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New polymers with N-phenyl pyrrole fragments obtained by chemical modifications of diacetylene containing-polymers

G. Huerta[1], L. Fomina[1], L. Rumsh[2] and M. G. Zolotukhin[1]

1.-Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, 04510, Apartado Postal 70-230, Coyoacan, Mexico, DF, Mexico
2.-M. M. Shemyakin and Yu. A. Ovchinnikov, Institute of Bioorganic Chemistry, Russian Academy of Sciences, Ul. Miklukho-Maklaya, 16/10, 117997 GSP, Moscow V-437, Russia

E-mail: lioud@servidor.unam.mx, Fax: (+ 52 55) 5 616 12 01

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Summary

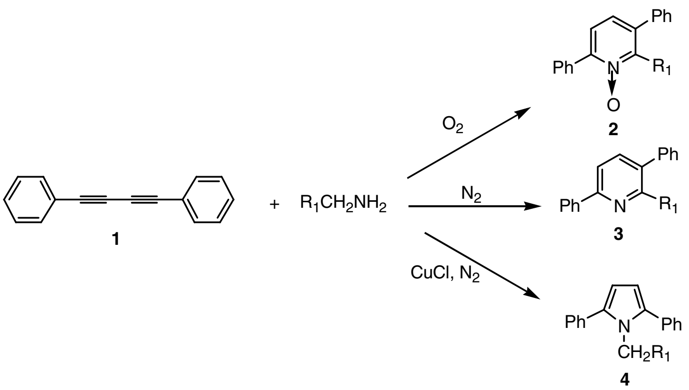
New polymers containing pyrrole units in the main chain were obtained by chemical modification of diacetylene-containing polymers, which were prepared by oxidative coupling of terminal diacetylenes or superelectrophilic polycondensation of diphenoxydiacetylene with isatin. Diacetylenic fragments in the polymers thus obtained reacted with aromatic amines in the presence of copper chloride to yield the corresponding pyrroles. The reaction between diacetylenic compounds and amines was studied to determine the proper reaction conditions for introduction of pyrrole groups into the polymer backbone. The new polymers and their model compounds were fully characterized by NMR, IR and thermal analysis.

Introduction

Polymeric reactions are commonly practiced to modify and impart new properties to conventional polymeric materials. In some cases, chemical modification either is the only way to obtain a polymer which otherwise is difficult or not possible to prepare directly. Numerous books and reviews on polymeric reactions have been published, many of them recently [1].

Diacetylene-containing polymers have been widely investigated due to their possible applications in optoelectronics and non-linear optics [2-3]. It is known that the diacetylene group can react with many nucleophilic and electrophilic agents. For example, diacetylene undergoes halogenation [4] and readily reacts with primary aliphatic and aromatic amines [5]. Depending on the reaction conditions, different products can be obtained from this synthesis (Scheme 1) [6].

Clearly, the selective modification of the diacetylene groups in a polymer by reaction with amines is an important synthetic route to the synthesis of new polymers, particularly those containing pyrrole units. Pyrroles are important heterocycles widely used in materials science [7]. This route opens up a number of opportunities for the



Scheme 1. Reaction of diphenylbutadiyne with a primary amine

synthesis of potentially soluble and processable pyrrole-containing polymers [8]. In addition, it also provides an opportunity to generate polymers containing both diacetylene and pyrrole units in the backbone. The aim of the present work was to devise a flexible practical synthesis of polymers containing pyrrole groups in the main chain. The synthetic approach to these materials involved preparation of polydiacetylenes followed by their reaction with amines.

Experimental part

Materials and Instruments: Reagents were provided by Aldrich Chemical Company and used as received. FT-IR spectra were taken using a Nicolet 510p spectrophotometer. NMR ^{1}H and ^{13}C spectra were recorded using a Varian Unity Inova 500 MHz, Bruker Avance 400 MHz and Jeol Eclipse 300 MHz spectrometers. The chemical shifts are reported in ppm scaled relative to TMS. Melting points are uncorrected. Thermogravimetric analyses (TGA) were carried out in air at a heating rate of 10°C min^{-1} on a TGA 2950 Instrument and Differential Scanning Calorimetry (DSC) was carried out on a DSC 2910 instrument. Gel Permeation Chromatographic Analysis was carried out on a Varian 9012, columns (TSK-gel 64008H8), detector (Varian RI-4) and integrator (Varian 4400), software GPC- plus. THF and DMF were employed as eluents at 25 °C and flux speed of 1.0 mLmin-1 after calibration with polystyrene standards.

