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ORIGINAL PAPER

Synthesis and study of the effect of carboxyvinyl group position on the properties of polyamides. Crosslinked polymers

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Abstract Several aromatic polyamides containing carboxyvinyl bonds in the main chain were synthesized by self-condensation from β-(2-,3-,4-aminophenyl)propenoic acid using the phosphorylation method. In addition, aromatic polyamides containing carboxyalkyl bonds in the backbone were synthesized under the same conditions for comparative purposes (model polyamides) and used as pattern. The model polyamides were synthesized from 3-,4-aminophenyl acetic acid and β-(3-aminophenyl)propanoic acid. Polymers were characterized by UV–vis, FT-IR and ^{1}H-NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and inherent-viscosity measurement. The effect of the carboxyvinyl group position in the aromatic ring was correlated to polyamides properties. Thereby, solubility, thermal stability, viscosities, optical properties, and polymers crosslinking were studied. Some polyamides were soluble in polar solvents and inorganic acids. Upon thermal curing crosslinked polymers were obtained. The thermal stability and crosslinking of polyamides were evaluated with respect to position of carboxyvinyl in the aromatic ring. The crosslinked polymers exhibited improved thermal stability.

Keywords Polyamides · Synthesis · Cured · Thermal stability · Vinyl · Crosslinked polymers

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Introduction

Aromatic polyamides have high thermal stability and good mechanical properties, usually are intractable materials of low solubility and high melting or softening temperature and therefore, poor processability [1–4]. Introduction of aromatic ether bonding to the polymer backbone is known to provide processability to the polymer [5–7]. Various studies have been done through synthetic modifications using, for example, flexible bonds [7–11], pendent, bulky, alkyl side groups, luminous aliphatic, and cyclic [12–16] in the polymer backbone. The aromatic azo bond in polyamides not only provides color, but also the *cis–trans* isomerism exerts an effect on their photochromic properties [17–19]. In some cases the azo group allows that the polyamides be light resistant [20]. Triphenylamine groups in polyamides backbone would allow using them as potential charge-carrier materials [21] and pyrolysed polyamides, with carboxyvinyl groups exhibiting a broad range of electrical conductivity [22]. Mikroyannidis et al. [23, 24] reported that several homopolyamides and copolyamides have high thermal stability (up to 370 °C), with soluble pendent cyano groups and can be used in the synthesis of heat-resistant crosslinkable polymers. Others polymers that can be crosslinked are those containing vinyl bonds in the main chain, crosslinking is caused by photo or thermal energy irradiation and the mechanism proceeds by cycloaddition reaction between the vinyl bonds of different chains [10, 25–27]. Moreover, vinyl bond containing polyamides possess attractive properties, e.g., from butene dioic acid with fluorescent properties [28] and polyamides with photoresponsive properties from norbornadiene dicarboxylic acid [29] have been synthesized. Polymers that contain crosslinkable functional groups are interesting since they have practical applications, e.g., for liquid crystal alignment [30] and optoelectronics [31].

The current investigation deals with the synthesis and characterization of a new series of aromatic polyamides containing carboxyvinyl bond in its backbone. The polyamides were prepared from β-(2-,3-,4-aminophenyl)propenoic acid. Studies of the effect of the carboxyvinyl group position in the aromatic ring on the optical properties, solubility, inherent viscosities, and thermal stability of the polyamides are reported. Upon thermal curing, the polyamides with carboxyvinyl bond yielded polymers with low crosslinking and moderate thermal stability. In addition, several aromatic polyamides were synthesized from 3-aminophenylacetic acid, 4-aminophenyl acetic acid, and β-(3-aminophenyl)propanoic acid, and were used for comparative purposes.

Experimental

Measurements

IR spectra were recorded on a JASCO FT-IR 4200 spectrometer. NMR spectra were obtained using TMS as internal reference on a 400 MHz Bruker spectrometer. Elemental analysis was performed on an EA-1108 Fisons Elemental Analyzer. Inherent viscosity was determined on a Desreux-Bischoff type viscometer at 26 °C using 0.32 g dL^{-1} H_2SO_4 solution. Polymer thermal analysis was carried out under nitrogen at 20 °C min^{-1} heating rate on a TGA Q 50 V20.5 thermal analyzer. Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments Q200 Differential Scanning Calorimeter. Samples (3–5 mg) were placed into aluminum pans and heated at 10 °C min^{-1} in the range 0–350 °C under flowing nitrogen (50 mL min^{-1}). Ultraviolet–Visible (UV–Vis) spectra were run on a Perkin–Elmer Lambda 35UV/VIS spectrometer. Spectra were obtained from a 0.02 g L^{-1} polymers solution. Melting points were determined on a Kofler melting point apparatus SMP10.

Reagents

β-(2-Nitrophenyl)propenoic acid, β-(3-nitrophenyl)propenoic acid, β-(4-aminophenyl)propenoic acid, 4-aminophenyl acetic acid, DMF, triphenylphosphite, LiCl, diethyl malonate, 3-nitrobenzyl chloride were from Sigma–Aldrich Co. Pyridine, NH_4Cl, Zn powder, and Sn were purchased from Arquimed Co.

