



Fluorescent aromatic polyamides with urea binding sites and fluorene or dansyl signaling units

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ABSTRACT

This work describes six novel fluorescent aromatic polyamides with bulky dansyl or fluorene pendant groups or with the fluorene moiety in the main chain. The fluorescent signaling dansyl or fluorene moieties are chemically connected to, or within, the main polymer chains through a urea group, a well-known binding site in supramolecular chemistry. These polyamides are amorphous and soluble in polar aprotic solvents and demonstrate a film-forming capability. They also show yellowish-green or blue fluorescence in solution and in the solid state depending on the signaling unit, with the former corresponding to the dansyl and the latter to the fluorene residue. The water uptake and the thermal behavior have also been evaluated and related to the chemical structure. The polar amide, urea, and sulfonamide groups give rise to a high water sorption of up to 3.8 water molecules per repeating unit. The thermal behavior has been investigated by means of DSC and TGA. The glass transition temperatures of the polymers are high (up to 331 °C) and the decomposition temperatures (around 300 °C) are due to the moderate thermal stability of the urea group.

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1. Introduction

Fluorescent chemosensors have attracted the interest of researchers due to their potential applications in chemistry and biology [1–4]. These discrete *probes* are generally low molecular weight compounds, which limits their technological uses as they are soluble in most solvents and thus their separation and recovery is difficult. In addition, they have low thermal and chemical stability and need to be bound to a physical support for most of their applications. The preparation of polymers with signaling moieties chemically anchored to the backbone provides an excellent means of immobilization, and the inclusion of these supramolecular subunits in a polymer structure opens up the technological application of these materials to areas such as sensors, actuators, permselective membranes, catalysts, etc [5–12]. Following this approach, polymers with both a

fluorescent signaling group and a host moiety in their structural unit can act as fluorescent chemosensing probes for the development of sensing devices [13–17]. Moreover, if a highly mechanically and thermally resistant polymer backbone is used, the materials derived from it can be used under extreme conditions, thereby increasing the added value of these materials.

In light of the above, we have prepared novel aromatic polyamides with a urea binding site in the polymer backbone or in the pendant substructure and with fluorescent dansyl or fluorene moieties as pendant subunits; the latter also form part of the main chain. We have studied the fluorescent behavior of these polymers in solution and in the solid state and we have also studied the materials from a macromolecular point of view, especially their thermal behavior, crystallinity, water sorption, etc.

Wholly aromatic polyamides (aramides) are high-performance materials due to their high temperature resistance and excellent mechanical behavior, characteristics which make them useful for advanced technologies (i.e.,

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flame-resistant and high tensile strength synthetic fibers, coatings, and fillers) [18]. Our previous work concerned with the preparation of novel aramides has focused on the chemical modification of poly(isophthalamide)s or poly(terephthalamide)s in order to increase their solubility – one of the major drawbacks of these materials is their insolubility – and at the same time to improve other properties, especially their thermal or mechanical behavior and water uptake, etc [19–28]. These objectives have also been pursued by other research groups [29–36], and the objective of improving the traditional properties of polyamide has often been accompanied by the development of new ones related to new technologies, such as photoluminescence, electrochromicity, etc [37–41].

The sensing behaviour of these materials, mainly as dense membranes, towards anions or neutral molecules will be described in a future paper. Thus far we have described the preparation of polyamides with urea groups in the main chain and in the pendant substructure. These materials have outstanding mechanical properties [42,43] and are excellent anion receptor units for the solid–liquid extraction/elimination of environmentally harmful cations when combined with cation receptor units such as crown ethers [44–46].

In short, we consider that polyamides containing urea binding sites and fluorescent signalling subunits are potentially excellent candidates for advanced technological applications in the fields of anion sensing, waste recovery of anions through reversible and reusable solid–liquid extraction technology, and anion membrane transport applications for purification or recovery, etc.

2. Experimental

All materials and solvents were obtained commercially and were used as received, unless otherwise indicated. 5-Aminoisophthalic acid diethyl ester was prepared by a previously described procedure [19]. *N*-Methyl-2-pyrrolidone (NMP; Aldrich) was vacuum-distilled twice over phosphorus pentoxide and then stored over 4-Å molecular sieves. Lithium chloride (Aldrich) was dried at 400 °C for 12 h prior to use. Triphenylphosphite (TPP; Aldrich) was vacuum-distilled twice over calcium hydride and then stored over 4-Å molecular sieves. Pyridine (Merck) was dried by refluxing over sodium hydroxide for 24 h and then distilled over 4-Å molecular sieves. *m*-Phenylenediamine (MPD) and *p*-phenylenediamine (PPD) were purchased from Aldrich and purified by double vacuum sublimation. Isophthaloyl chloride and terephthaloyl chloride were purchased from Aldrich and were crystallized from dry heptane. 9H-Fluoren-2-yl isocyanate (Aldrich, 98%), 4-[9-(4-aminophenyl)-9H-fluoren-9-yl]phenylamine (Aldrich, 99%), and dansyl chloride [5-(dimethylamino)-1-naphthalenesulfonyl chloride; Aldrich, 99%] were used as received.

2.1. Intermediates and monomers

2.1.1. 5-[3-(9H-fluoren-2-yl)ureido]isophthalic acid (**1**)

5-Aminoisophthalic acid (50 mmol) was dissolved in 10 mL of *N,N*-dimethylacetamide in a 50-mL round-bottomed flask fitted with a mechanical stirrer and 9H-fluo-

ren-2-yl isocyanate (50 mmol) was added portionwise. The resulting solution was stirred at room temperature for 24 h and then precipitated in 300 mL of slightly acidified water. The product, 5-[3-(9H-fluoren-2-yl)ureido]isophthalic acid (**1**), was filtered off and washed thoroughly with distilled water. It was then extracted with hot ethanol and dried in a vacuum oven at 80 °C overnight. Yield: 88%. M.p.: 299 °C (dec.).

