

# Synthesis and properties of PPE-type conjugated polymers containing tricarbonyl(arene)chromium unit in the main chain

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## Abstract

Novel  $\pi$ -conjugated polymers containing  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  in the main chain based on poly(*p*-phenylene-ethynylene) were prepared by the Sonogashira coupling reaction of  $\eta^6\text{-(1,4-diethynylbenzene)}$ tricarbonylchromium with 1,4-diiodo-2,5-dialkoxybenzenes. The polymers were soluble in common organic solvents and characterized by NMR and FT-IR spectra. The polymers exhibited an absorption maximum at around 390 nm, which showed a red shift of approximately 30 nm compared to that of the model compound. Cyclic voltammogram showed a single reversible oxidation peak derived from the  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  unit. © 2004 Elsevier B.V. All rights reserved.

**Keywords:**  $\pi$ -Conjugated polymer; Poly(*p*-phenylene-ethynylene); Tricarbonyl(arene)chromium; Redox activity

## 1. Introduction

Poly(phenylene-ethynylene)s, PPEs, are an important class of  $\pi$ -conjugated polymers and promising materials in such applications as molecular wires, sensors, and light-emitting devices [1]. The first soluble PPE was synthesized successfully by Giesa and Schultz [2] through the attachment of a long alkoxy side chain to the rigid rod of the PPE backbone. One particularly significant recent research activity regarding PPEs has focused on tuning the spectral and electrical properties of  $\pi$ -conjugated polymers based on PPE. Among them, conjugated polymers containing transition metal complexes are of increasing interest [3] because they not only provide an enormous opportunity to easily change the physical properties of the resulting materials by exchange of a ligand coordinated to the metal center, but can also be converted to various kinds of functional organic polymers by means of polymer reactions. In addition, since the first report of the synthesis of organometallic PPEs by Wright [4], several PPEs including transition metals have been synthesized and showed

attractive properties such as redox activity [5,6] and liquid crystallinity [7,8].

On the other hand, it is well known that the tricarbonylchromium fragment,  $\text{Cr}(\text{CO})_3$ , has the characteristic of strongly withdrawing electrons and activates the coordinated arene ligand toward nucleophilic substitution [9–11]. Namely, the tricarbonyl(arene)chromium complex,  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ , can act as an electron acceptor, since the electron density of coordinated arenes to a  $\text{Cr}(\text{CO})_3$  unit is highly deficient. Furthermore, there has also been much interest in  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  complexes due to their redox activity [12–15], ligand exchange reaction [16], possible application in nonlinear optical molecules [17], and catalysts [18]. However, little research has been performed regarding the synthesis of a conjugated polymer containing a  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  unit in the main chain [4,19–21]. Wright [4] reported the first synthesis of PPE including a  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  moiety in the main chain by means of the Stille coupling reaction of  $(\eta^6\text{-1,4-dichlorobenzene})\text{Cr}(\text{CO})_3$  with organostannane reagents. According to TGA analysis, these polymers showed thermal stability; however, they showed low solubility in common organic solvents. Recently, we reported the first soluble  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ -containing  $\pi$ -conjugated polymers by the Sonogashira coupling reaction (for PPE) [22] or the

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Horner–Emmons–Wadsworth coupling reaction (for PPVs) [23,24], which showed redox activity and conductivity. In this paper, the synthesis of soluble PPE-type  $\pi$ -conjugated polymers containing a ( $\eta^6$ -arene)-Cr(CO)<sub>3</sub> unit in the main chain catalyzed by palladium is described, and their optical, electrochemical, and thermal properties are discussed.

## 2. Results and discussion

Monomers **1** [25] and **2a–c** [26] were prepared according to the synthesis procedures previously published. In order to enhance the solubility of the resulting polymers, monomers **2a–c** having long alkoxy chains were synthesized. Subsequently, equimolar amounts of **1** and **2** were reacted in a catalytic system [27] using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI in THF–HNPr<sub>2</sub><sup>i</sup> at 60 °C for 24 h, as shown in Scheme 1. For capping of the polymer ends, small amounts of ethynylbenzene were added to the solution, and the reaction mixture was stirred for an additional 2 h. After the work-up procedures, for example, polymer **3c** was obtained in 90% isolated yield with a number-average molecular weight of 22 800 and a polydispersity of 2.8 determined by gel permeation chromatography (CHCl<sub>3</sub> eluent, polystyrene standards). Polymer **4** (Chart 1) without a Cr(CO)<sub>3</sub> fragment as the reference polymer was prepared using the same coupling reaction. The results of polymerization are summarized in Table 1. The longer substituted alkoxy side chain gave the higher molecular weight polymer, because the long alkoxy group can increase the solubility of high molecular weight polymer. The reaction of **1** with **2a** gave a low molecular weight polymer **3a** ( $M_n = 2900$ ) due to the formation of insoluble high molecular weight products. The obtained polymers had good solubility in common organic solvents, such as THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and toluene.

