Received: 15 July 2009

Revised: 11 October 2009

(www.interscience.com) DOI 10.1002/aoc.1593

Accepted: 26 October 2009

Published online in Wiley Interscience: 22 January 2010

pplied Irganometallic

hemistry

Synthesis of π -conjugated polymers via regioregular organometallic polymers 2. Transformation of titanacyclopentadienecontaining polymer into poly(*p*-phenylene) derivative

Tomoko Kino, Hiroki Nishiyama and Ikuyoshi Tomita*

The transformation of a regioregular organometallic polymer possessing titanacyclopentadiene-2,5-diyl units into a poly(*p*-phenylene) derivative by means of a novel polymer reaction method is described. The organotitianium polymer was prepared by the polymerization of 1,4-diethynyl-2,5-dioctyloxybenzene and a low-valent titanium complex, generated *in situ* from titanium(IV) isopropoxide and isopropylmagnesium chloride, and was subjected to the reaction with 3-bromo-1-propyne followed by the protonation. Consequently, a polymer consisting of the substituted phenylene-1,4-diyl units could be produced in a high yield, which is soluble in organic solvents such as chloroform. The number-average molecular weight and the molecular weight distribution of the polymer were estimated as 4800 and 1.8, respectively (GPC, polystyrene). The UV-vis absorption spectrum of the polymer exhibited the absorption maximum (λ_{max}) at 329 nm, which was bathochromically shifted by 53 nm compared with that of a model compound, 1,4-bis(2-methoxyphenyl)-2-methylbenzene ($\lambda_{max} = 276$ nm). Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: organometallic polymer; π -conjugated polymer; polymer reaction; poly(p-phenylene)

Introduction

Organometallic polymers have been extensively studied with expectation of their diverse applications to advanced functional materials.^[1] In addition, polymers possessing reactive carbon-metal bonds are attractive candidates of reactive polymers that serve as synthetic precursors for functional organic and/or inorganic polymers applicable to many research fields. In particular, organometallic polymers possessing reactive functions in the main chain are attractive for attaining novel macromolecular design of the target polymers with unique functions in the main chain. Recently, polymers containing reactive organometallic building blocks such as organoboron,^[2] cobaltacyclopentadiene,^[3] zirconacyclopentadiene,^[4] titana $cyclobutene^{[5]}$ and $titanacyclopentadiene^{[6,7]}$ in the main chain have been prepared and they have been applied as powerful synthetic precursors for main chain functionalized materials. Through our studies on the reactive organometallic polymers, it turned out that the control of regioregularity of the main chain connection at each metallacycle unit is an important point to obtain novel functional materials such as π -conjugated polymers via the reactive polymers. Previously, we reported the synthesis of a regioregular organotitanium polymer (3) by the regiospecific metallacyclization of a diethynylbenzene derivative (1) and a low-valent titanium complex (2), generated in situ from titanium(IV) isopropoxide [Ti(OPr')₄] and isopropylmagnesium chloride ('PrMgCl), and the polymer was converted into novel π -conjugated polymers containing 1,3-butadiene-1,4-diyl units (4) (Scheme 1).^[7]

In the course of our studies to evaluate the reactivity of the organotitanium polymer (**3**) and to determine the possibility of preparing π -conjugated materials possessing diverse main chain functionality, we describe here the transformation into poly(*p*-phenylene) derivative (**4**) using 3-bromo-1-propyne as a reagent for the polymer reaction (Scheme 2). Properties of the poly(*p*-phenylene) derivative obtained in the present method are also discussed.

Experimental

Materials

A diethyl ether solution of ^{*i*}PrMgCl was prepared from 2-chloropropane and magnesium in diethyl ether. $Ti(OPr^i)_4$ was distilled and stored under argon. 1,4-Dioctyloxybenzene was prepared from hydroquinone and 1-bromooctane and purified by recrystallization from ethanol. 3-Bromo-1-propyne was distilled under argon. Diethyl ether was dried over sodium benzophenone

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatuta-cho 4259-G1-9, Midori-ku, Yokohama 226-8502, Japan

^{*} Correspondence to: Ikuyoshi Tomita, Tokyo Institute of Technology, Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Nagatsuta-cho 4259-G1-9, Midori-ku, Yokohama 226-8502, Japan. E-mail: tomita@echem.titech.ac.jp



Scheme 1. Synthetic route for diene-containing π -conjugated polymers (**4**).



Scheme 2. Synthetic route for a poly(p-phenylene) derivative (5) by the reaction of 3 with 3-bromo-1-propyne.

ketyl and distilled under argon. All reagents used for precipitation and analyses were used without further purification.