¹H NMR (400 MHz, [D₆]DMSO, δ , ppm): 13.24 (s, 2H), 9.22 (s, 1H), 8.88 (s, 1H), 8.39 (s, 2H), 8.19 (s, 1H), 7.87 (s, 1H), 7.83 (d, 1H), 7.81 (d, 1H), 7.56 (d, 1H), 7.48 (d, 1H), 7.36 (t, 1H), 7.26 (t, 1H), 3.93 (s, 2H). ¹³C NMR (100.6 MHz, [D₆]DMSO, δ , ppm): 167.66, 153.55, 144.94, 143.61, 142.12, 141.55, 139.46, 136.48, 132.78, 127.68, 126.86, 125.96, 124.26, 123.69, 121.17, 120.26, 118.46, 116.44, 37.53. EI-LRMS *m/z*: 388 (M⁺; 2), 207 (82), 181 (100), 165 (34), 152 (20), 90 (12). FTIR (cm⁻¹): $\nu_{\text{N-H}}$: 3302; $\nu_{\text{O-H}}$: 3389–2736 (br); $\nu_{\text{C=O}}$: 1708, 1650; $\delta_{\text{N-H}}$: 1601; $\nu_{\text{C=C}}$: 1552.

2.1.2. 9,9-Bis[4-[3-(4-aminophenyl)ureido]phenyl]-9H-fluorene (**2**)

4-[9-(4-Aminophenyl)-9H-fluoren-9-yl]phenylamine (11.5 mmol) was dissolved in 50 mL of dichloromethane in a 100-mL Erlenmeyer flask fitted with a mechanical stirrer and 4-nitrophenyl isocyanate (23 mmol) was added portionwise. The solution was stirred at room temperature for 24 h and then filtered and the precipitate washed with dichloromethane. The product, 9,9-bis[4-[3-(4-nitrophenyl)ureido]phenyl]-9H-fluorene, was extracted with hot ethanol and dried in a vacuum oven at 60 °C overnight. Yield: 85%.

Dry 9,9-bis[4-[3-(4-nitrophenyl)ureido]phenyl]-9H-fluorene (4.5 mmol) was mixed with 150 mL of absolute ethanol and 60 mg of Pd/C (10% Pd) in a hydrogenation flask and the system purged and pressured with hydrogen to 75 psi. The mixture was stirred at 60 °C for 6 h and the hydrogen consumed was replaced every 15 min. The solution was then filtered, the solid thus obtained dissolved in *N,N*-dimethylformamide, and this solution filtered through celite to eliminate the hydrogenation catalyst (Pd/C). The resulting clear solution was then added dropwise to 150 mL of water to precipitate 9,9-bis[4-[3-(4-aminophenyl)ureido]phenyl]-9H-fluorene (**2**), which was then filtered off and washed thoroughly with distilled water. The product was extracted with hot ethanol and dried in a vacuum oven at 60 °C overnight. Yield: 82%. M.p.: 239 °C (dec.).

¹H NMR (400 MHz, [D₆]DMSO, δ , ppm): 8.52 (s, 2H), 8.15 (s, 2H), 7.95 (d, 2H), 7.49 (d, 2H), 7.42 (t, 2H), 7.36 (d, 4H), 7.35 (t, 2H), 7.12 (d, 4H), 7.07 (d, 4H), 6.56 (d, 4H), 4.81 (d, 4H). ¹³C NMR (100.6 MHz, [D₆]DMSO, δ , ppm): 153.77, 152.09, 144.93, 140.36, 139.63, 139.40, 129.51, 128.93, 128.68, 128.38, 126.91, 121.58, 121.36, 118.83, 115.09, 64.86. EI-LRMS *m/z*: 617 (M⁺; 2), 374 (22), 348 (38), 256 (20), 134 (48), 108 (100), 80 (32). FTIR (cm⁻¹): $\nu_{\text{N-H}}$: 3354, 3314; $\nu_{\text{C=O}}$: 1656; $\delta_{\text{N-H}}$: 1604; $\nu_{\text{C=C}}$: 1546.

2.1.3. 5-[3-[4-[1-(dimethylamino)naphthalene-5-sulfonamido]phenyl]ureido]isophthalic acid (**3**)

5-Aminoisophthalic acid diethyl ester (35 mmol) was dissolved in 500 mL of dichloromethane in a 1-L

Erlenmeyer flask fitted with a mechanical stirrer and 4-nitrophenyl isocyanate (35 mmol) was added portionwise. The solution was stirred at room temperature for 48 h and then filtered. The product, 5-[3-(4-nitrophenyl)ureido]isophthalic acid diethyl ester, was washed thoroughly with dichloromethane and dried in a vacuum oven at 80 °C overnight. Yield: 89%.

Dry 5-[3-(4-nitrophenyl)ureido]isophthalic acid diethyl ester (12 mmol) was mixed with 200 mL of absolute ethanol and 95 mg of Pd/C (10% Pd) in a hydrogenation flask and the system purged and pressured with hydrogen to 75 psi. The mixture was stirred at 60 °C for 4 h and the hydrogen consumed replaced every 15 min. The solution was then filtered and the solid thus obtained dissolved in *N,N*-dimethylacetamide. This solution was filtered through celite to eliminate the insoluble Pd/C. The resulting clear solution was then added dropwise to 250 mL of water to precipitate the 5-[3-(4-aminophenyl)ureido]isophthalic acid diethyl ester, which was then filtered off, washed thoroughly with distilled water, and dried in a vacuum oven at 80 °C overnight. Yield: 93%.