The structure of the polymers was confirmed by <sup>1</sup>H NMR and FT-IR spectroscopies. The <sup>1</sup>H NMR spectrum of **3c** in CDCl<sub>3</sub> solution displayed the aromatic proton peaks coordinated to Cr(CO)<sub>3</sub> moieties at 5.6 ppm (Fig. 1). The protons of dialkoxybenzene appeared at 7.0 ppm. In addition, the peaks at around 7.4 ppm were derived from the end-capped phenyl groups as well as aromatic protons of phenylene units by the thermal-

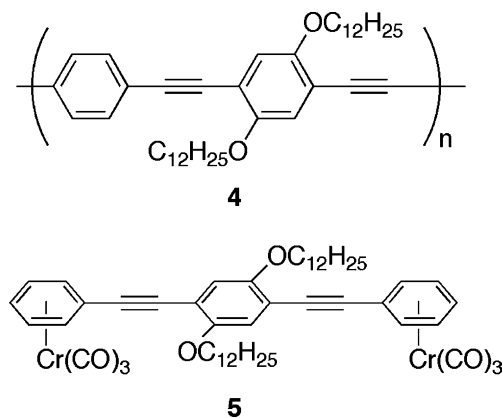


Chart 1.

Table 1  
The results of polycondensation of **1** with **2a–c**

| Polymer              | R       | Yield (%) <sup>a</sup> | $M_n^b$ | $M_w^b$ | $M_w/M_n^b$ |
|----------------------|---------|------------------------|---------|---------|-------------|
| <b>3a</b>            | butyl   | 63                     | 2900    | 7100    | 2.4         |
| <b>3b</b>            | octyl   | 80                     | 8400    | 18 000  | 2.2         |
| <b>3c</b>            | dodecyl | 90                     | 22 800  | 63 700  | 2.8         |
| <b>4<sup>c</sup></b> | dodecyl | 95                     | 11 300  | 24 800  | 2.4         |

<sup>a</sup> Isolated yield.

<sup>b</sup> GPC (CHCl<sub>3</sub>), polystyrene standards.

<sup>c</sup> Without Cr(CO)<sub>3</sub>.

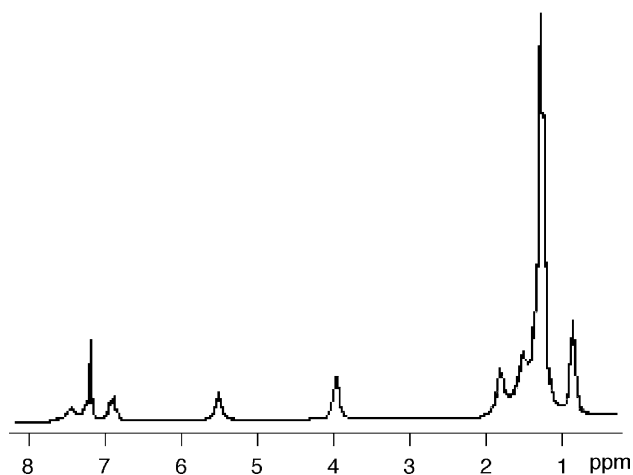
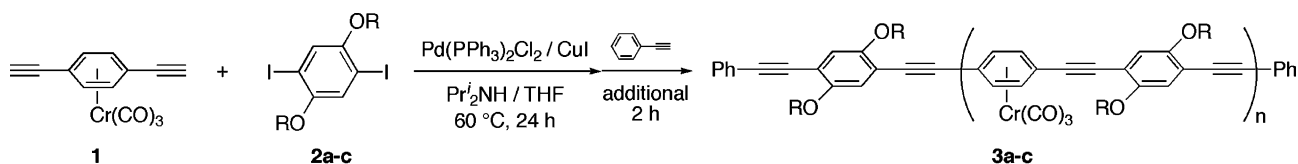


Fig. 1. <sup>1</sup>H NMR spectrum of **3c** in CDCl<sub>3</sub>.



