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Polyamide model compound containing the urea group as selective colorimetric sensing probe towards aromatic diamines

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A colorimetric diacid monomer for aromatic diamine sensing containing the urea binding site has been synthesised and characterised. A colour development from colourless to blue, brown or yellow was observed upon addition of *meta*, *para* or *ortho*-phenylenediamine, respectively, to polar aprotic organic solvent solutions of the monomers. The solutions remained colourless upon addition of other amines or diamines. The model polyamide compound derived from the diacid monomer maintains the colorimetric sensing selectivity towards the aromatic diamines; so the polyamides derived from the diacid monomer described herein are supposed to retain the ability to interact selectively with the aromatic diamines; hence cheap future sensing devices could be built by means of easy-to-use naked eye polyamide film chemosensor or by incorporating a polyamide coating in the end of an optic fibre connected to a portable diode array visible detector.

Keywords: polyamide model compounds; amine sensing; urea; host–guest chemistry

1. Introduction

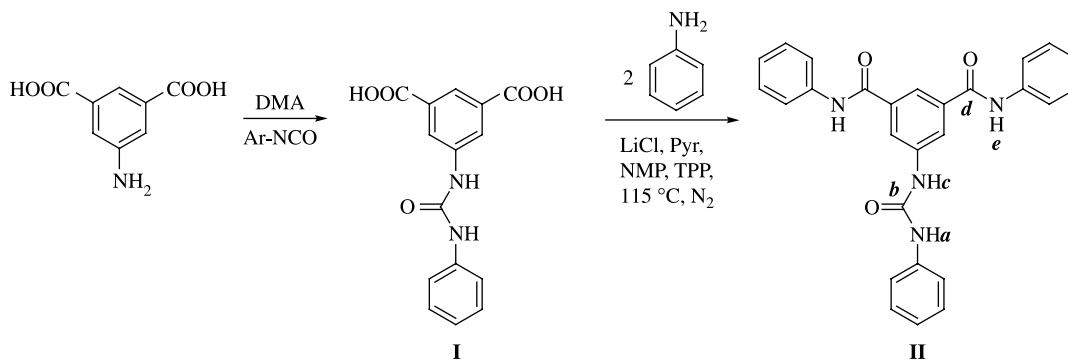
The development of selective and sensitive materials for sensing anion, cation and neutral molecules is a topical research area (1–4). Interest in materials that behave as hosts toward guest molecules arises from the importance attached to easy and quick detection and quantification of chemicals in environmental, biological and chemical processes. Thus, detection and quantification of chemicals, such as aromatic diamines, have a certain technological importance. Compounds such as *ortho*, *meta* or *para*-phenylenediamines are important intermediates in engineering polymers and composites, aramid fibres, hair dyes, adhesive and rubber chemicals, textile dyes, ion exchange and decolorizing resins, urethanes, petroleum additives and corrosion inhibitors, and are also important building blocks in heterocyclic chemistry.

The reported examples of chromogenic sensing systems for neutral molecules, i.e. amines, generally rely on the reactivity of certain functional groups (5–11). Thus, amine colorimetric signalling is generally based on a chemodosimeter approach involving a nucleophilic substrate attack that generates a new fluorescent unit (5). Although in itself an interesting approach, its disadvantage lies in its poor selectivity due to the possibility of an attack by other nucleophiles, including the water OH[−] groups. Moreover, the signalling events of these systems

are usually shown near the UV zone, and rarely at more interesting longer wavelengths, in the visible region. Additionally, these optical transducers are generally designed to detect a set of related compounds that share the same functional group, without selectivity. Thus, the most interesting systems for amine detection are molecules that interact with amines by means of hydrogen bonds, which produce variations in the fluorescence or in the UV–vis spectra of the system (12–14).

