Dyes and Pigments 122 (2015) 177-183

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Intrinsically colored wholly aromatic polyamides (aramids)

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ARTICLE INFO

Article history: Received 22 May 2015 Accepted 22 June 2015 Available online 30 June 2015

Keywords: Aramids Aromatic polyamides High performance polymers Inherently colored polymers Intrinsically colored polymers Self-colored polymers

ABSTRACT

This work describes the preparation of intrinsically blue-colored, high-performance aromatic polyamides (aramids). The color was achieved by preparing a diamine monomer containing a chromogenic azadipyrromethene (ADPM) core, which after polymerizing it with commercially available *m*-phenyleneisophtahlamide and isophthaloyl chloride gave the blue-colored polyisophthalamide copolymers. These materials were structurally compared to commercialized and high-value-added *meta*-aramid fibers [poly(*m*-phenyleneisophthalamide), **MPIA**, brand names: NOMEX[®] and Teijinconex[®]]. Blue is the highest demanded color in the market of protective aramid fibers. The coloration efficiency of this special monomer is very high. Furthermore, the aramids showed even better thermal properties than commercial **MPIA**.

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1. Introduction

Wholly aromatic polyamides, usually termed as aramids, are high value-added high-performance materials. They are prepared and commercialized as outstanding thermally and mechanically resistant fibers. The commercial success of the aramids started in the 1960s with the discovery of the all-*para*-phenylene oriented aramid fiber, poly(*p*-phenylene terphthalamide), by Stephanie Kwolek at DuPont, which is commercialized under the trade name Kevlar[®]. Concomitantly, this put into the market the all-*meta*-phenylene oriented aramid fiber, **MPIA**, under the trade name Nomex[®]. Two decades later, the company Teijin made the only break-through in 50 years of commercial success of aramids with the commercialization of Technora[®], the aramid with a copolymer structure comprising *meta*- and *para*-phenylene oriented rings, poly(*p*-phenylene-*co*-3,4'-oxydiphenylene terephthalamide) [1–6].

Both the remarkable thermal and fire resistance, and the mechanical strength of aramids come from their chemical structure. Thus, the rigidity of the main polymer chain due to the wholly aromatic structure conjugated with the amide groups, the high average bond energy, along with the strong and highly directional interchain hydrogen bonds between amide moieties, provide the materials with extraordinary cohesive energy. The fibers are obtained by wet, dry or dry-jet wet spinning of aramid solutions. The properties of the fibers are physically enhanced by improving the rod-like structure and the percentage and quality of crystalline microdomains by cold and heat drawing after fiber spinning and coagulation. This increases the intermolecular packing and also the cohesive energy even further. The fibers are obtained as flogs, staple and continuous fibers that are used for preparing yarns and fabrics for apparel (protective clothing such as fire, chemical and saw protection suits, and bullet-proof body armor), isolating paper, composites, and high temperature industrial filters, among others, covering the broad range of value-added products related with the following industrial sectors: transport (e.g., automotive and aerospace), oil and gas, protection and defense, telecom, and civil engineering [7–16].

Although in some industrial applications (e.g., composites and hot gas filtration) the natural yellowish color of the fibers is used, generally most of the applications require colored fibers, specifically those related with apparels, carpets, drapes, etc. However, the aramid fibers have poor dyeing properties for the same reasons that make them extremely thermal and mechanical resistant, i.e., the dense molecular packaging, the cohesive energy, the molecular interactions and the chain orientation and crystallinity. Colored yarns can be obtained by dying the fibers or by dope dyed. In conventional dying of aramid fibers, the affinity toward conventional dyes has to be improved by expansion of the amorphous regions with the combination of swelling agents and extremely high temperatures, over 190 °C [17]. For this reason, the dope





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dyeing using pigments is usually preferred, and dope dyed yarns are usually used for garments woven with aramids. Anyhow, dying impairs the properties of the fibers and at the same time the resistance to fading is barely achieved.