Instrumentation

Nuclear magnetic resonance spectra were obtained on a Jeol ECP300 spectrometer (300 and 75 MHz for ¹H NMR and ¹³C NMR, respectively). Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS liquid chromatograph equipped with Tosoh TSK-gel GMH_{HR}-M tandem columns using chloroform (CHCl₃) as an eluent at 35 °C. Polystyrene standards were used for the calibration. Thermogravimetic analyses (TGA) were performed on a Shimadzu TGA-50 instrument. Differential scanning calorimetric (DSC) measurements were carried out on a Shimadzu DSC-60 instrument. TGA and DSC measurements were performed under nitrogen at the scan rate of 10 °C/min. Ultraviolet–visible (UV–vis) spectra and photoluminescence spectra were measured in CHCl₃ on a Shimadzu UV-3100PC spectrometer and a Shimadzu RF-5300PC spectrometer, respectively.

Synthesis of 1,4-Diethynyl-2,5-dioctyloxybenzene (1)

To a 200 ml round bottom flask containing 1,4-dioctyloxybenzene (5.0 g, 15 mmol), were added iodine (3.1 g, 24.3 mmol), periodic acid monohydrate (1.4 g, 6.0 mmol), acetic acid (45 ml), water (8 ml) and concentrated sulfuric acid (1.7 ml), and the mixture was heated under gentle reflux overnight. After the addition of aqueous sodium thiosulfate, the mixture was extracted three times with hexane. The intermediate, 1,4-diiodo-2,5-dioctyloxybenzene, was obtained in a 78% yield (7.19 g, 11.7 mmol) by recrystallization from ethanol.

¹H-NMR (300 MHz, CDCl₃, δ in ppm) 0.88 (t, J = 6.8 Hz, 6H, -CH₃), 1.29–1.50 [20H, -OCH₂CH₂(CH₂)₅-], 1.80 (m, 3H, -OCH₂CH₂-), 3.92 (t, J = 6.5 Hz, 4H, -OCH₂CH₂-), 7.17 (s, 2H, -C₆H₂-).

Introduction of two ethynyl groups were performed by the Sonogashira coupling reaction.^[8] To a 100 ml round bottom flask containing copper(I) iodide (0.04 g, 0.05 mmol), palladium(II) chloride (0.02 g, 0.1 mmol), triphenylphosphine (0.05 g, 0.1 mmol),

and 1,4-diiodo-2,5-dioctyloxybenzene (5.9 g, 10 mmol), were added diiospropylamine (40 ml) and tetrahydrofuran (15 ml), and the mixture was stirred for 30 min at ambient temperature. Then, trimethylsilylacetylene (2.5 g, 25 mmol) was added and the mixture was heated under gentle reflux overnight. After the addition of benzene (100 ml), the mixture was washed with brine and the organic layer was dried over magnesium sulfate. 1,4-Bis(trimethylsilylethynyl)-2,5-dioctyloxybenzene was obtained in a quantitative yield (4.8 g, 10 mmol) by SiO₂ column chromatography (eluent: benzene).

¹H-NMR (300 MHz, CDCl₃, δ in ppm) 0.25 [s, 18H, -Si(CH₃)₃], 0.88 (t, J = 6.2 Hz, 6H, -CH₃), 1.25–1.53 [20H, -OCH₂CH₂(CH₂)₅-], 1.78 (m, 4H, -OCH₂CH₂-), 3.94 (t, J = 6.3 Hz, 4H, -OCH₂CH₂-), 6.89 (s, 2H, -C₆H₂-).

To a methanol (20 ml) solution of 1,4-bis(trimethylsilylethynyl)-2,5-dioctyloxybenzene (4.8 g, 10 mmol), a methanol solution of potassium hydroxide (1.0 M, 12 ml) was added and the mixture was stirred at ambient temperature for 4 h. Then, diethyl ether (20 ml) was added and the mixture was washed with water. The organic layer was collected and dried over magnesium sulfate. 1,4-Diethynyl-2,5-dioctyloxybenzene (1) was isolated in a 77% yield (2.6 g, 7.7 mmol) by SiO₂ column chromatography (eluent: hexane).

¹H-NMR (300 MHz, CDCl₃, δ in ppm) 0.88 (t, $J = 5.7, 6H, -CH_3$), 1.28–1.54 [20H, -OCH₂CH₂(CH₂)₅-], 1.79 (m, 4H, -OCH₂CH₂-), 3.33 (s, 2H, -C=CH), 3.96 (t, J = 7.2 Hz, 4H, -OCH₂-), 6.95 (s, 2H, -C₆H₂-).

