3,5-dinitroaniline (Aldrich) and reduction of the dinitro intermediate [20,21].

2,2′-Bis(4-aminophenyl)hexafluoropropane (**6FD**) (Chriskev Company) and 2,2′-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (**6FDA**) (Chriskev Company) were commercially available and were sublimated just before used.

4-*tert*-Butylphenyl boronic acid (Aldrich), 4-*tert*-butylphenyl acetylene (Aldrich), solvents and other reactants were of reagent-grade quality, and used without further purification.

2.2. Monomer synthesis

2.2.1. 1,3-Bis(3,4-dicarboxybenzoyl)-5-bromobenzene dianhydride (BrDA)

The dianhydride **BrDA** was prepared by refluxing 10 mmol of 1,3 bis(3,4-dicarboxybenzoyl)-5-bromobenzene in a mixture 6/1 (v/v) of acetic anhydride (108 mL)/acetic acid (18 mL) for 3 h. The product crystallized on cooling and was filtered out and recrystallized from a 4/1 (v/v) mixture of acetic anhydride/acetic acid.

Yield: 88%; mp 233 °C; ^{1}H NMR (pyridine-d_5, ppm): ($\delta=$ 8.17 (dd, 2H, H_d), 8.25 (d, 2H, H_e), 8.36 (s, 2H, H_b), 8.40 (s, 1H, H_h), 8.84 (d, 2H, H_j); ^{13}C NMR (pyridine-d_5, ppm): $\delta=$ 129.8 (C_h), 129.9 (C_i), 131.4 (C_e), 132.4 (C_b), 135.1 (C_a), 136.6 (C_d), 138.0 (C_j), 139.5 (C_c and C_g), 139.9 (C_f), 170.6 and 169.8 (C anhydride), 193.0 (C carbonyl); *m/z* 504 and 506 ($M+H^+$); Elemental analysis ($C_{24}H_9BrO_8$), (505.23) calcd C 57.05, H 1.80, Br 15.81; found C 56.10, H 1.82, Br 15.30.

2.3. Polymer synthesis

Five millimole of diamine were dissolved in 20 mL of *m*-cresol in a 100 mL three-necked flask with mechanical stirring blanketed by nitrogen. Then, 5.0 mmol of dianhydride were added to the solution. The mixture was gradually heated up to 80 °C and then, 0.3 mL of pyridine was added. The reaction was held at that temperature for 2 h. Then, the temperature was gradually risen up to 190 °C and benzoic acid (3 mmol) was added to the viscous clear solution of poly(amic acid). The reaction was maintained at that temperature overnight, except for polyimide **Br–6F** which was heated only for 3 h to avoid gelation of the polymer solution. After cooling, the viscous solution was poured into ethanol forming a fibrous polymer precipitate, which was removed by filtration and thoroughly washed with water and ethanol. Polyimides **Br–6F** and **6F–I** were further purified by dissolving them in chloroform and pouring into methanol. Polyimide **Br–I** was dissolved in DMF and poured into ethanol. All polymers were finally extracted with ethanol in a Soxhlet apparatus for 8 h and dried in a vacuum oven at 80 °C overnight. Yields were quantitative for all polymerizations.

2.3.1. Br–6F

^{1}H NMR (80 °C, DMSO-d_6, ppm): ($\delta=7.57$ (m, 4H, H_m), 7.64 (m, 4H, H_l), 7.98 (s, 1H, H_h), 8.07–8.38 (m, 8H, H_b, H_d, H_e, H_j); ^{13}C NMR (DMSO-d_6, ppm): $\delta=122.5$ (C_n), 123.9 (C_h), 127.5 (C_e and C_l), 130.2 (C_b and C_m), 130.6 (C_j), 131.7 (C_a), 132.8 (C_f), 134.7 (C_k), 135.9 (C_i), 136.1 (C_d), 138.4 (C_g), 141.6 (C_c), 165.9 (C imide), 192.4 (C carbonylic); FT-IR (film, cm^{-1}) 709 (C–Br), 1093 and 1174 (C–F), 1735 and 1781 (C=O imide), 3068 (C–H ar); Elemental analysis ($C_{39}H_{17}BrF_6N_2O_6$), (803.45) calcd C 58.24, H 2.13, N 3.48, Br 9.94; found C 57.72, H 2.17, N 3.65, Br 9.60.

2.3.2. 6F–I

^{1}H NMR (CDCl$_3$, ppm): ($\delta=7.64$ (t, 1H, H_h), 7.84 and 7.85 (2×m, 4H, $H_{d,j}$), 7.92 (m, 2H, H_b), 8.02 (d, 2H, H_e); ^{13}C NMR (CDCl$_3$, ppm): $\delta=93.1$ (C_i), 123.1 (C_h), 124.4 (C_e), 125.5 (C_b), 132.0, 132.3 and 132.7 (C_a, C_c and C_f), 134.2 and 136.2 (C_d and C_j), 139.4 (C_g), 165.1 and 165.2 (C imide); FT-IR (film, cm^{-1}) 630 (C–I), 1102, 1143 and 1192 (C–F), 1747 and 1786 (C=O imide), 3085 (C–H ar); Elemental analysis ($C_{25}H_9F_6IN_2O_4$), (642.24) calcd C 46.71, H 1.41, N 4.36, I 19.75; found C 46.90, H 1.46, N 4.47, I 19.96.