In previous articles we have reported on the synthesis and characterisation of polymer materials with the following host units: crown ether (15–17), urea (18, 19) or pyrylium (20, 21), along with their interaction with cations (22–25), anions (20, 21) or gas molecules (26). This work concerns the development of polymeric optical transducers that intimately detect related compounds. We therefore report herein on a polyamide model compound (Scheme 1; Figure 1) that exhibits colorimetric sensing selectivity towards isomeric aromatic diamines (Figure 2). Thus, the models probably mimic the polyamides, polymers derived from the diacid monomers (**I**), which are intermediates in the synthesis of the models. The polymeric materials are supposed to retain the ability to interact selectively with these diamines, such that cheap future sensing devices might well take the form of user-friendly naked eye polyamide film sensors or might

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Scheme 1. Synthesis of the diacid monomer (I) and the model polyamide compound (II).

incorporate a polyamide coating at the end of an optic fibre connected to a portable UV–vis diode-array detector. Moreover, as the aromatic polyamide belongs to a class of polymers of great technological importance, mainly due to its mechanical and electrical properties and outstanding thermal resistance, the sensing devices prepared with these materials could be utilised in a wide range of thermal and mechanical conditions, in smooth to extreme environments, making them unique components in control of industrial chemical concentrations, i.e. in air, gases, inside reactors or waste products, and also

environmental protection and occupational safety and health, through determination of pollutant concentrations.

2. Experimental

2.1 Materials

All materials and solvents were commercially available and were used as received, unless otherwise indicated. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMA) were vacuum-distilled twice, over phosphorus pentoxide, and then stored over 4 Å molecular

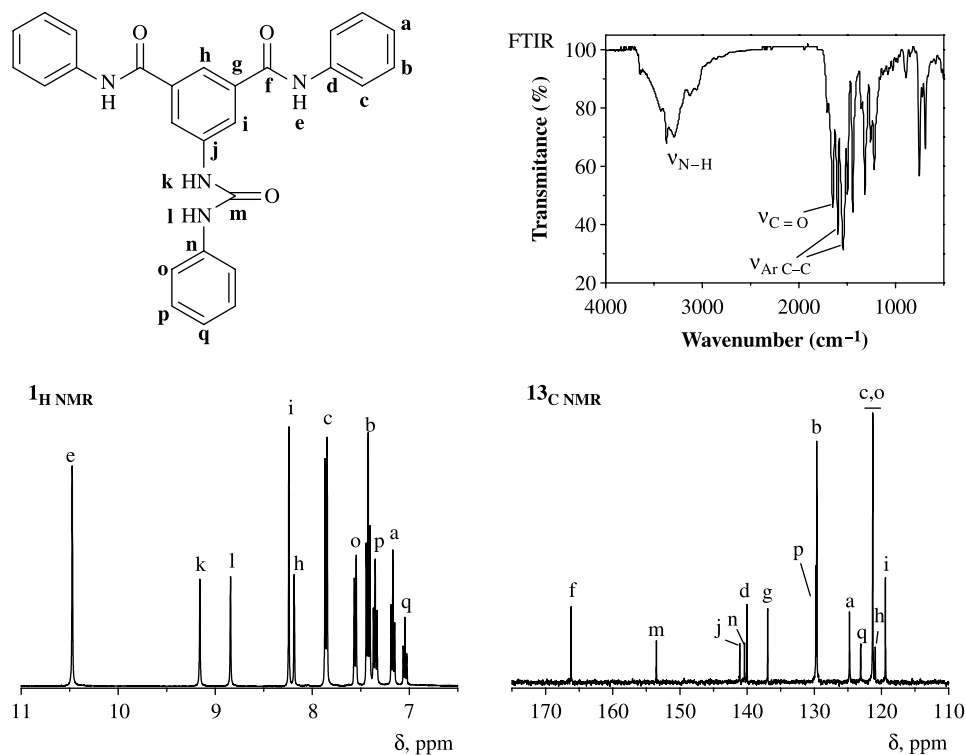


Figure 1. Characterisation of polyamide model II: (a) FTIR, (b) ¹H NMR and (c) ¹³C NMR. FTIR spectra were recorded on KBr pellets, and DMSO-*d*₆ was used as solvent in the NMR experiments.