Monomers

Monomers β-(2-aminophenyl)propenoic acid, β-(3-aminophenyl)propenoic acid were synthesized by hydrolysis from methyl β-(2-aminophenyl)propenoate and methyl β-(3-aminophenyl)propenoate. 3-Aminophenyl acetic acid and β-(3-aminophenyl)propanoic acid were prepared as described elsewhere [32, 33] but synthesis of the latter was slightly modified.

β-(2-Aminophenyl)propenoic acid

Methyl β-(2-nitrophenyl)propenoate In a 250 mL round-bottom flask equipped with a reflux condenser, 4.0 g (21 mmol) of β-(2-nitrophenyl)propenoic acid and 200 mL methanol were placed. 0.2 mL 98% H_2SO_4 was then added dropwise. The mixture was heated under reflux for 17 h. The reaction mixture was let to cool at room temperature and then 1.34 g $NaHCO_3$ dissolved in 15 mL of water was added. Methanol was removed by distillation under vacuum using a rotary-evaporator and then the residue was extracted with CH_2Cl_2, dried with Na_2SO_4, CH_2Cl_2 was removed and the white solid was purified by re-crystallization from ethanol. Yield 58%, mp = 73–74 °C. FT-IR: C=O at 1713 cm^{-1}, C=C at 1518 cm^{-1}, C–O at 1204 cm^{-1}, vinyl bond at 1638 cm^{-1}. ^{1}H-NMR (acetone-d6): aromatic CH at 8.08 ppm (1H,d); CH at 7.91 ppm (1H,d); CH at 7.78 ppm (1H,t); CH at 7.68 ppm (1H,t); vinyl CH at 8.04 ppm (1H,d), vinyl CH at 6.54 ppm (1H,d); $-OCH_3$ at 3.78 ppm (3H,s).

Methyl β-(2-aminophenyl)propenoate 0.90 g (4.34 mmol) of methyl β-(2-nitrophenyl)propenoate, 19 mL methanol, 2.2 mL of water, and 0.40 g NH_4Cl were placed into a 50 mL round-bottom flask equipped with a reflux condenser. The mixture was heated and 2.79 g Zn powder added slowly under stirring. The mixture was refluxed at 75–80 °C for 2 h heated up to boiling, filtered, and finally the solvent was removed using a rotary-evaporator. The product was dissolved in 40 mL of methanol, activated carbon added, then, the mixture was heated and filtered, cooled at room temperature and finally 1.8 mL of water added. The mixture was left for 1 day and the dark-yellow product was filtered and dried at room temperature. Yield 28%, mp = 65–66 °C. FT-IR: NH_2 3 bands at 3413, 3358, and 3234 cm^{-1}; aliphatic CH at 2956 cm^{-1}, C=O at 1698 cm^{-1}, C=C at 1623 cm^{-1}, C–O at 1197 cm^{-1}, vinyl bond at 1630 cm^{-1}. ^{1}H-NMR (acetone-d6): NH_2 at 5.17 ppm, (2H,s); aromatic CH at 7.14 ppm (1H,t); CH at 6.64 ppm (1H,t); aromatic CH (1H,d) at 6.79 ppm, aromatic CH at 7.45 ppm (1H,d), vinyl CH at 7.88 ppm (1H,d), 6.34 ppm (1H,d); $-OCH_3$ at 3.75 ppm (3H,s). Elemental analysis, Calcd. C 67.8, H 6.3, N 7.9%; Found C 66.80, H 8.24, N 7.97%.

Ester hydrolysis 0.20 g (1.13 mmol) of methyl β-(2-aminophenyl)propenoate and NaOH aqueous solution (0.090 g dissolved in 9 mL water) were placed into a 20 mL round-bottom flask equipped with a reflux condenser. The solution was refluxed by 16 h, cooled at room temperature and 0.3 mL 5.75 M HCl added. The mixture was cooled in an ice-water bath and the yellow product was filtered off. 0.13 g of β-(2-aminophenyl)propenoic acid was obtained. Yield 71%, mp = 152–153 °C (decomposed). FT-IR: NH_2 at 3356 cm^{-1}, 3239 cm^{-1}, OH (broad band) at 2916 cm^{-1}, C=O at 1683 cm^{-1}, C=C + vinyl bonds at 1600 cm^{-1}. ^{1}H-NMR (acetone-d6): aromatic CH at 6.78 ppm (1H,d), aromatic CH at 6.62 ppm (1H,t), aromatic CH at 7.09 ppm (1H,t), aromatic CH at 7.44 ppm (1H,d), vinyl CH at 7.84 and 6.31 ppm, OH at 5.1 ppm, NH_2 at 3.50 ppm. Elemental analysis, Calcd. C 66.25, H 5.56, N 8.58%; Found C 62.9, H 6.9, N 8.3%.

