

Novel hyperbranched molecules containing pyrrole units from diacetylene compounds

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Abstract Novel hyperbranched molecules containing pyrrole units were obtained from *ortho*-, *meta*-, and *para*-diaminodiphenyldiacetylenes, as AB₂ type monomers by one-step polymerization. Diacetylenic fragments reacted with terminal amino groups in the presence of copper chloride to give pyrrole units. Diaminodiphenyldiacetylene monomers have been synthesized from ethynylanilines in three steps. The novel monomers and hyperbranched molecules were characterized by NMR, IR and thermal analysis.

Keywords Synthesis · Diacetylene · Pyrrole · AB₂ type monomers · One-step polymerization · Hyperbranched molecules · Copper chloride

Introduction

The hyperbranched macromolecules are highly branched structures with three-dimensional dendritic architecture, globular shape, absence of chain entanglements and large number of functional terminal groups. These special characteristics of hyperbranched macromolecules improve solubility, compatibility, reactivity, adhesion to various surfaces, self assembly, chemical recognition, electrochemical, luminescence, optoelectronics, and non-linear optical properties compared with their linear analogs [1, 2].

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Hyperbranched macromolecules can be conveniently divided in two major groups. The first is the perfect dendritic macromolecules prepared by stepwise synthetic approaches [3–6]. Their properties are easy to control, but they are obtained only in limited quantities and after much effort. The second is the hyperbranched polymers obtained by the direct polymerization of AB_n monomers [7–10].

Hyperbranched polymers generally have less perfect branching, show polydispersity, and their properties are not so easily tailored; however, they are readily available by simply one-step polymerization.

The authors are interested in the development of polymers with new chemical structures for electronics, photonics, and nonlinear optics using reaction between diacetylenes with amines to yield the pyrrole units. Previously, our research group reported synthesis of linear polymers containing diacetylenes and their modification by reaction between fragments of polymers with aromatic amines in the presence of copper chloride to yield the corresponding pyrrole units in the main chain of polymer [11].

This route opens up a number of opportunities for the synthesis of polymers containing two important fragments in the same structure, diacetylene responsible for possible applications in optoelectronics and nonlinear optics [12–20], and pyrrole, an important heterocycle widely used in material science [21–27].

The goal of this work is to synthesize novel hyperbranched compounds by one-step polymerization using the reaction between diacetylenic fragments and terminal amino groups of AB₂ type monomers in the presence of copper chloride to yield pyrrole fragments in the hyperbranched structure.

Experimental part

Materials and instruments

Reagents were provided by Aldrich Chemical Company and were used as-received. FT-IR spectra were taken using a Nicolet 6700 spectrophotometer. NMR ¹H and ¹³C spectra were recorded using a Bruker Avance 400 MHz spectrometer. The chemical shifts are reported in ppm on the scale relative to TMS. Melting points are uncorrected. Thermogravimetric analyses (TGAs) were carried out in air at a heating rate of 20 °C min⁻¹ on a Mettler DTG 760 instrument, and differential scanning calorimetry (DSC) was carried out at 20 °C min⁻¹ on a Mettler DSC 20 system.

Synthesis of the monomer compounds

(1) (*N*-Boc-amino)phenylacetylene [28]. To a solution of di-*tert*-butyl dicarbonate (BOC₂O) (27.56 g, 126.28 mmol) in 42 mL THF was added aminophenylacetylene (4.85 g, 41.39 mmol). Solution was stirred and refluxed for 3 h. The solvent was removed in vacuum, and the product was purified by column chromatography using hexane–ethyl acetate 10:1–5:1 as eluent.

