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**SYNTHESIS AND CHARACTERIZATION OF AROMATIC POLY(AMIDES)
BASED ON 3,5-DIAMINO-N-CYCLOPROPYLBENZAMIDE**

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ABSTRACT

Three aromatic poly(amides) (**PAs**) were prepared, one of them containing a dimethyldiphenylsilane unit from a new aromatic diamine monomer with a bulky pendant polar group. All **PAs** were obtained in high yield and the inherent viscosities were in the range of 0.30 and 0.47 dL/g. The obtained poly(amides) showed excellent solubility in a variety of aprotic polar organic solvents. **PAs** evidence thermal stability with thermal decomposition temperature (TDT_{10%}) between 300 – 371 °C and the glass transition temperatures (T_g) values were high (between 215 and 250 °C). **PAs** containing silicon atom in the main chain captures the highest moles number of water per mole of repeating unit. Contact angles were also tested in order to know the hydrophilicity of the polymer films.

Keywords: aromatic poly(amides), thermally stable, diphenylsilane units, water uptake.

1. Introduction

Thermally stable polymers are important because they can replace metal and ceramics in several fields of science. Specifically, aromatic poly(amides) exhibit excellent mechanical, electrical and chemical properties, making them very interesting for their study as high performance materials [1-3]. However, their industrial processing is affected by their remarkable intractability caused by the strong molecular interactions through hydrogen bonding of amide groups [4].

With the aim to reduce the intermolecular bonding energy, many structural modifications have been made in poly(amides), such as the incorporation of flexible units, 1,3-substituted monomers, bulky pendant groups or heteroatoms in the main chain [5-8]. These chemical modifications provide interchain distance, and consequently, higher free volume and solubility, without affecting the thermal properties [9-10]. Adamantylcarbamoyl pendant group or other cyclic side group such as fluorene or phenylcyclohexane were effective to improve the solubility of the polymers derivatives [11-13].

In other works, and also in our previous works, it was found that the introduction of diphenylsilane units in the polymer backbone improves the solubility and maintains the thermal properties of the polymeric materials [7,14,15]. Silicon atom has a lower electronegativity than carbon atom causing a small dipole moment inside the chain, which increases the polarity of the polymeric chain and therefore, its solubility in specific solvents.

Rigid aromatic poly(amides) with other polar groups into the main or side chain are interesting in the reverse osmosis field because it increases the hydrophilicity of the membrane, allowing better diffusion of water through the polymeric matrix [16]. Structural rigidity of this sort of polymers is a critical property for the adequate functioning of the membrane [17]. Such high stiffness degree is usually associated with high T_g values.

This work reports the synthesis and characterization of a novel aromatic diamine with a cyclopropylcarbamoyl pendant group and three aromatic poly(amides) derived from it. One of them contains a dimethyldiphenylsilane unit in the repeating unit. Solubility, water uptake, contact angle, inherent viscosity and thermal properties of the polymers are also investigated and discussed.

2. Experimental

2.1. Materials

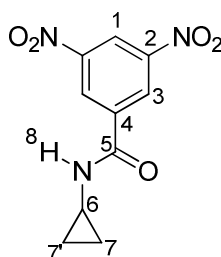
Anhydrous *N,N*-dimethylacetamide (DMAc), 3,5-dinitrobenzoyl chloride, cyclopropylamine, Pd/C (10 % w/w), 4,4'-sulfonyldibenzoic acid and tert-butylisophthalic acid were obtained from Aldrich Chemical (Milwaukee, WI). Bis(4-carboxyphenyl)dimethylsilane was synthesized following a procedure already reported by our research group [18]. Diethyl ether and *n*-hexane were refluxed over metallic sodium under nitrogen atmosphere. All other reagents and solvents were purchased commercially as analytical-grade and used without further purification.

2.2. Instrumentation and measurements

IR-TF spectra (KBr pellets) were recorded on a Perkin-Elmer (Fremont CA) 1310 spectrophotometer over the range of 4000–450 cm^{-1} . Melting points (uncorrected) were obtained on a SMP3 Stuart Scientific melting point apparatus. ^1H , ^{13}C and ^{29}Si NMR spectra were carried out on a 400 MHz instrument (Bruker AC-200) using $\text{DMSO-}d_6$ as solvent and TMS as internal standard. Viscosimetric measurements were made in a Desreux-Bischof type dilution viscosimeter at 25 °C ($c = 0.5 \text{ g/dL}$). Glass transition temperature (T_g) values were obtained with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system (10 °C/min under N_2 flow). Thermogravimetric analyses were carried out in a Mettler (Switzerland) TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance (temperature range between 25 °C and 900 °C at 10 °C/min under N_2 flow). Elemental analyses were made on a Fisons EA 1108-CHNS-O equipment. A Dataphysics OCA 20 device with a conventional goniometer and high performance video camera, controlled by SCA20 software, was used to measure the optical contact angle. Water sorption measurements were determined gravimetrically at room temperature. Powder polymer samples (0.3 g), previously dried at 120 °C for 24 h, were placed in a closed desiccator containing a saturated aqueous solution of NaNO_2 , which provided a relative humidity of 65 %. The samples were frequently weighed during 15 h and then allowed to humidify for 5 more days until constant weight.

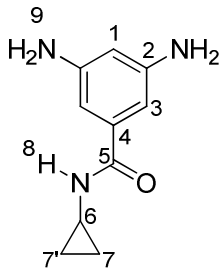
2.3. Monomer synthesis and characterization

3,5-dinitro-*N*-cyclopropylbenzamide (**1**). To a two-necked round-bottomed flask equipped with magnetic stirrer, 3 mL (43.37 mmol) of cyclopropylamine in 125 mL of dry diethyl ether were added. The mixture was stirred under a gentle nitrogen stream. Small amounts (500 mg) of 3,5-dinitrobenzoyl chloride in solid state were added every 5 minutes, until a total of 5 g (21.68 mmol). Suspension was maintained with stirring at room temperature for 30 minutes and then filtered. White precipitate was washed three times with 50 mL of HCl/water mixture (1:1 vol/vol) and then with water until neutral pH. Finally, the white solid was dried in a vacuum oven. Crude product was recrystallized from dichloromethane to afford 5 g of white needles.



Yield: 92 %. M.p.: 158 - 159 °C. IR (KBr, ν , cm^{-1}): 3289 (N-H); 3099, 3086 (C-H arom.); 2871 (C-H aliph.); 1644 (C=O); 1536, 1343 (NO_2); 1457, 1422 (C=C); 730 (1,3,5-arom. subs.). ^1H RMN (DMSO- d_6 , δ , ppm): 0.65 (m, 2H(7,7')); 0.77 (m, 2H(7,7')); 2.93 (m, 1H(6)); 8.94 (s, 1H(1)); 9.01 (s, 2H(3)); 9.12 (s, 1H(8)). ^{13}C RMN (DMSO- d_6 , δ , ppm), 5.97 (C7,7'); 23.76 (C6); 121.05 (C1); 127.73 (C3); 137.21 (C4); 148.47 (C2); 163.46 (C5). Elem. Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_5$; (251.05): C, 47.81 %; H, 3.61 %, N, 16.73 %. Found: C, 47.18 %; H, 3.35 %, N, 16.66 %.