β-(3-Aminophenyl)propenoic acid

Methyl β-(3-nitrophenyl)propenoate 4.0 g β-(3-nitrophenyl)propenoic acid, 200 mL methanol, and 0.2 mL 98% H_2SO_4 were placed into a 250 mL round-bottom flask equipped with a reflux condenser. The mixture was refluxed under stirring for 31 h, cooled at room temperature and 15 mL solution 9.0% $NaHCO_3$ was added. Methanol was removed using a rotary-evaporator and the residue was extracted with CH_2Cl_2, dried with Na_2SO_4, the solvent was removed, re-crystallized with 40 mL ethanol. The white product was finally dried at room temperature. Yield 56%, mp = 126–127 °C. FT-IR: aromatic CH at 3090 cm^{-1}, CH_3 at 2956 cm^{-1}, C=O at 1698 cm^{-1}, aromatic C=C at 1524 cm^{-1}, vinyl C=C at 1633 cm^{-1}, δ CH=CH vinyl (*trans*) at 992 cm^{-1}; ^{1}H-NMR (acetone-d6): aromatic CH at 8.52 ppm (1H,s), aromatic CH at 8.28 ppm (1H,d), aromatic CH at 8.15 ppm (1H,d), aromatic CH at 7.75 ppm (1H,t), vinyl CH at 7.79 and 6.78 ppm (1H,d),
$-CH_3$ at 3.78 ppm (3H,s). Elemental analysis, Calcd. C 57.9, H 4.4, N 6.8; Found C 58.0, H 5.5, N 7.0%.

Methyl β-(3-aminophenyl)propenoate 0.90 g methyl β-(3-nitrophenyl)propenoate, 19 mL methanol, 2.2 mL of water, and 0.40 g NH_4Cl was placed in a 50 mL round-bottom flask equipped with a reflux condenser. The mixture was heated and 2.79 g Zn powder was slowly added under stirring. The system was refluxed for 2 h at 80 °C, heated up to boiling, filtered, and the solvent was removed using a rotary-evaporator. The product was re-crystallized with 20 mL ethanol (after standing for several days the precipitate was filtered off), dried at 60 °C. Yield 47%, mp = 179–180 °C, FT-IR: NH_2 at 3274 and 3228 cm^{-1}, aromatic CH at 3137 cm^{-1}, CH_3 at 2954 cm^{-1}, C=O at 1711 cm^{-1}, vinyl at 1642 cm^{-1}, aromatic C=C at 1583 cm^{-1}. ^{1}H-NMR (acetone-d6): aromatic CH at 7.12 ppm (1H,s), aromatic CH at 7.42 (1H,d), aromatic CH at 6.88 ppm (1H,d), aromatic CH at 7.43 ppm (1H,t), vinyl CH at 7.54 and 6.54 ppm (1H,d), $–OCH_3$ at 3.73 ppm (3H,s), NH_2 at 3.38 ppm (2H,s). isomers ratio *cis*/*trans* 1:1.

Ester hydrolysis 0.20 g methyl *β*-(3-aminophenyl)propenoate and 4 mL methanol were placed into 20 mL round-bottom flask equipped with a reflux condenser. The mixture was heated and then 0.5 mL of a 20% p/v NaOH solution was poured under stirring. The mixture was refluxed for 7 h, cooled at room temperature and 0.48 mL of a 5.5 M HCl (pH 0–1) solution and a little amount of water added. Finally, the mixture was left aside until the solid separates. The precipitate was filtered off and the solid was purified by recrystallization from water. The mother liquor was cooled in an ice-water bath and the obtained product was separated by filtration. *β*-(3-Aminophenyl)propenoic acid was dried at room temperature for several days. Yield 48.9%, mp = 250 °C (decomposition), FT-IR: NH_2 + OH at 3002–2555 cm^{-1}, C=O at 1702 cm^{-1}, vinyl C=C at 1629 cm^{-1}, aromatic C=C at 1594 cm^{-1}, δ CH=CH vinyl (*trans*) at 1094 cm^{-1}. ^{1}H-NMR (D_2O): aromatic CH at 7.70 ppm (1H,d), aromatic CH at 7.59 ppm (1H,s), aromatic CH at 7.56 ppm (1H,t), aromatic CH at 7.41 ppm (1H,d), vinyl CH at 7.68 and 6.55 ppm. OH and NH_2 not were observed. Elemental analysis, Calcd. C 66.2, H 5.6, N 8.6; Found C 64.8, H 6.2, N 7.9.

β-(3-Aminophenyl)propanoic acid

β-(3-Nitrophenyl)propanoic acid Diethyl malonate (18.5 g) was added to a warm solution of sodium ethoxide prepared from 2.61 g of Na in 50 mL super-dried ethanol. The mixture was boiled and then rapidly added to the boiled solution of 3-nitrobenzyl chloride (10.0 g) dissolved in 80 mL of super-dried ethanol. The mixture was refluxed for 2.5 h and the alcohol was removed by vacuum distillation (Caution, bath temperature lower at 60 °C). The residue was acidified with a 12.3% HCl solution (17 mL) and extracted twice with 40 mL $CHCl_3$. $CHCl_3$ was removed and the residue was refluxed at 70–80 °C during 2.5 h with a 30% KOH solution (44 mL) and then diluted with water (50 mL). The mixture was left standing for 24 h, filtered and the mixture was acidified with 20 mL HCl (37%) and finally extracted twice with 80 mL of diethyl ether. The extract was dried with Na_2SO_4 and the ether was removed by distillation. The product (3-nitrobenzyl malonic acid) was recrystallized from water, dried and then heated to 180–190 °C until the evolution of carbon dioxide ceased. Next, the obtained oil was extracted several times using a little volume of boiling water (50 mL), cooled at room temperature, filtered and dried at 65 °C. Yield 2.0 g. mp = 111–112 °C. FT-IR: C=O at 1704 cm^{-1}, aromatic C=C at 1519 cm^{-1}, CH aliphatic at 2916 cm^{-1}, aromatic CH at 3085 cm^{-1}. ^{1}H-NMR (DMSO-d6): Aromatic CH at 8.16 ppm (1H,s), aromatic CH at 8.11 ppm (1H,d), aromatic CH at 7.79 ppm (1H,d), aromatic CH at 7.64 ppm (1H,t), –CH_2– at 3.03 ppm (2H,t), –CH_2– at 2.70 ppm (2H,t).