5-[3-(4-aminophenyl)ureido]isophthalic acid diethyl ester (6 mmol) was dissolved in 40 mL of *N,N*-dimethylformamide in a 500-mL Erlenmeyer flask fitted with a mechanical stirrer. After cooling the solution to 0 °C, dantyl chloride (6 mmol) was added dropwise and the solution stirred at room temperature for 1 h, 60 °C for 4 h, and then precipitated in 150 mL of water. The 5-[3-{4-[1-(dimethylamino)naphthalene-5-sulfonamido]phenyl}ureido]isophthalic acid diethyl ester was filtered off and washed thoroughly with distilled water. Ester hydrolysis was carried out by dissolving this product in *N,N*-dimethylacetamide and adding this solution dropwise to 100 mL of aqueous sodium carbonate solution. The solution was then filtered and precipitated in 300 mL of slightly acidified water. The product, 5-[3-{4-[1-(dimethylamino)naphthalene-5-sulfonamido]phenyl}ureido]isophthalic acid (**3**), was filtered off, washed thoroughly with distilled water, and dried in a vacuum oven at 80 °C overnight. Yield: 91%. M.p.: 198 °C (dec.).

¹H NMR (400 MHz, [D₆]DMSO, δ , ppm): 13.20 (s, 2H), 10.45 (s, 1H), 9.11 (s, 1H), 8.65 (s, 1H), 8.47 (d, 1H), 8.43 (d, 1H), 8.27 (s, 2H), 8.18 (d, 1H), 8.11 (s, 1H), 7.66 (t, 1H), 7.61 (t, 1H), 7.30 (d, 2H), 7.28 (d, 1H), 6.98 (d, 2H), 2.82 (s, 6H). ¹³C NMR (100.6 MHz, [D₆]DMSO, δ , ppm): 167.55, 153.35, 152.36, 141.39, 136.60, 135.87, 132.68, 130.90, 130.62, 130.00, 129.87, 129.02, 124.43, 124.09, 123.51, 121.68, 120.33, 119.72, 119.71, 116.16, 45.98. EI-LRMS *m/z*: 367 (78), 341 (30), 235 (42), 181 (58), 170 (100), 107 (56), 78 (28), 69 (86). FTIR (cm⁻¹): $\nu_{\text{N-H}}$: 3372; $\nu_{\text{O-H}}$: 3667–2708 (br); $\nu_{\text{C=O}}$: 1702, 1646; $\delta_{\text{N-H}}$: 1607; $\nu_{\text{C=C}}$: 1552.

The overall monomer synthesis is shown in Scheme 1.

2.2. Polymer synthesis

A typical polymerization reaction is as follows. The diamine (10 mmol), diacid (10 mmol), and lithium chloride (1.4 g) were dissolved in a mixture of pyridine (6 mL), TPP (22 mmol), and NMP (20 mL) in a 50-mL three-necked flask fitted with a mechanical stirrer and the resulting

solution stirred and heated at 110 °C under dry nitrogen for 4 h. The system was then cooled to room temperature and the solution precipitated in 300 mL of methanol to give a swollen fibrous precipitate. The polymer obtained was filtered off and washed with distilled water and acetone, after which it was extracted with acetone for 24 h in a Soxhlet apparatus and dried in a vacuum oven at 80 °C overnight. Yields were quantitative for all polymers.

The polymer synthesis and acronyms are depicted in Scheme 2.

2.3. Measurements and Instrumentation

¹H and ¹³C NMR spectra were recorded with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively, using deuterated chloroform (CDCl₃) or deuterated dimethylsulfoxide ([D₆]DMSO) as solvents. Low resolution electron impact (EI-LR) mass spectra were obtained at 70 eV on an Agilent 6890 N mass spectrometer. High-resolution mass spectrometry (HRMS) was carried out on a Micromass AutoSpec Waters mass spectrometer. Infrared spectra (FTIR) were recorded with a Nicolet Impact spectrometer. Elemental analyses were performed with a LECO CHNS-932 microanalyser. Inherent viscosities were measured with an Ubbelohde viscometer at 25 ± 0.1 °C with NMP as solvent at a concentration of 0.5 g/dL. Differential scanning calorimetry (DSC) data were recorded with a Perkin-Elmer Pyris I analyzer for 10 mg of sample under nitrogen at a scan rate of 20 °C/min. Thermogravimetric analysis (TGA) data were recorded for 5 mg of sample under nitrogen or oxygen with a Mettler-Toledo TGA/SBTA851 analyzer at a scan rate of 10 °C/min.

