

Synthesis of Ferrocene-containing Polyacetylenes by Click Chemistry

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Ferrocene-containing polyacetylenes are synthesized in good yields by Cu-catalyzed click reactions of azido moieties of poly[(6-chloro-1-phenyl-1-hexyne)-*co*-(6-azido-1-phenyl-1-hexyne)] and poly{1-[4-azidohexyloxy]phenyl}-2-phenylacetylene} with ethynylferrocene. All the organometallic polymers are completely soluble in common organic solvents such as chloroform, THF and toluene. Spectroscopic analyses reveal that all the azido functional groups have cyclized with ethynylferrocene. With the incorporation of ferrocene rings into the polyacetylene structure, the resulting polymers show enhanced thermal stability and redox activity.

KEY WORDS: Azide; alkyne; click chemistry; ferrocene; polyacetylene

1. INTRODUCTION

Synthesis of organometallic macromolecules has attracted much attention among polymer scientists due to the unique magnetic, electronic, catalytic, sensoric and optical properties of the polymers and their potential applications in data storage and superconducting systems [1–6]. Much research has been done to attach different metal or metalloid units onto side and/or main chains of polymers. Ferrocene is probably the most widely used species for the construction of organometallic polymers [7–11] because of its ready availability, high stability, unique structure, and redox activity. The ring-opening polymerizations of silaferrocenophanes yield poly(ferrocenylsilene)s, which show an array of novel functional properties and have served as processable

polymer precursors to magnetic ceramics [12]. Polyacetylene is the best-known conjugated polymer and its functionalization has attracted much attention in recent years [13, 14]. Thanks to the enthusiastic efforts of polymer scientists, a variety of polyacetylenes carrying different functional pendants have been synthesized. Polyacetylenes containing metallic species have, however, been rarely synthesized [15] because metal-containing acetylenes are difficult to polymerize and/or their polymerizations generally give insoluble products.

1,3-Dipolar cycloadditions of azides with alkynes produce 1,4- and 1,5-disubstituted 1,2,3-triazoles [16]. The cycloadditions catalyzed by copper(I) complexes are known as “click reactions” because of their fast, mild conditions and high tolerance towards functional groups [17]. The regioselectivity of the reactions can be controlled to give only 1,4-disubstituted 1,2,3-triazoles. The click reactions have been successfully applied to macromolecular chemistry [18], surface modification of nanoparticles [19] and electrodes [20], hydrogels synthesis [21], construction of degradable network [22], etc. In this work, we utilized click chemistry for the synthesis of organometallic polyacetylenes.

This communication is dedicated to Professor Ian Manners and his scientific accomplishments

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2. EXPERIMENTAL

2.1. Materials and Instrumentations

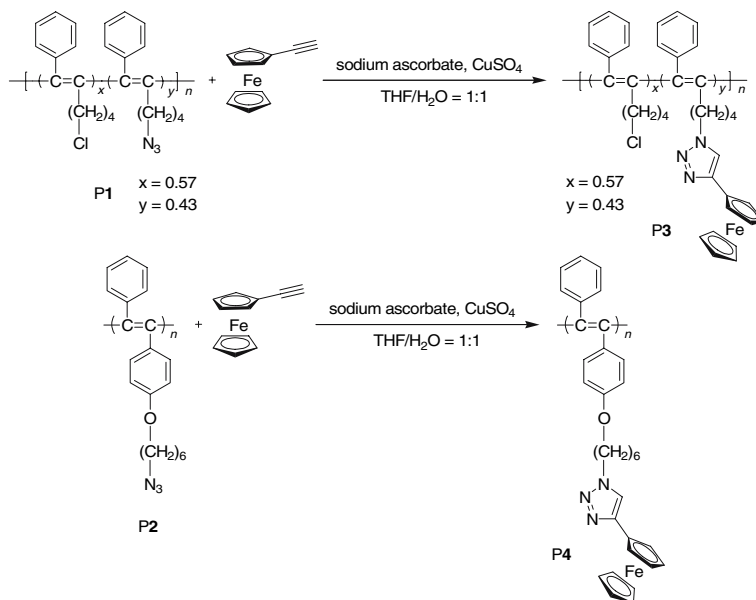
Azide-containing poly(1-phenyl-1-hexyne) **P1** (M_w 27800, M_w/M_n 1.8) and poly(diphenylacetylene) **P2** (M_w 15400, M_w/M_n 2.2) were prepared according to our previously published procedures [23]. Sodium ascorbate, copper(II) sulphate, and other reagents were all purchased from Aldrich and used as received without further purification. THF (Labskan) were distilled under nitrogen from sodium benzophenone ketyl under nitrogen immediately prior to use.