¹³C-NMR (75 MHz, CDCl₃, δ in ppm) 14.1, 22.6, 25.9, 29.1, 29.2, 29.3, 31.7, 69.7, 79.8, 82.4, 113.3, 117.8, 154.0.

IR (KBr disk, cm⁻¹) 3287, 2926, 2872, 2852, 1637, 1543, 1500, 1469, 1385, 1273, 1219, 1199, 1039, 999, 860, 761, 727, 671, 648, 526.

Likewise, 2-ethynylanisole was obtained by the reaction of 2-iodoanisole with trimethylsilylacetylene followed by the deprotection of the trimethylsilyl group.

¹H-NMR (300 MHz, CDCl₃, δ in ppm) 3.30 (s, 1H, -C \equiv CH), 3.86 (s, 3H, -OCH₃), 6.84–6.91 (2H, aromatic), 7.29 (m, 1H, aromatic), 7.45 (d, J = 7.2 Hz, 1H, aromatic).

¹³C-NMR (75 MHz, CDCl₃, δ in ppm) 55.8, 80.1, 81.1, 110.6, 111.1, 120.4, 130.3, 134.1, 160.6.

IR (KBr disk, cm⁻¹) 3285, 3074, 3007, 2964, 2945, 2914, 2837, 2542, 2106, 2065, 1909, 1597, 1575, 1491, 1464, 1435, 1290, 1253, 1178, 1163, 1111, 1047, 1024, 937, 814, 754, 653, 614, 582, 569.

Synthesis of Poly(p-phenylene) Derivative (5)

To a 50 ml flask containing 1 (0.167 g, 0.43 mmol) in diethyl ether (20 ml), were added Ti(OPr^i)₄ (0.178 g, 0.63 mmol) and ^{*i*}PrMgCl (1.0 M, 1.3 ml, 1.3 mmol) at -78 °C under argon. After stirring for 30 min at that temperature and then at -50 °C for 12 h, a diethyl ether (0.13 ml) solution of 3-bromo-1-propyne (0.060 g, 0.50 mmol) was added and the mixture was warmed slowly to ambient temperature. After the addition of a methanol solution of hydrochloric acid (1.0 M, 0.50 ml, 0.50 mmol), the mixture was kept stirring for an additional 1 h. Then water (10 ml) was added and the mixture was extracted with CHCl₃. The organic layer was collected and dried over magnesium sulfate. The polymer (5) was obtained in a 78% yield (0.15 g) by precipitation into methanol.

¹H-NMR (300 MHz, CDCl₃, δ in ppm) 0.84 (br, 6H, -CH₃), 1.22 – 1.85 [br, 24H, -OCH₂(CH₂)₆-], 2.23 (br, 3H, Ar-CH₃), 3.96 (br, 4H, -OCH₂-), 7.05-7.71 (5H, aromatic).

¹³C-NMR (75 MHz, CDCl₃, δ in ppm) 14.1, 21.4, 22.6, 25.9, 26.2, 29.2, 29.3, 31.8, 68.1, 125.3, 128.2, 128.8, 137.8, 150.5.

IR (KBr disk, cm⁻¹) 2926, 2854, 1685, 1608, 1560, 1467, 1377, 1261, 1205, 1028, 866, 802, 721, 669, 528.

Synthesis of 1,4-Bis(2-methoxyphenyl)-2-methylbenzene (6)

To a 50 ml flask containing 2-ethynylanisole (0.155 g, 1.20 mmol) in diethyl ether, were added Ti $(OPr^{i})_{4}$ (0.235 g, 0.83 mmol) and ⁱPrMgCl (1.0 M, 1.6 mmol, 1.6 ml) at -78 °C under argon. After stirring for 30 min at that temperature and then at -50 °C for 12 h, a diethyl ether (0.13 ml) solution of 3-bromo-1-propyne (0.074 g, 0.625 mmol) was added and the mixture was warmed slowly to ambient temperature. After the addition of a methanol solution of hydrochloric acid (1.0 M, 0.63 ml, 0.63 mmol), the mixture was kept stirring for an additional 1 h and was washed with brine. The organic layer was collected and dried over magnesium sulfate. A p-terphenyl derivative (6) was obtained as yellow oil in an 88% yield (0.16 g, 0.53 mmol) by column chromatography on Al_2O_3 (eluent: benzene).

¹H-NMR (300 MHz, CDCl₃, δ in ppm) 2.18 (s, 3H, Ar–CH₃), 3.77 (s, 3H, -OCH₃), 3.82 (s, 3H, -OCH₃), 6.94 – 7.04 (4H, aromatic), 7.18 – 7.41 (7H, aromatic).