3,5-diamine-*N*-cyclopropylbenzamide (**2**). A mixture of 5 g (20 mmol) of 3,5-dinitro-*N*-cyclopropylbenzamide (**1**), 10 % palladium on activated carbon (0.250 g) and 100 mL of absolute ethanol were placed under an atmosphere of hydrogen (30 psi) and allowed to react with stirring for 10 minutes. When the pressure of the system decreased, the reaction bottle was loaded with 30 psi of additional of hydrogen, until the pressure of hydrogen was kept constant. Catalyst was removed by filtration through a Celite plug, and the solvent removed under reduced pressure to afford 3.5 g of a yellow solid. The crude product was recrystallized from ethanol to afford 3.2 g of yellow crystals.



Yield: 92 %. M.p.: 201 - 202 °C. IR (KBr, ν , cm^{-1}): 3460, 3378, 3341 (NH_2); 3236 (N-H); 3080 (C-H arom.); 2998 (C-H aliph.); 1644 (C=O), 1593 (N-H bending); 1527, 1456 (C=C); 1283 (C-N bending); 746 (1,3,5-arom. subs.). ^1H RMN (DMSO- d_6 , δ , ppm): 0.51 (m, 2H(7,7')); 0.62 (m, 2H(7,7')); 2.77 (m, 1H(6)); 4.81 (s, 4H(9)); 5.93 (s, 1H(1)); 6.18 (s, 2H(3)); 8.00 (s, 1H(8)). ^{13}C RMN (DMSO- d_6 , δ , ppm), 6.07 (C7,7'); 23.28 (C6); 102.43 (C1); 102.54 (C3); 136.74 (C4); 149.24 (C2); 169.63 (C5). Elem. Anal. Calcd. for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}$; (191.11): C, 62.81 %; H, 6.85 %, N, 21.97 %. Found: C, 62.16 %; H, 6.06 %, N, 21.88 %.

Aromatic acid dichlorides (**3**, **4** and **5**, scheme 2). The corresponding dicarboxylic acid (10.0 mmol), 30 mL of thionyl chloride and a few drops of DMF were reacted in a round bottomed flask at 90 °C for 3 h. Thionyl chloride excess was removed from the solution by simple distillation. Crude **3** was washed with dry *n*-hexane and then recrystallized from *n*-hexane to afford 2.8 g of crystalline solid. Crude **4** was dissolved in dry *n*-hexane and then cooled overnight at -30 °C. The solid was filtered and washed with cold *n*-hexane to afford 2.0 g of crystalline solid. Crude **5** was washed with dry *n*-hexane and then recrystallized from *n*-hexane/toluene mixture (1:1 vol/vol) to afford 2.7 g of white fluffy solid.

4,4'-(dimethylsilyl)phthaloyl chloride (**3**). Yield: 83 %. M.p.: 78 - 80 °C. IR (KBr, ν , cm^{-1}): 3030 (C-H arom.); 2980 (C-H aliph.); 1774 (C=O), 1589, 1492 (C=C); 1413, 1106 (Si-C arom.); 1375 (Si-C aliph); 832 (arom. *p*-subst.).

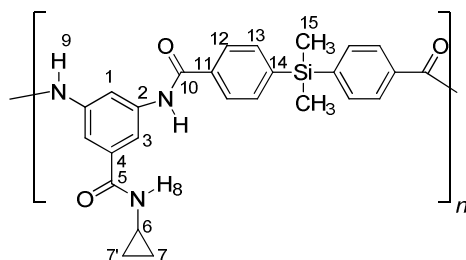
5-(tert-butyl)isophthaloyl dichloride (**4**). Yield: 77 %. M.p.: 44 - 45 °C. IR (KBr, ν , cm^{-1}): 3087 (C-H arom.); 2967, 2905 (C-H aliph.); 1757 (C=O), 1587, 1473 (C=C); 1396, 1367 (-C(CH₃)₃ bending); 752 (1,3,5-arom.).

4,4'-sulfonyldibenzoyl chloride (**5**). Yield: 78 %. M.p.: 159 - 160 °C. IR (KBr, ν , cm^{-1}): 3093, 3041 (C-H arom.); 1782, 1745 (C=O), 1590, 1575 (C=C); 1328, 1154 (S=O bending); 881 (arom. *p*-subst.).

2.4. Polymer synthesis and characterization

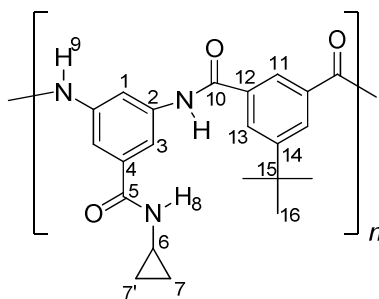
A typical polymerization procedure for the synthesis of poly(amides) was as follows. To a three-necked round-bottomed flask equipped with mechanical stirrer, was added 1.18 mmol of 3,5-diamino-*N*-cyclopropylbenzamide (**2**) and 1.5 mL of dry DMAc. When the solution was completed, it was cooled with an ice-water bath and 1.18 mmol of the corresponding acid dichloride (**3**, **4** or **5**) and 1.0 mL of dry DMAc were added. The ice-water bath was removed when acid dichloride was entirely dissolved. Then, the mixture was stirred at room temperature during 6 hours. The resulting mixture was poured into 300 mL of water with stirring. White solid was filtered, washed thoroughly with water and dried at 100 °C during 12 hours. Thus, **PA-1** was obtained from acid dichloride **3**, **PA-2** from acid dichloride **4** and **PA-3** using acid dichloride **5**.

PA-1: Yield: 99 %. IR (KBr, ν , cm^{-1}), 3444 (N-H); 3021 (C-H arom.); 2956 (C-H aliph.); 1643 (C=O); 1555, 1538 (C=C); 1415, 1093 (Si-C arom.); 1376 (Si-C aliph); 814 (arom. *p*-subs.); 746 (1,3,5-arom. subs.). ^1H NMR (DMSO- d_6 , δ , ppm), 0.49 – 0.60 (m, 10H(7,7',15)); 2.77 (m, 1H(6)); 7.62 (d, $J = 7.5$ Hz, 4H(13)); 7.80 (s, 2H(3)); 7.89 (d, $J = 7.6$ Hz, 4H(12)); 8.36 (s, 1H(1)); 8.37 (s, 1H(8)); 10.36 (s, 2H(9)). ^{13}C NMR (DMSO- d_6 , δ , ppm), 167.3 (C10); 165.1 (C5); 141.3 (C2); 138.6 (C4); 135.2 (C14); 134.9 (C11); 133.4 (C13); 126.4 (C12); 114.9 (C3); 114.8 (C1); 22.6 (C6); 5.2 (C7,7'); -3.4 (C15). ^{29}Si NMR (DMSO- d_6 , δ , ppm), -8.47. Elem. Anal. Calcd. for $[\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_3\text{Si}]_n$ (455.58) $_n$, C, 68.55 %; H, 5.53 %; N, 9.22 %. Found: C, 68.36 %; H, 5.43 %; N, 9.12 %.