2.3.3. Br–I

^{1}H NMR (DMSO-d_6, ppm): (($\delta=7.62$ (m, 1H, H_h), 7.91 and 7.94 (m, 3H, H_j and H_h), 8.05–8.27 (m, 8H, H_b, H_d, H_e, H_j), 8.07–8.28 (m, 9H, $H_{b,d,e,h,j}$); ^{13}C NMR (DMSO-d_6, ppm): 93.6 (C_m), 123.8 (C_l), 124.5 (C_h), 126.1 (C_e), 131.8 (C_j), 132.8, 133 and 133 (C_a, C_f, C_n), 135.8 (C_i), 136.1 (C_d), 137.5 (C_g and C_k), 141.6 (C_c), 165.9 (C imide), 192.4 (C carbonylic); FT-IR (film, cm^{-1}) 630 (C–I), 715 (C–Br), 1744 and 1780 (C=O imide), 3069 (C–H ar); Elemental analysis ($C_{30}H_{12}BrIN_2O_6$), (703.23) calcd C 51.19, H 1.72; N 3.98, Br 11.36, I 18.04; found C 50, 40, H 2.10, N 3.67, Br 11.24, I 18.29.

2.4. Polymer modification

*2.4.1. Substitution of bromine group via Suzuki reaction of **Br–6F***

A 100 mL three neck round bottom flask equipped with condenser, mechanical stirrer and nitrogen inlet–outlet was charged under a nitrogen flux with 0.300 g (0.37 mmol) of polyimide **Br–6F**, 0.133 g (0.74 mmol) of 4-*tert*-butylphenylboronic acid, 0.206 g (1.48 mmol) of potassium carbonate, 0.008 g (0.007 mmol) of $Pd(PPh_3)_4$ and 10 mL of anhydrous THF, previously degassed by bubbling nitrogen over a period of 30 min. The solution was refluxed for 48 h. After cooling, the solution was passed through Celite® and concentrated by rotary distillation. The yellow solid obtained was redissolved in chloroform and poured into methanol. The precipitate was refluxed 3 h with hot hexane and 3 h with methanol to remove any trace of reactants. The polymer was separated by filtration and dried in a vacuum oven at 80 °C overnight. Yield: 75 ± 5% for polymer modification.

^{1}H NMR (80 °C, DMSO-d_6, ppm): 1.33 (s, $C(CH_3)_3$), 7.35 (m, H_r), 7.59 (d, H_m, $H_{m'}$), 7.68 (d, H_l, $H_{l'}$), 7.80 (m, H_q), 7.89 (m, H_d, H_j), 8.05 and 8.09 (2 × s, H_h, $H_{h'}$), 8.16–8.34 (m, H_b, H_e, H_d, H_j, $H_{b'}$, $H_{e'}$, $H_{d'}$, $H_{j'}$); FT-IR (KBr, cm^{-1}) 705 (C–Br), 1086 and 1174 (C–F), 1737 and 1785 (C=O imide), 3067 (C–H ar).

*2.4.2. Substitution of iodine group via Sonogashira reaction of **6F–I***

A 100 mL three neck round bottom flask equipped with condenser, mechanical stirrer and nitrogen inlet–outlet was charged under a nitrogen flux with 0.250 g (0.38 mmol) of polyimide **6F–I**, 1.3 mg (0.002 mmol) of $Cl_2Pd(PPh_3)_2$, 7.4 mg (0.038 mmol) of CuI and 3 mL of freshly distilled DMF. After the polymer was dissolved, 2.3 mL of freshly distilled Et_2NH and 0.061 g (0.38 mmol) of 4-*tert*-butylphenyl acetylene were added to the solution. The reaction mixture was stirred 24 h at room temperature and 2 h at 50 °C yielding a brown viscous liquid. The resulting solution was passed through Celite® and precipitated in water. The beige solid obtained was refluxed 3 h with hot methanol to remove any trace of reactants. The polymer was separated by filtration and dried in a vacuum oven at 80 °C overnight. Yield: 65 ± 5 for polymer modification.