Ideal color fastness of fibers is achieved by intrinsically, inherently or self-colored polymers [18–21]. Inherently colored macromolecules are polymers with chromophores in their structure, i.e., polymers that have dye motifs chemically anchored. Accordingly, we designed and prepared a blue chromophore as an aromatic diamine monomer, and we used it to synthesize blue *meta*-aramids. The color hue was modified by tuning molar content of the chromophore monomer in relation with the conventional diamine monomer, i.e., *m*-phenylenediamine. The chromophore motifs cannot migrate and are evenly distributed along the polymer chains due random copolymerization. Moreover, the impressive thermal properties of the aramids are even improved by using this colored monomer.

2. Experimental

All materials and solvents were commercially available and used as received, unless otherwise indicated. p-aminoacetophenone (99%, Aldrich), NaOH (99.9%, VWR-Prolabo), *p*-anisaldehyde (>98%, Merck), diethylamine (DEA) (98%, Aldrich), nitromethane (>95%, Aldrich), ammonium acetate (97%, Alfa Aesar), benzoyl chloride (99%, Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF₆) (98%, Aldrich), ethanol (99.9%, VWR-Prolabo), methanol (>99.8%, Aldrich), dimethyl sulfoxide (DMSO) (99%, Prolabo), deuterated dimethyl sulfoxide (DMSO- d_6) (99.80D, VWR-Prolabo), and sulfuric acid (100%, Merck) were used as received. N,N-dimethylacetamide (DMA) (>99%, Aldrich) was vacuum distilled over phosphorous pentoxide twice and then stored over 4 Å molecular sieves. *m*-phenylenediamine (MPD) is commercially available (>99%; Aldrich) and was purified by double vacuum sublimation. Isophthaloyl dichloride (ICL) (>99%, Aldrich) was purified by double crystallization from dry heptane (99.9%, VWR-Prolabo).

2.1. Synthesis

2.1.1. Synthesis of intermediates, monomer and model

The synthetic steps carried out to prepare monomer (**3**) and model (**M1**) are depicted in Scheme 1.

Synthesis of (E)-1-(4-aminophenyl)-3-(4-methoxvphenvl)prop-2en-1-one (1): A stirred mixture of 5.0 g (37 mmol) of p-aminoacetophenone, 140 mL of ethanol and 240 mL of aqueous NaOH 4M solution was brought to 0 °C. 5.05 g (37 mmol) of *p*-anisaldehyde was added and the mixture was stirred at room temperature for 4 h. The flask was kept at 4 °C for 12 h, and then filtered off. The compound was dissolved in 300 mL of boiling methanol. The hot solution was filtered off and the solvent was evaporated to give compound (1). Yield: 4.8 g (51%). M.p.: 120 \pm 1 °C. ¹H NMR $\delta_{\rm H}$ (400 MHz, DMSO-d₆, Me₄Si): 7.95 (2H, d, / 8.7 Hz, Ph); 7.83 (2H, d, / 8.8 Hz, Ph); 7.77 (1H, d, / 15.5 Hz, CH); 7.63 (1H, d, / 15.5 Hz, CH); 7.03 (2H, d, / 8.8 Hz, Ph); 6.65 (2H, d, / 8.8 Hz, Ph); 6.14 (2H, s, NH₂); 3.85 (3H, s, CH₃). ¹³C NMR, δ_C (100.6 MHz, DMSO-*d*₆, Me₄Si): 186.80, 161.74, 154.61, 142.24, 131.87, 131.17, 128.71, 126.46, 120.84, 115.23, 113.62, 56.24. EI-LRMS m/z: 253.11 (M+, 100), 252.10 (35), 238.08 (38), 225.11 (18), 210.08 (22), 161.06 (18), 145.05 (15), 120.04 (73), 92.05 (22), 65.04 (18). HRMS calcd. for (C₁₆H₁₅NO₂): 253.1103; Found: 253.1102. FT-IR [wavenumbers (cm^{-1})]: v_{NH_2} : 3350; $v_C=_0$: 1640.