**a** R = butyl, **b** R = octyl, **c** R = dodecyl

Scheme 1.

or photo-dissociation of  $\text{Cr}(\text{CO})_3$  moieties. This result indicates that **3c** consists of 65% chromium-coordinated phenylene and 35% normal phenylene units as determined by calculation from a proton integral ratio. The disappearance of the alkyne proton peaks at 3.0 ppm confirmed complete polymerization. In the IR spectrum (Fig. 2), **3c** showed characteristic absorption bands at 1970 and 1906  $\text{cm}^{-1}$  (stretching vibrations of coordinated carbon monoxide), and at 2218  $\text{cm}^{-1}$  corresponding to the weak stretching vibrations of the internal carbon–carbon triple bond.

The optical properties of the polymer obtained were investigated by UV–Vis absorption measurement in  $\text{CHCl}_3$  solution at room temperature, and the spectra are shown in Fig. 3. The absorption maxima of the polymer **3c** corresponding to the  $\pi$ – $\pi^*$  transition in the conjugated polymer backbone were observed at 321 nm ( $\log \epsilon = 4.23$ ) and 396 nm ( $\log \epsilon = 4.25$ ), respectively. On the other hand, the model compound **5** (Chart 1) was prepared, and its UV–Vis absorption spectrum is also shown in Fig. 3. The UV–Vis spectrum of **5** in  $\text{CHCl}_3$  solution exhibited a  $\pi$ – $\pi^*$  transition band similar to those of the polymers, and the absorption maxima at 306 nm ( $\log \epsilon = 4.61$ ) and 363 nm ( $\log \epsilon = 4.53$ ), respectively. This result indicates the effective extension of  $\pi$ -delocalization length through the polymer chain. Furthermore, **5** showed the MLCT band in the (arene) $\text{Cr}(\text{CO})_3$  moiety at around 420 nm ( $\log \epsilon = 4.11$ ), while **3c** exhibited a broadened  $\pi$ – $\pi^*$  transition band which covered the MLCT band.

The polymers **3a–c** displayed emission peaks at around 440 nm in the visible blue region; the results are listed in Table 2. However, these polymers exhibited low emission efficiency in  $\text{CHCl}_3$  solution, and their photoluminescence (PL) quantum yields ( $\Phi_{\text{PL}}$ ), which were determined relative to 9-anthracenecarboxylic acid in

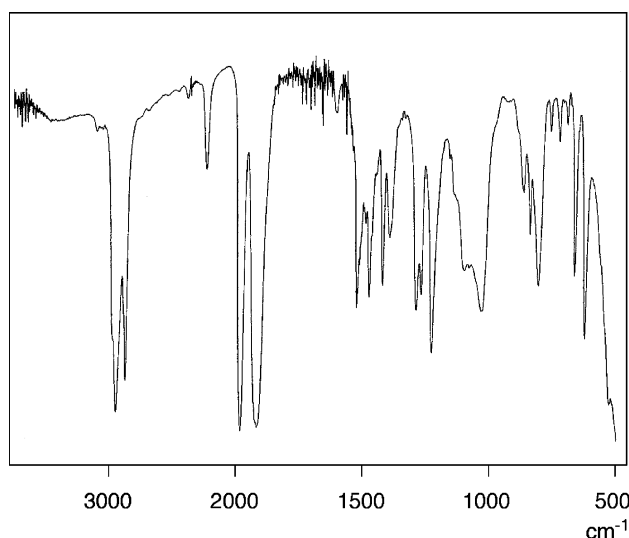


Fig. 2. IR spectrum of **3c** (KBr).

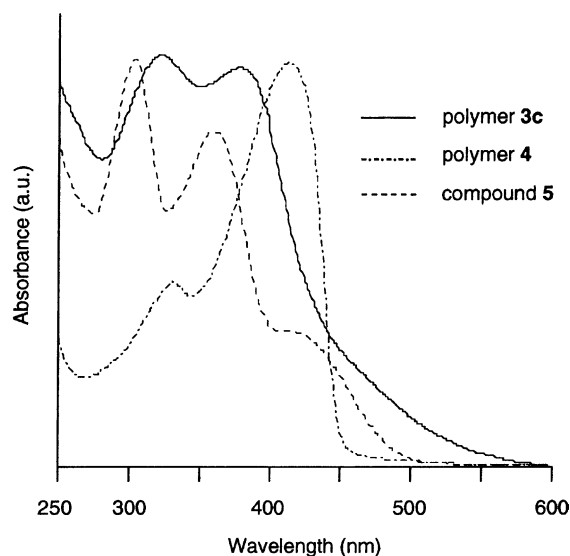


Fig. 3. UV–Vis absorption spectra of **3c**, **4**, and **5**.