^{1}H NMR (DMSO-d_6, ppm): ($\delta = 1.28$ (s, $C(CH_3)_3$), 7.44–7.58 (m, $H_{k'}$, $H_{l'}$), 7.62 and 7.63 (2 × s, H_h, $H_{h'}$), 7.73 and 7.67 (2 × s, H_j, $H_{j'}$), 7.95 (m, H_b, $H_{b'}$, H_d, $H_{d'}$), 8.20 (m, H_e, $H_{e'}$); FT-IR (KBr, cm^{-1}) 634 (C–I), 1099, 1143 and 1191 (C–F), 1731 and 1785 (C=O imide), 2204 (C≡C), 2950 (C–H ar).

2.5. Measurements

FT-IR spectra were recorded on a Perkin Elmer RX-1 Instrument from 30 μm thick polymer films for the unmodified polymers. The modified polymers were recorded from KBr pellets.

^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini 300 spectrometer operating at 300 and 75 MHz, respectively. Dimethylsulfoxide-d_6, chloroform-d_1 and pyridine-d_5 were used as solvents.

Microanalyses were made with a Carlo Erba EA1108 elemental analyzer.

Inherent viscosities were measured with an automated Ubbelohde viscosimeter at 25 ± 0.1 °C with NMP as solvent at 0.5 g/dL concentration.

Differential scanning calorimetry (DSC) data were obtained on a Perkin–Elmer DSC 7 analyzer from 5 mg of sample under a nitrogen atmosphere at a 20 °C/min scan rate.

Thermogravimetric analysis (TGA) data were recorded on a TA TGQ500 analyzer from 5 to 10 mg of sample under a 50 mL/min nitrogen flux at 10 °C/min.

For the measurement of the mechanical properties, strips 5 mm wide, 30 mm long and 20–80 μm thick were cut from polymer films and tested on a MTS Synergie 200 Universal Testing Machine dynamometer at 25 °C. Mechanical clamps were used, and an extension rate of 5 mm/min was applied with a gauge length of 10 mm.

Water sorption measurements were determined gravimetrically at room temperature. Powdered polymer samples of 0.3 g, previously dried at 120 °C for 48 h over P_2O_5, were placed in a closed box containing a saturated aqueous solution of $NaNO_2$, which provided a relative humidity of 65%. The samples were frequently weighed during 8 h and then were allowed to humidify for seven more days, until they had equilibrated with their surrounding as denoted by no weight change.

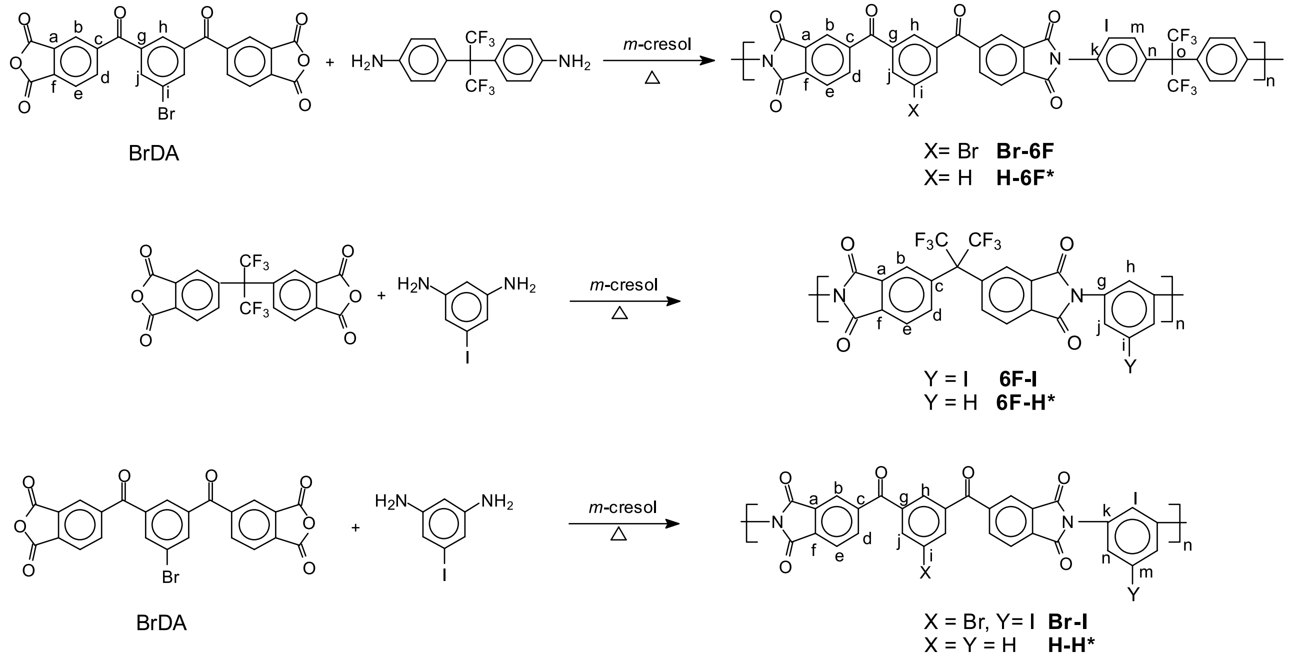
3. Results and discussion

3.1. Monomers and polymers synthesis and characterization

The new dianhydride **BrDA**, was obtained by cyclodehydration of 1,3-bis(3,4-dicarboxybenzoyl)-5-bromobenzene [2] using a mixture of acetic anhydride and acetic acid.