Synthesis of 1-(4-aminophenyl)-3-(4-methoxyphenyl)-4nitrobutan-1-one (2): 1 g (3.95 mmol) of compound (1) and 2.041 mL (19.73 mmol) of DEA were mixed in a pressure tube together with 10 mL of ethanol. Then, 2.138 mL (39.5 mmol) of nitromethane was added to the mixture. The solution was refluxed for 24 h. The solvent was evaporated under vacuum and 20 mL of diethyl ether was added to the brown oil. A palid yellow solid was formed, and it was filtered off and air dried. Yield: 0.74 g (60%). M.p.: 99 \pm 1 °C. ¹H NMR $\delta_{\rm H}$ (400 MHz, DMSO- d_6 , Me₄Si): 7.69 (2H, d, / 8.7 Hz, Ph); 7.30 (2H, d, / 8.6 Hz, Ph); 6.97 (2H, d, / 8.6 Hz, Ph); 6.58 (2H, d, / 8.7 Hz, Ph); 6.11 (2H, s, NH₂); 4.95 (1H, dd, / 12.7 Hz, / 5.6 Hz, CH₂-NO₂); 4.82 (1H, dd, / 12.6 Hz, / 10.0 Hz, CH₂-NO₂); 3.99 (1H, dd, / 9.6 Hz, / 6.1 Hz, CH); 3.74 (3H, s, CH₃); 3.35 (1H, dd, / 17.2 Hz, J 7.5 Hz, CH₂): 3.23 (1H, dd, J 17.1 Hz, J 6.8 Hz, CH₂). ¹³C NMR, δ_C (100.6 MHz, DMSO-*d*₆, Me₄Si): 195.17, 159.15, 154.74, 132.99, 131.31, 129.73, 125.19, 114.70, 113.40, 80.98, 55.87. EI-LRMS m/z: 314.10 (M+, <1), 268.10 (13), 239.10 (12), 134.06 (10), 121.03 (22), 120.03 (100), 106.05 (5). FT-IR [wavenumbers (cm⁻¹)]: v_{NH2}: 3364; $v_{C}=_{0}$: 1622; $\delta_{NH_{2}}$: 1596; $v_{as NO_{2}}$: 1580; $v_{s NO_{2}}$: 1349.

Synthesis of (*Z*)-5-(4-aminophenyl)-*N*-(5-(4-aminophenyl)-3-(4methoxyphenyl)-2H-pyrrol-2-ylidene)-3-(4-methoxyphenyl)-1Hpyrrol-2-amine (**3**): Compound (**2**) (1 g, 3.18 mmol), ammonium acetate (8.309 g, 107.7 mmol) and ethanol (18 mL) were heated under reflux for 24 h in a pressure tube. The reaction solvent was



Scheme 1. Synthesis of monomer (3) and model (M1).

evaporated under vacuum, and 50 mL of distilled water was added to the crude product. The mixture was stirred at room temperature for 10 min, and the green solid was filtered off and air dried. Yield: 0.67 g (80%). M.p.: 235 \pm 1 °C (decomp.).¹H NMR $\delta_{\rm H}$ (400 MHz, DMSO- d_6 , Me₄Si): 12.87 (1H, s, NH); 8.10 (4H, d, J 8.7 Hz, Ph); 7.78 (4H, d, J 8.6 Hz, Ph); 7.36 (2H, s, CH); 7.07 (4H, d, J 8.8 Hz, Ph); 6.78 (4H, d, J 8.6 Hz, Ph); 6.02 (4H, s, NH₂); 3.88 (6H, s, CH₃). ¹³C NMR, $\delta_{\rm C}$ (100.6 MHz, DMSO- d_6 , Me₄Si): 159.99, 154.40, 152.30, 149.26, 140.51, 130.60, 128.98, 127.44, 119.77, 115.08, 114.72, 113.66, 56.13. EI-LRMS m/z: 539.23 (M+, 100), 540.23 (40), 524.21 (8), 280.15 (6), 279.15 (26), 269.63 (16), 264.14 (20), 249.15 (6), 120.07 (6), 69.02 (5). HRMS calcd. for (C₃₄H₂₉N₅O₂): 539.2321; Found: 539.2310. FT-IR [wavenumbers (cm⁻¹)]: v_{NH}: 3466, 3320, 3210; v_C=_N: 1627, 1594; $\delta_{\rm NH+}$: 1565, 1544.