Synthesis of the monomer compounds

(**1**) 1, 4-diphenylbuta-1,3-diyne [5a] . Copper (I) chloride (0.02g, 0.2 mmol) and N, N, N´, N´- tetramethylethylendiamine (TMEDA), 0.05 mL (0.038g, 0.3 mmol) were added to the solution of phenyl acetylene (2.00 g, 19.6 mmol) in iso-propanol. The mixture was left stirring under an oxygen atmosphere for 3 hours, and the resulting solution added to acidified water. The product was separated by filtration, dried in vacuum and purified by recrystallization from hexane. Yield: 96%, white solid, m.p. 87-88°C. NMR ^{1}H (400 MHz, $CDCl_3$): δ 7.33 (m, 3H), 7.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 73.9 (CC), 81.6(CC), 121.8, 128.5, 129.2, 132.5.

(**11**) 1-(prop-2-ynyloxy) benzene. To a solution of phenol (10.0 g, 0.10 mol) in dry acetone, was added anhydrous potassium carbonate (17.6 g, 0.12 mol), the solution was stirred for one hour at room temperature, and propargyl bromide then added (19.0 g, 0.155 mol). The resulting mixture was stirred at 50°C for 22 h. The residue was treated with water, extracted with ethyl acetate and dried over anhydrous magnesium sulphate. The product was purified by vacuum distillation and obtained as colorless oil. Yield: 90%, b.p.: 65-68°C at 5 mm Hg [9] , IR (film, cm-^{1}): 3293, 2122. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.52 (1H, t, J = 2.5 Hz, CCH), 4.72 (2H, d, J= 2.5Hz, CH$_2$O), 7.01 (3H, m, H-Ar), 7.34 (2H, m, H-Ar). ^{13}C NMR (100 MHz, CDCl$_3$): δ 55.9, 75.6, 78.8, 115.1, 121.8, 129.9, 157.7.

(**1a**) 1-(6-phenoxyhexa-2,4-diynyloxy)benzene [21]. **1a** was prepared analogously to the procedure described for **1**. A white solid was obtained, m.p.: 80ºC. Yield: 90%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.76 (2H), 7.00 (3H, m, H-Ar), 7.32 (1H, H-Ar). ^{13}C NMR (100 MHz, CDCl$_3$): δ 56.1 (CH$_2$O), 71.0, 74.7, 114.9(Co), 121.8(Cp), 129.6(Cm), 157.4(Ci).

(**6**) 2,2-bis(4-(prop-2-ynyloxy)phenyl)propane. The procedure was similar to the found in the literature. Yield: 90 %. M.p.: 79°C (m.p.: 80 °C [10]).

Synthesis of model compounds

A typical procedure was as follows. A mixture of diacetylene (0.50 g, 2.47 mmol), copper (I) chloride (0.04g 0.49 mmol) and the corresponding amine (4.94 mmol), in dioxane (10 mL), was refluxed under nitrogen for 24 hours at 70°C in an oil-bath, and allowed to cool to room temperature. The solvent was removed in vacuum and the product was purified by column chromatography using hexanes-ethyl acetate (9:1) as eluent.

(**4a**) 1, 2, 5-triphenylpyrrole. Yield: 80%, white solid, m.p.: 233-234°C; (m.p.: 233-234, [11]).

(**4b**) 2, 5-bis-phenoxymethyl-1-phenyl-1-*H*-pyrrole [12]. Yield: 40%, yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.71 (s, 2H, H-3), 6.39 (s, 1H, H-1), 6.77(m, 2H, H-5), 6.80 (dd, 2H, H-9), 6.91(m, 1H, H-7), 7.15 (m, 2H, H-6), 7.20 (dd, 2H, H-10). ^{13}C NMR (100 MHz, CDCl$_3$): δ 62.0, 110.7, 114.1, 115.0, 121.0, 129.7, 130.7, 158.5, 159.4.

(**4c**) 1-(*p*-methoxyphenyl)-2,5-triphenylpyrrole. Yield: 90%, white solid, m.p.: 229°C (m.p.: 229-227°C [13]).