(1a) 2-(*N*-Boc-amino)phenylacetylene. mp: 47–48 °C, yellow solid, yield 80.2%; IR (film, cm^{-1}): 3404, 3287, 1734, 1613, 1583; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.17 (1H, d, H-7), 7.39 (1H, dd, H-6), 7.29 (1H, dt, H-5), 6.95 (NH, dt, H-9), 3.55 (1H, s, H-1), and 1.50 (9H, s, H-12). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 79.1 ($\equiv\text{CH}$, C-1), 84.4 ($-\text{C}\equiv$, C-2), 109.8 (C aromatic, C-3), 132.1 (C aromatic, C-4), 117.5 (C aromatic, C-5), 130.0 (C aromatic, C-6), 122.0 (C aromatic, C-7), 140.2 (C aromatic, C-8), 152.2 (C=O, C-10), 80.7 (C, C-11), 28.2 ($-\text{CH}_3$, C-12).

(1b) 3-(*N*-Boc-amino)phenylacetylene. mp: 64–66 °C, yellow transparent solid, yield 79%. IR (film, cm^{-1}): 3367, 3287, 2104, 1723, 1583, and 1475. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.55 (1H, s, H-7), 7.01 (NH, s, H-9), 7.17 (H, d, H-6), 7.35 (H, d, H-4), 3.04 (1H, s, H-1), 7.13 (1H, t, H-5), and 1.49 (9H, s, H-12). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 78.6 ($\equiv\text{CH}$, C-1), 83.7 ($-\text{C}\equiv$, C-2), 125.8 (C aromatic, C-3), 127.4 (C aromatic, C-4), 129.7 (C aromatic, C-5), 120.1 (C aromatic, C-6), 122.7 (C aromatic, C-7), 138.5 (C aromatic, C-8), 152.8 (C=O, C-10), 80.6 (C, C-11), 28.8 ($-\text{CH}_3$, C-12).

(1c) 4-(*N*-Boc-amino)phenylacetylene. mp: 70–72 °C, dark yellow solid, yield 96%. IR (film, cm^{-1}): 3400, 3280, 2104, 1699, 1606, 1509. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.34 (H, dd, H-4), 7.43 (H, dd, H-5), 6.59 (NH, s, H-9), 3.03 (H, s, H-1), 1.52 (9H, s, H-12). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 83.7 ($\equiv\text{CH}$, C-1), 81.2 ($-\text{C}\equiv$, C-2), 116.5 (C aromatic, C-3), 133.2 (C aromatic, C-4), 118.2 (C aromatic, C-5), 152.6 (C=O, C-10), 81.2 (C, C-11), 28.5 ($-\text{CH}_3$, C-12).

(2) di(*N*-Boc-amino)diphenyldiacetylene [11]. To a solution of compound 1 (2.00 g, 9.2 mmol) in 20 mL isopropanol was added (0.025 g, 0.252 mmol) of copper chloride and 0.3 mL of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), the mixture was stirred under oxygen atmosphere for 3 h, and the resulting solution was added to acidified water. The product was separated by filtration, dried in vacuum, and purified by recrystallization from hexane.

(2a) 2,2'-di(*N*-Boc-amino)diphenyldiacetylene. mp: 118–120 °C, yellow solid, yield 91.6%. IR (film, cm^{-1}): 3408, 2131, 2205, 1734, 1524, 1583. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 8.19 (H, d, H-7), 7.51 (H, dd, H-4), 7.37 (H, t, H-6), 7.01 (H, t, H-5), 7.19 (NH, s, H-9), 1.57 (9H, s, H-12). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 78.9 ($-\text{C}\equiv$, C-1), 79.7 ($\equiv\text{C}-$, C-2), 110.0 (C aromatic, C-3), 133.2 (C aromatic, C-4), 118.1 (C aromatic, C-5), 130.9 (C aromatic, C-6), 122.4 (C aromatic, C-7), 141.1 (C aromatic, C-8), 152.3 (C=O, C-10), 81.7 (C, C-11), 28.3 ($-\text{CH}_3$, C-12).