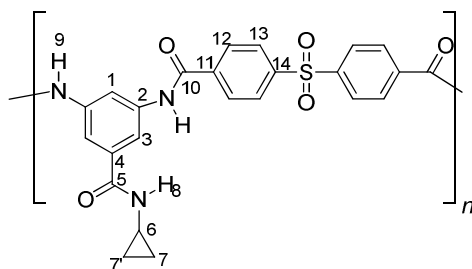


PA-2: Yield: 99 %. IR (KBr, ν , cm^{-1}), 3440 (N-H); 3088 (C-H arom.); 2961 (C-H aliph.); 1654 (C=O); 1598, 1543 (C=C); 739 (1,3,5-arom. subs.). ^1H NMR (DMSO- d_6 , δ , ppm), 0.46 (m, 2H(7,7')); 0.56 (m, 2H(7,7')); 1.29 (s, 9H(16)); 2.74 (m, 1H(6)); 7.80 (s, 2H(3)); 8.07 (s, 2H(13)); 8.36 (s, 1H(11)); 8.37 (s, 1H(1)); 8.41 (s, 1H(8)); 10.52 (s, 2H(9)). ^{13}C NMR (DMSO- d_6 , δ , ppm), 168.2 (C10); 165.8 (C5); 151.8 (C14); 139.5 (C2); 136.1 (C4); 135.1 (C12); 128.1 (C13); 125.2 (C11); 116.4 (C3); 116.2 (C1); 35.4 (C15); 31.4 (C16); 23.6 (C6); 6.1 (C7,7'). Elem. Anal. Calcd.

for $[\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_3]_n$ (377.44) $_n$, C, 70.01 %; H, 6.14 %; N, 11.13 %. Found: C, 69.79 %; H, 6.09 %; N, 11.01 %.



PA-3: Yield: 86 %. IR (KBr, ν , cm^{-1}), 3442 (N-H); 3094 (C-H arom.); 2935 (C-H aliph.); 1654 (C=O) 1560, 1543 (C=C); 855 (arom. *p*-subs.); 747 (1,3,5-arom. subs.). ^1H NMR (DMSO- d_6 , δ , ppm), 0.58 (s, 2H(7,7')); 0.68 (s, 2H(7,7')); 2.87 (s, 1H(6)); 7.90 (s, 2H(3)); 8.20 (s, 8H(12,13)); 8.45 (s, 1H(1)); 8.50 (s, 1H(8)); 10.71 (s, 2H(9)). ^{13}C NMR (DMSO- d_6 , δ , ppm), 168.1 (C10); 164.8 (C5); 143.4 (C14); 140.0 (C2); 139.3 (C4); 136.3 (C11); 129.6 (C13); 128.2 (C12); 116.0 (C3); 115.7 (C1); 23.6 (C6); 6.1 (C7,7'). Elem. Anal. Calcd. for $[\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_5\text{S}]_n$ (461.49) $_n$, C, 62.46 %; H, 4.15 %; N, 9.11 %. Found: C, 62.16 %; H, 4.11 %; N, 9.03 %.



3. Results and discussion

3.1. Monomer synthesis and characterization

A new diamine, 3,5-diamino-*N*-cyclopropylbenzamide, was synthesized by reacting 3,5-dinitrobenzoyl chloride with cyclopropylamine in anhydrous diethyl ether, followed by a reduction reaction using hydrogen gas, Pd/C as catalyst and absolute ethanol as solvent (Scheme 1).

Scheme 1. Here

Dinitro compound **1** was insoluble in the medium reaction (anhydrous diethyl ether), favoring the isolation process. The next step (reduction reaction) was conducted in a dark media to prevent color change due to photodegradation of the diamine **2** (this diamine derivative is sensitive to light, changing from yellow to red color).

The FT-IR spectra in Fig. 1 confirmed the presence of both compounds. The bands at 3289 cm^{-1} and 1644 cm^{-1} correspond to stretching of N-H and C=O groups, respectively, while those at 1536 and 1343 cm^{-1} were assigned to the vibration of the nitro group. Disappearance of these two signals and the appearance of sharp bands at 3460 and 3378 cm^{-1} , corresponding to the stretching of the amino group, confirmed the formation of the monomer.

Figure 1. Here

The ^1H NMR spectrum in Fig. 2 also confirmed the structure of the diamine. The peak at 8.00 ppm was assigned to amidic hydrogen. The singlet at 4.81 ppm, integrating for 4 nuclei corresponds to the hydrogens of the amino groups. Also, a clear pattern of cyclopropyl fragment was possible to observe. The multiplet at 2.77 ppm was assigned to hydrogen H6, while one of the hydrogens H7 appears at 0.62 ppm and the other at 0.51 ppm. The same happened for hydrogens H7'. The difference in chemical shift of the hydrogens H7 and H7' is due to the axial and equatorial positions of both in the cyclopropyl ring. Meanwhile, the ^{13}C NMR spectrum showed the seven expected carbon signals. The peak at 169.6 ppm corresponds to the carbonyl carbon of the amide group. The carbons C1 and C3 showed similar chemical shifts due to the mesomeric effect induced by the amine group, by shielding the carbon nucleus.

Figure 2. Here

The FT-IR spectra in Fig. 3 confirmed the absence of OH bands in the all aromatic acid dichloride. Characterization by NMR techniques was not necessary in order to continue with the synthesis of polymers.

Figure 3. Here

3.2. Polymer synthesis and characterization

Poly(amides) were prepared in solution, by reacting the appropriate acid dichloride with the diamine in *N,N*-dimethylacetamide as solvent (Scheme 2).

Scheme 2. Here

Successful conversion from acid dichloride and diamine to amide was confirmed by the FT-IR spectra, in which the characteristic absorptions due to the amide group moiety around 3440 cm^{-1} ($\nu_{\text{N-H}}$) and 1650 cm^{-1} ($\nu_{\text{C=O}}$) can be clearly identified (Fig. 4).

Figure 4. Here

Fig. 5 shows the ^1H NMR spectrum of **PA-1** in $\text{DMSO-}d_6$. The singlet at 10.36 ppm confirms the formation of an amide linkage. Other peaks were assigned to hydrogens of the repeating unit. The hydrogens H8 and H1 appeared with a very similar chemical shift, as shown in the enlarged figure. The signals of hydrogens H12 and H13 appear as doublets, characteristic pattern of substitution in the *para* position of the aromatic ring (*AB* system). Also, the coupling constant (J) of hydrogens H12 and H13 was determined ($J = 7.5\text{ Hz}$ approximately). The chemical shifts of hydrogens H7 and H7' appear overlapped with the singlet at 0.5 ppm, which corresponds to hydrogens of the methyl groups bound to the silicon atom.