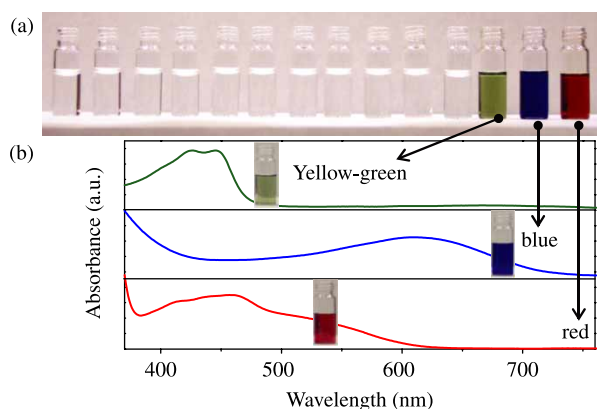


Figure 2. (a) Photograph of **II** solutions in DMA upon addition, from left to right, of ethanolamine, triethylamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 4,4'-diamino-diphenylsulfone, tris-(2-aminoethyl) amine, 1,2-diaminocyclohexane, aniline, *o*-phenylenediamine, MPD and *p*-phenylenediamine. (b) UV-vis spectra of solutions of **II** with *o*-phenylenediamine (yellow-green), MPD (blue) and *p*-phenylenediamine (red).

sieves. Lithium chloride was dried at 400°C for 12 h prior to use. Triphenylphosphite (TPP) was vacuum-distilled twice over calcium hydride, and then stored over 4 Å molecular sieves. Pyridine was dried under reflux over sodium hydroxide for 24 h, and distilled over 4 Å molecular sieves. *m*-Phenylenediamine (MPD) was commercially available and purified by double vacuum sublimation.

2.2 Synthesis and characterisation of the polyamide model compound

2.2.1 5-(3-phenylureido)isophthalic acid (I)

5-aminoisophthalic acid of 50 mmol was dissolved in 10 ml of *N,N*-dimethylacetamide in a 50 ml Erlenmeyer flask fitted with mechanical stirring. Afterwards, 50 mmol of phenylisocyanate was added dropwise. The solution was stirred at room temperature for 24 h, and then precipitated in 300 ml of slightly acidified water. The product, 5-(3-phenylureido)isophthalic acid, was filtered off and washed thoroughly with distilled water. The crude product was recrystallised from ethanol. Yield: 88%. M.p.: 281°C (d). ¹H-NMR (400 MHz, DMSO-*d*₆): δ (ppm), 13.27 (s, 2H); 9.18 (s, 1H); 8.78 (s, 1H); 8.33 (m, 2H); 8.14 (m, 1H); 7.52 (dd, 2H); 7.33 (t, 2H); 7.03 (t, 1H). ¹³C-NMR (100,6 MHz, DMSO-*d*₆): δ (ppm), 167.62; 153.50; 141.50; 140.37; 132.72; 129.79; 124.21; 123.64; 122.16; 119.54. EI-LRMS *m/z*: 300 (M⁺; 4), 207 (59), 190 (35), 181 (50), 164 (14), 119 (59), 93 (100), 66 (32). FTIR [Wavenumbers (cm⁻¹)]: ν_{N-H}: 3286; ν_{acid,O-H}: broad band (3657-2752); ν_{C=O}: 1716, 1646; δ_{N-H}: 1603; ν_{ArC=C}: 1567.

2.2.2 *N,N'*-diphenyl-5-(3-phenyl-ureido)-isophthalamide (II)

In a 50 ml three-necked flask fitted with mechanical stirring, 20 mmol of aniline, 10 mmol of 5-(3-phenylureido)isophthalic acid and 1.4 g of lithium chloride were dissolved in a mixture of 6 ml of pyridine, 22 mmol of TPP and 20 ml of NMP. The solution was stirred and heated at 110°C under a dry nitrogen blanket for 4 h. The system was then cooled at room temperature and the solution precipitated in 300 ml of methanol to render a swollen fibrous precipitate. The model obtained was filtered off and washed with distilled water and acetone and then extracted with acetone for 24 h in a Soxhlet and dried in a vacuum oven at 80°C overnight. Yield: 94%. It was obtained as a semicrystalline solid (55% crystallinity) that crystallised at 169°C. M.p: 256°C. The IR-FT and the ¹H and ¹³C NMR spectra, along with the signals assigned, are shown in Figure 1. LRMS (70 eV, EI), *m/z* (%): 331 (55), 239 (100), 185 (11), 119 (60), 93 (62), 65 (16). Elemental analysis for C₂₇H₂₂N₄O₃ (450.50): calc (%) C 71.99, H 4.92, N 12.44; found (%) C 71.73, H 5.07, N 12.19.