β-(3-Aminophenyl)propanoic acid 0.97 g of β-(3-nitrophenyl)propanoic acid, 16 mL of glacial acetic acid and 0.60 g tin were placed into a 50 mL round-bottom flask equipped with a reflux condenser. The mixture was heated at 98 °C for 22 min, and then 1.2 mL water and six drops of 37% HCl added. Once tin was consumed, 0.70 g tin was added followed by slow addition of six drops 37% HCl. When the mixture begins to turn orange (113 min), the product was filtered off, the solvent was removed by distillation using a rotary-evaporator, and 50 mL of water added. After standing for 30 min the mixture was filtered, concentrated down to a small volume, filtered again and the solvent was almost completely removed. The product was then dried in the paper at 65 °C. 0.53 g of 3-(aminophenyl)propanoic acid was obtained, yield 53%, mp = 160 °C. FT-IR: NH + OH (broad) at 3279–2881 cm^{-1}, C=O at 1703 cm^{-1}, aromatic C=C at 1593 cm^{-1}, CH aliphatic at 2881 cm^{-1}, aromatic CH at 3020 cm^{-1}. ^{1}H-NMR (DMSO-d6): OH at 10.1 ppm (s,1H), aromatic CH at 7.36 ppm (1H,d), aromatic CH at 7.18 ppm (3H,m), NH at 3.5 ppm (1H,s), –CH_2– at 2.84 ppm (2H,t), –CH_2– at 2.54 ppm (2H,t). Elemental analysis, Calcd. C 53.6, H 6.00, N 6.95; Found C 51.5, H 4.8, N 6.65%.

Polymers synthesis

All polyamides were synthesized under the same experimental conditions using the phosphorylation method. In this approach triphenylphosphite was used as initiator and polymers can be obtained with an increased molecular weight [34].

In a 20 mL round-bottom flask, containing 4.39 mmol of monomer, 2.2 mL DMF, 2.2 mL of pyridine, 4.38 mmol of triphenylphosphite, and 0.15 g LiCl, a condenser was attached. The mixture was heated to 110–120 °C for 6 h, concentrated to 2/3 its volume, cooled at room temperature and 10 mL of cold water added. The mixture was stirred for 30 min, the solvent removed by decantation and the solid washed twice with 6 mL of 12.4 M HCl solution and methanol. The polymers were dried at 65 °C.

In this paper, the polyamides obtained from β-(2-aminophenyl)propenoic acid, β-(3-aminophenyl)propenoic acid, β-(4-aminophenyl)propenoic acid were called P2APC, P3APC, and P4APC, respectively. Model polyamides obtained from 3-aminophenyl acetic acid, 4-aminophenyl acetic acid, and β-(3-aminophenyl)propanoic acid were called P3APA, P4APA, P3APP, respectively.

Polyamides curing Each polyamide was placed in a glass tube and cured by heating in an oven provided with a digital thermometer, P2APC, P4APC at 220 °C for 90 min and P3APC at 240 °C for 90 min.

Results and discussion

Several attempts were made in order to obtain the monomers β-(2-aminophenyl)propenoic acid, β-(3-aminophenyl)propenoic acid, and β-(3-aminophenyl)propanoic acid by direct hydrogenation of the respective β-(2-nitrophenyl)propenoic acid, β-(3-nitrophenyl)propenoic acid, and β-(3-nitrophenyl)propanoic acid. Usually, hydrogen gas simultaneously reduces the nitro group and the double bond of the vinyl group and lengthy hydrogenation induces decomposition of the vinyl group or the aliphatic chain of β-(3-nitrophenyl)propanoic acid. The selective reduction of the nitro group from methyl β-(2-nitrophenyl)propenoate and methyl β-(3-nitrophenyl)propenoate in the presence of vinyl bonding was accomplished using a methanol, water, and powder zinc mixture. Amino acids were then obtained by alkaline hydrolysis of the aminophenyl esters. Moreover, the synthesis of β-(3-aminophenyl)propanoic acid was attempted by direct reduction of β-(3-nitrophenyl)propanoic acid using hydrazine hydrate or a $Zn/H_2O/NH_4Cl$ mixture; however, either the purification process was complicated or aliphatic bond cleavage occurred. The reduction of nitro group from β-(3-nitrophenyl)propanoic acid was achieved using a mixture of acetic acid, tin, and hydrochloric acid.

Synthesis of monomers, aromatic polyamides bearing carboxyvinyl bonds in the main chain, and model polyamides are depicted in Fig. 1.