(**4d**) 1-(*p*-methoxy-phenyl)-2,5-bis-phenoxymethyl-1-phenyl-1-*H*-pyrrole.Yield: 50%, yellow solid, m.p.: 60-62°C. NMR (400 MHz, CDCl$_3$): δ 3.22 (s, 3H), 4.71 (s, 2H, H3), 6.39 (s, 1H, H pyrrole), 6.77(m, 2H, H-5), 6.80 (dd, 2H, H-9), 6.91(m, 1H, H-7), 7.15 (m, 2H, H-6), 7.20 (dd, 2H, H-10). ^{13}C NMR (100 MHz, CDCl$_3$): δ 30.5, 62.0 , 110.7 , 114.1 115.0 , 121.0 , 129.7 , 130.7, 158.5 , 159.4 .

(**4e**) 2,5-diphenyl-1-*p*-tolyl-1-*H*-pyrrole [13b]. Yield: 85%, white solid, m.p.: 200 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.32 (s, 3H, -Me), 6.47(s, 2H, H-pyrrole), 6.90 (2H, d, H-9), 7.02 (2H, d, H-8), 7.07 (4H,m) 7.16 (6H,m). ^{13}C NMR (100 MHz, CDCl$_3$): 21.4, 110.0, 126.4, 128.1, 128.8, 128.9, 129.6, 133.6, 136.0, 136.6, 137.2.

(**4f**) 1-(4-methyl-phenyl)-2, 5-bis-phenoxymethyl-1-phenyl-1-*H*-pyrrole. Yield: 45%, yellow solid, m.p.: 224-226°C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.30(s, 3H), 4.72 (s, 2H, H-3), 6.39 (s, 1H, H-pyrrole), 6.77 (m, 2H, H-5), 6.80 (dd, 2H, H-9) 6.91(m, 1H, H-7), 7.15 (m, 2H, H-6), 7.20 (dd, 2H, H-10). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 62.0, 110.7, 114.1, 115.0, 121.0, 129.7, 130.7, 158.5, 159.4.

(**4g**) 1-(*p*-nitro-phenyl)-2,5-triphenylpyrrole [5b]. Yield: 50%. Yellow solid, m.p.: 253-255°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (s, 1H), 7.24 (2H, m), 7.35 (m), 7.52 (m), 8.2 (d, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.3, 121.8, 124.1, 127.5, 128.5, 130.1, 132.5, 135.7, 146.0.

(**4h**) 1-(*p*-carboxy-phenyl)-2,5-triphenylpyrrole [5c]. Yield: 70%, white solid. M.p.: 256°C. ^{1}H NMR (400 MHz, DMSO-*d6*): δ 6.45 (s, H-1), 7.02 (bs, H-5, H-6), 7.17 (bs, H-4, H-8), 7.48 (H-9).

Polymerization

(**7**) To a solution of **6** (1 g, 3.28mmol) in 1,2-dichlorobenzene was added copper (I) chloride (0.02g ,0.2 mmol) and a few drops of N,N,N',N'-tetramethyl-ethylenediamine (TMEDA). The reaction mixture was stirred under a stream of oxygen at 75°C for 2 hours. The solution was then diluted with excess methanol. The precipitate was collected by filtration, washed with methanol and dried in vacuum. The polymer yield was quantitative. IR(film): υ= 2054 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (s, 6H, $-CH_3$), 4.68 (t, J = 2.4Hz, 4H, $-OCH_2$), 6.88 (d, 4H, $-C_6H_4$), 7.18(d, 4H,$-C_6H_4$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.0(CMe), 41.8,56.2($-OCH_2$), 70.1(CC),74.8(CC),114.2, 127.1, 144.0, 155.3(C-Ar).

