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New Route to Conjugated Polymer Networks: Synthesis of Poly(4-ethynyl)phenylacetylene and Its Transformation into a Conjugated Network

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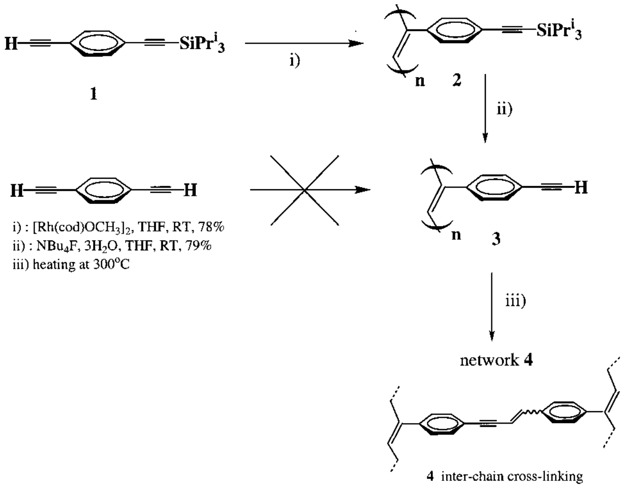
The interest for conjugated organic networks as new materials possessing unique properties[1] motivates efforts for the development of a highly selective and clean synthesis, preferably without evolution of volatiles. Alkynes present two relevant properties useful as precursors of conjugated polymeric networks. On the one hand the polymerization of acetylenic compounds is well-known for the elaboration of polyene-type polymers.[2] The application of these conjugated polymers in the fields of organic conductors,[3] nonlinear optics,[4] optoelectronics,[5] and permselective membranes[6] have definitely boosted the development of polymerization reactions of alkynes. On the other hand, the capability of the terminal carbon−carbon triple bond to give cross-linking reactions is of interest to produce thermosetting materials,[7] 3D carbon-rich network precursors,[8] hyper-cross-linked organic solids,[9] and flame retardants[10] via the cross-linking of molecular and polymeric compounds containing terminal alkyne groups. The combination of both these properties, i.e., polymerization and cross-linking, represents a simple way to elaborate cross-linked conjugated materials. Thus, we have investigated the synthesis of linear conjugated polymers containing terminal ethynyl groups in pendant chains that allowed cross-linking reaction.

The direct polymerization of monomers containing two terminal ethynyl groups, such as the 1,4-diethynylbenzene, cannot be retained for the preparation of polyacetylene type polymers with terminal triple bonds in pendant chains. These terminal alkyne groups could be involved, to some extent, in the polymerization reaction to generate undefined cross-linked side products. The clean preparation of a conjugated cross-linked polymer from a diyne monomer requires an indirect approach. The polymerization of monomers containing both terminal and internal triple bond with transition metal catalysts, which are highly selective for the activation of terminal triple bonds, can be suggested for this purpose. Such a polymerization has been reported for the preparation of polyacetylene-type polymers with internal triple bonds in the pendant chains.[11]

Herein we report: (i) the selective catalytic polymerization of the monoprotected monomer $HC{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}Si^iPr_3$ **1** and the access to polyphenylacetylene polymer **2** containing silylated acetylenic pendant groups, (ii) the clean desilylation of **2** to generate the new polymer **3** carrying phenylacetylene groups in pendant chains, and (iii) the thermal cross-linking reaction of these acetylenic groups, as a simple and very efficient way of accessing a conjugated polymeric network **4**.