(2b) 3,3'-di(*N*-Boc-amino)diphenyldiacetylene. mp: 230–234 °C, yellow solid, yield 90.02%. IR (film cm^{-1}): 3338, 2143, 2213, 1701, 1543, 1582. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 7.68 (1H, s, H-8), 7.55 (H, d, H-6), 7.20 (H, d, H-4), 7.31 (H, t, H-5), 1.47 (9H, s, H-12). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 73.9 ($-\text{C}\equiv$, C-1), 81.3 ($\equiv\text{C}-$, C-2), 122.1 (C aromatic, C-3), 127.2 (C aromatic, C-4), 129.1 (C aromatic, C-5), 119.4 (C aromatic, C-6), 138.5 (C aromatic, C-7), 122.4 (C aromatic, C-8), 152.5 (C=O, C-10), 80.9 (C, C-11), 28.3 ($-\text{CH}_3$, C-10).

(2c) 4,4'-di(*N*-Boc-amino)diphenyldiacetylene. mp: 229–232 °C, yellow solid, yield 92.48%. IR (film cm^{-1}): 3373, 2147, 2213, 1696, 1579, 1513. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 7.49 (1H, dd, H-4), 7.48 (1H, dd, H-5), 1.47 (9H, s, H-12), 5.78 (NH, s, H-9). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 73.7 ($-\text{C}\equiv$, C-1), 82.4

($\equiv\text{C}-$, C-2), 114.0 (C aromatic, C-3), 118.4 (C aromatic, C-4), 141.5 (C aromatic, C-5), 133.6 (C aromatic, C-6), 153.0 (C=O, C-10), 80.1 (C, C-11), 28.5 ($-\text{CH}_3$, C-12).

(3) diaminodiphenyldiacetylene [29]. To a suspension of (1.25 g, 2.89 mmol) of compound **2** in 110 mL of MeOH was added 125 mL of concentrated HCl, and the mixture was stirred for 42 h at room temperature. The supernate was pipetted off, and the solid was stirred in 100 mL of acetone overnight, after which it was filtered off, washed four times with 15 mL of acetone, and pumped dry.

(3a) 2,2'-diaminodiphenyldiacetylene. mp: 146 °C, light brown solid, yield 64.24%. IR(film cm^{-1}): 3514, 3340, 1982, 2222, 1627, 1583, 1538. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 5.74 (NH_2 , s, H-9), 7.07 (H, d, H-7), 6.86 (H, t, H-5), 7.28 (H, t, H-6), 7.39 (H, d, H-4). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 74.3 ($-\text{C}\equiv$, C-1), 81.8 ($\equiv\text{C}-$, C-2), 121.7 (C aromatic, C-3), 130.8 (C aromatic, C-4), 125.0 (C aromatic, C-5), 129.6 (C aromatic, C-6), 123.6 (C aromatic, C-7), 136.9 (C- NH_2 , C-8).

(3b) 3,3'-diaminodiphenyldiacetylene. mp: 188–190 °C, light brown solid, yield 67.12%. IR(film cm^{-1}): 3439, 3357, 2047, 2270, 1627, 1552, 1514. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 3.67 (NH_2 , s, H-9), 7.26 (1H, s, H-8), 6.79 (1H, d, H-6), 7.15 (1H, t, H-5), 7.4 (1H, d, H-4). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 73.9 ($-\text{C}\equiv$, C-1), 81.3 ($\equiv\text{C}-$, C-2), 123.6 (C aromatic, C-3), 129.9 (C aromatic, C-4), 130.4 (C aromatic, C-5), 121.3 (C aromatic, C-6), 135.7 (C- NH_2 , C-9), 125.0 (C aromatic, C-8).