(**12**) A typical polymer synthesis was conducted in a single-necked 10 mL flask equipped with magnetic stirrer. To a mixture of **1a** (0.50 g, .9 mmol) and (0.28 g, 1.9 mmol) of isatin were added trifluoromethansulfonic acid (TFSA) (5 mL) and Eaton´s reagent (2mL) (a mixture of methanesulfonic acid (MSA) with 10% of P_2O_5). The reaction mixture was stirred for 2 hours at room temperature and poured into water. The slightly greenish fiber formed was filtered off, washed with water and extracted with hot methanol. ^{1}H NMR (400MHz, $CDCl_3$): δ 4.91 (s, 4H,$-OCH_2$), 6.96 (m, 6H, H-o in 1a, H-5, H-6 isatin ring) 7.06 (m, 4H, H-m in 1a), 7.23 (m, 2H, H-7, H-8 isatin ring), 10.71 (bs, 1H, N-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.2 ($-CH_2O$), 61.2(Cq), 70.4(CC), 76.5(CC), 110.5, 115.0, 122.4, 126.4, 128.7, 129.7, 133.9, 135.5, 141.7, 156.5, 179.0 (C-Ar).

Polymer reactions with amines: general procedure

To a stirred solution of **7** (0.5 g, 1.64mmol) in dioxane (10 mL) under nitrogen were added copper (I) chloride (0.05g, 0.5mmol) and the corresponding amine (3.28 mmol). After 24 hours stirring at a temperature of 70°C, the solution was diluted with excess acidified water. The precipitate was collected by filtration and dried in vacuum.

(**8**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (s, 6H, -Me), 4.69 (2H, $-OCH_2$), 6.39 (s, 1H, H-pyrrole), 6.68 (m, 2H), 7.05 (m, 2H), 7.20 (dd, 2H), 7.43 (m, 1H), 7.43 (dd, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 31.1, 41.6, 62.0, 110.8(C-pyrrole), 114.4, 127.6, 127.8, 130.6, 132.6, 156.2.

(**9**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (s, 6H, -Me), 4.69 (s, 2H, $-OCH_2$), 6.39 (s, 1H, H-pyrrole), 6.70- 7.43 (m, 12H). ^{13}C NMR (100MHz, $CDCl_3$): δ 31.1, 41.6, 62.0, 110.8 (C-pyrrole), 114.4, 127.6, 127.8, 130.6, 132.6, 156.2.

(**10**) ^{1}H NMR (400MHz, $CDCl_3$): δ 1.59 (s, 6H, Me), 2.17 (s, 3H, -*p*Me), 4.72 (2H, $-OCH_2$), 6.39 (s, 1H, H-pyrrole), 6.71-7.29 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 31.1, 41.6, 62.0, 110.8(C-pyrrole), 114.4, 127.6, 127.8, 130.6, 134.4, 156.3.

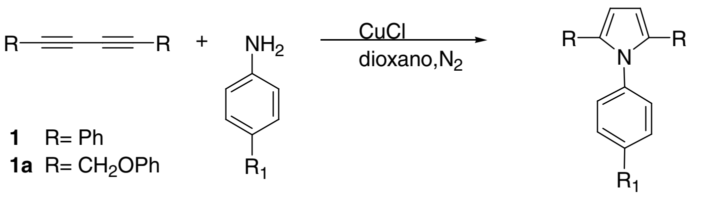
(**13**) A mixture of **12** (0.1 g, 0.25 mmol), 0.1 mL of aniline (0.09g, 1 mmol), copper (I) chloride (0.01 g, 0.01 mmol) and 5 mL of dioxane was placed in a flask equipped with a magnetic stirring bar and a reflux condenser under a nitrogen atmosphere. The mixture was maintained at 70°C for 24 hours with stirring, then cooled and poured into water. The precipitated polymer was filtered, washed with hot methanol and dried in vacuum. ^{1}H NMR (300 MHz, DMSO-d6): δ 4.71 (s, 4H), 6.35 (s, 1H, H-pyrrole), 6.66 (3H, m), 6.90 (9 H, m), 7.21 (m). 10.64 (bs, 1H, N-H). ^{13}C NMR (75 MHz, DMSO-d6): δ 56.2 ($-CH_2O$), 61.3 (Cq), 110.4 (C-pyrrole), 110.5, 115.0, 122.3, 112.4, 126.4, 128.5, 128.7, 129.7, 129.9, 133.0, 135.5, 141.7, 156.5, 179.0 (C-Ar).