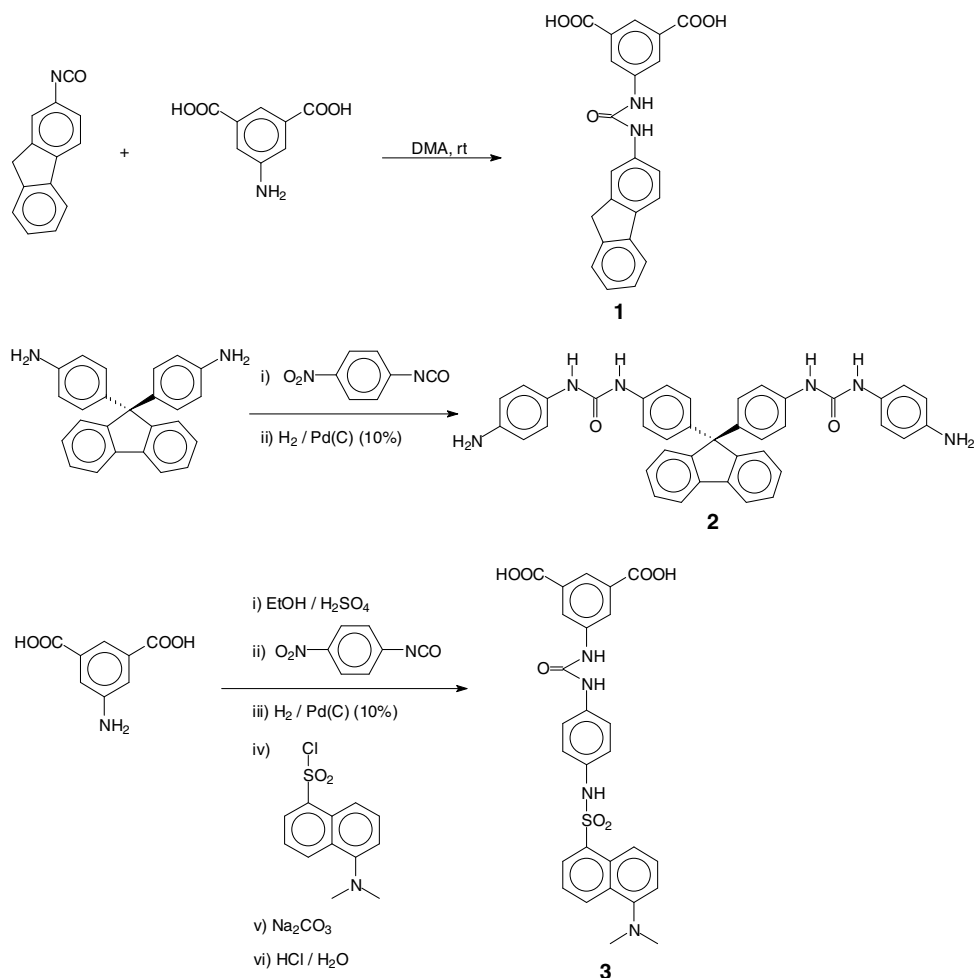
Polymer solubility was determined by mixing 10 mg with 1 mL of solvent and stirring for 24 h at room temperature. Polymer films were prepared by evaporation of cast solutions in DMA. In most cases, a concentration of 10% by polymer weight was used and the solvent was eliminated by heating at 100 °C for 4 h in an air-circulating oven and then at 120 °C for 4 h under vacuum (1 mmHg).

The X-ray diffraction patterns were obtained using a Philips model X-Pert X-ray diffractometer operating at 40 kV, using Co as the radiation source and a graphite filter. The scans were obtained using a scan step size of 0.025° with a scan step time of 0.5 s.

Water sorption values were determined gravimetrically at room temperature. Powdered polymeric samples of about 200 mg, previously dried at 120 °C for 24 h over phosphorus pentoxide, were placed in a closed box containing a saturated aqueous solution of NaNO₂ at a temperature of 20 °C, which provided a relative humidity of 65%. The samples were weighed periodically over a period of 8 days until they had equilibrated with their surroundings and presented no further changes in weight.

3. Results and discussion

Our work concerns the design, preparation, and characterization of high-performance materials for future use in advanced applications such as molecular recognition. Thus, we describe poly(isophthalamide)s containing urea binding sites in the polyamide backbone or in the lateral chain



Scheme 1. Experimental monomer synthesis sequences.

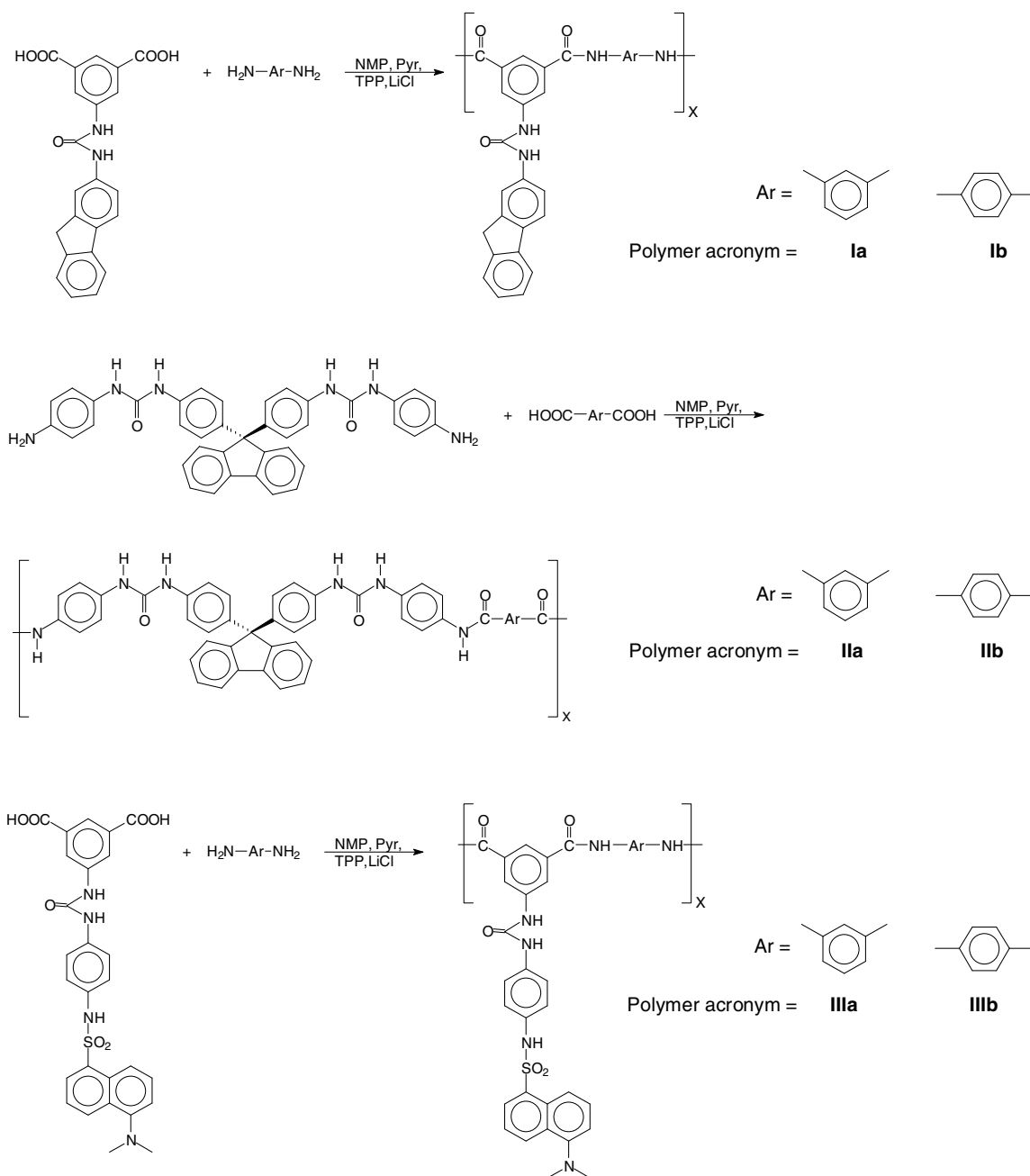
along with a fluorescent signaling subunit (fluorene or dansyl moiety) anchored to the pendant structure as a sulfonamide (Scheme 2). Urea is a polar group that establishes highly directional urea–urea and urea–amide hydrogen bonds and can interact effectively with water, thereby increasing polyamide hydrophilicity, as with the sulfonamide moiety. Moreover, the well-known selective anion binding capability of the urea moiety, along with that of the fluorescent signaling units, creates new possibilities for the production of sensing materials for use under extreme conditions.