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, with deuterated dimethylsulfoxide (DMSO-*d*₆) as solvent.

Fast atom bombardment (FAB) and low resolution electron impact mass spectra (EI-LRMS, 70 eV) were carried out on a Micromass AutoSpect Waters mass spectrometer.

Infrared spectra (FT-IR) were recorded with a Nicolet Impact spectrometer.

UV-vis spectra were recorded with a Varian Cary3-Bio UV-vis spectrophotometer.

Elemental analyses were performed on a LECO CHNS-932 microanalyser.

Thermogravimetric analysis (TGA) data were recorded under a nitrogen atmosphere on a Mettler-Toledo TGA/SBTA851 analyser from 5 mg of sample at a scan rate of 10°C/min.

3. Results and discussion

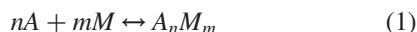
The new model polyamide compound (**II**) and its diacid monomer precursor (**I**) contain an urea group and two aromatic amide linkages, in which the carbonyl groups of the amides act as a slightly electron-withdrawing group and the urea moiety acts as a slightly electron-donating one. Although, the urea group has been exploited in compounds that mainly exhibit their sensing behaviour towards anions (27–31) and hardly ever towards cations

(32), their strong hydrogen-bonding ability, both in solution and in the solid state, either with other groups or alone – i.e. to give clathrates – opens the door to specific interactions with neutral molecules in the field of molecular recognition, or host–guest chemistry (33–35). Moreover, aromatic urea derivatives have shown the ability to form oligomeric assemblies, or capsules, in which guests can be encapsulated in solution, and the complex capsules persist even in the solid state, as demonstrated by X-ray analysis (36–38).

The diacid monomer (**I**) and the polyamide model compound (**II**) are prepared straightforwardly (Scheme 1) by cheap and conventional methods that render the products with a high yield and purity. As an illustrative example, the characterisation of **II** is depicted in Figure 1, the spectra showing the high purity of the model.

The chromogenic sensing properties of model polyamide compounds **II** in DMA solutions were tested in the presence of certain aliphatic and aromatic amines and diamines. In a typical assay, 43 mg of the proper diamine (0.23 mmol) were added to a colourless DMA solution (1 ml) of the proper **II** (0.1 M). The system was sealed and stored in the dark for 24 h. The results are shown in Figure 1. The DMA solution of **II** remained unchanged in the presence of a wide set of different amines, whereas **II** was highly selective towards diamines derived from benzene, and developed either a yellow-greenish, blue or red colour upon addition of *ortho*, *meta* or *para*-phenylenediamine, respectively (Figure 1).

The interaction between **II** and MPD in DMSO solution was studied using ^1H and ^{13}C NMR spectroscopy. By starting with a 0.1 M solution of **II** in DMSO- d_6 , and gradually adding MPD, the variations in the ^1H and ^{13}C NMR chemical shifts of both chemicals in response to the increasing concentration of MPD were evaluated. The MPD/**II** concentration ratio (C_{A_0}/C_{M_0}) ranged from 0.1/1 to 10/1. For each sample, the chemical shift of amidic and urea protons and the carbonyl carbon of the urea and amide groups were compared with their values in a pure **II** in DMSO- d_6 solution. The chemical shift variations of the amine proton of the MPD were analysed by the same procedure. The chemical shifts of the analysed protons and carbons in **II** increase with the increased concentration of MPD, and it approaches a constant value. In the case of the diamine proton, the chemical shift decreased when the concentration of this compound increased in the sample, and it approached the chemical shift of pure MPD in DMSO- d_6 solution. Thus, the interaction between **II** and MPD, responsible for the chemical shift variations, can be described as a binding of a diamine, *A*, to the model, *M*, according to the equilibrium described by Equation (1) (39).