Scheme 1



Results and Discussion. 1. Synthesis and Characterization of Polymers. $[Rh(cod)(\mu\text{-}OMe)]_2$ catalyst, described as an efficient catalyst for the polymerization of phenylacetylene derivatives via an insertion mechanism,[12] was used for the polymerization of the 1-ethynyl-4-triisopropylsilylphenylacetylene monomer **1**[13] at room temperature in THF as solvent (Scheme 1). The resulting polymer **2** was isolated in a high yield as a yellow solid soluble in aromatics and various low-polarity solvents. Both the NMR and vibrational spectroscopies (Figures 1 and 2) indicated clearly that only terminal ethynyl groups are involved in the polymerization reaction. All resonance and bands characteristic of the $C{\equiv}CH$ group of **1** are absent [^1H NMR 3.12 ppm; ^{13}C NMR 83.3 and 78.9 ppm; IR 3293 cm^{-1} ν ($\equiv$C−H), 2108 cm^{-1} ν ($C{\equiv}CH$); Raman 2111 cm^{-1} ν ($C{\equiv}CH$)], whereas bands characteristic of the internal triple bond are present in the spectra of **2** [^{13}C NMR 93 and 106 ppm; IR 2153 cm^{-1} ν ($C{\equiv}CSi$); Raman 2157 cm^{-1} ν ($C{\equiv}CSi$)]. The transformation of terminal triple bonds into conjugated double bonds is evidenced: (i) in NMR spectra of **2** by the observation of ^1H signals at 5.76 ppm (vinylic protons in cis−transoid units[14−16]) and 6.44 ppm (ortho hydrogen of phenyl in cis−transoid units[14−16]) and ^{13}C signals at 142.5 ppm (quaternary main-chain carbon in cis−transoid units[14−16]), and (ii) in the Raman spectra of **2** the presence of the ν (C=C) band[17] at 1579 cm^{-1} with shoulder at 1549 cm^{-1} (the phenyl ν (C=C) band is found at 1603 cm^{-1}). According to these spectral features the polymer microstructure can be assigned to a cis−transoid head-to-tail type. The SEC (size exclusion chromatography) analysis showed an unimodal molecular weight distribution for the polymer **2** and provided values of average molecular weight $\langle M\rangle_w = 150\ 000$ and $\langle M\rangle_n = 24\ 000$ g mol^{-1}.

The trialkylsilyl group was reported[13,18] to be an excellent protecting group of terminal alkyne. To generate free ethynyl groups, the polymer **2** was reacted with tetrabutylammonium fluoride trihydrate in THF at room temperature. A new polymer **3** was formed and

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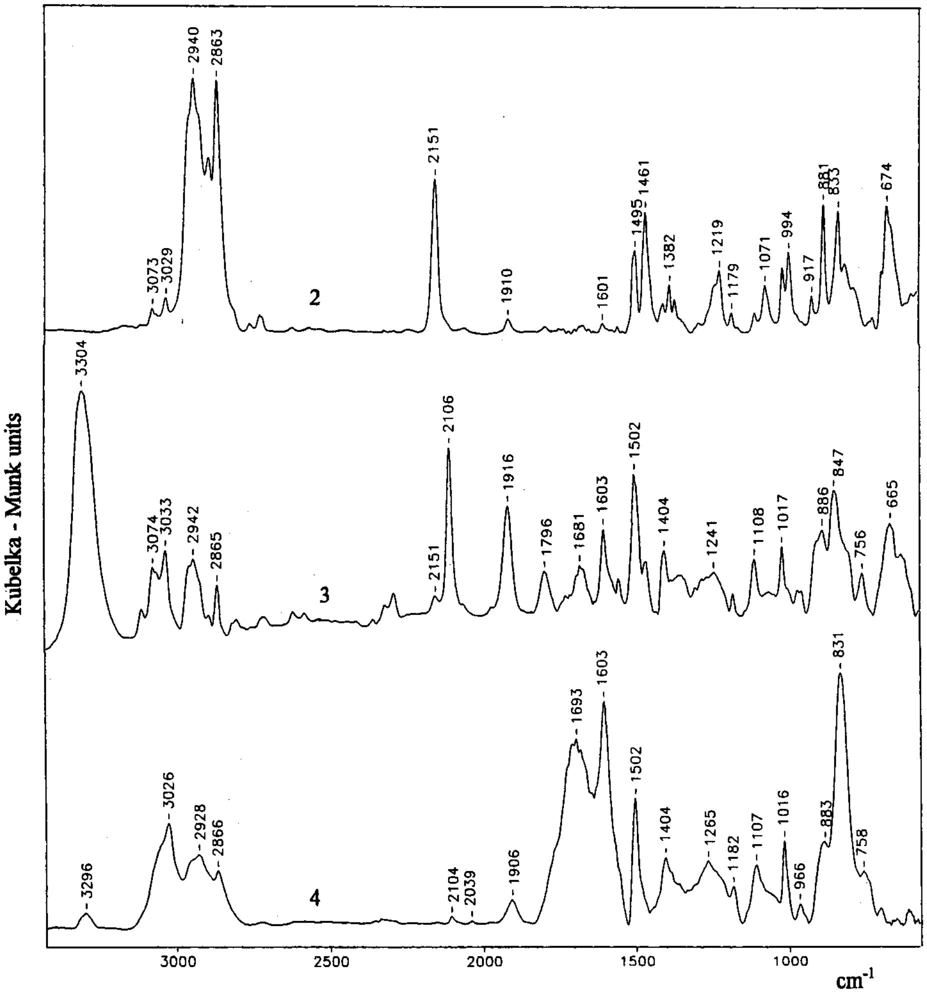