(3c) 4,4'-diaminodiphenyldiacetylene. mp: 198–200 °C, yellow solid, yield 68.2%. IR(film cm^{-1}): 3447, 3424, 2209, 2129, 1610, 1552, 1501. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 4.97 (NH_2 , s, H-7), 7.05 (H, d, H-4), 7.48 (H, d, H-5). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 73.6 ($-\text{C}\equiv$, C-1), 81.9 ($\equiv\text{C}-$, C-2), 115.6 (C aromatic, C-3), 120.7 (C aromatic, C-4), 133.8 (C aromatic, C-5), 138.8 (C- NH_2 , C-6).

Synthesis of hyperbranched compounds

(4). Method A. A mixture of compound **3** (0.1 g, 0.43 mmol), and copper (I) chloride (0.05 g, 0.5 mmol) in 10 mL dimethylformamide was refluxed under nitrogen for 24–48 h at 110 °C in an oil bath and allowed to cool to room temperature. The mixture was diluted with excess of acidified water. The precipitate was collected by filtration and dried in vacuum. Method B. A mixture of compound **3** (0.5 g, 2.15 mmol), and copper (I) chloride (0.05 g, 0.5 mmol) in dioxane (10 mL) was refluxed under nitrogen for 24 h at 70 °C in an oil bath and allowed to cool to room temperature. The solution was diluted with excess of acidified water. The precipitate was collected by filtration and dried in vacuum.

(4a) hyperbranched *ortho*-phenylpyrrole. Method A: 30% yield, Method B: 20% yield, dark green solid, insoluble in organic solvents, TGA onset decomposition begins at 189 °C, at 600 °C 45.5% weight loss, ^{13}C CPMAS NMR (100 MHz, 5000 Hz): δ 111.5 (pyrrole, C-15, C-16), 83.5, 79.5 (diacetylenic, C-1, C-2), 136.9, 129.6, 122.9, 120.7, 99.8 (aromatic).

(4b) hyperbranched *meta*-phenylpyrrole. Method A: 91% yield, Method B: 70% yield, black solid, insoluble in organics solvents, TGA onset decomposition begins at 199 °C, at 500 °C 36% weight loss. IR(pellet cm^{-1}): 3442, 3329, 1559, 1558,

1517. ^{13}C CPMAS NMR (100 MHz, 5000 Hz): δ 109.8 (pyrrole, C-15, C-16), 156.0 (C–NH₂), 85.9, 80.1 (diacetylenic, C-1, C-2), 136.1, 131.9, 127.0 (aromatic).

(4c) hyperbranched *para*-phenylpyrrole. Method A: 94% yield, Method B: 73% yield, black solid, insoluble in organic solvents (a little part was soluble in DMF to correspond to ^1H -NMR (400 MHz, DMSO-*d*₆), TGA onset decomposition begins at 165 °C, at 600 °C 45% weight loss. IR (film cm^{-1}): 3442, 2201, 2116, 1685, 1620. ^1H -NMR (400 MHz, DMSO-*d*₆): δ 6.59 (H-pyrrole, H-15, H-16), 5.66 (NH₂, H-17), 7.46 (aromatic, H-4, H-8), 8.30 (aromatic, H-10, H-14), 7.60 (aromatic, H-11, H-13), 7.25 (aromatic, H-5, H-7). ^{13}C CPMAS NMR (100 MHz, 5000 Hz): δ 105.1 (pyrrole, C-15, C-16), 148.9 (C–NH₂) 74.1, 71.1 (diacetylenic), 129.4, 120.5, 114.4, 118.5 (aromatic).

