

Homo-Coupling Polycondensation of Bis(alkynylsilane)s Mediated by Copper(I) Chloride: A New Synthesis of Poly(arylenebutadiynylene)s

Yasushi Nishihara, Tsuyoshi Kato, Jun-ichi Ando, Atsunori Mori,* and Tamejiro Hiyama[†]

Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta, Yokohama 226-8503

[†]Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501

(Received March 23, 2001; CL-010262)

Homo-coupling polycondensation of aromatic compounds bearing two (trimethylsilyl)ethynyl groups mediated by copper(I) chloride in DMF gives conjugated poly(arylenebutadiynylene)s in up to 94% yield with molecular weight of 4000–8900 ($M_w/M_n = 1.78$ –2.09).

Studies on conjugated polymers have been a subject of great interest owing to their potential applications as new materials. Poly(aryleneethynylene)s (PAEs) containing conjugated carbon–carbon triple bonds in the polymer chain exhibit unique photo- and electroluminescence, nonlinear optical properties, and electrical conductivity.^{1,2}

In contrast, there have been fewer examples of the synthesis of poly(arylenebutadiynylene)s than PAEs. Poly(arylenebutadiynylene)s were prepared by polycondensation of dihaloarene with butadiyne catalyzed by palladium complexes³ or oxidative polycondensation of diethynylarenes^{4,5} in the presence of Cu-TMEDA catalyst (Hay's coupling⁶). These polymers show intense fluorescence, semiconducting properties, and thermotropic liquid crystalline characteristics. Terminal alkynes used in the above polycondensation have been, in general, prepared from the corresponding trimethylsilylated derivatives via desilylation, and the diethynyl monomers thus deprotected are known to be thermally unstable.

On the other hand, we have documented the copper(I) salt-promoted desilylative homo-coupling reaction of alkynylsilanes to afford 1,3-diynes.⁷ Therefore, polymerization by the direct coupling of the silylated dialkynes would provide a facile synthesis of the polymers bearing a butadiynylene backbone

(C≡C–C≡C) in the main chain. Herein, we report the novel synthetic method of poly(arylenebutadiynylene) using bifunctional monomers with a (trimethylsilyl)ethynyl group as an alternative method of the Hay's coupling polycondensation.

We first examined the polycondensation of 2,5-dinonyloxy-1,4-[bis(trimethylsilyl)ethynyl]benzene (**1a**) in order to obtain soluble polymers, since insoluble nature of the polymers limits their characterization in solution. This polymer may offer much improved solubility over unsubstituted poly(1,4-phenylenebutadiynylene). Several polymerization conditions were investigated for this monomer **1a** in order to optimize desirable solubility and molecular weight. Results on the polymerization are summarized in Table 1 together with molecular weights determined by SEC (Size Exclusion Chromatography) relative to polystyrene standards.

In Run 1, crude **2a** was obtained by work-up with pouring of the resulting dark brown DMF solution into a mixture of methanol and 3 M HCl to yield orange-yellow precipitates. Reprecipitation of the chloroform solution into methanol gave 48% of **2a** with number average molecular weight (M_n) of 2900 as a yellow powder. We assumed that the polymerization at 60 °C was found to be ineffective to obtain the high yield and M_n of **2a** due to the formation of low molecular weight oligomers. At higher temperature (80 °C), polymer **2a** was obtained in 77% yield with M_n of 5100 (Run 2). Consequently, the reaction carried out in a lower concentration (0.2 M) improved M_n of **2a** to 8900 (Run 3).⁸

The polymer **2a** was soluble in chloroform and THF, and characterized by IR, ¹³C and ¹H NMR analyses. IR spectrum of the polymer **2a** exhibited $\nu_{C=C}$ stretching at 2155 cm⁻¹. The ¹³C