Figure 1. Infrared spectrum of polymers **2** and **3** and polymeric network **4**.

isolated in 79% yield as a yellow orange solid, poorly soluble in THF and insoluble in aromatic hydrocarbons and $CHCl_3$. The lack of solubility of polymer **3** prevented us from obtaining the corresponding ^1H and ^{13}C NMR spectra. The SEC trace of polymer **3** was unimodal, as that of **2** and provided values of $\langle M\rangle_w = 83\ 000$ and $\langle M\rangle_n = 31\ 000$ g mol^{-1}. No oligomers resulting from a chain cleavage were detected. The presence of terminal ethynyl groups is evidenced in vibrational spectra of **3** (Figures 1 and 2), by the absence of the absorption band of **2** (C≡CSi) at 2153 cm^{-1} (IR) and 2157 cm^{-1} (Raman), and by occurrence of ν (≡C—H) band at 3293 cm^{-1} (IR) and ν (C≡CH) at 2108 cm^{-1} (IR) and 2111 cm^{-1} (Raman). The desilylation of the triple bond is further evidenced by the disappearance of the ν (C—H) bands of isopropyl groups in the region from 2800 to 3000 cm^{-1} (IR, Raman). The Raman band of the skeletal ν (C=C) mode of π-conjugated sequences is found at 1578 cm^{-1} (shoulder at 1544 cm^{-1}) in the spectrum of **3**. Moreover, the UV/vis spectrum of **3** exhibits absorptions reaching 500 nm, similar to that of **2**, proving the presence of long π-conjugated sequences in the polymer. The above observations showed that the deprotection reaction was virtually quantitative and the main-chain linearity and the π-conjugation remained intact.

2. Thermal Properties and Cross-Linking Reactions. TGA (thermogravimetric analysis) spectra obtained for polymers **2** and **3** as well as DSC (differential scanning calorimetry) spectrum for polymer **3** are shown in Figure 3.

Polymer **2**, carrying protected ethynyl groups, started to decompose at 286 °C (curve a). An initial rapid weight loss was slowed after the temperature exceeded the value of 550 °C. The weight loss of 60%, achieved at 760 °C, slightly exceeded the weight fraction of Si^iPr_3 groups in polymer **2** (56%). On the other hand, the deprotected polymer **3** started to decompose only above 370 °C (2% weight loss) and the final weight loss at 760 °C is 13.5% (curve b). DSC spectrum for polymer **3** (Figure 2, curve c) exibited a strong exothermic peak starting at 148 °C, reaching maximum at 211 °C, and ending at 305 °C. Thus, the exotherm occurred in the temperature range in which no loss of weight has been observed for polymer **3** (see TGA curve b). In contrast, no exotherm was detected for the polymer **2**. This clearly proves that the exothermic process underlying the DSC peak observed for polymer **3** is related to the presence of terminal triple bonds in this polymer. The repeated DSC analysis of the same sample of **3**, performed after scanning up to 320 °C and cooling to room temperature, did not show any exotherm. This strongly suggests that the anticipated irreversible cross-linking reaction of terminal ethynyl groups took place during the first heating cycle.