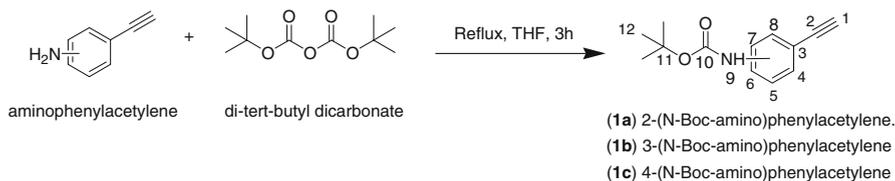
Results and discussion

Monomer synthesis

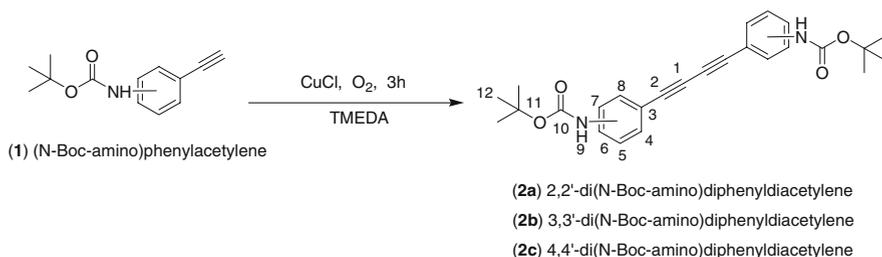
The synthetic route to the monomers **3a**, **3b**, and **3c** are shown in Schemes 1–3. These monomers were prepared from *ortho*-, *meta*-, and *para*-aminophenylacetylenes, in three steps.

Terminal amino groups have been converted into *N*-Boc-amino groups by treating aminophenylacetylene with di-*tert*-butyl dicarbonate (BOC₂O) in THF (Scheme 1) to preserve the amino groups for the subsequent reaction of oxidative coupling (Scheme 2).

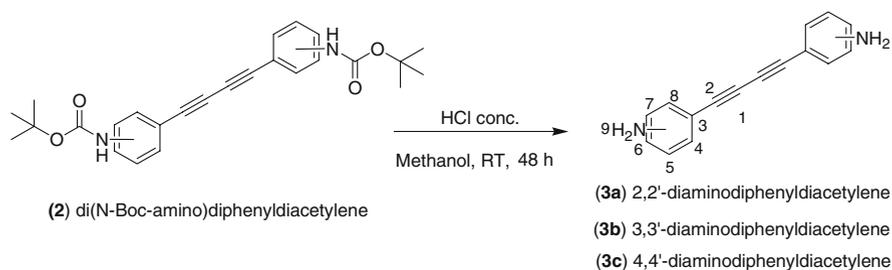
The compound **1a**, **1b**, and **1c** were characterized by FT-IR. In all the cases, the signal corresponding to amino group (3450, 3357 cm^{-1} 3-aminophenylacetylene)



Scheme 1 Synthesis of (*N*-Boc-amino)phenylacetylene (1)



Scheme 2 Synthesis of di(*N*-Boc-amino)diphenyldiacetylene (2)



Scheme 3 Synthesis of diaminodiphenyldiacetylenes (3)

changed to amide group (3353 cm^{-1}) showing a singlet: the result of the reaction between Boc group and amino group. $^1\text{H-NMR}$ spectra showed signals at 7.34, 7.43, (aromatic), 6.59 (amide), 3.03 (acetylenic), 1.52 (BOC), and $^{13}\text{C-NMR}$ spectra at 83.8, 81.2 (acetylenic), 116.5, 133.2, 118.2 (C aromatic, C-5), 152.6, 81.2, 28.5 (BOC).