3.1. Monomer and polymer synthesis and characterization

We have prepared new diacid and diamine monomers in one or two synthetic steps by treatment of the appropriate isocyanate with commercial aromatic amines, sometimes followed by reduction of a nitro group and occasionally a sulfonamidation, in an easy, clean way to form monomers that contain a urea binding site and a fluorophore in high yield and purity (Scheme 1). Purification by crystallization or by the solution–reprecipitation meth-

od yields high purity monomers, as confirmed by NMR techniques. The intermediates and monomers were characterized by elemental analysis and IR, ^1H , and ^{13}C NMR spectroscopy, thereby fully confirming the chemical structure of all the products.

The polyamides have been synthesized by combining isophthalic and terephthalic acid, or *m*-phenylenediamine and *p*-phenylenediamine, with three novel monomers, two of which contain a urea host moiety as a pendant substructure of the isophthalic acid along with a fluorene or a dansyl signaling unit, and the other of which contains an aromatic diamine with two urea groups and a fluorene moiety in its main structure (Scheme 1). The polymers were synthesized according to the method described by Yamazaki and co-workers [47]. Their structures are shown in Scheme 2, and their inherent viscosities and elemental analyses are listed in Table 1. Fig. 1 shows the chemical characterization of polymer **1a** as an example. The inherent viscosity of this polymer, which is higher than 0.50 dL/g and the ^1H and ^{13}C NMR spectra, the peaks of which were assigned on the basis of the monomer's spectra, are consistent with a high degree of polycondensation.



Scheme 2. Synthesis, chemical structure and acronyms of the polyamides.

3.2. Properties of the polymers

3.2.1. Thermal properties

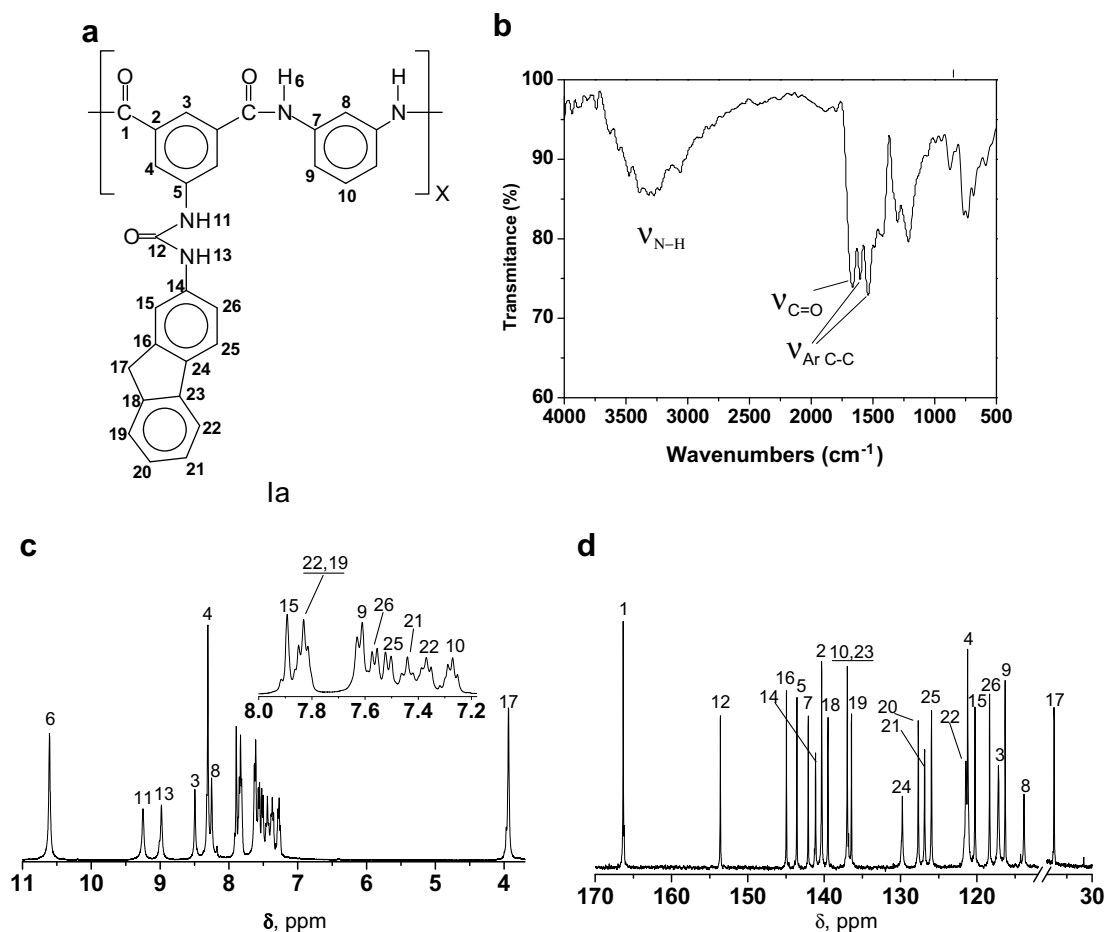
The thermal behavior of the polyamides was evaluated by DSC and TGA. The glass transition temperatures of the polyamides, as determined by DSC, are high and close to their decomposition temperatures. DSC scans at a rate of 20 °C/min allowed detection of the transitions between 174 and 331 °C, with the highest values corresponding to the poly(amide urea)s **IIa** and **IIb**, which have the most rigid main chain and do not possess bulky side chains. Thus,