Synthesis of model (M1): To a solution of benzoyl chloride (0.80 mmol, 0.112 g) in 0.6 mL of DMA at 0 °C, 0.178 g (0.33 mmol) of compound 3 was added portionwise keeping vigorous stirring for 30 min under nitrogen, and then at room temperature for an additional 3.5 h. The final solution was slowly poured into distilled water, forming a dark blue solid that was filtered and washed thoroughly with water. Yield: 0.21 g (83%). ¹H NMR $\delta_{\rm H}$ (400 MHz, DMSO-d₆, Me₄Si): 12.76 (1H, s, NH); 10.62 (2H, s, NH); 8.11-8.04 (14H, m, Ph); 7.69–7.57 (10H, m, Ph, CH); 7.05 (4H, d, / 8.8 Hz, Ph); 3.88 (6H, s, CH₃). ¹³C NMR, δ_C (100.6 MHz, DMSO-*d*₆, Me₄Si): 165.96, 159.62, 153.85, 141.54, 134.76, 131.97, 130.27, 128.72, 128.60, 127.91, 127.78, 127.55, 126.17, 125.97, 120.54, 114.07, 113.93, 55.31. EI-LRMS m/z: 747.28 (M+, 3), 628.26 (5), 384.20 (30), 383.20 (97), 368.19 (100), 353.17 (5), 279.17 (10), 278.17 (37), 263.16 (28), 181.04 (8), 169.04 (9), 131.04 (11), 119.04 (12), 105.09 (77), HRMS calcd, for (C₄₈H₃₇N₅O₄): 747.2846; Found: 747.2841. FT-IR [wavenumbers (cm^{-1})]: v_{NH}: 3283; v_C=0: 1654; v_{C-N}: 1243.

2.1.2. Synthesis of polymers

The preparation of copolyamides **I**, **II**, and **III** is schematically shown in Scheme 2. The synthesis of copolyamide **I** is described below as an illustrative example.

A three necked flask with a nitrogen inlet and a mechanical stirrer was charged with 4.3 mL of DMA under a blanket of nitrogen at room temperature. Then, 0.23 g (0.426 mmol) of diamine **1** and 0.41 g (3.834 mmol) of MPD were added. The solution was stirred at room temperature until the solution of the diamine. The system was then cooled to 0 °C, and 0.86 g (4.260 mmol) of ICL was added portionwise (four equal amounts) over 5 min. The mixture was allowed to react under nitrogen at 0 °C for 30 min, and then at room temperature for additional 3.5 h. The final solution was slowly poured into distilled water, forming a dark blue, fibrous, swollen polymer precipitate that was filtered, washed thoroughly with water and acetone. The yield was quantitative.

2.2. Measurements

¹H and ¹³C NMR spectra were recorded with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively, with deuterated dimethyl sulfoxide (DMSO- d_6) as solvent.

Infrared spectra (FT-IR) were recorded with an FT/IR-4200 FT-IR Jasco Spectrometer with an ATR-PRO410-S single reflection accessory. Low-resolution electron impact mass spectra (EI-LRMS) and high resolution electron impact mass spectra (EI-HRMS) were obtained at 70 eV on an Aligent 6890N mass spectrometer and on a Micromass AutoSpec mass spectrometer respectively.