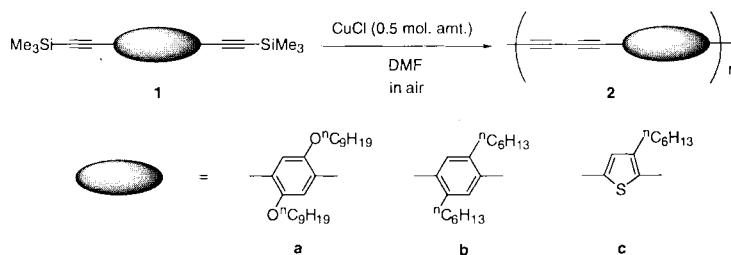


Table 1. Yields and molecular weight data for polymers **2a–c**^a

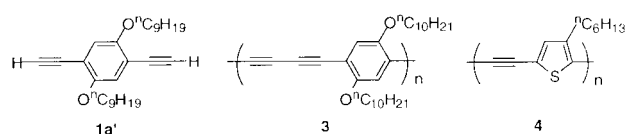
Run	Polymer	[Monomer] mol dm ⁻³	Temp. / °C	Time / h	Yield ^b / %	M_n^c	M_w/M_n^c	DP ^d
1	2a	0.4	60	42	48	2900	1.05	7
2	2a	0.4	80	3	77	5100	1.35	12
3	2a	0.2	80	3	74	8900	1.78	21(15) ^e
4	2b	0.4	80	36	45	7900	2.04	27
5	2c	0.2	60	4	94	4000	2.09	19

^aConditions: polymerization of monomers **1a–c** with copper(I) chloride in DMF in air. ^bCHCl₃ soluble part. ^cDetermined by SEC with THF as an eluent relative to polystyrene standards. ^dDegree of polymerization based on M_n (SEC). ^eDetermined from integration ratio in ¹H NMR signals.

NMR spectrum showed nine signals assignable to a nonyloxy group (14–70 ppm), acetylenic carbons (79.7 and 79.8 ppm), and the aromatic carbons (114, 118, and 155 ppm). The ^1H NMR spectra of polymer **2a** showed a weak resonance at 0.26 ppm. This signal disappeared and a new signal at 3.36 ppm appeared by treatment of the polymer with tetrabutylammonium fluoride (TBAF). This result indicates the presence of a trimethylsilyl group as end groups of the polymer **2a**.

Polycondensation of monomers **1b** and **1c** was carried out similarly and the results showing the optimized yield are also summarized in Table 1. Reaction of 1,4-[bis(trimethylsilyl)ethynyl]-2,5-dihexylbenzene (**1b**) afforded polymer **2b**⁶ in 45% yield (Run 4). Polycondensation using 3-hexyl-2,5-[bis(trimethylsilyl)ethynyl]thiophene (**1c**) gave polymer **2c** with M_n of 4000 (Run 5). The SEC data may not truly reflect the average molecular weights and the molecular weight distributions of polymers **2a–c**, since insoluble fractions of the polymers remained unassayed.

Data on UV–vis absorption spectra of polymers **2a–c** are collected and compared together with the corresponding monomer **1a**, desilylated dialkyne **1a'**, and reported polymers **3** and **4**. The synthesized polymers **2a–c** showed absorption maxima at 397–430 nm which were considerably shifted to longer wavelengths in comparison with monomers **1a–c**. Polymer **2a** showed strong UV absorption maximum at 427 nm, red-shifted by ca. 80 nm from that of the corresponding monomer **1a**. The red-shifted absorption maximum is responsible for the effect of π -conjugation through aromatic rings and acetylenic moieties in the polymer main chain. Poly(3-hexyl-2,5-thienylenebutadiynylene) (**2c**)⁹ showed the longest λ_{max} at 430 nm, which was rather higher than that of analogous poly(3-hexyl-2,5-thienyleneethynylene) (**4**) (λ_{max} : 403 nm).¹⁰ The peak is located at a longer wavelength compared with that of polymer **4**, indicating that polymer **2c** has a longer effective π -conjugation system due to negligible steric repulsion between substituents in the neighboring units. This trend is consistent with that poly(arylenebutadiynylene)s show the longer wavelength maxima in absorption spectra than those of poly(aryleneethynylene)s.



In summary, we have demonstrated that copper(I) chloride-mediated homo-coupling of alkynylsilanes can be applied into the synthesis of poly(arylenebutadiynylene)s. Thus, the present methodology that can be performed using the starting monomer without desilylation would provide an alternative to the Hay's coupling. Further investigations on the high yield synthesis and fluorescence characters and thermal properties of polymers are currently under way.

The present work was partially supported by the Inamori Foundation, and the Grants-in-Aid for Scientific Research (A) No. 07405042 and Scientific Research in Priority Area of Inter-element Linkage No. 09239102, from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank Shin-Etsu Chemical Co., Ltd. and Chisso Co., Ltd. for a generous gift of organosilicon reagents.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