incorporation of the fluorene moiety into the main chain through an sp^3 carbon (C9) has a rigidifying effect. Comparing series **a** and **b**, it can be seen that series **b** polymers have a higher *p*-phenylene ring content in the main structural unit and consequently their T_g 's are higher. If we consider polyamides with bulky side groups, the bulkier pendant structure of polymers **IIIa** and **IIIb** leads to lower T_g 's than polymers **Ia** and **Ib** due to the greater interchain distance, which lowers the strength of the amide-amide hydrogen bonds that are partly responsible for the generally high T_g 's of these aromatic polyamides.

Table 1

Inherent viscosities, polymerization conditions and elemental analysis of the polymers

Polymer	$\eta_{inh}(\text{dL g}^{-1})$	Elemental analysis					
		Theoretical			Found		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
Ia	0.99	73.03	4.38	12.17	72.60	4.63	11.94
IIa	1.04	75.59	4.59	11.25	75.13	4.86	10.91
IIIa	0.61	63.86	4.55	13.54	63.47	4.78	13.50
Ib	1.32	73.03	4.38	12.17	72.85	4.69	11.80
IIb	0.50	75.59	4.59	11.25	75.41	4.63	11.02
IIIb	1.5	63.86	4.55	13.54	63.52	4.66	13.20

**Fig. 1.** Characterization of polyamide Ia: (a) FT-IR-FT, (b) ^1H NMR and (c) ^{13}C NMR.

The TGA results are shown in Table 2. The decomposition temperatures (T_d) of all polymers range between 275 and 330 °C, with the polyamides containing no pendant structure (IIa and IIb) having the highest T_d 's as the breaking of a bond in a pendant structure gives rise to the elimination of a low molecular weight fragment, which is detected by TGA, whereas the breaking of a bond in the main chain does not. As regards the degradation processes, different authors have described the oxidative degradation of urea units to occur at temperatures of between 250 and 300 °C in urea–formaldehyde resins

[48,49]. Two degradation steps were detected in our systems (Fig. 2). Although the T_d 's are similar under O_2 and N_2 , the degradation mechanism should be considered different. Thus, the weight loss of the first degradation step for polyamides with lateral fluorene moieties (polyamides Ia and Ib) under oxygen corresponds to the loss of the fluorene group due to breaking of the $\text{C}_{\text{fluorene}}\text{--N}_{\text{urea}}$ bond, whereas the whole pendant structure is lost under nitrogen. In polyamides with pendant dansyl moieties (IIIa and IIIb), the first degradation step under N_2 probably corresponds to loss of the dimethylamino residue from

Table 2
Thermal DSC and TGA data of the polyamides

Polymer	DSC		TGA ^a	
	T_g (°C)	T_d (°C)	N ₂ atmosphere	
			T_d (°C)	Char yield (%)
Ia	265	275	38	
IIa	295	330	40	
IIIa	174	290	42	
Ib	331	275	37	
IIb	316 ^b	320	33	
IIIb	250 ^b	280	42	

^a T_d is the initial temperature at the onset of the first stage of thermal weight loss. Char yield at 700 °C.

^b Weak transition; not clearly observed.

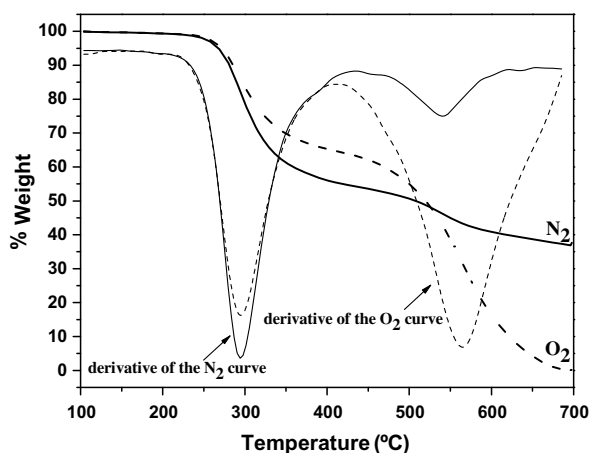


Fig. 2. TGA curves of polyamide **Ia** under N₂ and O₂.

the dansyl group, while under O₂ the first step is probably loss of the entire dansyl residue. Nevertheless, a slow weight loss continues in these polyamides with lateral ureas after the first step, and loss of the whole pendant group is observed just before the second step. Thus, the second step corresponds to a poly(*m*-phenylene isophthalamide)-like structure. The first degradation step for polyamides **IIa** and **IIb** can be assigned to the elimination of a biphenyl residue from the main chain.

3.2.2. Wide-angle X-ray scattering

The polyamide crystallinity, as evaluated by WAXS, was found to show an amorphous pattern in all cases. Fig. 3 shows the wide-angle X-ray scattering patterns for **Ia**, **IIa**, and **IIIa**. Thus, the polyamides reported in this paper may be considered as amorphous materials with medium thermal resistance and very high T_g 's.