Table 2  
Optical properties of the polymers<sup>a</sup>

| Polymer              | Absorption ( $\log \epsilon$ ) (nm) | Emission <sup>b</sup> (nm) | $\Phi^c$ |
|----------------------|-------------------------------------|----------------------------|----------|
| <b>3a</b>            | 322 (4.18) 382 (4.34)               | 438                        | 0.08     |
| <b>3b</b>            | 328 (4.13) 382 (4.34)               | 443                        | 0.14     |
| <b>3c</b>            | 321 (4.23) 396 (4.25)               | 443                        | 0.02     |
| <b>4<sup>d</sup></b> | 332 (4.09) 410 (4.34)               | 445                        | 0.42     |

<sup>a</sup> In  $\text{CHCl}_3$  at room temperature.

<sup>b</sup> Excited at the absorption maximum.

<sup>c</sup> Fluorescence quantum efficiencies.

<sup>d</sup> Without  $\text{Cr}(\text{CO})_3$ .

$\text{CH}_2\text{Cl}_2$  as a standard [28], were 0.02–0.14 (Table 2). While the polymer **4** showed moderate quantum yield ( $\Phi_{\text{PL}} = 0.42$ ), the emissions of **3a–c** were highly quenched by the presence of  $\text{Cr}(\text{CO})_3$ . This result implies that intramolecular charge transfer between the coordinated  $\text{Cr}(\text{CO})_3$  unit and the conjugated polymer chain occurs in the excited state.

Measurement of thermogravimetric analysis (TGA) was carried out for **3c** and **4** under nitrogen at a heating rate of 10  $^\circ\text{C min}^{-1}$  (Fig. 4). In the case of **3c**, pyrolysis took place in two steps. The first step started at 210  $^\circ\text{C}$  and was attributed to the liberation of carbon monoxide from the chromium center, while the second step started at around 300  $^\circ\text{C}$  and was attributed to the decomposition of the polymer backbone. The polymer **4** showed a high decomposition temperature stable up to approximately 370  $^\circ\text{C}$  under the same conditions. Both **3c** and **4** gave similar curves except for the first decomposition of the  $\text{Cr}(\text{CO})_3$  unit in the polymer **3c**. In addition, the weight loss of this first step, i.e., the escape of carbon monoxide in **3c**, is in close agreement with the calculated

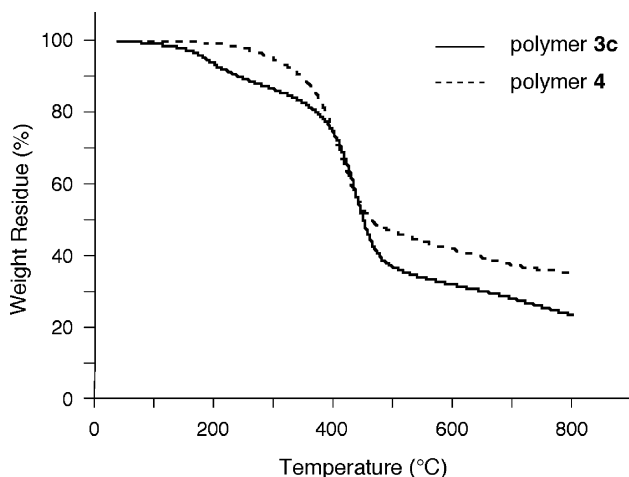


Fig. 4. TGA curves of **3c** and **4** under nitrogen ( $10\text{ }^\circ\text{C min}^{-1}$ ).

value of the amount of carbon monoxide incorporated in **3c**.

On the other hand, the photolysis of the polymers **3a–c** was investigated in the solution state. Tricarbonylchromium groups could be removed completely by irradiation from a high pressure UV lamp for 20 min (Scheme 2). In the  $^1\text{H}$  NMR spectrum of the resulting polymer after work-up, a peak at 5.6 ppm, i.e., aromatic proton peaks coordinated to the  $\text{Cr}(\text{CO})_3$  unit, disappeared completely, and its spectrum was consistent with that of the polymer **4**.