Polyamides FT-IR spectra are shown in Fig. 2. Polyamides P2APC, P3APC, and P4APC show characteristic absorption bands at 3235, 3272, 3221 cm^{-1} (N–H); 1658, 1659, 1661 cm^{-1} (C=O); 1614, 1612, 1590 cm^{-1} (vinyl bond); and 1525, 1537, 1507 cm^{-1} (aromatic CH=CH). The characteristic bands of carbonyl and hydrogen-bonded amide groups in all polyamides spectra confirm the formation of amide bond.

P4APC absorption band at 818 indicates a *para*-substituted polyamide, while *meta*- and *ortho*-substituted showed three and one strong absorption bands located at 852, 741, 670, and 750 cm^{-1}, which agrees well with the pattern of a di-substituted aromatic ring of different polymers. P4APC, P3APC, and P2APC showed an absorption band at 974, 970, and 974 cm^{-1}, respectively, typical of a *trans* olefinic bond [35]. P2APC *trans*-isomer is predominant; nevertheless, the P2APC spectrum shows an additional band at 858 cm^{-1} related to the *cis*-isomer. P2APC *trans*-, *cis*-geometry minimizes the repulsion between neighboring functional groups, allowing the polymer to become a more extended conformation.

Figures 3 and 4 show P3APC and P2APC ^{1}H-NMR spectra. The more important signals correspond to vinyl bonds, these signals were assigned considering a coupling constants of 17 cps, typical of vinyl bonds [35]. Coupling constant of 17 cps was also observed for monomers spectra. P4APC was insoluble in deuterated solvents. Some other signals such as doublet and triplet corresponding to the aromatic ring are also observed in such spectra.

As shown in Table 1, the synthesized polyamides, P2APC, P3APC, P4APC and model polyamides present inherent viscosities in the range 0.33–0.18 dL g^{-1}, indicating a low degree of polymerization. The viscosity depends on the position of the carboxyvinyl group in the main chain. P4APC exhibited the highest inherent viscosity and P2APC the lowest one. P2APC viscosity is the result of steric

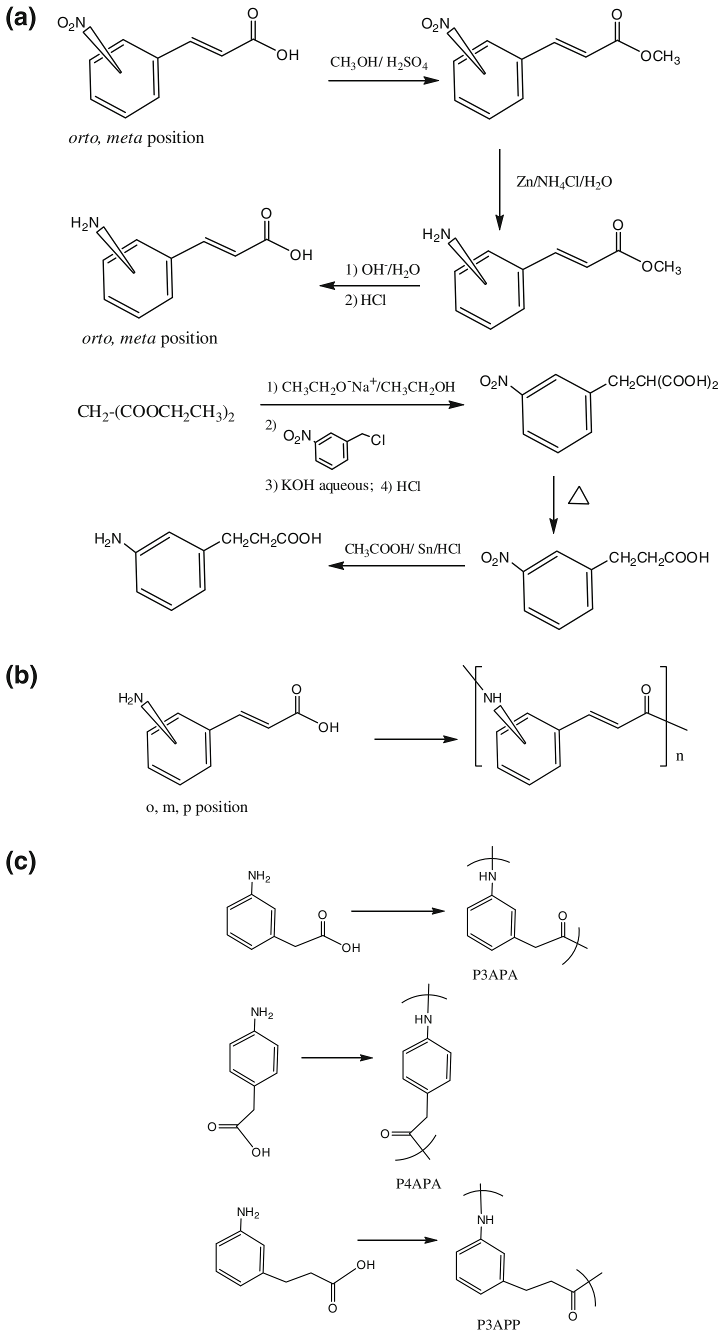

Fig. 1 **a** Synthesis of *β*-(2-aminophenyl)propenoic acid, *β*-(3-aminophenyl)propenoic acid, and *β*-(3-aminophenyl)propanoic acid monomers; **b** synthesis of polyamides with carboxyvinyl; and **c** synthesis of model polyamides