Figure 5. Here

The ^{13}C NMR spectrum of **PA-1** (Fig. 6) shows two peaks at 167.3 and 165.1 ppm, corresponding to carbonyl carbon C10 and C5 of the amide groups, respectively, which exhibit different chemical environments. Aliphatic carbon C15 appears with a δ value below zero due to the lower electronegativity of silicon atom respect to carbon. Thus, the respective signal is shifted to higher field. Similar behavior was observed for the methyl hydrogens in the ^1H NMR spectra. Chemical shifts of the remaining carbons were in accordance with the proposed structure.

Figure 6. Here

Polymeric samples were also characterized by ^{29}Si NMR. Fig. 7 shows the spectrum of **PA-1**, where a single signal at -8.47 ppm is observed. This chemical shift is expected when the silicon atom is surrounded by two aromatic rings and two methyl groups [19,20].

Figure 7. Here

3.3. Inherent viscosity and solubility

Inherent viscosity was measured at a single point, in *N*-methyl-2-pyrrolidone (NMP) solution at 25 ± 0.1 °C (0.5 g/dL). Inherent viscosity values were in the range of 0.30 to 0.47 dL/g. On the other hand, the solubility of poly(amides) was tested in various organic solvents, and the results are listed in Table 1. Unmodified polyamides such as **PPTA** and **PPMI** were insoluble in *m*-cresol and, in some cases; LiCl was required for their complete dissolution. The chemical modifications made on the new poly(amides) improve solubility, mainly in polar aprotic solvents and *m*-cresol.

Table 1. Here

3.4. Thermal properties

Thermal stability of all poly(amides) was evaluated by TGA and DSC techniques under a nitrogen atmosphere and the results are summarized in Table 2. Fig. 8 shows the TGA curves for all **PA**s. Three **PA**s exhibited good thermal stability, with the 10 % weight loss temperature ($TDT_{10\%}$) in the range of 300 – 371 °C.

Figure 8. Here

PA-1 exhibited the highest thermal stability among them, probably due to the presence of the silicon atom, which increases the ionic character of the silicon-carbon bond along the chain [7,22]. DTGA curves show a complex degradative process between 300 - 400 °C. However, a peak near 500 °C, corresponding to the main polymer degradation, was observed. **PA-3** exhibited the lower value of $TDT_{10\%}$. Taking into account the values of inherent viscosity, **PA-3** showed chains shorter than the other **PA**s (lower inherent viscosity), which could be associated to the low value of $TDT_{10\%}$.

Table 2. Here

In all cases, the char yield at 800 °C was nearly to 40 %. High aromatic content of all poly(amides) was responsible for the high char yields after calcinations.

DSC analyses were performed in order to obtain the T_g values of all poly(amides) and the results are summarized in table 2. Fig. 9 shows the DSC curves obtained from the second heating scan. Polymers did not show melting peaks, indicating the amorphous nature of the materials.

Figure 9. Here

One transition was detected in all poly(amides) corresponding to the T_g. **PA**s showed T_g values greater than 215 °C. **PA-1** and **PA-3** showed similar T_g values and they were larger than those of **PA-2**. Regarding the structures of the poly(amides), **PA-1** and **PA-3** have *para*-position linkage while **PA-2** has *meta*-position linkage. The chains in **PA-2** could be less packed. This, and the fact that repeating unit in **PA-2** has the lower aromatic content could be responsible for its lower T_g value. In general, the T_g values were large compared to other structurally modified poly(amides) [14, 23-25]. These results could be interesting for applications in the gas separation membrane field or reverse osmosis membrane field. These technological applications, from the point of view of thermal properties, seek to obtain polymers with high values of the glass transition temperature [26-28].

Table 2 also shows the T_g values for **PMPI** and **PPTA**. These values are very high, indicating that the structural modifications made on the poly(amides) synthesized in this work allowed to reduce structural rigidity, favoring industrial processability and reducing energy costs in case that mold the material to a temperature above the T_g be necessary.

3.5. Water uptake and contact angle

Water sorption measurements were performed gravimetrically at room temperature using poly(amides) powder samples previously dried at 120 °C for 24 h. Samples were introduced in a closed desiccator containing a relative humidity of 65 %. The samples were frequently weighed during 15 h and then allowed to humidify for 5 more days until constant weight.

Table 3 shows the percentage of water uptake for each poly(amide). **PA-2** had the largest value of water uptake. However, analyzing the moles of water per mol of repeat unit, **PA-1** has more moles of water in the repeat unit than **PA-2**. As the amount of amide groups in both repeating units is the same, the higher water content in the repeating unit of **PA-1** could be associated to the presence of the silicon atom. It is known that the affinity of silicon to oxygen is very strong [29], being there an additional interaction between the silicon atom and the water oxygen.

PA-3 had the lowest value of water uptake and the least amount of moles of water per mol of repeating unit. The most plausible explanation for this result is that the sulfone group could form intra and/or intermolecular H-bonds with nearby amide groups, thereby reducing the number of moles of water per mol of amide groups. This fact is related with the large T_g value obtained for

PA-3. The greater structural rigidity would hinder penetration of water molecules through the polymer matrix.

For comparison, the results obtained from an unmodified poly(amide), *m*-phenylene isophthalamide (**PMPI**) [30], were included in Table 3. This poly(amide) is used as membrane for reverse osmosis separation [31]. The poly(amides) prepared in this work have similar values of water uptake and exhibit water absorption values larger than 1.2 mol of water per repeating unit, while **PMPI** only has 0.7. Preliminarily, the prepared poly(amides) could have application in the field of reverse osmosis separation.

Table 3. Here

Another technique to investigate the wettability of a surface of film samples is by contact angle measurements. Dense films were prepared from all **PAs** by casting 10 % (w/v) filtered *N,N*-dimethylacetamide polymer solutions onto a glass plate and heating at 60 °C overnight. Then, the films were stripped off and were dried in a vacuum oven at 100 °C overnight and at 150 °C for 48 h. Table 3 also shows contact angles measured for **PAs** and the image of the drop (Fig. 10) was captured five seconds after placed.

Figure 10. Here

PA-1 and **PA-3** had higher contact angles than **PA-2**, therefore, the surface of **PA-2** is the most hydrophilic, since it showed the smallest contact angle. This result would be inconsistent with those obtained in the experiment of water absorption, but morphology of the film sample is a very important issue in wettability properties. The explanation to these results should be sought in the capability that has the chain for adopting different conformations and molecular packing. From this point of view, **PA-2** has only two aromatic rings in their repeating unit, while **PA-1** and **PA-3** have three aromatic rings, therefore **PA-2** has the lower aromatic content, which implies a lower hydrophobicity and therefore, more wettability.

4. Conclusions

Based on the synthesis of a novel aromatic diamine containing a bulky pendant polar group, a series of three aromatic poly(amides) were successfully prepared by low temperature solution polycondensation technique. One **PAs** had a silicon atom in the repeating unit, which possibly contributes to the increased water uptake per mole of the repeating unit. In general, all **PAs** had water absorption values per repeating unit larger than **PMPI**. All **PAs** were thermally stable and the glass transition temperature values were in the range of 215 - 250 °C. The obtained **PAs** were characterized by good solubility in aprotic solvents and *m*-cresol. **PA-2** showed the smallest contact angle, indicating the most hydrophilic surface.