The synthetic route of the novel halogenated polyimides is depicted in Scheme 1. A one-pot condensation method in solution at high temperature was adopted in this work. The mixture of monomers was heated slowly to 80 °C to form a transparent solution in *m*-cresol in 2 h and then, the temperature was raised to 190–200 °C and kept for several hours. In that stage the formation of long chain polymers and imidization, catalyzed by benzoic acid, took place simultaneously. Polyimides **6F–I** and **Br–I** were kept at that temperature overnight but polyimide **Br–6F** was heated at 190–200 °C only for 3 h because a longer reaction, either 6 h or overnight, caused a gel formation probably due to cross-linking. However, up to the present we do not know the reason for that cross-linking.

The reactivity of the monomers was estimated by semiempirical methods (PM3) [22]. At the early stages of any organic reaction, the frontier molecular orbital, FMO, theory works reasonably well [23]. The reactivity of the diamine monomers can be related to the energy of the highest occupied molecular orbital (HOMO) while the reactivity of dianhydrides depends on the energy of the lowest unoccupied



Scheme 1. Structures and designation of halogenated polyimides and reference polyimides (*). * For the synthesis of reference polyimides see Refs. [3,25].

molecular orbital (LUMO). Thus, the polymerization reaction rate can be predicted by the $\mathrm{HOMO_{diamine}}$–$\mathrm{LUMO_{dianhydride}}$ energy difference. The calculated values of these parameters (Table 1) indicate that the new dianhydride **BrDA** is less reactive as electrophyle than the commercial dianhydride **6FDA**. Regards the diamines, **6FD** is less reactive than **ID**. For this reason, the $\mathrm{HOMO_{diamine}}$–$\mathrm{LUMO_{dianhydride}}$ interaction energy gap in polyimide **Br–6F** is the lowest, and hence the polyimidation reaction rate is the least favored. Despite of that, the energy gaps are low enough to justify a good reactivity, and thus all polyimides have shown similar inherent viscosities of around 0.38 dL/g (Table 2), which can be considered as moderate values for this type of macromolecular structures.

Elemental analyses were consistent with the chemical composition. FT-IR spectroscopic characterization was performed on films obtained by solvent evaporation from polymer solutions. The most remarkable features were the absorption bands around 1780 and 1740 $\mathrm{cm^{-1}}$ associated to the carbonyls of the imide group. Polyimides with iodine and bromine showed also a strong band around 630 and 710 $\mathrm{cm^{-1}}$ corresponding to C–I and C–Br stretching, respectively. No absorption bands associated to N–H vibrations (polyamic acid) were observed.

The structures of the novel halogenated polyimides were also confirmed by ^{1}H NMR and ^{13}C NMR. All peaks were properly assigned (Section 2) and no signal corresponding to poly(amic acid) structures were observed in any case. The carbons were assigned by comparing the structures and with the help of additional DEPT and HMQC experiments. The carbons corresponding to the hexafluoroisopropylidene moiety could not be observed in any case probably due to the short relaxation time used to record the spectra.

Table 1
Electronic parameters of halogenated monomers and gap energies (cross cells)

Dianhydride	Diamine	**6FD**	**ID**
	E_{HOMO} (eV)	−8.93	−8.57
	E_{LUMO} (eV)		
BrDA	−1.85	−7.08	−6.72
6FDA	−2.14		−6.43

3.2. Polymer properties

3.2.1. Solubility

The three polyimides were highly soluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, dimethyl sulfoxide, *N*,*N*-dimethylformamide, protic solvents such as *m*-cresol and even in organic solvents such as cyclohexanone. Moreover, **Br–6F** and **6F–I** could also be dissolved in more common organic solvents, such as tetrahydrofuran and chloroform at room temperature. The introduction of a more bulky halogen group such as iodine should probably produce a decrease in the intermolecular

Table 2
Inherent viscosity values and thermal properties of the halogenated and reference polyimides

Polymer	η[a] (dL/g)	T_g (°C)[b]	$\mathrm{Td_{onset}}$ (°C)[c]	T_{10} (%)	Char yield (800 °C)
Br-6F	0.40	285	540	550	50
H-6F*	0.81	257	555	–	–
6F-I	0.38	315	495	510	35
6F-H*	0.71	298	–	–	–
Br-I	0.35	n.d	430	465	52
H-H*	0.37	255	585	–	–

* Data obtained from literature [3,25].
[a] Ubbelohde viscometer; 25±0.1 °C; 0.5 g/dL in NMP.
[b] Perkin–Elmer DSC 7; 5 mg of sample; nitrogen atmosphere; 20 °C/min.
[c] TA TGQ500 analyzer; 50 mL/min nitrogen flux; 10 °C/min.