Thermogravimetric analysis (TGA) data were recorded on a 5 mg sample under a nitrogen or oxygen atmosphere on a TA Instrument Q50 TGA analyzer at a scan rate of 10 °C min⁻¹. LOI was estimated using the experimental Van Krevelen equation, LOI = 17.5 + 0.4 CR, where CR is the char yield weight percentage at 800 °C, which was obtained from TGA measurements in a nitrogen atmosphere [22].

Melting points (m.p.) were visually determined with a Gallenkamp melting point apparatus.

UV/Vis spectroelectrochemical measurements were carried out using an SPELEC (DropSens), a commercial fully integrated synchronized spectroelectrochemical device. The light beam, supplied by a 360–2500 nm tungsten-halogen light source was both conducted to and collected from the spectroelectrochemical cell by a



Scheme 2. Synthesis of copolyamides I, II and III.

200 µm reflection probe (RPROBE, DropSens). A standard threeelectrode cell was used in all experiments, consisting of a commercial Pt working electrode, a Pt wire as auxiliary electrode and a homemade Ag/AgCl/KCl (3 M) reference electrode. The polymer was deposited on the Pt working electrode by drop casting. Reflection UV/Vis data were recorded using a spectrometer QE-65000 (Ocean Optics) with a light beam supplied by an Avalight-DH-s-BAL Deuterium-halogen light source(Avantes), guided and collected by a reflection probe FCR-7IR200-2-2.5 × 100 (Avantes).

The polymer solubility was determined by mixing 10 mg of the polymer with 1 mL of a solvent, followed by stirring for 24 h at 20 °C. The polymer was considered soluble at room temperature if a homogeneous solution was obtained. If the polymer was not soluble, the system was heated to reflux to 2 h, and the polymer was considered soluble on heating if a homogeneous solution was obtained. Otherwise, the polymer was considered insoluble. The polymer inherent viscosities were measured with a Ubbelohde viscometer using *N*-methyl-2-pirrolidone and sulfuric acid (100%) as solvents at 25 ± 0.1 °C and a polymer concentration of 0.5 g dL⁻¹.

Water sorption experiments were conducted gravimetrically at room temperature. 200 mg of the sample was dried at 60 °C for 24 h over phosphorus pentoxide, and the sample was placed in a closed box containing a saturated aqueous solution of NaNO₂ at 25 °C, which provided a relative humidity of 65%. The samples were weighed periodically over a period of 8 days until they equilibrated with their surroundings and presented no further changes in weight.

Polyamide films were prepared by evaporation of cast solutions of 12% by polymer weight in DMA. The solvent was eliminated by heating at 80 °C overnight. To determine the tensile properties of the polyamide, strips (5 mm in width and 30 mm in length) were cut from a polymer film of 551 μ m thickness for I on an SHIMADZU EZ Test Compact Table-Top Universal Tester at 20 °C. Mechanical clamps were used and an extension rate of 5 mm min⁻¹ was applied using a gauge length of 9.44 mm. At least 6 samples were tested, and the data was then averaged.

3. Results and discussion

The preparation of inherently colored aromatic polyamides is a promising methodology for the exploitation of the highperformance thermal and mechanical properties of the aramids in the preparation of fibers for protective clothes. In this regard, it is advisable to modify as little as possible the aromatic nature of the main chain to maintain the outstanding properties of the aramids and at the same time achieving the new functionalities of the materials, i.e., permanent color in the development we are reporting, that increases even more their value added. In our case, we prepared a diamine monomer as novel blue chromophore for the preparation of a set of inherently blue copolyamides I, II and III, in which the color hue can be easily tuned by adjusting its feed percentage in the synthesis of the aramids. In our study, we have prepared aromatic copolyamides as MPIA derivatives with 0.1, 1.0 and 10.0% of structural units containing the chromophore (3) (Scheme 2).