For spectroscopic investigation, a sample of cross-linked polymer **4** was prepared by heating the polymer **3** to 300 °C over 1 h under a nitrogen atmosphere. The very poor solubility of the polymer **4** prevented us from investigating the ^1H and ^{13}C NMR spectroscopy. However, the infrared spectroscopy showed clearly the disappearance of the very intense vibration at 3292 cm^{-1}

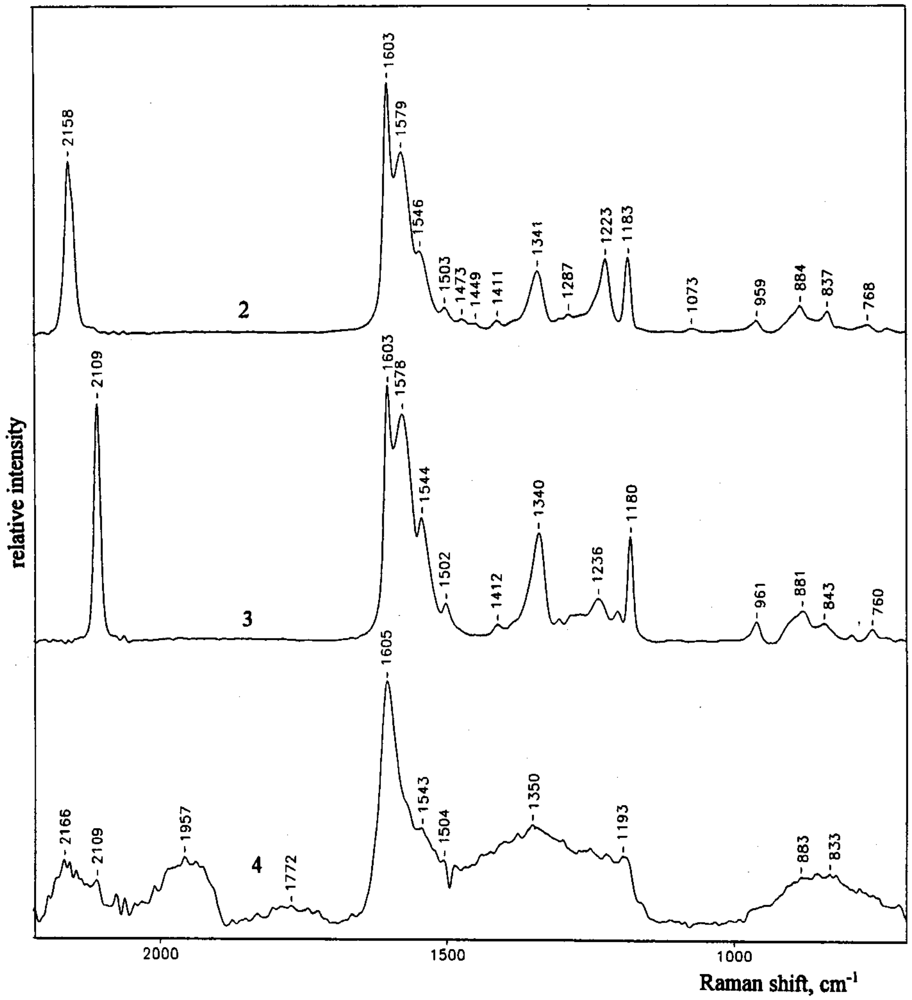

Figure 2. Raman spectrum of polymers **2** and **3** and polymeric network **4**.

(≡C—H), indicating the complete reaction of all terminal acetylene groups. The generation of ene–yne structure by the curing of acetylenic compound was already described.[19] By comparison with the infrared data of the 1,4-diphenyl-1-buten-3-yne[20] (3041, 3010, 1605, 1471, and 843 cm^{-1}), the two new strong absorptions at 1606 and 823 cm^{-1} observed for the product **4** strongly suggest the formation of ene–yne fragments —C=C—C≡C— during the cross-linking reaction. This interchain cross-linking (Scheme 1) is in agreement with the complete insolubility of product **4** in common solvents. However, an intrachain cross-linking via a zip-closing mechanism could be also possible if several acetylenic groups are close to each other. For such an interchain cross-linking there is no mass loss expected, and the resulting polymer **4** is fully conjugated. In Raman spectroscopy, the absorptions of the phenyl ring and of the conjugated poly-enyl chain at 1650–1500 cm^{-1} indicated that the π-conjugation was not affected by the cross-linking process.