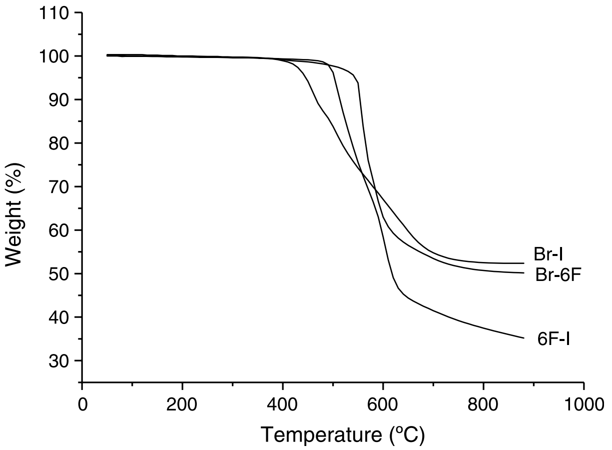


Fig. 1. TGA curves of the halogenated polyimides.

association forces, which should bring about an enhanced solubility. However, both polymers (**Br–6F** and **6F–I**) showed the same solubility behavior, which can be attributed to the strong effect of the hexafluoroisopropylidine group on solubility. In fact, the polyimide **Br–I**, which does not have this group, showed the poorest solubility.

3.2.2. Thermal properties

Thermal properties were evaluated by DSC and dynamic TGA. DSC thermograms were registered up to 400 °C and only the inflection corresponding to glass transition was observed on the curves (Table 2). The T_g values of polyimides **Br–6F** and **6F–I** were 285 and 315 °C, respectively, while the reported T_g values for the homologous polyimides without halogen group (**H–6F** and **6F–H**) are 260 °C [3] and 298 °C [24]. Thus, the introduction of bromine or iodine group brought about a slight increase of the T_g value. This is probably attributable to the fact that the decrease in the intermolecular forces of the halogen-substituted polyimides was compensated by the simultaneous effect of molecular mobility restriction. For the polyimide with two halogen groups (**Br–I**), no T_g could be detected by DSC measurements.

The thermal stability results, measured under nitrogen, are presented in Fig. 1 and summarized in Table 2. Polyimide **Br–6F** exhibited the highest thermal stability with a decomposition temperature of 540 °C. However, polyimides with iodine substituents (**6F–I** and **Br–I**) shared a lower thermally stability with decomposition temperatures of 490 and 430 °C, respectively. These results can be explained on the basis of the bond dissociation energy of the aromatic-halogen bond, which decrease in the following order: C–Br (300 kJ/mol) > C–I (230 kJ/mol) [25]. Thus, the weak C–I bond energy causes the lowest decomposition temperatures in comparison with the bromine substituted polyimide.

When these results were compared with the homologous polyimides without halogen group, it could be noticed that the introduction of bromine group in polyimide **Br–6F** slightly decreased the thermal resistance, since polyimide **H–6F** shows a decomposition temperature of 555 °C [3]. However, when bromine and iodine groups were simultaneously introduced (polyimide **Br–I**), the thermal stability decreased significantly when compared with polyimide **H–H**.

These results are in agreement with the highest bond dissociation energy of the aromatic-hydrogen bond C–H (460 kJ/mol) [25].

3.2.3. Mechanical properties

Polyimides films were tested to evaluate their tensile modulus, tensile strength and elongation (Table 3). Polyimides **Br–6F** and **Br–I** showed elastic moduli of 2.5 GPa, values very close to those of the reference polyimides without halogen groups [3]. However, the tensile strengths found for halogenated species were lower than those of the non-halogenated references, which, on spite of the lower molecular weight of the halogenated polymers, could be attributable to the chain separation caused by the introduction of the halogen side groups, which decrease the strength of inter-chain interactions. Elongations at break were not very high, around 4.5 and 4%, respectively, in agreement with the molecular rigidity of aromatic polyimides. Polyimide **6F–I** showed the worst mechanical properties of the series with a tensile strength of only 45 MPa and 1.4 GPa for the Young's modulus. On the basis of these results, it can be pointed out that polyimides containing iodine usually show lower mechanical properties than non-substituted polyimides.