5. Acknowledgements

Tundidor-Camba, A. acknowledges the financial assistance by Comisión Nacional de Investigación Científica y Tecnológica, CONICYT, through Project 79130011.

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List of figure and scheme captions

Scheme 1. Synthetic route to obtain 3,5-diamino-*N*-cyclopropylbenzamide.

Scheme 2. Synthetic route of poly(amides).

Fig. 1. FT-IR spectra of both dinitro (**1**) and diamine (**2**) compounds.

Fig. 2. ^1H and ^{13}C NMR spectrum of aromatic diamine **2**.

Fig. 3. FT-IR spectra of all aromatic acid dichloride derivatives.

Fig. 4. FT-IR spectra of poly(amides).

Fig. 5. ^1H NMR spectrum of **PA-1** in $\text{DMSO-}d_6$.

Fig. 6. ^{13}C NMR spectrum of **PA-1** in $\text{DMSO-}d_6$.

Fig. 7. ^{29}Si NMR spectrum of **PA-1** in $\text{DMSO-}d_6$.

Fig. 8. TGA and DTGA curves of **PAs**.

Fig. 9. DSC curves of **PAs**.

Fig. 10. The profiles of a droplet on the **PAs**. **A)** correspond to **PA-1**, **B)** to **PA-2** and **C)** to **PA-3**.

Tables.

Table 1. Inherent viscosity and solubility results of PAs.

PA	η_{inh} (dL/g) ^a	Solubility					
		DMSO	NMP	DMF	DMAc	<i>m</i> -cresol	THF
PA-1	0.45	+	+	+	+	+	-
PA-2	0.47	+	+	+	+	+	-
PA-3	0.30	+	+	+	+	+	-
PMPI*		+	+	+ ^b	+	-	-
PPTA**		+ ^b	+ ^b	+ ^b	+ ^b	-	-

^aMeasured in NMP (0.5 g/dL at 25 °C) Solubility: +, Soluble at room temperature; -, Insoluble.

*Poly(*m*-phenylene isophthalamide) used as reference [21]. **Poly(*p*-phenylene terephthalamide) used as reference [21]. ^b5 % wt of LiCl was required.

Table 2. Summary of thermal properties of the PAs.

PA	^a TDT _{10%} (°C)	^b Tg (°C)	^c Char Yield (%)
PA-1	371	245	39
PA-2	359	215	40
PA-3	300	250	37
PMPI*		280	
PPTA**		425	

^aThermal decomposition temperature at which 10 % weight loss was recovered by TGA at a heating rate of 10 °C/min in nitrogen atmosphere. ^bGlass transition temperature taken at 10 °C/min in nitrogen atmosphere. ^cResidual weight (%) when heated to 800 °C. *Poly(*m*-phenylene isophthalamide) used as reference [21]. **Poly(*p*-phenylene terephthalamide) used as reference [21].

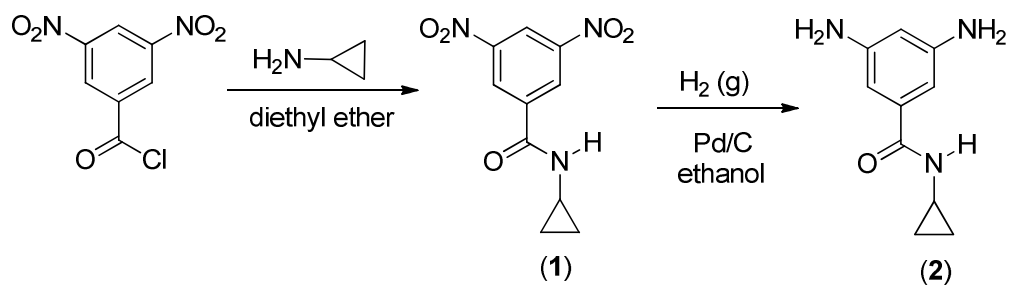
Table 3. Summary of the water sorption and contact angles of PAs.

PA	Water uptake (%) ^a	mol H ₂ O/mol repeat unit	mol H ₂ O/mol amide	θ (°) ^b
PA-1	5.4	1.5	0.44	84 ± 1.8
PA-2	6.0	1.4	0.48	69 ± 0.4
PA-3	4.5	1.2	0.34	81 ± 2.0
PMPI*	5.5	0.7	0.35	-

^aMeasurements were performed using the same conditions as in Reference 30. ^bContact angle recorded at a rate of 10 μ L/s at 25 °C. *Poly(*m*-phenylene isophthalamide) used as reference [30]

Schemes and figures

Scheme 1.



Scheme 2.

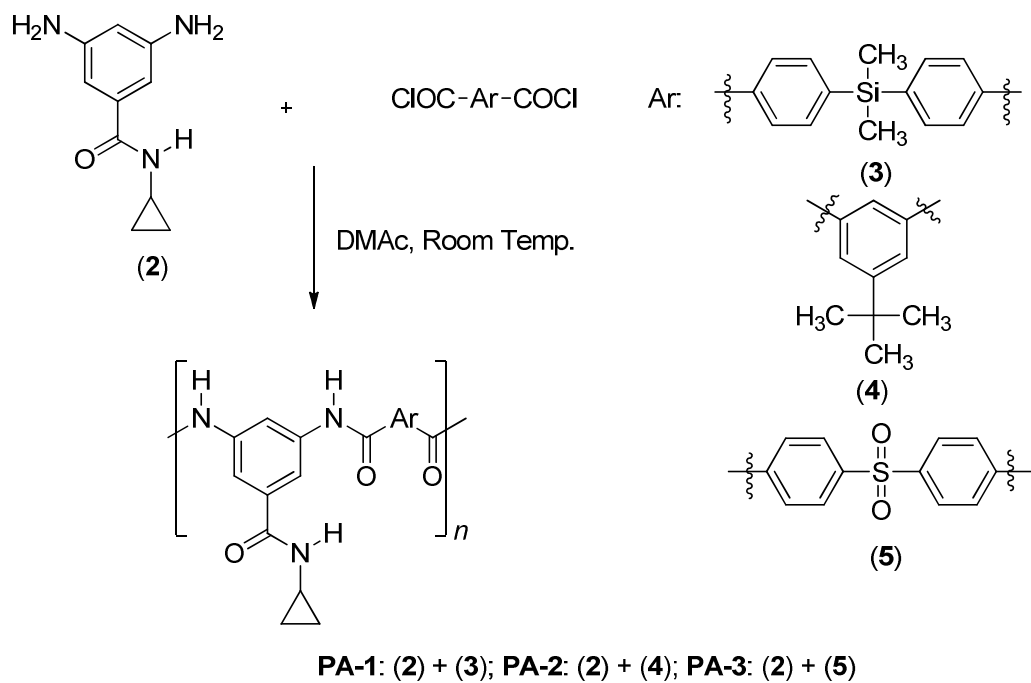


Figure 1.