Conclusion. The above results show that the new polyphenylacetylene **3** containing terminal acetylenic group is a good and well-defined precursor to provide cross-linked conjugated system, without evolution of volatiles. The easy access to the monomer **1** and the high selectivity and yield of polymerization and desilylation reactions represent an efficient way to obtain this new functionalized polymer **3**, which cannot be obtained directly, via the polymerization of the 1,4-diethynylbenzene.

Experimental Section. Characterization. IR spectra were performed with the use of an FTIR Nicolet 21 spectrometer and the diffuse reflectance technique with nondiluted, powdered samples (128 scans at 4 cm^{-1} resolution). FT Raman spectra were acquired on a Bruker IFS 55/S Equinox spectrometer fitted with quartz beam splitter and equipped with FRA 106/S FT-Raman module with a liquid nitrogen-cooled germanium detector. The defocused 1064-nm line of an air-cooled Nd:YAG near-IR laser (coherent) was used to excite spectra. All samples were excitated in 180° arrangement with the laser power at the sample less than 30 mW. The spectra were collected with 4 cm^{-1} resolution; 256 scans were co-added for one spectrum. The following abreviations are used to describe peak patterns where appropriate: s, strong; br, broad; m, medium; w, weak. UV/vis optical absorption spectra were recorded on a Hewlett-Packard 8452 diode-array spectrometer using quartz cuvettes (0.2 cm) and fresly distilled THF. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DSX 200 NMR spectrometer, operating at 50.32 MHz for ^{13}C and 200.11 MHz for ^{1}H, using 4-mm broad band probe.

The TGA and DSC values were obtained with the use of a TGA 2950 thermogravimetric analyzer and a DSC 2010 differential scanning calorimeter of TA Instruments at a heating rate of 20 °C/min under N_2.

SEC measurements were made on a TSP (Thermo Separation Products) chromatograph equipped with a UV detector, operating at 254 nm. A series of two PL