According to Halasa et al. [50,51] the average molecular interchain spacing ($\langle R \rangle$, in Angstroms) for amorphous polymers can be estimated from the strong maximum (θ_{\max}) in the WAXS diffraction scan using Eq. (1), where λ is the radiation wavelength (Table 3). The value of $\langle R \rangle$ is approximately the same for polymers **Ia** and **IIIa**, which have pendant groups and volumes of 234 and 369 Å³, respectively, while it is higher for polymer **IIa**. This indi-

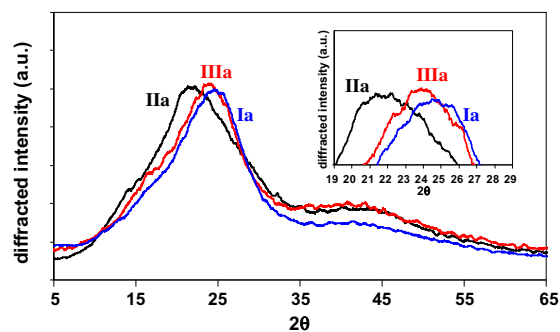


Fig. 3. X-ray diffraction patterns of polyamides **Ia**, **IIa** and **IIIa**.

cates that the 9*H*-fluorene moiety of the main chain, with an sp³ carbon in the backbone, exerts a strong influence on the chain packing by partially inhibiting the strong urea–urea, urea–amide, and amide–amide hydrogen bonds, which more than compensates for the lowering of the cohesive energy due to the bulky side groups.

$$\langle R \rangle = 5/8(\lambda / \sin \theta_{\max}) \quad (1)$$

3.2.3. Solubility

The polymer solubilities are shown in Table 4. The solubility of the aromatic polyamides with bulky pendant groups depends mainly on the polyamide backbone structure, which means that the diamine residue plays the most important role. Thus, a poly(*m*-phenylene isophthalamide) structure with an all-*meta* aromatic ring substitution (polymers **Ia** and **IIIa**) gives rise to polyamides with an enhanced solubility in polar aprotic solvents, while a poly(*p*-phenylene isophthalamide) backbone substructure, which has a *para* aromatic ring substitution in the diamine residue (polyamides **Ia** and **IIIa**), leads to highly insoluble materials. This could be because the bulk of the lateral residue is not sufficient to override the effect of the interchain interactions superimposed by the backbone. We believe, however, that the polar urea and sulfonamide groups contribute effectively to the cohesive energy counteracting their influence in the increment in the main chain–main chain distance. Hence the orientation of the main chain aromatic rings plays the most important role. Moreover, a *meta* orientation give rise to a less rigid structure that also reduces the effectiveness of the side chain–side chain interactions.

The influence of the orientation of the acid residue (*meta* or *para*) in polyamides **IIa** and **IIb** on the solubility is negligible, and both aromatic poly(amide urea)s can be considered to be highly soluble. The main chain 9*H*-fluorene substructure residue, which has an sp³ carbon, could

Table 3
Average molecular interchain spacing $\langle R \rangle$

Polymer	2θ (°)	$\langle R \rangle$ [Å]
Ia	24.1	4.6
IIa	21.5	5.2
IIIa	23.6	4.7

Table 4
Solubility of the poly(amide urea)s^a

Polymer	NMP	DMA	DMF	DMSO	THF	<i>m</i> -Cresol, cyclohexanone, CHCl ₃ , AcOH
Ia	++	++	++	++	+–	–
IIa	++	++	++	++	+–	–
IIIa	++	++	++	++	+–	–
Ib	+–	+–	+–	+–	–	–
IIb	++	++	++	++	–	–
IIIb	+–	+–	+–	+–	–	–

^a ++, soluble at room temperature; +, soluble on heating; +–, partially soluble; –, insoluble.

be responsible for this high solubility due to the weakening of the interchain interactions caused by this carbon due to steric effects. This fact is also reflected in the higher average interchain spacing of polymer **IIa** in comparison with bulky side chain polymers **Ia** and **IIa**.

3.2.4. Water sorption

Aromatic polyamides are hydrophilic polymers due to their polar amide groups, whose interaction with water leads to a water uptake from the environment. These water molecules interact with the amide groups by weakening the amide–amide interactions that endow the polyamides with their high cohesive energy and, as a result, their high thermal transitions and resistance and superior mechanical properties. The water uptake therefore determines the final application of these high performance materials as the absorbed water diminishes the T_g and influences the mechanical, electrical, and dielectric properties. Conversely, in other technological fields, such as membrane technology, greater water uptake in water-treatment membranes or even in dense gas-separation membranes implies better performance.

The polyamides described herein have two amide and one or two urea groups per structural unit, and sometimes a sulfonamide pendant moiety. Amide, urea, and sulfonamide moieties are highly polar groups that can influence water uptake by forming hydrogen-bonding interactions with water. Measurement of the isothermal sorption of water at 65% relative humidity gave values that are related to the polyamide chemical structure. The absorption iso-

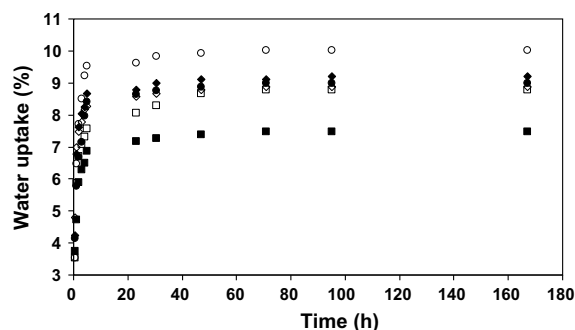


Fig. 4. Isothermal water absorption of polyamides **Ia** (●), **IIa** (◆), **IIIa** (■), **Ib** (○), **IIb** (◇) and **IIIb** (□).

Table 5
Moisture absorption of the polyamides

Polymer	Water uptake (%)	Molecules of H ₂ O per repeating unit	Molecules H ₂ O per equiv of urea ^a	Molecules H ₂ O per equiv of sulfonamide ^b
Ia	9.0	2.3	1.1	
IIa	9.2	3.8	1.3	
IIIa	7.5	2.6		0.3
Ib	10.0	2.6	1.4	
IIb	8.9	3.7	1.8	
IIIb	8.8	3.0		0.4

^a Considering an uptake of 0.6 water molecules per amide group [27].