Results and discussion

Synthesis of model compounds

It has been reported that the reaction of diacetylene with amines depends strongly on the reaction conditions [6]. Non-catalyzed syntheses under oxygen or nitrogen atmospheres, or reactions under nitrogen catalyzed by Cu [5] and Ti salts [14], afforded mixtures of products with a dominating content of 2,3,6-triphenylpyridine (**3**), pyridine-N-oxide (**2**) or 1,2,5-triphenylpyrrole (**4**). Model reactions to find conditions for selective formation of 1,2,5-triphenylpyrrole units were therefore carried out. Diyne compounds (**1, 1a**) for these reactions were easily obtained through a modification of Hay´s oxidative coupling using copper (I) chloride as a catalyst [15].

The diacetylenes obtained were then reacted with different amines (Scheme 2). The presence of an electrodonating group in the *p*-position was found to increase the yield of the pyrrole obtained. In the case of **4b**, **4d** and **4f,** the starting compounds were recovered. Polar solvents like dioxane or DMF favour the formation of pyrroles. It



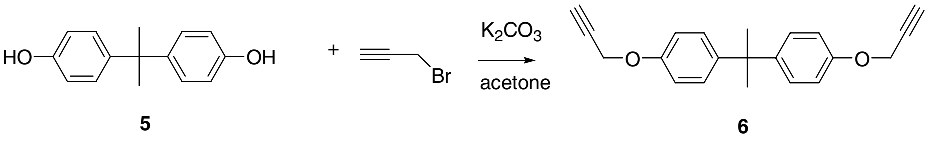
4a	R=Ph,	R_1= H
4b	R=CH_2OPh,	R_1= H
4c	R=Ph,	R_1= OMe
4d	R=CH_2OPh,	R_1= OMe
4e	R=Ph,	R_1= Me
4f	R=CH_2OPh,	R_1= Me
4g	R=Ph,	R_1= NO_2
4h	R=Ph,	R_1= COOH

Scheme 2. Model reactions of diacetylenes with amines

was found that the reaction of **1a** with *p*-substituted amines in presence of copper (I) chloride (20 % mol) at 70°C in DMF gave the highest yields of the corresponding 2, 5-disubstituted pyrroles. The conversion of the diacetylenic group was studied by FTIR and NMR spectroscopy. The ^{1}H spectrum of the model compounds showed a singlet at 6.4 ppm. In the ^{13}C NMR spectrum, signals at 71.0 and 74.7 ppm disappear after reaction. The signal at 110 ppm in the ^{13}C spectrum is attributed to 2,5-disubstituted pyrrole. The structure of the polymeric compounds was established on the basis of monomer spectra.

Monomer synthesis

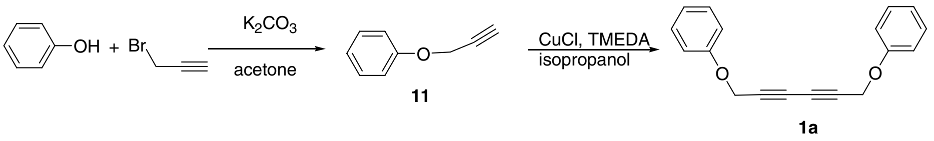
Monomer **6** was prepared from propargyl chloride and bisphenol A (**5**) in presence of an excess of potassium carbonate in acetone (Scheme 3) [10].



Scheme 3. Alkylation of bisphenol A under basic conditions

Monomer **6** was characterized by FT-IR which showed characteristic absorption signals at 3285 and 2028 cm^{-1} corresponding to the stretching bands of $\equiv$CH and C$\equiv$C , respectively. The ^{1}H NMR spectrum showed the characteristic acetylene terminal signal at 2.6 ppm.

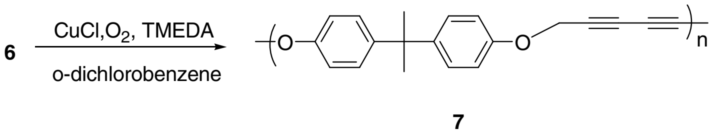
Synthesis of compound **11** was carried out by *O*-propargylation. Thus, **11** was obtained from phenol and propargyl bromide in acetone at 50°C in 90 % yield. Monomer **1a** for the superelectrophilic condensation was obtained in 95% yield using the oxidative coupling reaction (Scheme 4).