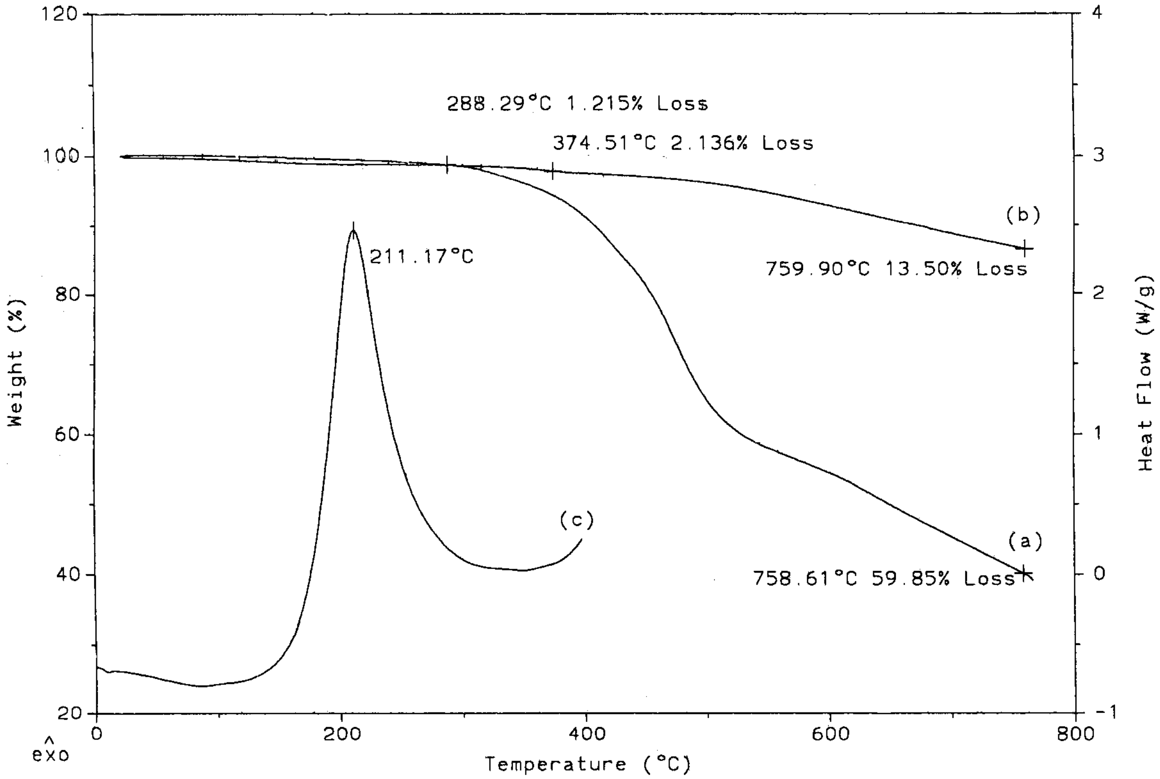

Figure 3. Thermic properties of polymers **2** (curve a, TGA) and **3** (curve b, TGA, and c, DSC)

gel columns (mixed bed B and mixed bed C, Polymer Laboratories, Bristol) and THF (flow rate 0.7 mL min^{-1}) were used. Molecular weight averages relative to polystyrene standards are reported.

Synthesis of the monomer **1** was described previously.[13] The catalyst $[Rh(cod)(\mu\text{-}OCH_3)]_2$ was prepared according to the Chatt procedure.[21] Purification of THF (Aldrich, 99.5%) as well as monitoring the polymerization by SEC are described elsewhere.[22,23]

Polymer 2. A solution of the catalyst $[Rh(cod))(\mu\text{-}OCH_3)]_2$ (20.5 mg, 0.042 mmol) in THF (4 mL) is added to a solution of the monomer 1-ethynyl-4-triisopropylsilylphenylacetylene **1** (0.606 g, 2.145 mmol) in 6 mL of THF. The mixture was stirred at room temperature for 1 h. The reaction mixture was then precipitated in MeOH. The methanol-insoluble polymer was isolated, washed with methanol and dried to a constant weight in a vacuum at room temperature. The drying gave a yellow powder: yield 0.473 g (78%). IR (KBr) ν (cm^{-1}): 2870−2964 (s, CH), 2153 (s, C≡CSi), 1469−1505 (s, C=C). Raman (KBr) ν (cm^{-1}): 2157 (s, C≡CSi), 1603−1540 (C=C). ^1H NMR (297 K, 200.11 MHz) δ (ppm): 6.48 and 7.13 (C_6H_4), 5.89 (H−C=), 1.10 (^iPr). $\{^1H\}^{13}C$ NMR (297 K, 50.32 MHz) δ (ppm): 142.5 and 132 (C=C), 139.5 and 122.2 (C ipso of C_6H_4), 127 and 131.8 (CH of C_6H_4), 107 (*C*≡CSi), 90.8 (C≡*C*Si), 18.68 (CH_3), 11.28 (CH). SEC (THF) M_w = 150 000; M_n = 31 000. UV−visible (THF, nm): 295, 450.

Polymer 3. Under N_2, a solution of tetrabutylammonium fluoride trihydrate in THF (0.055 g, 0.174 mmol) is added dropwise to a solution of the polymer **2** (0.198 g in 6.5 mL of THF). After addition was completed, the mixture was stirred at room temperature for 1 h. The reaction mixture was then precipitated in methanol, drop by drop. The methanol-insoluble polymer was isolated by filtration, washed by methanol, and dried to a constant weight in a vacuum at room temperature. The drying led to a yellow-orange powder: yield 0.057 g (79%). IR (KBr) ν (cm^{-1}): 3290 (s, ≡C−H), 2105 (m, C≡C), 1495−1602 (s, C=C). Raman (KBr) ν (cm^{-1}): 2107 (s, C≡C), 1603−1503 (s, C=C). SEC (THF) M_w = 83 000; M_n = 24 000. UV−visible (THF, nm): 285, 450.

Cross-Linked Network 4. The polymer **3** was heated at a rate of 20 °C/min to 300 °C and then maintained at 300 °C under N_2 for 30 min to provide a maroon powder of polymer **4**. IR (KBr) ν (cm^{-1}): 2105 (w, C≡C), 1606 (s, C=C), 823 (s, C=C). Raman (KBr) ν (cm^{-1}): 1600−1500 (s, C=C).

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