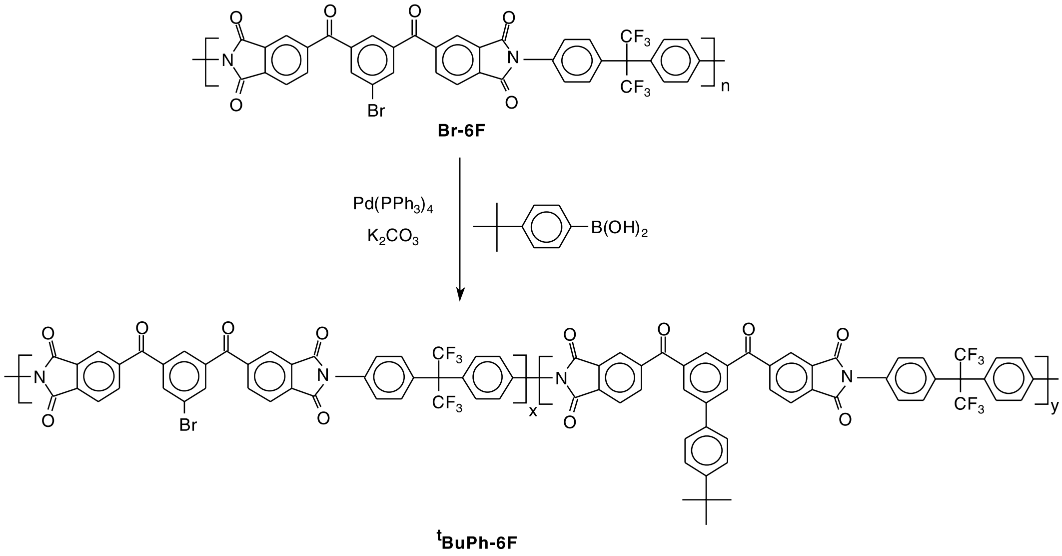
Table 3
Mechanical and water sorption properties of the halogenated polyimides

Polymer	Mechanical properties[a]			Water sorption properties[b]	
	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Moisture absorption (%)	Mol H_2O per repeat unit
Br–6F	2.50	86	4.5	1.01	0.45
H–6F*	2.51	117	8.5	–	–
6F–I	1.4	45	2	1.01	0.36
6F–H	–	–	–	–	–
Br–I	2.50	65	4	1.01	0.40
H–H*	3.02	135	4.9	–	–

* Data obtained from literature [3].

[a] MTS Synergie 200 Universal Testing Machine; films (30×5 mm, 20–80 μm); extension rate: 5 mm/min; gauge length: 10 mm.

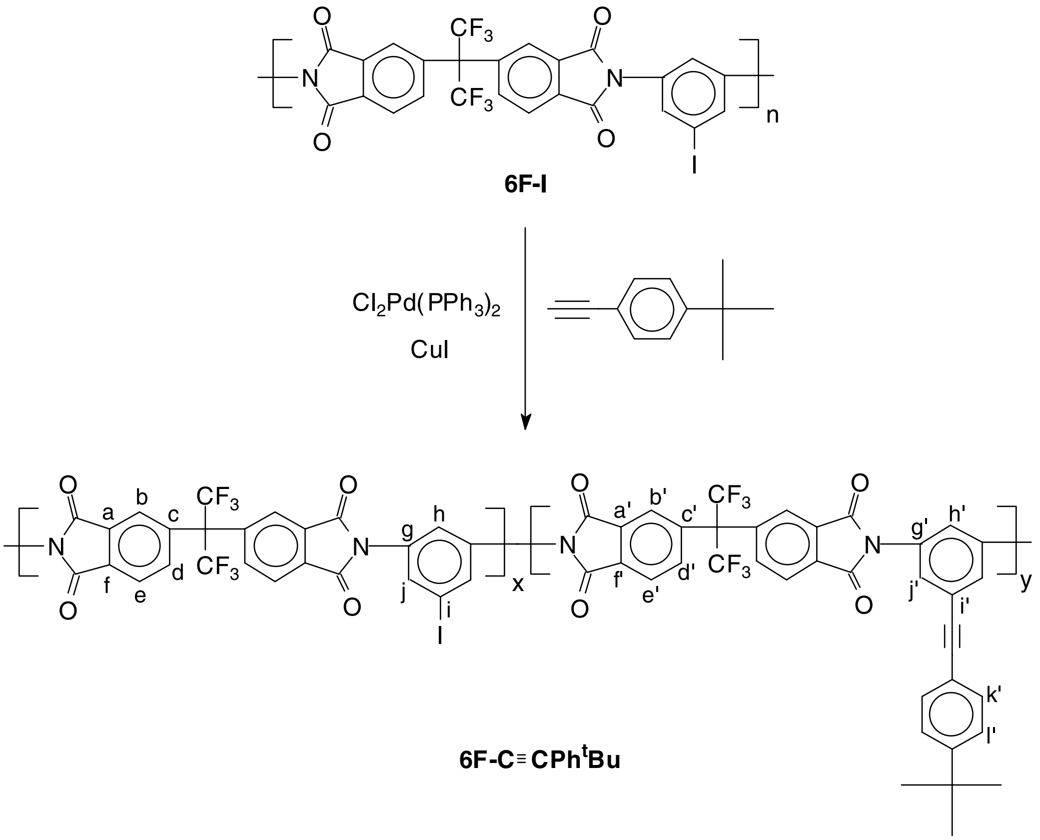
[b] 65% relative humidity.