Scheme 4. Synthesis of monomer **1a**

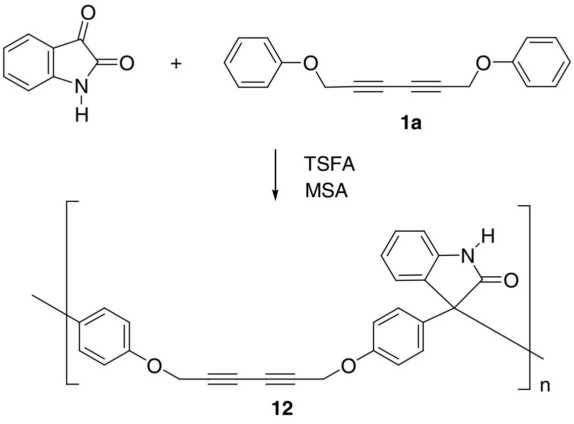
Polymerization

Oxidative polymerization of **6** was carried out according to the Scheme 5.



Scheme 5. Oxidative polymerization of monomer **6**.

Since phenyl propargyl ethers are known to undergo Claisen type sigmatropic rearrangements to give 2H-chromenes [16], the polymerization temperature was not allowed to rise above 70°C. Reaction under these conditions yielded a fully soluble polymer. The preparation of polymer **7** has been reported previously [17], but its structural characterization was very limited. Therefore, the polymer **7** thus obtained was characterized by NMR, IR and GPC before chemical modification. The ethynyl proton disappears during oxidative coupling polymerization, as evidenced by IR spectroscopy: the absorption band at 3285 cm^{-1} gradually disappears. In the ^{1}H NMR spectrum of **7,** the signal at 2.53 ppm disappeared. In ^{13}C spectrum of **7**, the acetylenic terminal carbon is shifted to lower frequencies ($\Delta\delta$=8 ppm) in comparison with that of monomer **6**. Thus, the spectroscopic pattern of polymer **7** was found to be in accordance with the proposed structure. GPC analysis showed a Mw of 10000 and polydispersity of 2.75. Polymer **7** has a T_g of 94°C and an exotherm at 202.5°C, which is characteristic of thermal diacetylenic polymerization. The new polymer **12** containing diacetylenic moieties in the main chain, was synthesized by condensation of isatin with diacetylenic monomer **1a** in a superacid medium. The yield of the polymer was close to quantitative. The synthesis proceeded as a superelectrophilic aromatic substitution reaction, and was carried out in similar fashion to recently reported polymerizations of isatin with aromatic hydrocarbons [18].



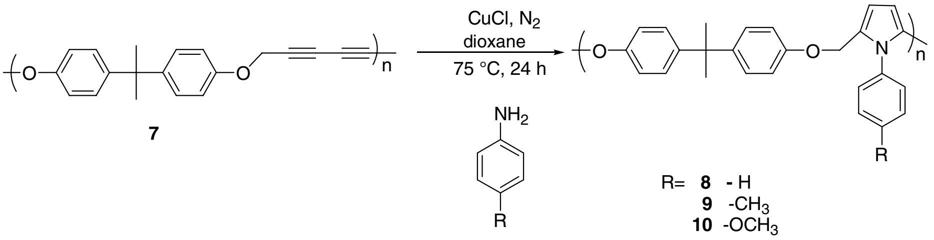
Scheme 6. Polycondensation of isatin with **1a**

Polymer **12** is insoluble in hydrocarbons or chlorinated solvents, but soluble in dipolar solvents as NMP or DMSO, which is consistent with the presence of significant interchain hydrogen bonding. The infrared spectrum showed a strong carbonyl band at 1718 cm-^{1}, assigned to the oxindole group. The TGA onset decomposition temperature of the polymer **12** is 351.8°C; it is lower than that of the corresponding polymers derived from isatin N-phenyl substituted [18]. DSC exhibited an exotherm at 227°C due to thermal cross-linking of the diacetylenic groups, but did not show an endothermic peak corresponding to melting of the material, thus indicating that the polymer was amorphous. Polymer **12** exhibits a Tg of 92°C. GPC data showed a Mw of 11000 and polydispersity of 1.51. Similarly to diacetylene **7**, the ^{13}C NMR spectrum of **12** shows signals at 70.4 and 56.2 ppm characteristic of diacetylenic carbons. The signal at 61.2 ppm is due to the quaternary carbon in the isatin ring (three carbon), this signal is showing the polycondensation. The signal attributed to *p*-substitution in the monomer is shifted to lower frequencies ($\Delta\delta$=14.7 ppm) characteristic of the aromatic polycondensation product.