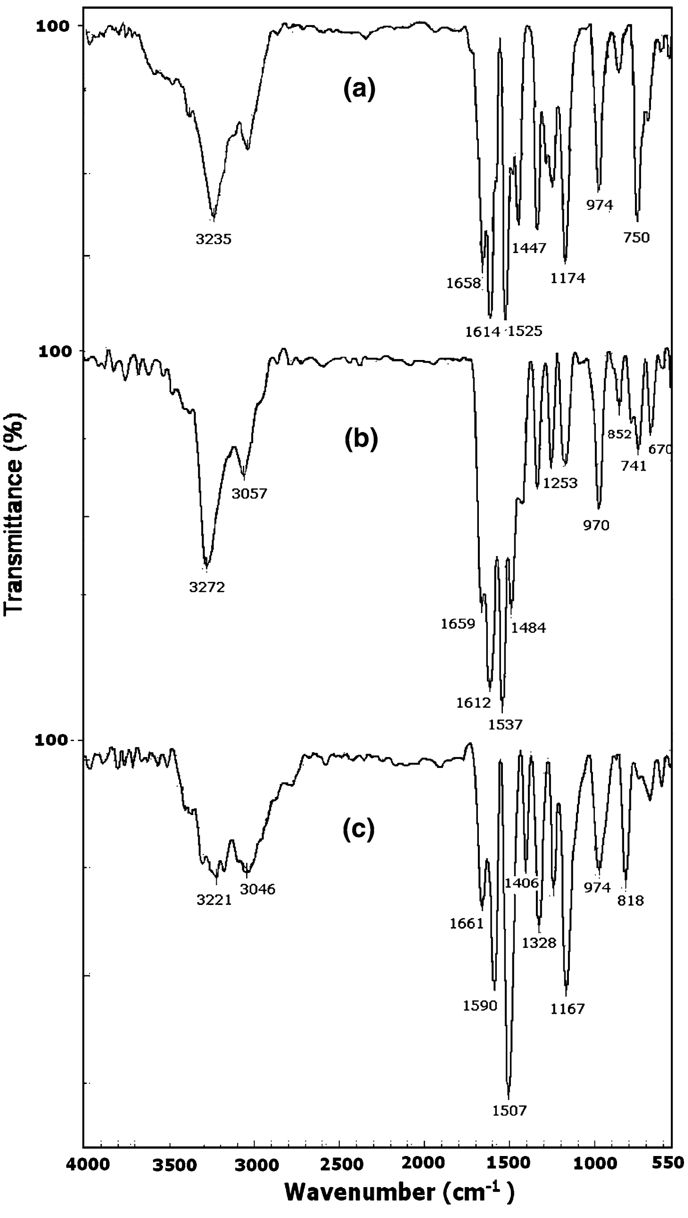

Fig. 2 FT-IR spectra of polyamides, (*a*) P2APC, (*b*) P3APC, and (*c*) P4APC

hindrance of the propenoic acid group that inhibits the polymerization process. This hindrance in the polymerization process was not observed for model polyamides since they show similar viscosity values.

Table 1 shows polyamides yield and solubility. Polyamides yield is as follows P4APC > P3APC > P2APC. The lower yield of P2APC was ascribed to steric

Fig. 3 ^{1}H-NMR spectrum of P3APC, recorded in DMSO-d6

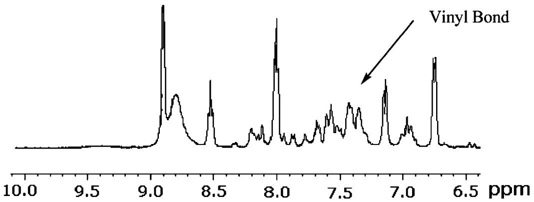

Fig. 4 ^{1}H-NMR spectrum of P2APC, recorded in DMSO-d6

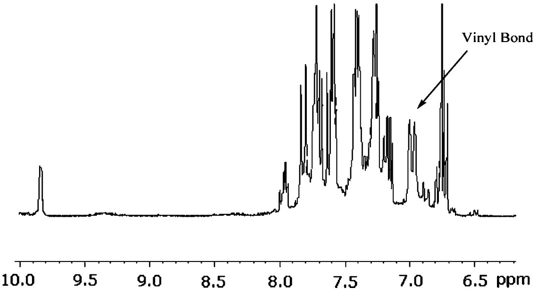

Table 1 Solubility, viscosity, and yield of polyamides with carboxyvinyl and model polyamides

	Solvent							η_{inh} (dL g^{-1})	Yield %
	CF_3COOH	H_2SO_4	DMF	DMSO	Pyridine	NMP	Toluene		
Synthesized polyamides									
P2APC	+	+++	+++	+++	+++	+	−−−	0.18	36
P3APC	+++	+++	+++	+++	+++	+++	−−−	0.20	48
P4APC	+	+++	−−−	−−−	−−−	−−−	−−−	0.33	90
Model polyamides									
P3APA	−−−	+	−−−	−−−	−−−	−−−	−−−	0.24	52
P4APA	−−−	+++[a]	−−−[b]	−−−[b]	−−−[b]	−−−[b]	−−−	0.23	65
P3APP	+++	+++[a]	+++	+++	−−−	+++	−−−	0.18	80