^b Considering an uptake of 1.1 water molecules per urea group (as estimated for polymer **Ia**).

therms of the polyamides are depicted in Fig. 4, while Table 5 shows the same data expressed as water absorption percentages for polyamides, the number of water molecules per structural unit, and the estimated number of water molecules per urea and per sulfonamide group [the former are calculated on the basis of an uptake of 0.6 water molecules per amide group, as predicted from the amount of water absorbed by poly(*m*-phenylene 5-benzoylaminoisophthalamide) [27], and the latter by considering an absorption of 1.1 molecules of water per urea moiety, as estimated for **Ia**].

The polyamide water sorptions are high (between 7.5% and 10.0%) and the number of water molecules per repeating unit ranges between 2.3 and 3.8, with the highest value corresponding to the polymer with two urea groups (**IIa**). Comparing the polyamides with pendant bulky groups, the presence of a sulfonamide moiety in polymer **IIIa** increases the water uptake in comparison with polyamide **Ia**. We have previously reported that the water sorption per repeating unit of polyamides is somewhat associated with its hydration energy, as estimated for polyamide models by a gas-phase equilibrium geometry optimization at the semiempirical level of theory with a Cramer and Truhlar SM5.4 model (Fig. 5) [52]. Surprisingly, however, the water sorption of the polyamides described in this work is not completely related to the hydration energy but instead is intimately correlated with the high content

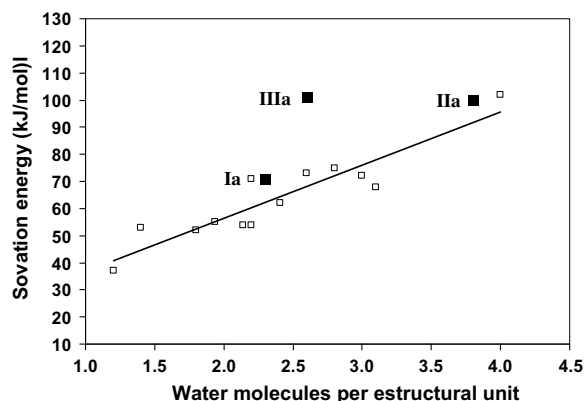


Fig. 5. Relationship between the water uptake and the aqueous solvation energy of different polyamides (the black squares represent the polyamides in this work).

of polar groups on the polymeric structural unit. We believe that strong amide–urea and urea–urea hydrogen bonding could be partly responsible for the lack of correlation of the hydration energy calculated for the isolated molecules in the gas phase with the water uptake observed in the solid state.

3.3. Fluorescence

Fig. 6 shows the fluorescence emission spectra of polymers **Ia** and **IIIa** in NMP solution and in the solid state (films obtained by casting). Polymer **IIIa**, which has a pendant dansyl group, shows intense yellowish-green fluorescence in dilute solution and as a thin films; this emission is due to the dansyl moiety emission. Polymer **Ia**, which has pendant fluorene moieties, shows blue fluorescence in the solid state and in solution. Films of polyamide **Ia** show an important bathochromic emission shift compared with the solution emission spectra, whereas polyamide **IIIa** shows a slight hypsochromic shift. When the fluorene moiety forms part of the main chain (**IIa**), the fluorescence is strongly reduced in comparison with **Ia** and cannot be observed by the naked eye. Fig. 7 shows a fluorescence image of polymers **Ia**, **IIa**, and **IIIa** in NMP solution.

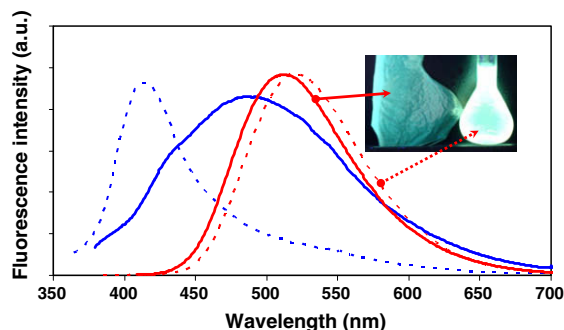


Fig. 6. Fluorescence emission of films (continuous lines) and NMP solutions (dashed lines) of polyamides **Ia** (blue) and **IIIa** (red), along with a fluorescence image of polyamide **IIIa** (left: film obtained by casting; right 3×10^{-3} M solution in NMP). (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)



Fig. 7. Fluorescence image of 3×10^{-3} M polyamide solutions in NMP (from left to right: **IIa**, **Ia**, **IIIa**).

4. Conclusion

This work has described the synthesis and characterization of six new fluorescent polyamides bearing a urea function in the bulky pendant structure or in the main chain along with fluorene or dansyl moieties. The fluorescent signaling dansyl or fluorene moieties are connected to, or within, the main chains through urea binding sites. The polyamides are amorphous, soluble in polar aprotic solvents, and demonstrate a film-forming capability, with yellow-greenish (dansyl) or blue fluorescence (fluorene) in solution and in the solid state. Their solubility, thermal behavior, water uptake, and WAXD spectra have been studied and related to the chemical structure. The polar amide, urea, and sulfonamide groups give rise to a high water sorption of up to 3.8 molecules of water per repeating unit. As regards the thermal behavior, the glass transition temperatures of the polymers are high (up to 331 °C) and the decomposition temperatures (around 300 °C) are due to the moderate thermal stability of the urea group. These polyamides are moderately soluble, which makes them useful materials for transformation into coatings, fibers, or films. Moreover, these polyamides combine a urea group, which is a potential anion receptor or host unit, with a fluorene or dansyl fluorescent signaling group, therefore we are currently studying the potential use of these specialty polymers as anion-sensing probes.

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