The chemical shift variations were analysed by using a two-site model, which assumes that the experimental chemical shift is the sum of two chemical shifts: the first one for the compound when it interacts with the other, δ_{bound} , and, the second for the compound when it is free in the solution, δ_{free} . This model is described by the relationship expressed in Equation (2),

$$(\delta_{\text{obs}})_i = x_{\text{free}}(\delta_{\text{free}})_i + x_{\text{bound}}(\delta_{\text{bound}})_i, \quad (2)$$

where *i* is the atom whose chemical shift is considered to evaluate the molar fraction, δ_{obs} is the observed chemical shift at a given concentration, x_{bound} and x_{free} are the molar fractions of the bound and free compounds, respectively, δ_{free} corresponds to the chemical shift of the pure solutions and δ_{bound} is given by Equation (3). Hence, δ_{bound} can be estimated by the extrapolation of observed chemical shift data to zero and infinite concentrations of MPD.

$$(\delta_{\text{bound}})_{i,A} = (\delta_{\text{obs}})_{i,A}; \quad (\delta_{\text{bound}})_{i,M} = (\delta_{\text{obs}})_{i,M}. \quad (3)$$

$C_{A_0} \rightarrow 0$ $C_{A_0} \rightarrow \infty$

Once the $(\delta_{\text{bound}})_i$ is estimated by Equation (3), the molar fractions of free MPD and **II** can be calculated by applying Equation (2). Figure 3 shows a plot of the molar fraction of both compounds as a function of the concentration ratio.

Taking material balance into account (Equation (4)), the stoichiometry of interaction between model **II** and MPD can be obtained by plotting the bound molar fraction relation, $(1 - x_M)/(1 - x_A)$, versus the initial concentration ratio. The slope of the linear fit corresponds to the model polyamide compound

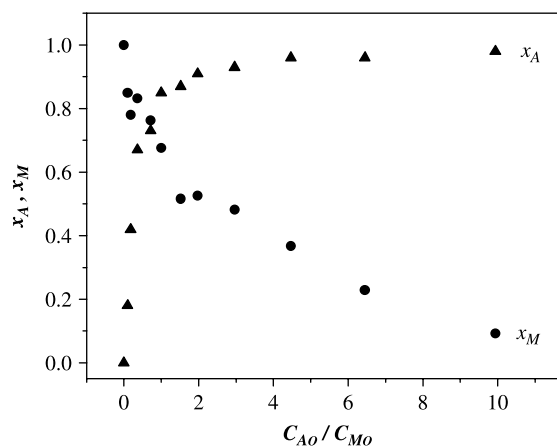


Figure 3. x_A and x_M vs. C_{A_0}/C_{M_0} . x_M are the averaged values obtained from the chemical shift variation of the amidic and urea protons and carbons of **II** after interaction with MPD (Equation (2)).

Table 1. Model polyamide compound–diamine interaction relation ($\mathbf{II}/\text{MPD} = m/n$, Equations (1) and (4)) as obtained by the linear regression of (C_{A_0}/C_{M_0}) vs. $(1 - x_M)/(1 - x_A)$ values, the slope representing the \mathbf{II} to MPD complex ratio.

Atom used to obtain the molar fraction data (Scheme 1)	m/n	R^2
Hc	4.5	0.988
Ha	4.5	0.991
He	4.1	0.973
Cd	3.7	0.974

\mathbf{II}/MPD interaction relation, m/n . The regression results appear to indicate an interaction \mathbf{II}/MPD of 4/1 (Table 1).