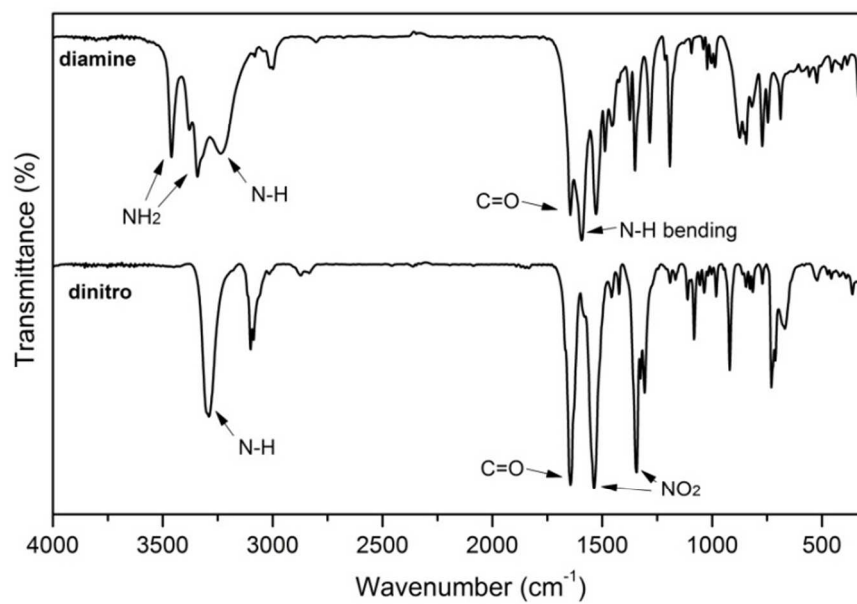


Figure 2.

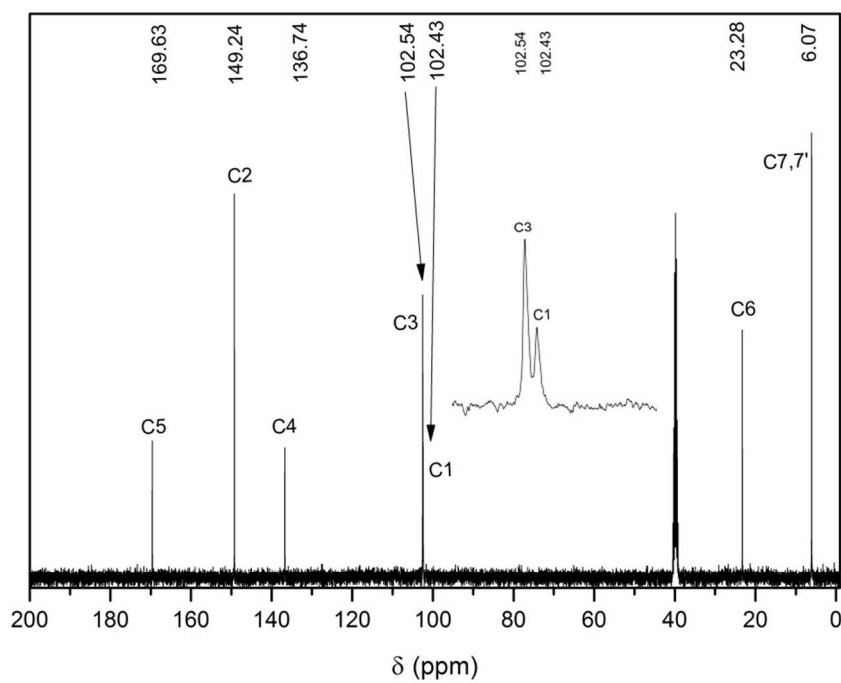
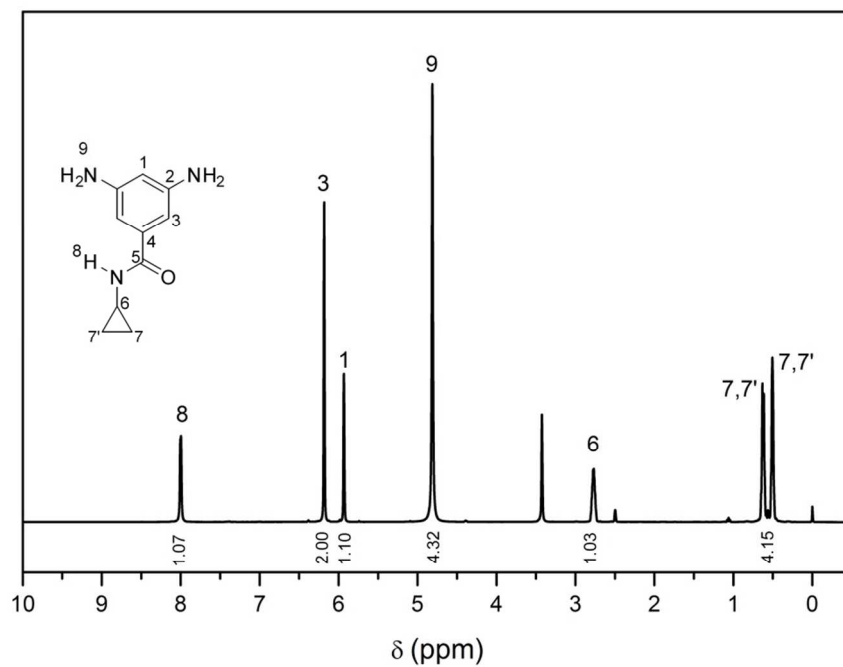


Figure 3.

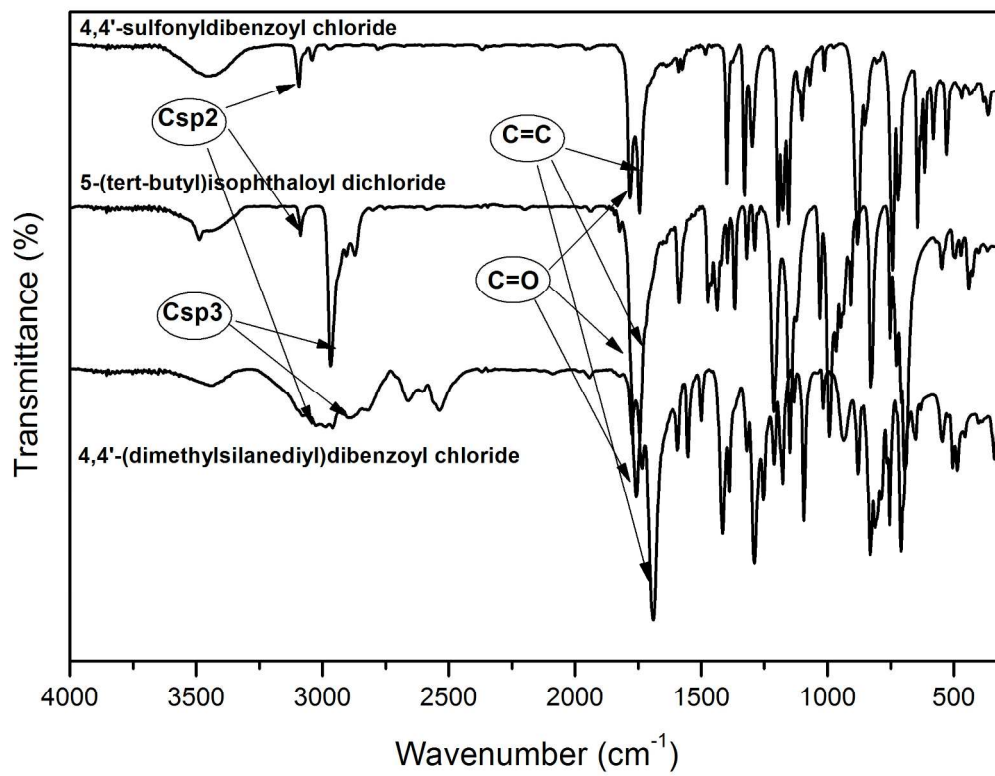


Figure 4.