+++ soluble, + sparingly soluble, −−− insoluble

DMF *N*,*N*-dimethylformamide, *DMSO* dimethylsulfoxide, *NMP* *N*-methylpyrrolidinone

[a] Polymer was slowly solubilized by the solvent, [b] Swollen

hindrance of the propenoic acid group. On other hand, polymers solubility in various solvents can be correlated to the structure, i.e., polyamides possessing a vinyl bond are more soluble in organic solvents than model polyamides which have aliphatic groups bonded to aromatic rings. The plane geometry of the carboxyvinyl group allows solvent molecules to easily penetrate the polymer to solubilize it. Diakoumakos et al. [36] reported that the vinyl moiety increases polymer crystallinity. Thus, having in mind the above mentioned reasons it was assumed that the polymers are more soluble. Table 2 shows the softening temperature, measured by DSC. The model polyamides P4APA and P3APA present no softening

Table 2 Thermal properties, color, and softening temperature (Ts)

Polyamide	Color	Ts (°C)	Decomposition temperature (°C)[a]			
			Td[b]	Td[5]	Td[10]	Residual weight (%)[d]
P2APC	Brown-orange	191.6	188	190	219	7
P3APC	Brown-clear	236.3	230	243	263	35
P4APC	Orange	228.5	150	187	237	52
Model polyamides						
P3APA	White	—[c]	180	306	375	65
P4APA	White	—[c]	195	200	262	60
P3APP	White	181.4[c]	185	192	237	50

[a] Temperature at which 5 or 10% weight loss occurred, recorded by TGA

[b] Polymer initial decomposition temperature

[c] No endothermic transition peak, associated with softening was detected by DSC

[d] Residual weight (%) at 550 °C under nitrogen

temperature, however, P3APP melted at 181.4 °C. The low melting temperature is related to lower polymer rigidity due to bigger extent of the aliphatic chains [37].

Figure 5 shows TGA thermograms of polyamides with carboxyvinyl bonds in the backbone. The weight loss below 150 °C can be attributed to adsorbed moisture release. P2APC and P3APC thermograms are similar, because significant curve break above 188 and 230 °C is observed. On the contrary, P4APC underwent significant weight loss above 150 °C. The shape of the three thermograms suggests that the thermal stability depends on the position of the carboxyvinyl groups in the aromatic ring. The sharp drop in P2APC and P3APC thermograms are related to carboxyvinyl group cleavage, while in P4APC the first bond cleavage corresponds to the carboxyl group. The initial decomposition temperature for P2APC, P3APC, and P4APC occurred at 188, 230, and 150 °C respectively; consequently P3APC presents the highest thermal stability. P4APA is thermally more stable than P3APA. Moreover, P3APP is the polymer with the lowest thermal stability of model polyamides (Table 2). From the structural point of view, the stability of P3APP model polyamide is comparable to the carboxyvinyl polyamide P3APC. Since the initial decomposition temperatures are similar; it might be stated that the vinyl bond has no effect on thermal stability. In general, if a 5% weight loss is considered, the model polyamides display higher thermal stability than polyamides with carboxyvinyl bonds.

Table 3 lists the maximum absorption values of the polymers dissolved in H_2SO_4. The absorption bands correspond to π–π^* transitions (n–π^* transitions in P4APC). The maximum absorption shift toward longer wavelengths is due to energy decrease between the ground and excited-state. As the excited state is relatively more stable, then the π–π^* transition takes place at larger wavelength [38]. The excited state is more stable when maximum overlapping between atomic orbitals is favored, i.e., the π-conjugation increases. The conjugation order is