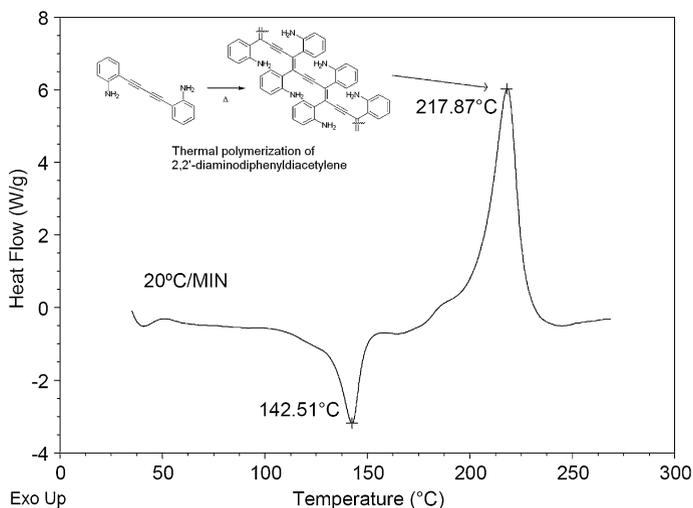
Diyne compounds **2a**, **2b**, and **2c** were obtained by a modified procedure of Hay's oxidative coupling using copper (I) chloride as a catalyst [11] (Scheme 2). The obtained diacetylenes were characterized by FT-IR analysis confirmed that characteristic absorptions of terminal acetylene bond at 3285 cm^{-1} disappeared after oxidative coupling reaction and double characteristic signal at 2200, 2100 cm^{-1} corresponding to diacetylenic group appeared. In $^1\text{H MNR}$, the signal corresponding to $\equiv\text{CH}$ (i.e., 79.14 ppm in compound **1b**) disappeared, and $^{13}\text{C MNR}$, showed two characteristic signals (i.e., 73.9, 81.3 ppm in compound **2b**) corresponding to $-\text{C}\equiv\text{C}-$.

The protective groups were removed by treating compounds **2a**, **2b**, and **2c** by concentrated HCl giving the resulting monomers **3a**, **3b**, and **3c** [29] (Scheme 3) containing diacetylenic and terminate amino groups in 64–68% yield.

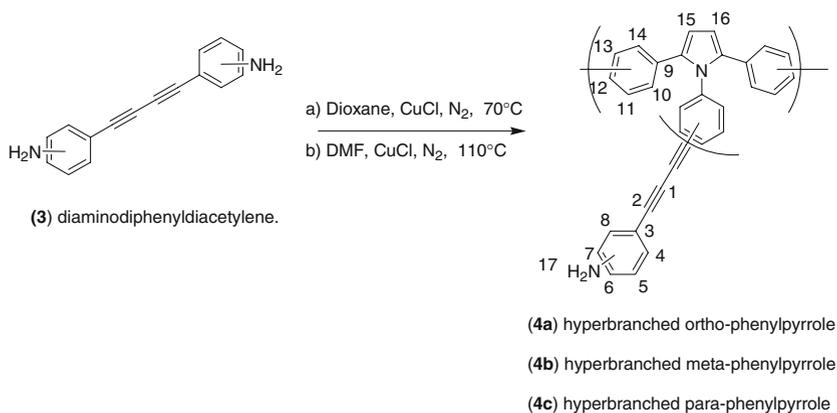
The deprotection reaction was monitored by FT-IR until signal $\text{C}=\text{O}$ (1700 cm^{-1}) disappeared, and the amino group signal appeared (3450 , 3350 cm^{-1}), showing that BOC group was removed. The $^1\text{H MNR}$ (1.47 ppm (9H, CH_3)) and $^{13}\text{C MNR}$ (152.9 (C=O), 80.1 (C), 28.5 (CH_3) ppm) signals corresponding to BOC group disappeared too (signals corresponding to compound **2b**). For obtained monomers (**3a**, **3b**, and **3c**)—thermal analysis by DSC was carried out—melting points of 142, 189, and 199 °C, respectively, were found. According to DSC data, monomers **3a**, **3b**, and **3c** showed exotherms at 217, 282, and 243 °C, respectively, characteristic of thermal diacetylenic polymerization (Scheme 4, DSC Thermogram of compound **3a**).