Polymer Reactions

There are examples in the literature reporting modification of diacetylene-containing polymers with amines and hydrogen sulfide producing pyrrole and thiophene containing polymers, respectively [19, 20]. However, the authors gave no solid proofs of the chemical structure. Furthermore, the drastic reaction conditions reported in those papers cannot be applied in all cases, because the diacetylenic group may suffer cross-linking before the chemical modification.

Polymer **7** was reacted with aniline, *p*-anisidine and *p*-toluidine to give new polymers **8**, **9** and **10** (Scheme 7).



Scheme 7. Reactions of polymer 7 with amines

The modification reaction was monitored by the disappearance of the band at 2152 cm^{-1} from the IR spectrum of the reaction. The singlet at 6.43 ppm in the ^{1}H NMR spectrum provides clear evidence for the formation of 2, 5-disubstituted pyrroles (Figure 1).

The ^{13}C NMR spectrum confirms the chemical transformation by the signal in the product at 110 ppm, characteristic of the pyrrole group. Interestingly, according to NMR data, the modified polymers **8**, **9** and **10** do not contain diacetylene groups, which means that conversion was near 100% efficient. New polymers **8, 9** and **10** are soluble in chlorinated solvents and show a Tg of around 100°C. GPC analysis showed a Mw of 2480 and polydispersity of 2.76 for polymer **8**; a Mw of 995 and polydispersity of 1.86 for polymer **9** and a Mw of 1329 and polydispersity of 2.12 for polymer **10**.

Polymer **12** was modified by reaction with aniline catalyzed by copper chloride under nitrogen atmosphere in order to obtain **13** (Scheme 8). The reaction was monitored by IR spectroscopy using the band at 2148 cm^{-1}, which is characteristic of triple bonds and disappears with the modification. The conversion was found to be 85% (determinated by ^{1}H NMR integration). The signal at 6.35 ppm is attributed to the pyrrole ring. New polymer **13** showed a Tg at 97°C and a TGA onset decomposition temperature at 227.4°C. Polymer **13** is insoluble in hydrocarbons or chlorinated solvents, and poorly soluble in NMP or DMSO. GPC data showed a Mw of 843 and polydispersity of 1.47.

The chemical modification was carried out under mild conditions making improbable chain scission. Therefore, from our point of view the apparent decrease of molecular