The electrochemical redox behavior of the polymer **3c** was studied using cyclic voltammetry. The measurement was performed in  $\text{CH}_2\text{Cl}_2$  solution containing  $1.5 \times 10^{-5}$  M of the polymer unit and 0.1 M of  $^n\text{Bu}_4\text{NPF}_6$  at a scan rate of  $100\text{ mV s}^{-1}$ . As shown in Fig. 5, **3c** showed a single broad reversible oxidation peak at 1.07 V vs.  $\text{Ag}/\text{Ag}^+$ , while no oxidation peaks appeared for the polymer **4** under the same conditions. These results indicate that this reversible wave could be attributed to the  $\text{Cr}(0)/\text{Cr}(\text{I})$  and  $\text{Cr}(\text{I})/\text{Cr}(0)$  system.

In summary, novel  $\pi$ -conjugated polymers containing  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  in the main chain based on PPE were synthesized using the Sonogashira coupling reaction. The polymers were soluble in common organic solvents and characterized by NMR and FT-IR spectra. The polymer **3c** exhibited an absorption maximum at 396 nm, which showed a red shift of 30 nm compared to that of the model compound **5**. According to the TGA analysis, the initial decomposition step of polymer **3c**

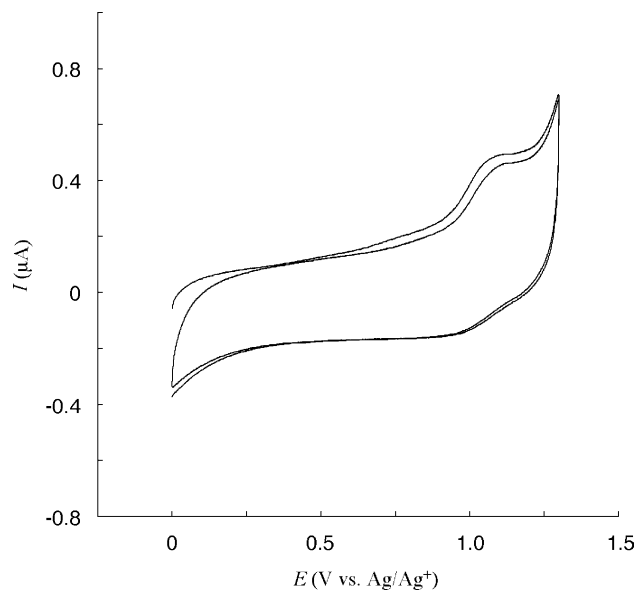
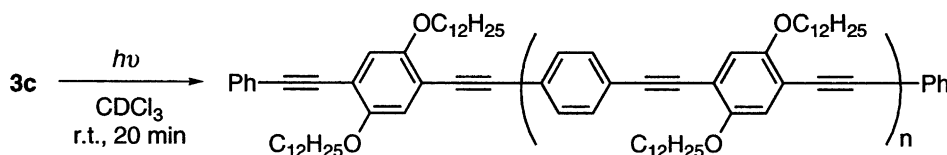


Fig. 5. Cyclic voltammogram of **3c** in  $\text{CH}_2\text{Cl}_2$  solution containing  $1.5 \times 10^{-5}$  M of the polymer unit and 0.1 M of  $^n\text{Bu}_4\text{NPF}_6$  using Pt electrode (vs.  $\text{Ag}/\text{Ag}^+$ ) at the sweep rate of  $100\text{ mV s}^{-1}$ . First and second cycles are shown.

showed a loss of carbon monoxide coordinated to the chromium center. Cyclic voltammogram showed a single reversible oxidation peak derived from the  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  unit. Further studies on the synthesis and properties of novel  $\pi$ -conjugated polymers possessing not only a  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  unit but a  $(\eta^6\text{-arene})\text{M}(\text{CO})_3$  unit ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) are now underway.

### 3. Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respectively. Samples were analyzed in  $\text{CDCl}_3$ , and the chemical shift values were expressed relative to  $\text{Me}_4\text{Si}$  as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-Vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in  $\text{CHCl}_3$  at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in  $\text{CHCl}_3$  at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L col-



Scheme 2.

umn) using  $\text{CHCl}_3$  as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument ( $10^\circ\text{C min}^{-1}$ ). Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer in  $\text{CH}_2\text{Cl}_2$  solution of  $0.1\text{ M } n\text{Bu}_4\text{NPF}_6$  as a supporting electrolyte. Platinum wire auxiliary electrode and  $\text{Ag}/\text{AgCl}$  RE-5 reference electrode were used in the CV measurement.