Polymerization

Ortho-, *meta*-, and *para*-diaminodiphenyldiacetylene (**3a**, **3b**, and **3c**) as AB_2 type monomers were polymerized by two methods [11]. Method A—in DMF under nitrogen at 110 °C, and method B—in dioxane under nitrogen at 70 °C using copper (I) chloride as catalyst in both cases (Scheme 5). Diacetylenic fragments and



Scheme 4 DSC Thermogram of compound 2,2'-diaminodiphenyldiacetylene (**3a**)

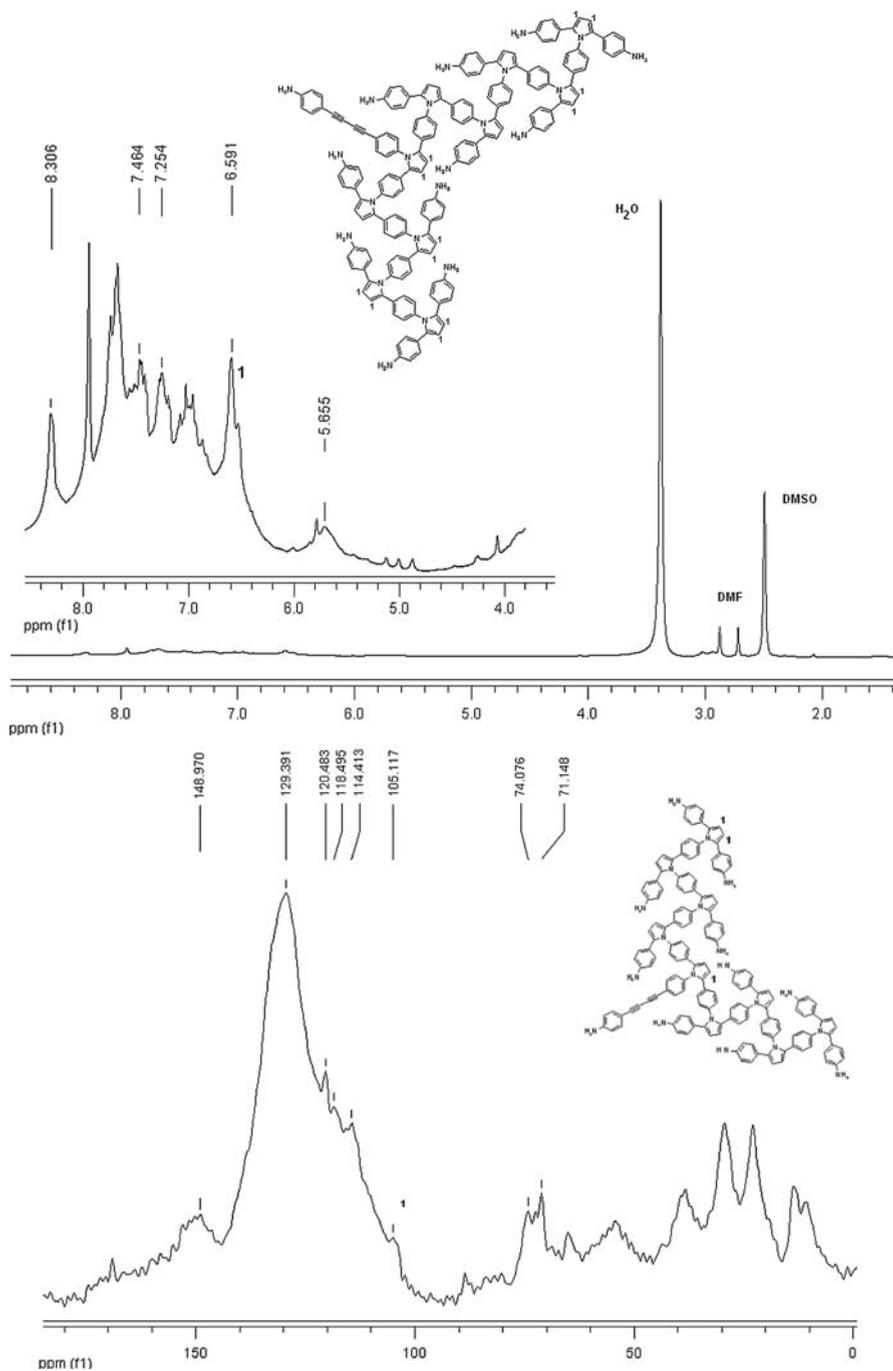


Scheme 5 Synthesis of hyperbranched molecules from diaminodiphenyldiacetylene (**4**)