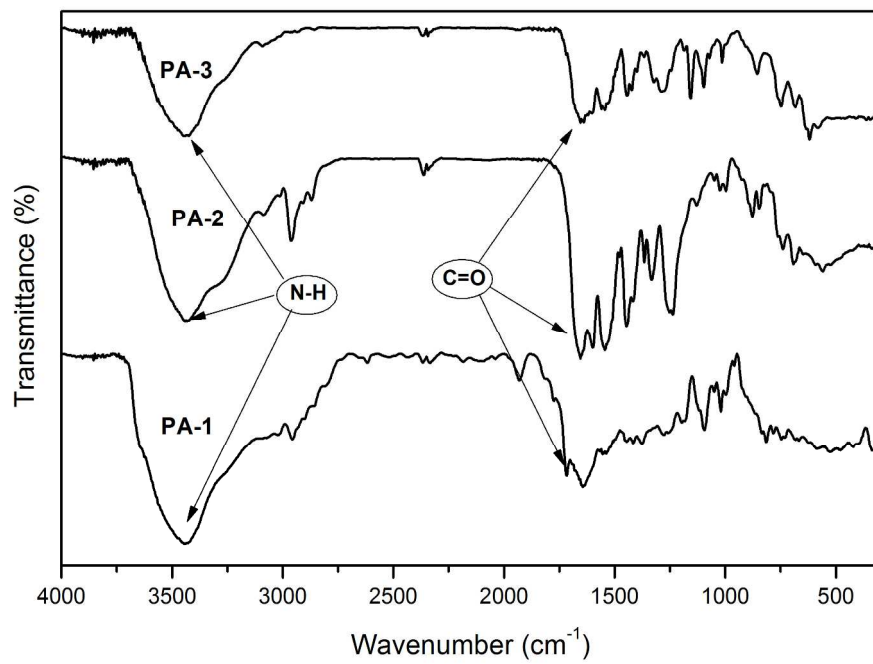


Figure 5.

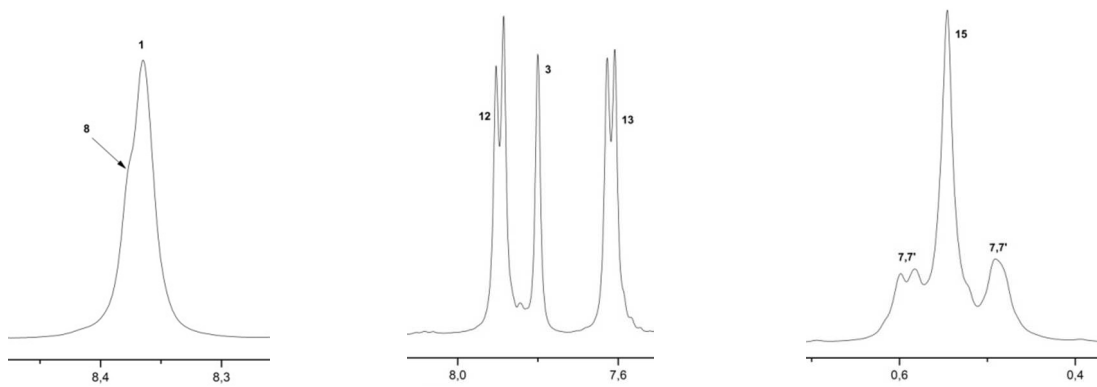
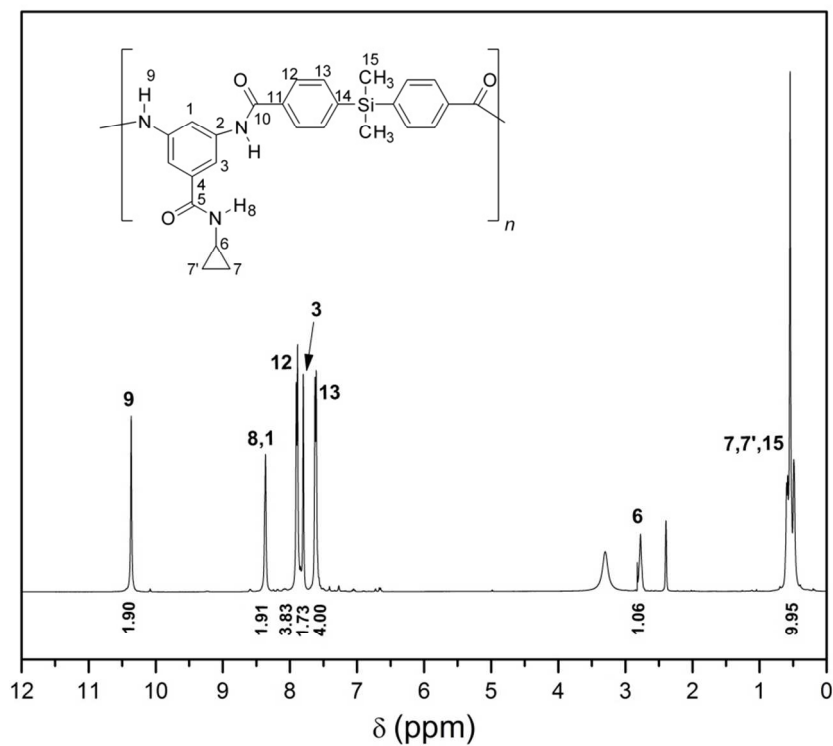


Figure 6.