### 3.1. Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Diisopropylamine was distilled from KOH under nitrogen.  $\text{Cr}(\text{CO})_6$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ , CuI, ethynylbenzene, and diiodobenzene were obtained commercially, and used without further purification. ( $\eta^6$ -1,4-Diethynylbenzene)tricarbonylchromium (**1**) [25], 1,4-diiodo-2,5-dialkoxybenzenes (**2a–c**) [26], ( $\eta^6$ -ethynylbenzene)tricarbonylchromium [29], and polymer **4** [30] were prepared as described in the literature.

### 3.2. Polymerization

A typical procedure is as follows. A 50 ml Pyrex flask was charged with **1** (52 mg, 0.20 mmol), **2c** (140 mg, 0.20 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (14 mg, 0.020 mmol), CuI (6.0 mg, 0.030 mmol), THF (2.0 ml),  $\text{HNPr}_2^i$  (2.0 ml), and a stirring bar under a flow of nitrogen. The reaction was carried out at  $60^\circ\text{C}$  for 24 h with stirring under a nitrogen atmosphere, and then ethynylbenzene (10 mg, 0.10 mmol) was added. The mixture was stirred for additional 2 h. After filtration of the precipitated ammonium salt, the filtrate was concentrated and dried in vacuo. The residue was dissolved in  $\text{CHCl}_3$  and poured into a large amount of MeOH to obtain the corresponding polymer **3c** in 90% yield (133 mg, 0.18 mmol) as a brown powder.

Polymer **3a**, yield 62%,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  0.89 (br, 6H), 1.20–1.47 (m, 8H), 2.61 (br, 4H), 4.00 (br, 4H), 5.47 (br, 3.2H), 6.99 (s, 2H), 7.54 (br, 0.8H). IR (KBr): 2202, 1970, 1899  $\text{cm}^{-1}$ .

Polymer **3b**, yield 80%,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  0.87 (br, 6H), 1.20–1.62 (m, 14H), 2.69 (br, 4H), 4.01 (br, 4H), 5.55 (br, 2.6H), 7.08 (s, 2H), 7.48 (br, 1.4H). IR (KBr): 2206, 1972, 1908  $\text{cm}^{-1}$ .

Polymer **3c**, yield 90%,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  0.88 (br, 6H), 1.27–1.54 (m, 36H), 1.85 (br, 4H), 4.03 (br, 4H), 5.57 (br, 3.2H), 7.06 (s, 2H), 7.53 (br, 0.8H). IR (KBr): 2218, 1970, 1906  $\text{cm}^{-1}$ .

### 3.3. Synthesis of the model compound **5**

A 50 ml Pyrex flask was charged with ( $\eta^6$ -ethynylbenzene)tricarbonylchromium [29] (100 mg, 0.42 mmol), **2c** (140 mg, 0.20 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (14 mg, 0.020

mmol), CuI (6.0 mg, 0.030 mmol), THF (4.0 ml),  $\text{HNPr}_2^i$  (2.0 ml), and a stirring bar under a flow of nitrogen. The reaction mixture was refluxed for 6 h with stirring under a nitrogen atmosphere. After cooling, the precipitated ammonium salts were filtered off. The filtrate was evaporated and the residue was purified by recrystallization from pentane/ $\text{CH}_2\text{Cl}_2$  to provide 95 mg (0.10 mmol, 52%) of **5** as a yellow solid.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  0.86 (t,  $J = 5.9$  Hz, 6H), 1.78 (m, 36H), 3.99 (t,  $J = 5.4$  Hz, 4H), 5.31 (m, 6H), 5.53 (d,  $J = 4.6$  Hz, 4H), 6.94 (s, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  14.2, 22.7, 26.0, 29.4, 29.7, 31.9, 69.6, 90.7, 91.2, 94.9, 114.1, 117.0, 132.7, 153.9, 232.0. IR (KBr): 2210, 1967, 1890  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{52}\text{H}_{62}\text{O}_8\text{Cr}_2$ : C, 67.96; H, 6.80. Found: C, 67.42; H, 7.07%.

### 3.4. Photolysis of the polymer **3c**

A mixture of the polymer **3c** (2.0 mg,  $2.7\ \mu\text{mol}$ ) and  $\text{CDCl}_3$  (0.75 ml) was placed in a NMR tube and irradiated by a 400 W high pressure mercury lamp. This sample was analyzed by  $^1\text{H NMR}$  at intervals of 5 min, and the dissociation of chromium moieties was completed after 20 min.  $^1\text{H NMR}$  spectrum was in agreement with that of the polymer **4**.

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