In an initial approach to the preparation of the inherently colored polyamides we modeled the chemical modification reactions using a polyamide model to assure that the condensation reaction is carried out in a clean manner, i.e., without side reactions or any modification of the chromophore core.

For comparative purposes, some of the properties of the colored aramids are compared with those of the commercial *m*-aramid, **MPIA**, which we prepared following the standard procedure for aramid synthesis depicted in Scheme 2.

3.1. Polymer synthesis and characterization

The monomer (**3**) was prepared in a straightforward manner from commercially available materials, as shown in Scheme 1. The synthesis of model **M1** (Scheme 1) was conducted according to a synthetic procedure similar to the one used in the preparation of the polymers (Scheme 2).

Thus, the preparation of the model containing the chromophore, **M1**, was easily achieved from (**3**) and benzoyl chloride. The FT-IR and ¹H and ¹³C NMR spectra of the model confirm its structure and purity (Supporting information, Fig. S4).

As previously mentioned, aromatic copolyamides with a low percentage of modification of the structural units from the commercial aramids are interesting materials that can impart new properties and characteristics without penalizing their outstanding mechanical and thermal properties. The structure of the copolymers was in agreement with the NMR data (Fig. 1) and the content of structural units corresponded with the feed molar ratio



Fig. 1. ¹H NMR spectra of copolyamides: a) **I**; b) **II**; and c) **III**.

of the chromophore monomer (**3**), as per the integral ratio of the methyl protons of methoxy group (\sim 3.9 ppm) to the aromatic region (7–9 ppm) in ¹H NMR spectra.

The chemical constitution limits the upper performance of materials. However, correct chemical structures do not guarantee the achievement of the highest properties, which are affected by different concomitant factors, such us molecular weight. This parameter is related with viscosity and in the field of high performance materials the inherent viscosity (η_{inh}) is usually studied for comparative purposes.

The viscosity is solvent dependent, and for this reason the inherent viscosity was measured in two different solvents (Table 1). Aramids with η_{inh} higher than 0.5 in NMP are usually considered as high molecular weight polymers, and our data are consistent with this approach.

Polymers with polar groups absorb water from the environment, influencing their performance. The amide linkage of aramids is highly polar and its interaction with water molecules is highly favorable. The water sorption lowers the thermal transitions by weakening the amide—amide strong interactions impairing the electrical insulation, the mechanical, and the thermal properties. Conversely, a high water uptake is interesting for other technological fields in which aramids play an important role, such as membrane technology for water desalination, i.e., reverse osmosis membranes. The water sorption is limited by the aramid crystallinity. The prepared aramids absorb 7% by weight of water, a data fully comparable with laboratory prepared **MPIA** samples (the reported water uptake for commercial **MPIA** fibers is 5.2%) [7].

The polymer II was characterized by time-resolved UV/Vis absorption spectroelectrochemistry. This multiple response technique allows us to obtain electrochemical and molecular information simultaneously. Polymer oxidation was studied using cyclic voltabsorptometry by scanning the potential between 0.00 V and +1.60 V at a scan rate of 0.02 V s⁻¹ in a 0.1 M TBAPF₆ acetonitrile solution. The cyclic voltammograms (Fig. 2a) shows an illdefined response providing little information on the oxidation process. However, the optical response is much more informative. Fig. 2b shows the UV/Vis spectra in which a band centered at 775 nm evolves during the oxidation process. This band is related to the oxidation of the ADPM [23]. The corresponding voltabsorptogram at 775 nm is shown in Fig. 2c. At lower potentials there is no change in the absorbance, but when the potential reaches a value of +0.70 V, the band centered at 775 nm starts to grow. At higher potentials the intensity of this band increases until the oxidation of the polymer is completed. As can be observed in Fig. 2c, absorbance does not decrease in the backward scan and, therefore, the initial value of absorbance is not recovered after the oxidation, indicating that an irreversible oxidation of the polymer is taking place.