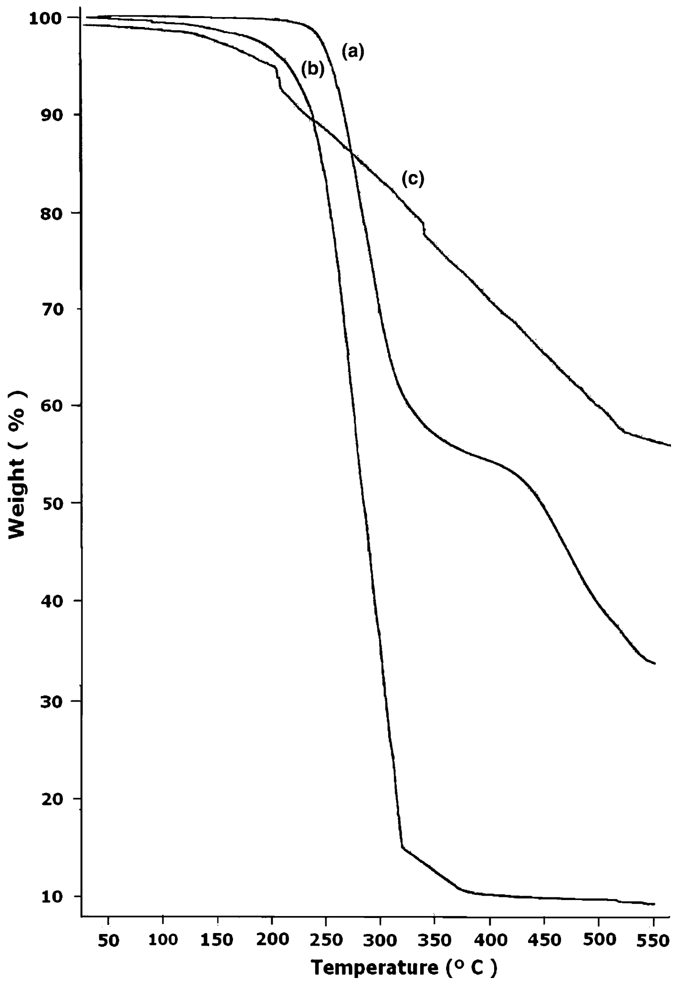

Fig. 5 Thermograms of polyamides (*a*) P3APC, (*b*) P2APC, and (*c*) P4APC

Table 3 UV–Vis maximum absorbance wavelength of polyamides

	P4APC	P3APC	P2APC	P4APA	P3APA	P3APP
Polyamides $\lambda_{\max}$ (nm)	414	334	304	254	244	250
Cured polyamides $\lambda_{\max}$ (nm)	316	330	298	–	–	–

P4APC > P3APC > P2APC model polyamides and P4APA > P3APA. It is evident that the *para*-position in the ring increases the conjugation in relation to *meta*- and *ortho*-position. Therefore, the *para*-disubstituted polymer presents higher conjugation because of the maximum overlapping of atomic orbitals.

Heat-resistant crosslinkable resins can be obtained by reaction between two vinylic bonds of the polymeric chain. Inter-chain crosslinking is caused by heating

Table 4 Relationship, *I*, between the absorption bands of polyamides

	P2APC	P3APC	P4APC
I_{cured}	1.07	1.02	1.04
$I_{\text{not-cured}}$	1.41	1.36	1.48
$I_0 = I_{\text{cured}}/I_{\text{not-cured}}$	0.76	0.75	0.70

Table 5 Cured polyamides decomposition temperature

Polyamide	Td^5 (°C)[a]	Td^{10} (°C)[a]	Residual weight (%)[b]
P2APC	147	306	48.3
P3APC	356	405	74.1
P4APC	326	375	65.1

[a] Temperature at which 5 or 10% weight loss occurred, recorded by TGA

[b] Residual weight (%) at 550 °C under nitrogen

the polymeric material at high temperature. In this reaction the mechanism proceeds by cycloaddition between vinyl bonds [10, 25–27]. Ideally, resins should be synthesized without mass loss, consequently polyamides bearing carboxyvinyl were heat-cured at different temperatures selected to obtain resins without substantial polymer decomposition. Consequently, P2APC and P4APC were cured for 90 min at 220 °C and P3APC at 240 °C for 90 min. It was observed that curing at temperatures lower than those mentioned above, affords low crosslinking level. The use of longer time and higher temperature substantially decomposed the polymers.

The relative crosslinking degree can be measured using the ratio between the absorption bands of FT-IR spectra. The ratio, *I*, vinyl absorption band/carbonyl absorption band from the spectrum of the cured polymer (I_{cured}) and the same ratio of the spectrum of a non-cured polymer ($I_{\text{not-cured}}$) affords the relative crosslinking extent of the polyamide, Table 4.

I_0 for P4APC is lower than of P2APC and P3PAC, *i.e.,* P4APC is a more reactive polymer. Besides, the crosslinking level in P4APC is higher than in P2APC and P3APC. This was confirmed by UV–Vis spectroscopy, the shift toward lower wavelength of the maximum absorption peak is greater for P4APC than for P2APC and P3APC (Table 3). This shift is due to a lower conjugation of the polymer caused by a decrease in the number of vinyl bonds in the polymer backbone.

Table 5 shows the decomposition temperature of crosslinked polyamides. It is known that, cycloaddition between two vinyl bonds produces an aliphatic cycle of four members, which confers increased thermal stability to the polymer. The increment in thermal stability of the crosslinked polymers does not depend on crosslinking degree, i.e., P4APC is a more crosslinked polymer than P2APC and P3APC, however, P3APC is the crosslinked polymer with the highest thermal stability, exhibiting 5% weight loss at 356 °C and 10% at 405 °C. On the other hand, cured polyamides are insoluble in organic solvents precluding thus their ^{1}H-NMR spectrum to be recorded.

Conclusion

Several polyamides containing carboxyvinyl groups in different positions in the aromatic ring were synthesized and characterized by spectroscopy. The polyamides displayed reasonable yield and viscosity (lower at 0.33 dL g^{-1}), ascribed to steric hindrance of the carboxyvinyl moieties in polymerization process. The carboxyvinyl groups allow an ameliorated solubility of the polymers and moderate thermal stability that depends on the position of carboxyvinyl groups in the aromatic ring. Partial polymer curing is possible, since at longer time and temperature above 220 °C the polyamides substantially decomposed. Upon curing, the thermal stability increases. P4APC showed the highest crosslinking degree and cured P3APC the highest thermal stability, which is independent of crosslinking extent.

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