$$C_{A_n M_m} = \frac{C_{A_0}}{n}(1 - x_A) = \frac{C_{M_0}}{m}(1 - x_M)$$

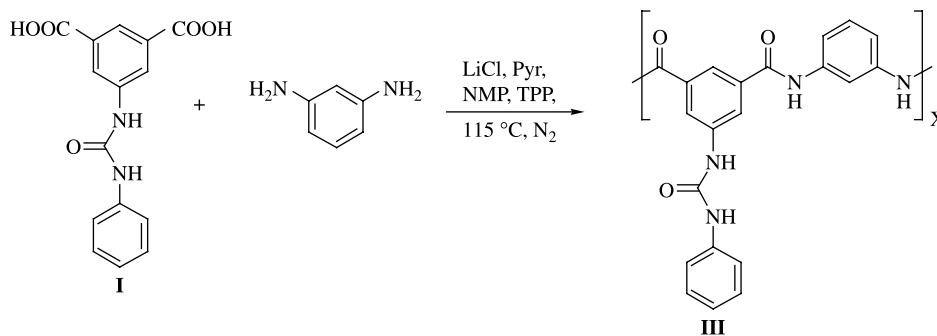
$$\therefore \frac{(1 - x_M)}{(1 - x_A)} = \frac{m}{n} \left(\frac{C_{A_0}}{C_{M_0}} \right) \quad (4)$$

Capsules formed through head-to-tail arrays of 12 hydrogen bonds formed by urea containing molecules have previously been described in solution, through a self-assembly processes (36–38). In our systems, we obtained a complex constituted by four molecules of model polyamide compound \mathbf{II} and one molecule of MPD. On the basis of this result, we conjecture that the formation of a capsule-like complex of four molecules of the model compound occurs with alternating up-and-down pendant urea groups encapsulating a diamine derived from benzene. The capsule might be maintained in solution by a belt of eight head-to-tail array hydrogen bonds, and two caps, up and down the belt, of amide–amide hydrogen-bond linkages. The cavity inside the capsule should have a shape in which guest diamines will fit, which in turn will establish new hydrogen bonds with urea and amide groups, thereby modifying the electronic structure of the supramolecular entity and giving rise to a charge transfer complex with the concomitant development of colour. Further studies should be carried out

to establish the structure of these complexes. The development of colour should also be investigated in depth, because it is not instantaneous. One possible hypothesis might be that decomposition species of the diamines could also be partially responsible, although the experimental fact that the polymerisation of \mathbf{I} with freshly purified MPD by double sublimation (Scheme 2) developed a deep blue colour instantaneously make us reject this possibility.

In order to get insight into the $\mathbf{II}/\text{diamine}$ complex structure, we have tried to obtain a monocrystal to study the structure of the complex in the solid state by the X-ray diffraction technique, but we have not succeeded. Anyway, we have obtained nice white crystals upon crystallisation of a mixture of \mathbf{II} and MPD in tetrahydrofuran (THF)/hexane (in this solvent mixture the development of colour was not observed) with a composition, as determined by ^1H NMR, of approx. four molecules of the model \mathbf{II} and one of the diamine. This fact does really not mean that the complex is a capsule, although it supports it, because it also could be another kind of structure, but it indicates that a supramolecular arrangement can be isolated even in the solid state. Additionally, the low-resolution FAB^+ mass spectra of these crystals show peaks at 559, 1008, 1458 and 1909, the mass of 1:1, 2:1, 3:1 and 4:1 \mathbf{II}/MPD complex, respectively, and although mass spectrometry only reflects the properties of gas-phase species, the correlation with the solid state is often reliable.

Moreover, the mass spectra of model \mathbf{II} indicates the presence of dimeric, trimeric and tetrameric species (FAB^+ , $m/z = 901, 1350, 1799$), indicating that the intermolecule interaction of \mathbf{II} is strong enough to give rise to supramolecular assemblies. Furthermore, the amidic and ureidic proton resonances of model \mathbf{II} (protons a, c and e in Scheme 1) in ^1H NMR experiments (using $\text{DMSO-}d_6$ as solvent) depend on the concentration. Thus, the increasing concentration gives rise to a highfield shifting of these protons, indicating that the amide and urea groups interact in solution by means of hydrogen bonds, even in a competitive polar solvent as DMSO.



Scheme 2. Polymerisation of the diacid monomer (**I**) with MPD to yield the polyamide (**III**).