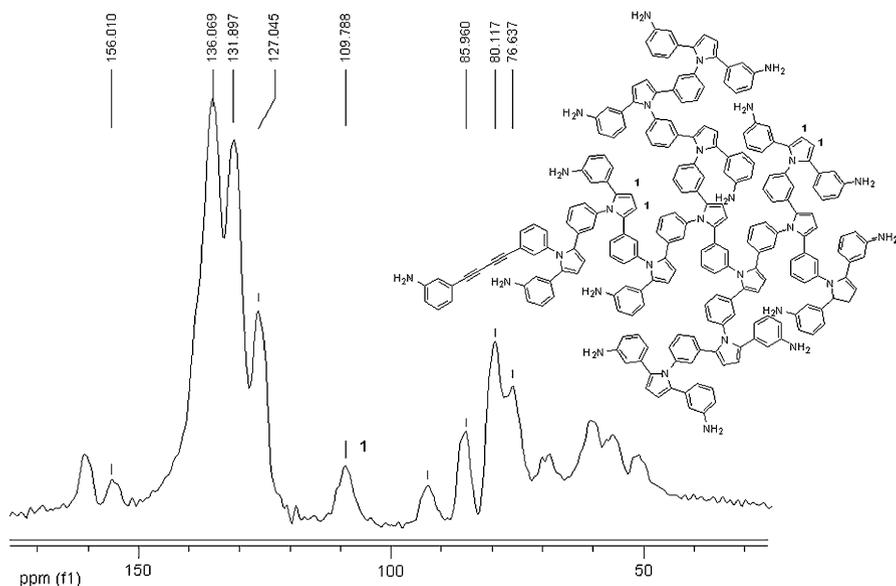
terminal amino groups reacted to yield pyrrole units. These reactions are carried out by one-step polymerization.

Hyperbranched products **4a**, **4b**, and **4c** were poorly soluble in organics solvents. Products obtained were characterized by FT-IR, which showed 1685, 1620 aromatic, 3442 amine, and 2201, 2116 cm⁻¹ diacetylenic groups signals.

The ¹³C CPMAS NMR spectrum of compounds **4a**, **4b**, and **4c** showed signals at 111.5, 109.8, and 105.1 ppm corresponding to pyrrole units (Schemes 6 and 7), respectively. Compound **4c** was partially soluble in DMF, in the ¹H-NMR spectrum can be appreciated the signal 6.59 ppm corresponding to pyrrole ring (Scheme 6) proving the chemical structure of formed hyperbranched structures. The TGA onset decomposition of the compound **4a** begins at 189 °C, and at 600 °C **4a** loses 45.5%



Scheme 6 $^1\text{H-NMR}$ and $^{13}\text{C CPMAS NMR}$ spectra of hyperbranched para-phenylpyrrole (**4c**)



Scheme 7 ^{13}C CPMAS NMR spectrum of hyperbranched meta-phenylpyrrole (**4b**)

of weight, that of the **4b** begins at 199 °C, and at 500 °C **4b** loses 36% of weight, and that of the **4c** begins at 165 °C and at 600 °C **4c** loses 45% of weight. Therefore, these products possess high thermal resistance.

Conclusions

Novel hyperbranched structures containing pyrrole units were obtained from *ortho*-, *meta*-, and *para*-diaminodiphenyl diacetylenes as AB_2 type monomers by one-step polymerization. Diacetylenic fragments and terminal amino groups reacted in the presence of copper chloride to yield the pyrrole units. These compounds have high thermal resistance, and show low solubility in organic solvents.

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