Scheme 2. Synthesis of polyimide **^{t}BuPh–6F** via Suzuki reaction of polyimide **Br–6F**.

3.2.4. Water sorption properties

Low moisture uptake in polyimide materials is a major concern for such applications as microelectronics and optical devices [26]. Generally, polyimides with CF_3 groups show very low water sorption because the CF_3 group imparts hydrophobicity [27,28]. Regards to that, the new halogenated polyimides exhibited very low water uptake, around 1.0% in standard conditions (Table 3). That is true even for the polyimide **Br–I** without trifluoromethyl groups in the repeat unit. Nevertheless, polyimides **Br–6F** and **Br–I** exhibited higher water absorption values per repeat unit than polyimide **6F–I**. This result seems to indicate that the extra carbonyl groups of these polymers are able to interact with water, and hence they are responsible for this higher water sorption.



Scheme 3. Synthesis of polyimide **6F–C≡CPh^{t}Bu** via Sonogashira reaction of polyimide **6F–I**.

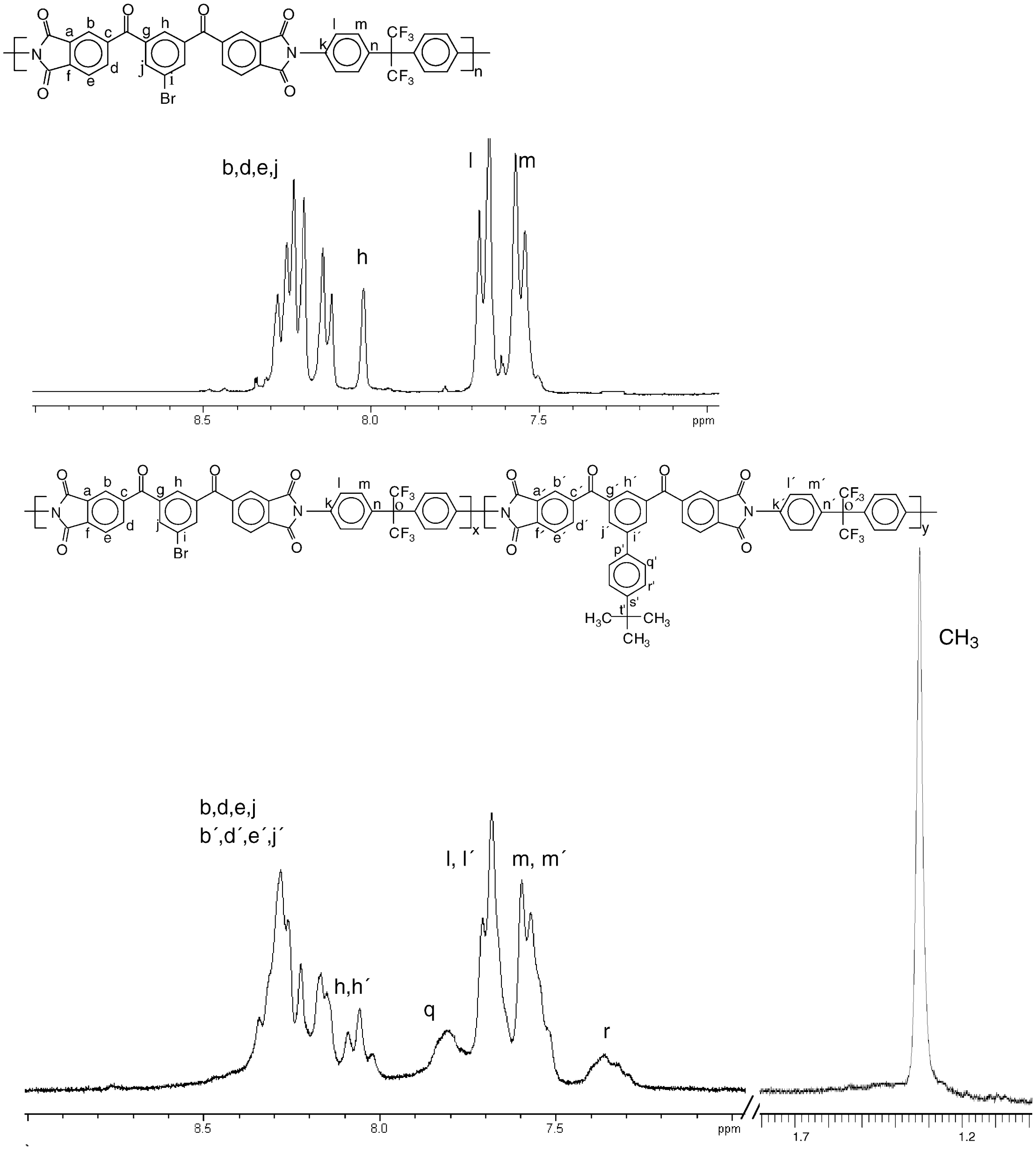


Fig. 2. ^{1}H NMR spectra of polyimide **Br–6F** and **^{t}BuPh–6F**.