^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. Fourier transform IR spectra were taken on a Perkin-Elmer 16 PC spectrometer. Thermogravimetric analysis (TGA) was carried out on a Setaram thermogravimetric analyzer TGA 92 at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen. Molecular weights (M_w and M_n) and polydispersity indices (M_w/M_n) of the polymers were estimated by a Waters 510 gel permeation chromatography (GPC) system equipped with RI and UV detectors at room temperature. Degassed THF was used as eluent at a flow rate of 1.0 ml/min. A set of monodisperse polystyrenes covering the molecular weight range of 10^3 – 10^7 was used for the molecular weight calibration.

2.2. Click Reaction

The ferrocene-containing polyacetylenes were prepared by the click reactions of **P1** and **P2** with ethynylferrocene (Scheme 1). Typical experimental procedures for the synthesis of **P3** were given below.

Into a 25 ml Schlenk tube were added 0.37 g of **P1** (1.9 mmol) and 0.6 g of ethynylferrocene (2.9 mmol) in 10 ml of THF/ H_2O mixture (1:1 by volume). Aqueous sodium ascorbate solution (1 M; 0.19 ml, 0.19 mmol) and 0.09 ml of 1 M (0.09 mmol) aqueous copper(II) sulphate solution were then added. The mixture was stirred vigorously overnight. THF was evaporated and the crude product was dissolved in dichloromethane (DCM). The solution was washed with dilute ammonium hydroxide solution. The organic phase was added dropwise to 500 ml of hexane under stirring. The precipitate was allowed to stand overnight, filtered, and dried to a constant weight in a vacuum oven. A yellowish powder was obtained in 52.5% yield (0.25 g). M_w 31300, M_w/M_n 1.46 (GPC polystyrene calibration). IR (thin film), ν (cm^{-1}): 1822–1618 [ferrocene (Fc)], 877 (Fc), 819 (C–Cl stretching). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 8.01–5.98 (Ph–H and triazole–H), 4.71 (Fc–H), 4.50–4.23 (NCH₂ and Fc–H), 4.06 (Fc–H), 3.29 (CH₂Cl), 2.61–0.26 [(CH₂)₃]. ^{13}C NMR (300 MHz, CDCl_3), δ (ppm): 146.5, 140.3, 128.7, 127.5, 118.6, 75.5, 69.5, 68.6, 66.5, 49.9, 44.8, 32.9, 30.8, 24.7.



Scheme 1. Synthesis of ferrocene-containing polyacetylenes **P3** and **P4** by click reaction.

Polymer **P4** was prepared following the similar procedures described above. The polymer was purified by precipitation into methanol. A yellow powder was obtained in 33.2% yield (0.08 g). M_w 19000, M_w/M_n 1.85 (GPC polystyrene calibration). IR (thin film), ν (cm^{-1}): 1812–1632 (Fc), 877 (Fc). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.47 (Triazole-H), 7.18–6.34 (Ph-H), 6.30–5.73 (Ph-H), 4.71 (Fc-H), 4.48–4.17 (CH_2N and Fc-H), 4.06 (Fc-H), 3.72 (CH_2O), 2.19–1.79 (CH_2), 1.79–1.54 (CH_2), 1.54–1.13 (CH_2). ^{13}C NMR (300 MHz, CDCl_3), δ (ppm): 156.6, 146.6, 145.2, 143.6, 136.7, 131.8, 130.7, 128.4, 127.4, 126.3, 124.8, 118.8, 112.7, 75.5, 69.5, 68.6, 66.5, 50.1, 30.2, 29.1, 26.3, 25.5.

3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis

We prepared azide-containing polyacetylenes according to our previous established procedures [23]. Because the azide functionality is toxic to the transition-metal catalysts for the polymerizations of acetylenes, **P1** and **P2** were prepared by post-polymerization reactions of poly(6-chloro-1-phenyl-1-hexyne) and poly{1-[4-bromohexyl]phenyl}-2-phenylacetylene} with sodium azide. Owing to the difference in the strength of the halogen-carbon bond, **P1** is only partially substituted, whereas 100% substitution is achieved in **P2**. Cycloadditions of **P1** and **P2** with ethynylferrocene are catalyzed by sodium ascorbate and CuSO_4 in THF/ H_2O , which furnish **P3** and **P4** with solely 1,4-disubstituted triazoles rings in good yields.