- For general reviews, see: T. Yamamoto, *Bull. Chem. Soc. Jpn.*, **72**, 621 (1999); U. H. F. Bunz, *Chem. Rev.*, **100**, 1605 (2000).
- The cross-coupling polycondensation of alkynylsilanes with aryl triflates catalyzed by $\text{CuCl}/\text{Pd}(\text{PPh}_3)_4$; see, Y. Nishihara, J. Ando, T. Kato, A. Mori, and T. Hiyama, *Macromolecules*, **33**, 2779 (2000).
- S. Takahashi, E. Murata, M. Kariya, K. Sonogashira, and N. Hagihara, *Macromolecules*, **12**, 1016 (1979).
- T. Mangel, A. Eberhardt, U. Scherf, U. H. F. Bunz, and K. Müllen, *Macromol. Rapid Commun.*, **16**, 571 (1995).
- M. Kijima, I. Kinoshita, T. Hattori, and H. Shirakawa, *J. Mater. Chem.*, **8**, 2165 (1998); M. Kijima, I. Kinoshita, T. Hattori, and H. Shirakawa, *Synth. Met.*, **100**, 61 (1999).
- A. S. Hay, *J. Polym. Sci., Part A-1*, **7**, 1625 (1969); C. Glaser, *Chem. Ber.*, **2**, 422 (1869); G. Eglinton and W. McRea, *Adv. Org. Chem.*, **4**, 225 (1963).
- K. Ikegashira, Y. Nishihara, K. Hirabayashi, A. Mori, and T. Hiyama, *Chem. Commun.*, **1997**, 1039; Y. Nishihara, K. Ikegashira, K. Hirabayashi, J. Ando, A. Mori, and T. Hiyama, *J. Org. Chem.*, **65**, 1780 (2000). Cu(I)-mediated homo-coupling reaction of alkenylsilanes has been reported by us, see: Y. Nishihara, K. Ikegashira, F. Torimaya, A. Mori, and T. Hiyama, *Bull. Chem. Soc. Jpn.*, **73**, 985 (2000).
- Representative procedure for the synthesis of **2a** is as follows: To a suspension of CuCl (25 mg, 0.25 mmol) in 0.6 mL of DMF was added 139 mg (0.25 mmol) of monomer **1a** with stirring. The reaction vessel was filled with an atmospheric air through a CaCl_2 drying tube. Consumption of the starting material was monitored by TLC (silica gel, hexane). After 3 h at 80 °C the resulting dark brown suspension was poured into a mixture of 100 mL of methanol and 5 mL of 3 M hydrochloric acid to afford orange-yellow precipitates. Reprecipitation of the solid dissolved in the minimum amount of chloroform into 50 mL of methanol gave 78.9 mg (0.19 mmol, 74%) of **2a** as a yellow powder. **2a**: IR (KBr) 2155 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 0.26 (SiMe_3 as end groups), 0.86 (t, $J = 7$ Hz, 6H, CH_3), 1.27–1.58 (br, 24H, CH_2), 1.74–1.88 (br, 4H, CH_2), 3.97 (t, $J = 7$ Hz, 4H, OCH_2), 6.96 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3): δ -0.07 (SiMe_3 as end groups), 14.1 (CH_3), 22.7, 25.9, 29.1, 29.27, 29.34, 29.6, 31.9 (CH_2), 69.8 (OCH_2), 79.7 and 79.8 ($\text{C}\equiv\text{C}$), 113.6, 117.7 and 154.8 (aromatic carbons). **2b**: IR (KBr) 2161 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (br, 6H, CH_3), 1.34 (br, 12H, CH_2), 1.63 (br, 4H, CH_2), 2.73 (br, 4H, CH_2), 7.35 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1 (CH_3), 22.6, 29.0, 30.3, 31.6, 33.8 (CH_2), 82.2 ($\text{C}\equiv\text{C}$), 122.4, 133.2, and 143.7 (aromatic carbons). **2c**: IR (KBr) 2137 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 0.90 (br, 3H, CH_3), 1.31 (br, 6H, CH_2), 1.61 (br, 2H, CH_2), 2.67 (br, 2H, CH_2), 7.09 (s, 1H, thienyl); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1 (CH_3), 22.6, 28.8, 29.6, 20.0, 31.6 (CH_2), 79.0, 81.2 ($\text{C}\equiv\text{C}$), 120.3, 123.1, 135.2 and 151.1 (thienyl carbons).
- This polymer was synthesized by an oxidative coupling of diethynyl monomer, but no UV–vis spectrum was reported; see, D. L. Rutherford, J. K. Stille, C. M. Elliott, and V. R. Reichert, *Macromolecules*, **25**, 2294 (1992).
- T. Yamamoto, W. Yamada, M. Takagi, K. Kizu, T. Maruyama, N. Ooba, S. Tamaru, T. Kurihara, T. Kaino, and K. Kubota, *Macromolecules*, **27**, 6620 (1994).