¹³C-NMR (75 MHz, CDCl₃, δ in ppm) 20.0, 55.3, 55.4, 110.6, 111.1, 120.4, 120.7, 126.6, 128.3, 128.4, 129.6, 130.6, 130.7, 130.9, 131.1, 136.3, 137.2, 137.3, 156.5, 156.7.

IR (KBr disk, cm⁻¹) 2961, 2928, 2833, 1595, 1579, 1483, 1460, 1431, 1392, 1292, 1234, 1174, 1159, 1118, 1049, 1022, 1005, 939, 889, 852, 829, 787, 754, 679, 619, 580.

Results and Discussion

Sato et al. has described that the transformation of titanacyclopentadiene derivatives, obtained by the cyclization of 2 and 1,6-heptadiyne derivatives, with 3-bromo-1-propyne proceeds smoothly to give benzene derivatives.^[9] In order to make sure the effective nature of the present process, a model experiment was performed using a titanacycle derived from 2-ethynylanisole (Scheme 3). That is, a 2,5-diaryltitanacyclopentadiene derivative was prepared by the reaction of 2-ethynylanisole and the lowvalent titanium complex (2), generated from Ti(OPrⁱ)₄ and ⁱPrMgCl, at -78 to -50 °C for 12 h^[10] and the titanacycle was subjected to the reaction with 3-bromo-1-propyne at -50 °C and the mixture was warmed up gradually to ambient temperature. It was found that the reaction took place nicely to give an objective *p*-terphenyl derivative (6), 1,4-bis(2-methoxyphenyl)-2-methylbenzene, in a high yield (88%) after isolation with column chromatography.

The high efficiency of the model reaction prompted us to carry out the polymer reaction under the same conditions. As a titanacyclopentadiene-containing polymer, we employed 3 which is obtainable from the diethynylbenzene derivative having solubilizing soft alkoxy substituents (1) and 2 as we described previously^[6,11] and **3** was reacted directly with 3-bromo-1-propyne at -50 °C to ambient temperature. As a result, a polymer (5) was isolated in a 78% yield by precipitation into methanol (Scheme 2). The polymer (5) is soluble in organic solvents such as chloroform and dichloromethane. The number-average molecular weight $(M_{\rm p})$ and the molecular weight distribution (M_W/M_n) of the polymer were estimated as 4800 and 1.8, respectively (GPC, with respect to polystyrene standards).

The structural elucidation of the polymer (5) was performed by the ¹H NMR and ¹³C NMR spectra in comparison with those of the model compound (**6**). In the ¹H NMR spectrum of **6**, a peak assignable to the methyl protons attached to the benzene ring is observable at 2.18 ppm besides two peaks for the methoxy protons at 3.77 ppm and 3.82 ppm (Fig. 1a). The integral ratio of the peak of the methyl protons and those of the methoxy protons



Scheme 3. Synthetic route for a terphenyl derivative (6) via a 2,5-diaryltitanacyclopentadiene derivative.



Figure 1. ¹H NMR spectra of a terphenyl derivative (6) (a) and a poly(*p*-phenylene) derivative (5) (b).



Figure 2. UV-vis spectra of 6 (a) and 5 (b), and photoluminescence spectra of 6 (c) and 5 (d) (measured in CHCl₃).

(3.0:6.0) is in good accordance with the proposed structure (3:6). In the case of the polymer (**5**), the peaks for the methyl protons and methylenes adjacent to the oxygen are observable at 2.23 and at 3.96 ppm as broad signals (Fig. 1b). In the ¹³C NMR spectrum of **6**, the methyl substituent attached to the benzene ring is observed at 20.0 ppm and the peaks for two methoxy moieties appear at 55.3 and 55.4 ppm. In the case of **5**, the corresponding peaks are clearly observable at 21.4 and at 68.1 ppm, respectively.

The thermal stability of the polymer (**5**) was evaluated by its TGA, where the temperature for 10% weight loss (T_{d10}) was observed at 305 °C, which was in good agreement with the reported decomposition temperatures for the alkoxy-substituted poly(*p*-phenylene)s.^[12] The DSC analysis of **5** was performed below its decomposition temperature, from which the glass transition temperature (T_g) was observed at 58.4 °C.

The polymer **5** was found to have the extended π -conjugated system along the backbone as supported by its UV–vis spectrum in comparison with that of the terphenyl derivative (**6**) as a model compound (Fig. 2). That is, the absorption spectrum of **6** measured

in CHCl₃ exhibited the absorption maximum (λ_{max}) and its onset (λ_{onset}) at 276 nm and 375 nm, respectively. In the case **5**, the absorption peak appeared at longer wavelength region where the λ_{max} and λ_{onset} are observable at 329 and 500 nm, respectively. The clear bathochromic shift is also observable in the emission spectra. In the photoluminescence spectrum of **5**, the emission maximum was found at 445 nm, while that of **6** appeared at 407 nm.