3.2. Structural Characterization

The organometallic polyacetylenes are soluble in common solvents, which enable us to characterize their structures by standard spectroscopic methods. An example of the IR spectrum of **P4** is shown in Fig. 1; for comparison, its precursor **P2** is also shown in the same figure. The stretching vibration of the azido groups of **P2** is found at 2096 cm^{-1} , which completely disappears in the spectrum of **P4**. The overtone and combination bands of the ferrocenyl moieties in the range of $1818\text{--}1638\text{ cm}^{-1}$ as well as their vibration and the deformation bands at 1051 and 880 cm^{-1} are readily observed in **P4**, revealing that the click reaction has gone to completion.

Analysis by ^1H NMR spectroscopy further confirms that all the azido moieties in **P2** have been

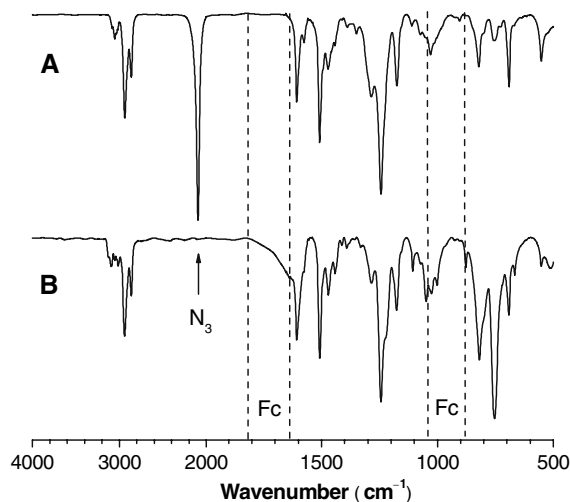


Fig. 1. IR spectra of (A) **P2** and (B) **P4**.

transformed to the 1,2,3-triazole units in **P4**. The spectrum of **P4** shows no peak at $\delta \sim 3.29$ associated with the resonance of the methylene protons next to the azido groups of **P2** (Fig. 2). Instead, new peaks corresponding to the resonances of the triazoles and ferrocene protons are observed at $\delta \sim 7.47$, 4.71, 4.23 and 4.05. No other unexpected signals are recorded, verifying that the molecular structure of the product

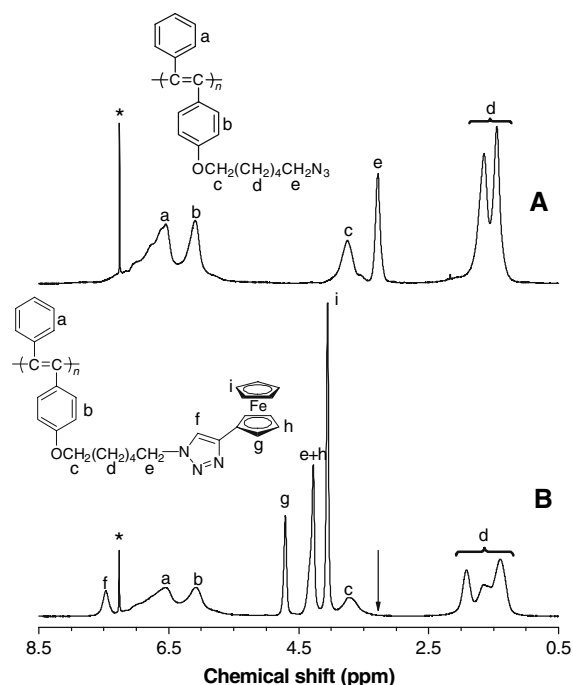


Fig. 2. ^1H NMR spectra of (A) **P2** and (B) **P4** in chloroform- d . The solvent peaks are marked with asterisks.

is indeed P4, as shown in Scheme 1. Because the methylene protons next to the chloro and azide moieties in P1 resonate at almost similar chemical shifts ($\delta \sim 3.3$), we had difficulty in calculating its azide content. However, after cycloaddition, the azide moieties are transformed to triazole rings, which largely deshield the resonances at the adjacent methylene protons to $\delta \sim 4.3$. By comparison between their integrals, the ferrocene content in P3 is determined to be $\sim 40\%$.