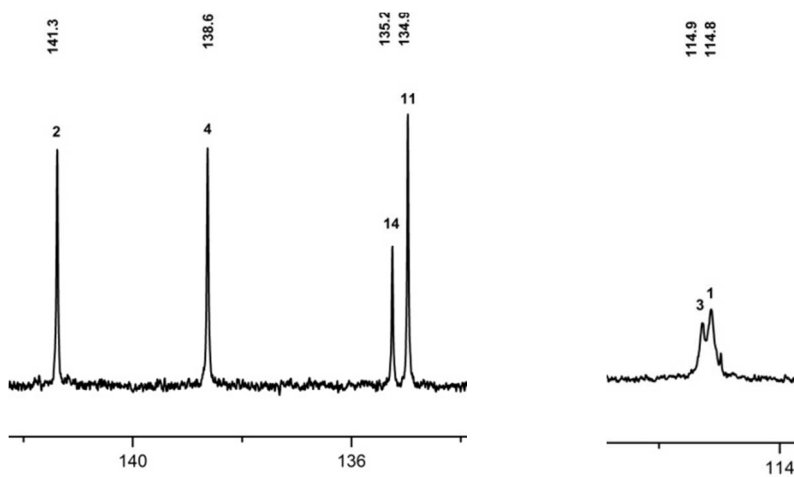
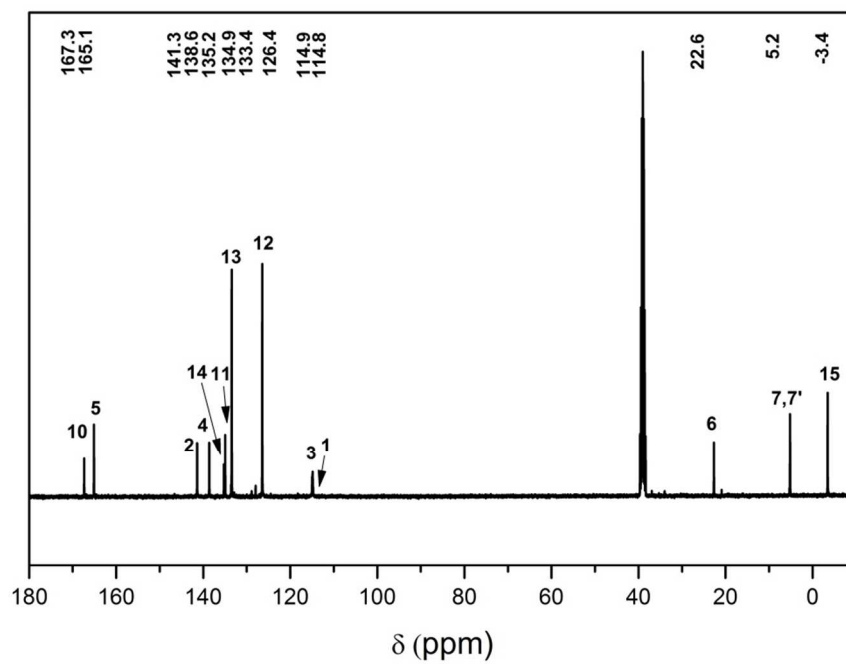


Figure 7.

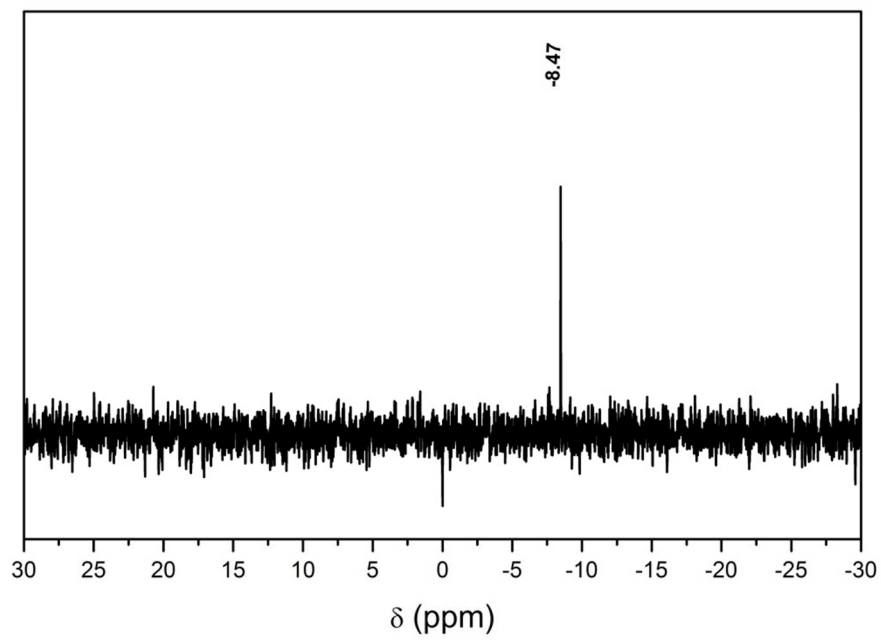


Figure 8

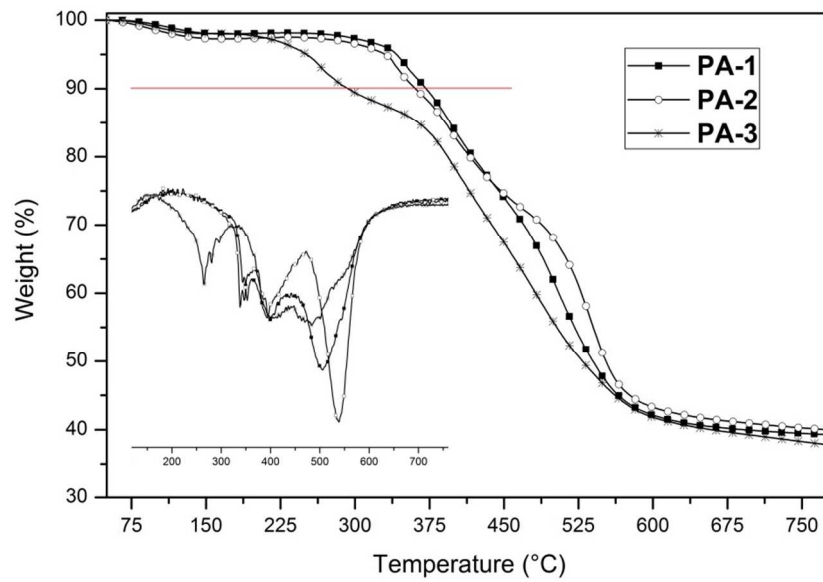


Figure 9

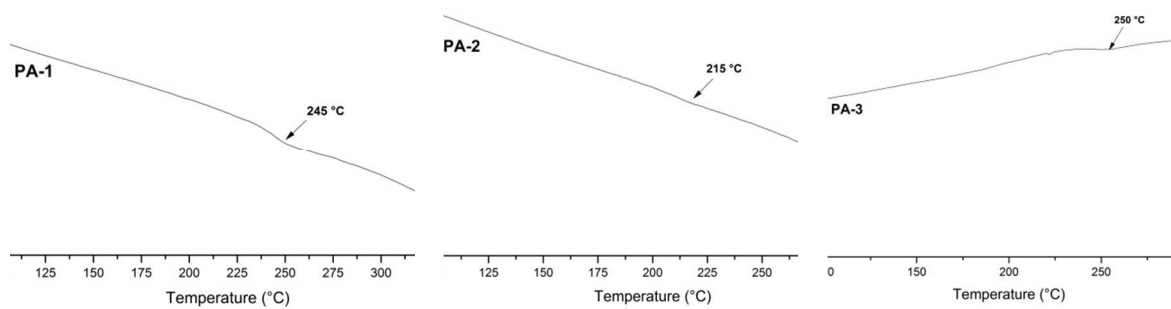


Figure 10