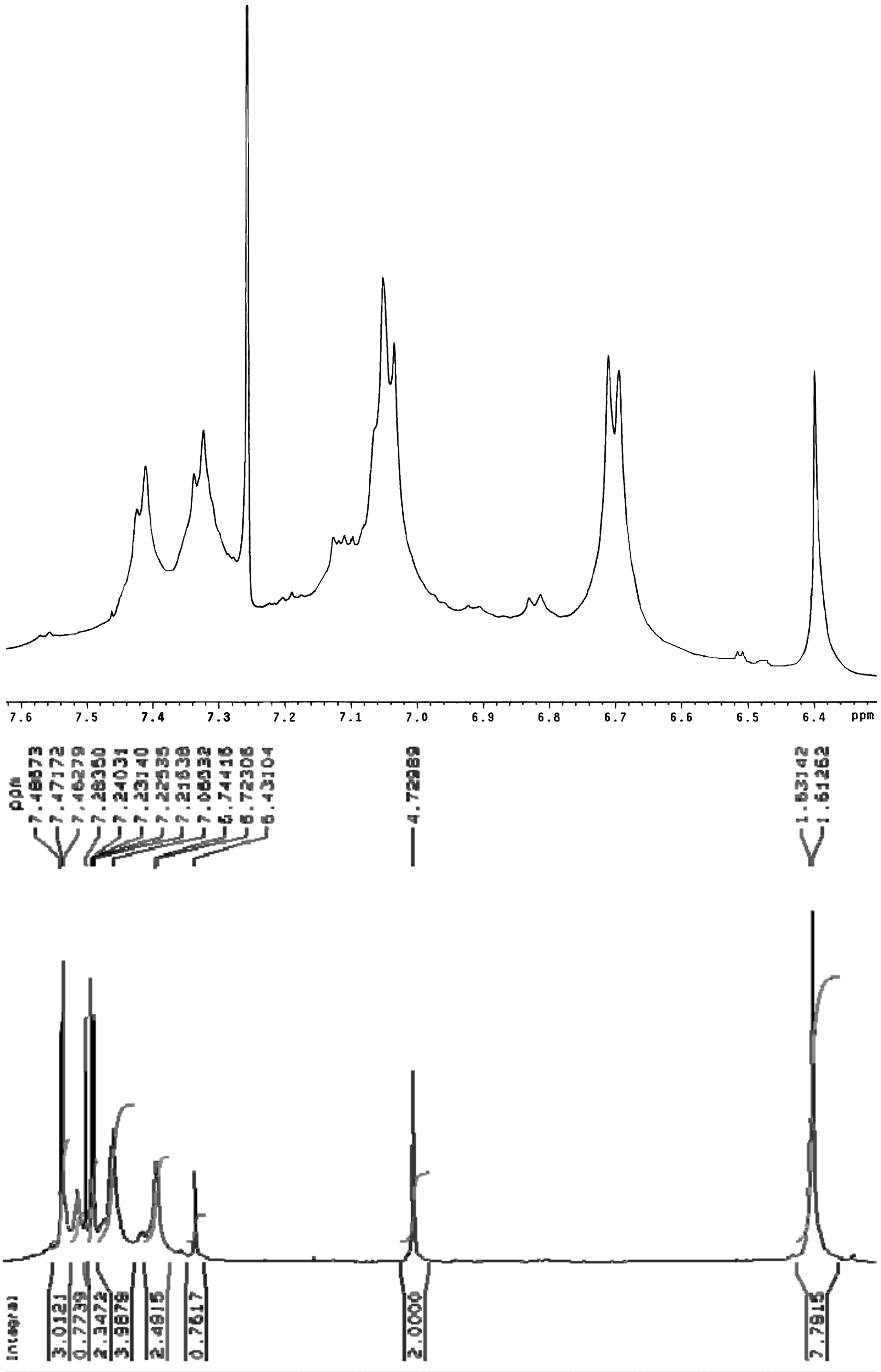
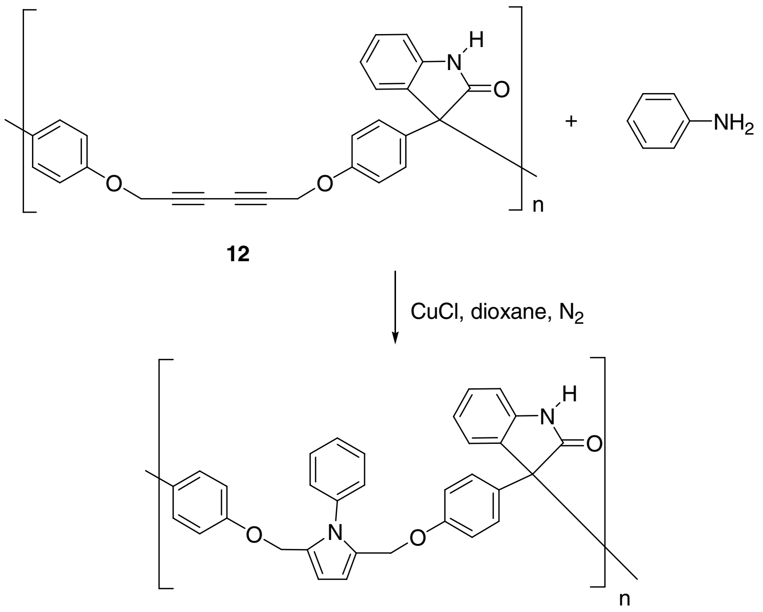


Figure 1. ^{1}H NMR spectrum of new polymer **8** (400 MHz). Ampliation (500 MHz).

weight is due to two factors; first one is that the modification of diacetilenic unit increases the flexibility of polymer chain, thus decreasing hydrodynamic radii of macromolecules. Second, the introducing of side groups also reduces hydrodynamic radii as noted for comb-like polymers thus reducing molecular weight measured by GPC.



13

Scheme 8. Chemical modification of polymer **12**

Conclusions

The chemical reactions of the diacetylene group can be employed to modify polydiacetylenes or to obtain totally different polymers. Reactions of diacetylene groups with aromatic amines in the presence of CuCl as a catalyst proceed under mild conditions to give diaryl-pyrrole fragments in high yield.

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