Conclusions

A poly(*p*-phenylene) derivative was successfully prepared by means of the polymer reaction of a regioregular organometallic polymer (**3**) containing titanacyclopentadiene units in the main chain. The effective nature of the transformation process was supported by the high efficiency of the model reaction and by the spectroscopic analyses. The polymer exhibited the π -conjugated character judging from the absorption and the emission spectra. On the basis of the present polymer reaction process, the diverse molecular design of the repeating structure of the polymer was attained from simple monomer structures. Also, the use of other electrophilic reagents for the polymer reactions might give versatile main chain functionalized macromolecules. Further synthetic studies utilizing the organotitanium polymers are currently being investigated and the results will be published in the forthcoming papers.

Acknowledgments

This work was partly supported by a Grant-in-Aid for Science Research in a Priority Area 'Super-Hierarchical Structures' from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The financial support of the New Energy and Industrial Technology Development Organization (NEDO) of Japan is gratefully acknowledged.

References

- See, for example: a) I. Manners, Synthetic Metal-Containing Polymers; Wiley-VCH: Weinheim, 2004; b) Macromolecules Containing Metal and Metal-Like Elements, Vol. 1–7 (Eds.: A. S. Abd-El-Aziz, C. E. Carraher, C. U. Pittman, J. E. Sheats, M. Zeldin), Wiley-Interscience: Hoboken, NJ, 2006.
- [2] A part of this work was presented previously: I. Tomita, ACS Polym. Prepr. 2004, 45, 415.
- [3] a) I. Tomita, A. Nishio, T. Endo, *Polym. Bull.* 1993, 30, 179; b) I. Tomita, A. Nishio, T. Endo, *Macromolecules* 1994, 27, 7009; c) I. Tomita, A. Nishio, T. Endo, *Macromolecules* 1995, 28, 3042; d) I. Rozhanskii, I. Tomita, T. Endo, *Macromolecules* 1996, 29, 1934; e) J.-C. Lee, A. Nishio, I. Tomita, T. Endo, *Macromolecules* 1997, 30, 5205; f) I. Tomita, A. Nishio, T. Endo, *Appl. Organomet. Chem.* 1998, 12, 735; g) I. Tomita, J.-C. Lee, T. Endo, *J. Organomet. Chem.* 2000, 611, 570.
- [4] a) S. S. H. Mao, T. D. Tilley, J. Am. Chem. Soc. 1995, 117, 5365;
 b) S. S. H. Mao, T. D. Tilley, Macromolecules 1997, 30, 5566;
 c) J. R. Nitschke, S. Zurcher, T. D. Tilley, J. Am. Chem. Soc. 2000, 122, 10345;
 d) S. A. Johnson, F. Q. Liu, M. C. Suh, S. Zurcher, M. Haufe, S. S. H. Mao, T. D. Tilley, J. Am. Chem. Soc. 2003, 125, 4199;
 e) B. L. Lucht, M. A. Buretea, T. D. Tilley, Organometallics 2000, 19, 3469.

- [5] a) I. Tomita, M. Ueda, J. Inorg. Organomet. Polym. Mater. 2005, 15, 511.
- [6] a) W.-M. Zhou, I. Tomita, Polym. Bull. 2008, 61, 603; b) W.-M. Zhou,
 I. Tomita, J. Inorg. Organomet. Polym. Mat. 2009, 19, 113.
- [7] For part 1, See: K. Atami, T. Kino, W.-M. Zhou, H. Nishiyama, and I. Tomita, Synth. Met. 2009, 159, 949.
- [8] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 1975, 50, 4467.
- [9] R. Tanaka, Y. Nakano, D. Suzuki, H. Urabe, F. Sato, J. Am. Chem. Soc. 2002, 124, 9682.
- [10] a) S. Yamaguchi, R.-Z. Jin, K. Tamao, F. Sato, J. Org. Chem. 1998, 63, 10060; b) T. Hamada, D. Suzuki, H. Urabe, F. Sato, J. Am. Chem. Soc. 1999, 121, 7342.
- [11] a) Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, T. Saegusa, *Macromolecules* **1991**, *24*, 345; b) Y. Chujo, I. Tomita, T. Saegusa, *Makromol. Chem. Macromol. Symp.* **1993**, *70*/71, 47.
- [12] See, for example: U. Lauter, W. H. Meyer, G. Wegner, Macromolecules, 1997, 30, 2092.