3.3. Physical Properties

All the polymers are thermally stable. Polymers P1 and P2 commence to lose their weights at a temperature (T_d) of $\sim 250^\circ\text{C}$, whereas their organometallic counterparts show superior performances ($T_d \sim 300^\circ\text{C}$; Fig. 3). Wrapping of the polymer chain by the bulky, stable ferrocenyl units should make the polymers resistant to thermolysis, which explains why P3 and P4 exhibit higher thermal stability. It is noteworthy that $\sim 40\%$ of weights are left for P3 and P4 after they have been pyrolyzed at 800°C . The pyrolysis products should contain iron nanoparticles and the polymers are thus promising candidates as precursors to magnetoceramic materials [11].

Due to the incorporation of ferrocene moieties into the macromolecular structure, the polyacetylenes become electrochemically active. Their redox behaviors are investigated by cyclic voltammeter. As can be

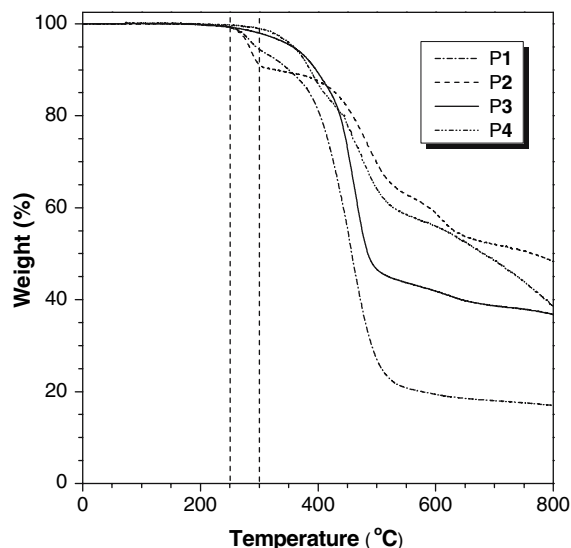


Fig. 3. TGA thermograms of P1–P4 measured under nitrogen at a heating rate of $20^\circ\text{C}/\text{min}$.

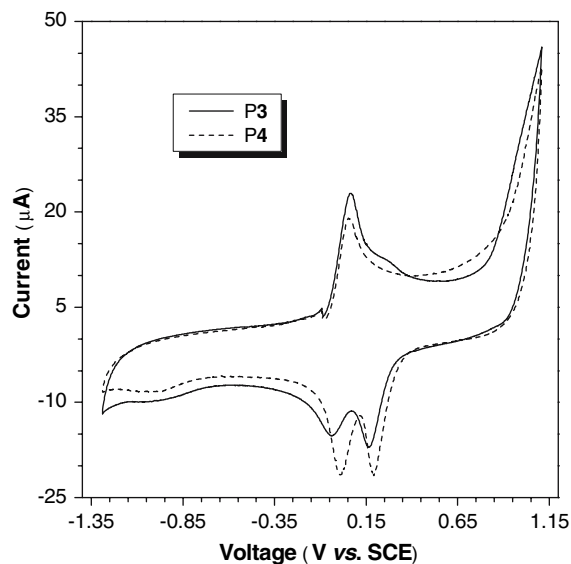


Fig. 4. Cyclic voltammograms of P3 and P4 in dichloromethane containing $0.2\text{ M } [(n\text{-Bu})_4\text{N}]\text{PF}_6$. Scan rate: 100 mV/s .

seen from Fig. 4, in the forward scan, P3 exhibits a single oxidation curve peaked at 0.05 V . In the reverse scan, two peaks at 0.15 and -0.05 V are observed. As the polymers possess electron-donating ferrocene and electron-deficient triazoles rings, the peak at 0.15 V may thus be due to charge transfer between the two species.

4. CONCLUSION

In this work, we have succeeded in synthesizing organometallic polymers by click reactions of the azido moieties of polyacetylenes with ethynylferrocene. The reactions rapidly proceeded to completion under mild conditions. The resultant polymers show good macroscopic processability, thermal stability, and electrochemical activity, demonstrating that this click methodology is a useful tool for endowing polyacetylenes with novel materials properties.

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