3.2. Solubility and water uptake

The lack of solubility has always been a drawback of polyamides and has limited their technological applications. However, the copolymers described in this work are highly soluble compared with aramids and can be dissolved at room temperature in polar aprotic

Table 1

Inherent viscosity and water sorption of the polymers.

Polymer	$\eta_{inh} \left(dL/g\right)^a$	Water uptake (%) ^b
I	0.76 (0.48)	7
II	1.15 (0.47)	7
III	1.03 (0.53)	7

 $^a\,$ Polymer concentration $=0.5\,g\,dL^{-1};$ temperature $=30\,^\circ\text{C};$ solvents: sulfuric acid 100% and NMP, the data obtained in NMP between brackets.

^b Water sorption at 65% RH.



Fig. 2. Electrochemical analysis of polymer **II** (film obtained by casting, 13 µm thickness): (a) Cyclic voltammogram obtained in 0.1 M TBAPF₆ acetonitrile solution. Potential was scanned between 0.00 V and +1.60 V at 0.020 V s⁻¹; (b) Evolution of the UV/Vis absorption spectra during the oxidation of the polymer; (c) Cyclic voltabsorptogram at 775 nm.

solvents, such as NMP, DMSO, and DMA (Table 2). At this point, it is important to comment that the commercial **MPIA** is transformed into fibers by wet, dry or dry-jet wet spinning from a DMA solution of approximately 19.2% **MPIA**. As expected, the low-molecular-weight model is soluble in conventional organic solvents.

Regarding the water uptake, the absorption of 7% by weight of water is similar to that of **MPIA**. This indicates that water affinity of the structural units containing the chromophore (**3**) of aramids **I**, **II** and **III** are similar to those of **MPIA**. Accordingly, this parameter will not affect the applicability of the materials as fibers in comparison with the commercial aramid fabrics.

3.3. Thermal and mechanical properties

The thermal resistance of the materials was considered to be related with the decomposition temperatures, in terms of weight

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Tabla	2

Table 2	
Solubility	of the polymers. ^a

Polymer	Solvents						
	DMSO, DMA	NMP, DMF	THF	Acetone	CHCl ₃ , CH ₂ Cl ₂ , EtOH	Cyclohexanone	
I	++	++	_	-	_	-	
П	++	++	_	_	_	-	
III	++	+	_	_	_	-	
MPIA	++	++	_	_	_	-	
M1	++	++	++	+	+-	++	

^a Essay: 10 mg of polymer in 1 mL of solvent. Solubility: ++ = soluble at room temperature, + = soluble on heating, +- = partially soluble, - = insoluble.

loss, and with the char yield at a given temperature. The thermal resistance was evaluated using TGA. The TGA data, summarized in Table 3, confirmed the good thermal stability of copolyamides, which surprisingly exhibited better thermal properties compared with the commercial aramid **MPIA**, which displayed 5% (T_5) and 10% (T_{10}) weight loss under nitrogen atmosphere of 432 and 452 °C, respectively.

Even more important than the weight loss at a given temperature is the minimum fraction of oxygen in a mixture of oxygen and nitrogen that will support combustion after ignition, that is, the LOI (limiting oxygen index), which is related to the char yield. The higher the char yield at 800 °C, the higher the LOI, and the better the flame resistance properties of the materials. LOI values higher than 21%, the oxygen content of air, will most likely not burn in an open-air situation. All LOI values are significantly higher than 21, and even higher than the LOI of MPIA calculated using the same method, which is 38. Considering this, the prepared materials have very good fireproof characteristics and must be considered as selfextinguishing materials.

In short, the results of the thermal behavior of the prepared aramids are quite shocking. We expected thermal property loss compared to commercial MPIA instead of an improvement. Remarkably, the improvement is more evident in oxidizing atmosphere (synthetic air) and even more striking in static thermogravimetric analysis at high temperature (350 °C) (Fig. 3).