3.3. Polymer modification

Polyimides **Br–6F** and **6F–I** were reacted with a boronic acid and with an acetylene derivative to demonstrate the utility of the halogenated polyimides of this work as functional polymers. Thus, polyimide **Br–6F** was reacted with 4-*tert*-butylphenyl boronic acid by a Pd(0)-catalyzed coupling reaction, to yield the corresponding modified polyimide **^{t}BuPh–6F** (Scheme 2). On the other hand, polyimide **6F–I** was reacted with 4-*tert*-butylphenyl acetylene by a cross-coupling methodology using the catalytic system of Pd(II) and CuI in freshly distilled DMF/Et_2NH as solvents to yield polyimide **6F–C≡CPh^{t}Bu** (Scheme 3).

The modified polymers were characterized by IR and ^{1}H NMR spectroscopy. As an example, ^{1}H NMR spectra of modified polyimide **^{t}BuPh–6F** and its precursor are shown in Fig. 2. The presence of a strong peak at 1.30 ppm, corresponding to the *tert*-butyl group, and two new signals at 7.35 and 7.80 ppm corresponding to the phenyl pendant moiety, clearly proved that the displacement of the halogen and the incorporation of the *tert*-butylphenyl group occurred in a great extension. The conversion of the reaction, estimated by aromatic signals integration, was $75\pm5\%$.

^{1}H NMR spectra of modified polyimide **6F–C≡CPh^{t}Bu** showed also a strong peak at 1.30 ppm due to the *tert*-butyl group and new signals in the aromatic area corresponding to the phenyl pendant moiety. In addition, the triple bond stretching of the ethynyl linkage appears at 2204 cm^{-1} in the IR spectra of modified polyimide **6F–C≡CPh^{t}Bu** (Fig. 3).

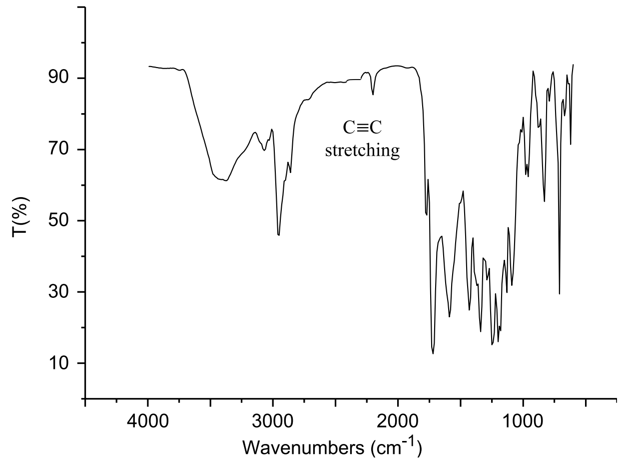


Fig. 3. FT-IR spectrum of polyimide **6F–C≡CPh^{t}Bu**.

Regards the thermal properties, the polyimides **^{t}BuPh–6F** and **6F–C≡CPh^{t}Bu** showed a T_g of 290 and 317 °C, respectively, very similar to that of the starting polymers. Polyimide **^{t}BuPh–6F** shows a decomposition temperature of 480 °C. Thus the partial substitution of bromine atoms by *tert*-butylphenyl groups caused a decrease of 60 °C in the thermal stability. However, the decomposition temperature of polyimide **6F–C≡CPh^{t}Bu** (505 °C) is slightly higher than the starting polymer, indicating that the partial substitution of iodine yields a more thermally stable polyimide. On the other hand, the TGA curve of the new polyimides showed a two-step decomposition path. The first one corresponds to the loss of the *tert*-butyl moiety while the second one could be associated to generalized polymer degradation.

4. Conclusions

Novel polyimides with replaceable halogen atoms have been synthesized following a one-pot condensation procedure, in solution at high temperature. The polymers have shown good solubility in organic solvents, film-forming abilities and acceptable thermal and mechanical properties. The halogenated polyimides here reported also exhibit very low values of water uptake, of only around 1%, which is a very low value for aromatic polyimides. The nature of the halogen incorporated and the composition of the repeat unit greatly influence the properties, particularly thermal resistance which is lower for polymers with iodine than for those containing bromine. The polymer having iodine and bromine in its repeat unit showed the lowest thermal resistance.

Halogen atoms can be replaced by a bulky group through Pd-catalyzed coupling reactions, which confirms the ability of these halogen-substituted polyimides as precursors for the preparation of novel polyimides.

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