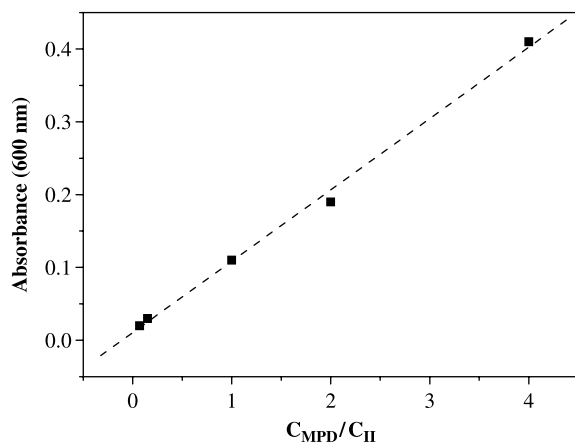


Figure 4. UV-vis absorbance (600 nm) of **II** upon exposure to increasing amounts of MPD in DMA.

From a macroscopic point of view, the concentration of MPD in solution could be followed colorimetrically adding a fixed quantity of **II**. Thus, the titration of MPD with the model **II** is shown in Figure 4, showing that the UV-vis absorbance (600 nm) of a solution of **II** in DMA increases proportionally to the **II**/MPD concentration ratio.

Upon adding the proper diamine to a solution of the model, the colour development is mainly observed in polar aprotic solvents, as DMA, *N*-methylpyrrolidone, dimethylformamide and DMSO.

In preliminary experiments, we have observed that the polymerisation of **I** with MPD in NMP (Scheme 2) takes place initially with the development of dark blue and red colours, respectively, that disappeared over time, owing to decreasing diamine concentrations as polymerisation progressed. This means that the diacid **I** also behaves as an aromatic diamine sensor and, more importantly, that the diamine concentrations can be monitored online during the polymerisation process. This is a significant fact because it could be employed to control synthetic procedures for aramids, which are of a certain economic significance, as well as other industrial processes involving diamines.

The polyamide **III** is an aromatic polyamide considered as a high-performance material with good chemical resistance and outstanding mechanical behaviour (18). Therefore, further work will be carried out to analyse the sensing characteristics of the polyamides. Preliminary experiments have shown that DMA solutions of the polyamide **III**, derived from **I**, retain the sensing behaviour of the models **II**. Thus, polymer **III** could be mixed with other polymers, or it could be crosslinked to yield a network in order to elaborate film strips to naked eye detection of aromatic amines or to manufacture detecting devices based on UV-vis spectroscopy. As an illustrative comparison of the diacid monomer, the model and the

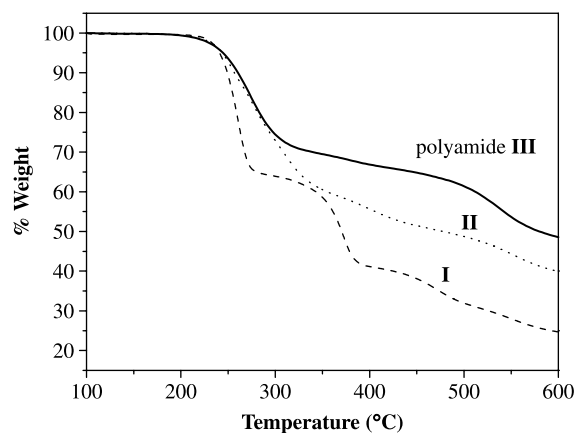


Figure 5. TGA of the diacid monomer **I** (dash), model compound **II** (dots) and polyamide derived from the polymerisation of the diacid monomer (**I**) and MPD (polyamide **III**, continuous line).

polyamide properties, Figure 5 shows the TGA patterns of all the compounds, showing all the same initial decomposition temperatures, between 200 and 250°C, typical of the thermal degradation of the urea group.

4. Conclusion

In summary, we have synthesised and characterised a model polyamide compound, which contains urea-binding sites, for the colorimetric sensing of aromatic diamines. The design of these receptors is intended to give them the ability to selectively recognise and sense the phenylene diamine isomers. Three colour developments from colourless to yellow-greenish, and blue and red were observed upon addition of either *ortho*, *meta* or *para*-phenylenediamine, respectively, to solutions of the model polyamide compounds (**II**) in polar aprotic organic solvents. The solutions remained colourless upon addition of other amines or diamines. Further, research will be carried out to extend the sensing capabilities of these model molecules in water environments and also to study the sensing capabilities of dense or semipermeable membranes obtained from the corresponding polyamides.

Acknowledgements

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