The mechanical properties were similar to those of the reference *m*-aramid, **MPIA**, with tensile strength and Young's modulus of 51 and 1530 MPa, respectively, with elongation of 5% [9]. At this point, it is important to take into account that the measurements were carried out with lab-made un-oriented and thermally un-treated films prepared by casting.

3.4. Applicability of the intrinsically colored aramids

Colored commercial aramid fibers are highly demanded for protected apparels and are extremely expensive materials. However, the loss of color upon use is usual in all kind of fibers dyed using standard dying procedures. We have worked to solve this to

Table 3	
Thermal behavior of polymers I, II and III compared to MPIA.	

Polymer	N ₂ atmosphere			O ₂ atmosphere (synthetic air))
	T₅ ^a (°C)	T ₁₀ ^b (°C)	CR ^c (%)	T₅ ^a (°C)	T ₁₀ ^b (°C)	CR ^c (%)	LOId
I	416	448	58	427	462	_	41
П	444	463	56	451	482	1	40
III	449	472	60	451	480	-	42
MPIA	432	452	50	419	445	9	38

^a T_5 : temperature at 5% weight loss is observed.

^b T_{10} : temperature at 10% weight loss is observed.

^c CR: char yield (%) at 800 °C.

 $^{\rm d}\,$ Limiting oxygen index, calculated from the TGA data (LOI = 17.5 + 0.4 CR).



Fig. 3. Weight loss of MPIA and aramid I after heating the polymers at 350 °C for 24 h in oxidizing (synthetic air) atmosphere.



Fig. 4. Color hue of the aramids as obtained upon precipitation after synthesis and films (a), and reflection UV/vis spectrum (b) of polyamide II. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Aspect of polymer **II** and model **M1**: a) Color change upon adding $Al(NO_3)_3 \cdot 9H_2O$ to polymer **II**; b) color change upon reduction and oxidation (-1.3 V and 1.6 V respectively) of polyamide model **M1** in solution of acetonitrile (5·10⁻⁵ M).

increase even more the value added of the aramids and have reported a novel methodology to get inherently colored aromatic polyamides.

For this purpose we have chosen the blue color, which is usually associated with the apparels used in civil defense, e.g., state security forces and firefighters. The color hue can be tuned by means of increasing or decreasing the percentage of structural units containing the dye motifs (Fig. 4). Moreover, different colors may be obtained by redox reaction affecting the chromophore motifs, as can be seen in the films with or without $Al(NO_3)_3 \cdot 9H_2O$ (Fig. 5).

Research on yellow and red diamine monomers is on progress for the preparation of intrinsically colored aramids. With the correct copolymerization of the blue, red and yellow chromophores, the full color range will be available.

4. Conclusions

We have synthetized a chromophore monomer that copolymerized with isophtaloyl dichloride and *m*-phenylendiamine results in a blue inherently colored wholly aromatic polyamide, specifically a *meta*-aramid. The blue is one of the highest demanded color in the market of protective aramid fibers. The coloration efficiency of this special monomer is very high. Moreover, it was intended to maintain the high mechanical and thermal properties or the reference aramids. Surprisingly, the thermal resistance has not only been maintained but notably improved. Furthermore, it has been demonstrated that the hue of the polyamide color can also be tuned by a redox process, and the evaluation of the application potential of this process is now under evaluation. Research is in progress for preparing yellow and red diamine monomers, and with the correct copolymerization of the described blue, and the forthcoming red and yellow chromophore monomers, the full color range will be available.

Acknowledgments

We gratefully acknowledge the financial support provided by the Spanish Ministerio de Economía y Competitividad-Feder (MAT2014-54137-R) and by the Consejería de Educación – Junta de Castilla y León (BU232U13).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.06.027.

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