A New Synthetic Method for Poly(arylene)s Using Bis(pinacolato)diboron as a Condensation Reagent

Atsushi Izumi, Ryoji Nomura, and Toshio Masuda
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501

(Received April 14, 2000; CL-000354)

We have developed a new convenient synthetic method for poly(arylene)s via dehalogenative coupling of dihaloarenes using bis(pinacolato)diboron as a condensation reagent. With this method, a variety of dihaloarenes including dihalobenzenes, dihaloazobenzenes, and dihalothiophenes were polymerized to give the corresponding poly(arylene)s.

A variety of π-conjugated polymers have been synthesized to date, which include poly(arylene)s as a typical category. One of the methods for preparing poly(arylene)s is dehalogenative coupling reaction of dihaloarenes, which is promoted by nickel(0) complex such as $Ni(cod)_2$ (cod = 1,5-cyclooctadiene).[1] Although this well-established Ni(0)-coupling is undoubtedly the mainstream in preparation of π-conjugated poly(arylene)s, there still remain some unavoidable problems: (i) $Ni(cod)_2$ is highly moisture-sensitive, so that the complete removal of moisture from the polymerization system is essential, and (ii) the working-up process is somewhat tedious due to the difficulty in removing the large amount of nickel residue (generally 1.0 to 1.2 equiv to the monomers).

Here we describe a new and more convenient method for the dehalogenative coupling of dihaloarenes **1** with bis(pinacolato)diboron[2] **2** as a condensation reagent (Scheme 1). Compound **2** is known to act as an excellent boron nucleophile toward alkynes, aryl halides, allenes and so on.[3] Both **2** and $PdCl_2(dppf)$[4] (dppf = 1,1'-bis(diphenylphosphino)ferrocene) are thermally stable and can be easily handled in air, which makes the whole synthetic procedures, from the reagents feeding to the working-up process, more facile than those for the $Ni(cod)_2$-promoted polymerizations; i.e., one can handle all reagents in air, and the catalytic amount of palladium complex as well as othere residues can be removed simply by washing the products with water and methanol.

We first examined the polymerization of 1,4-dihalo-2,5-dihexylbenzenes, **1a** and **1b**, to establish optimal conditions, and the results are summarized in Table 1. This method is based on the Suzuki–Miyaura coupling and water is often added to the solvent system to increase the efficiency of the bases; however, the polymerizations of **1a** in toluene/water and DMAc/water (DMAc = *N*,*N*-dimethylacetamide) mixtures at 90 °C did not proceed (runs 1, 2). In contrast, polymers with $M_n > 2 \times 10^3$ and $M_w > 4 \times 10^3$ were obtained in toluene or DMAc, and the polymerization in DMAc produced a polymer with higher yield and molecular weight than that in toluene (runs 3, 4). When **1a** was polymerized in DMAc at high temperature, both the yield and molecular weight improved (run 5). Similar tendencies were observed in the polymerization of diiodide **1b** (runs 6–8), and a high molecular weight polymer with M_n of 6360 was quantitatively obtained in DMAc at 130 °C (run 8). The formation of the corresponding poly(*p*-phenylene)s was verified by the ^1H NMR and IR spectra.

Scheme 1.

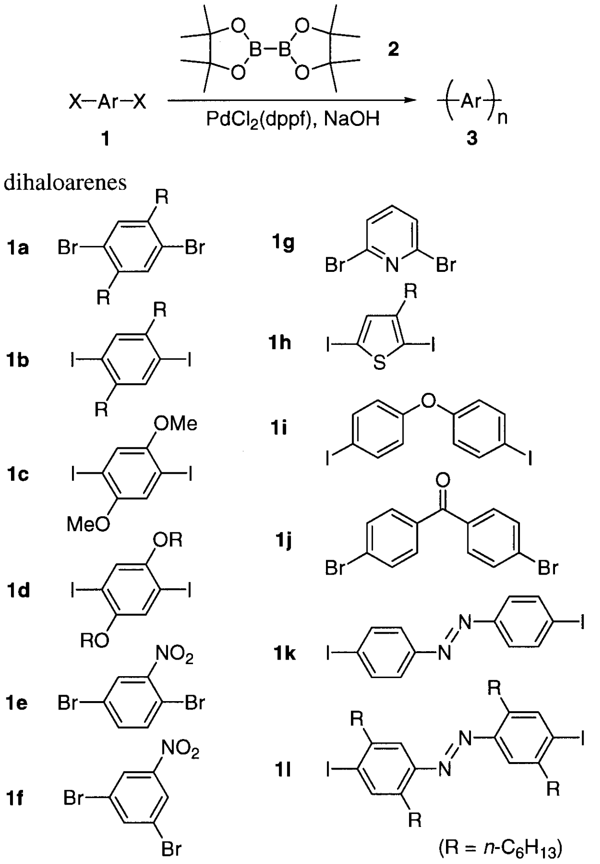

Table 1. Pd-Catalyzed polymerization of **1a** and **1b**[a]

Run	1	Solvent	Temp./°C	Yield/%[b]	M_n[c,d]	M_w[c,d]
1	**1a**	Toluene/H_2O	90	0	—	—
2	**1a**	DMAc/H_2O	90	0	—	—
3	**1a**	Toluene	90	36	2220	4570
4	**1a**	DMAc	90	67	2560	4190
5	**1a**	DMAc	130	80	4130	6880
6	**1b**	Toluene	90	19	1870	2490
7	**1b**	DMAc	90	42	2510	5140
8	**1b**	DMAc	130	100	6360	13900

[a] A mixture of **1** (0.40 mmol), **2** (0.40 mmol), $PdCl_2(dppf)$ (1.2 μmol) and NaOH (24 mmol) in toluene or DMAc (5.0 mL) (and water (1.0 mL) for runs 1, 2) were stirred for 24 h under nitrogen. [b] Methanol-insoluble part. [c] THF-soluble part. [d] Estimated by GPC (THF, PSt).

Copyright © 2000 The Chemical Society of Japan

Other dihaloarenes were employed to investigate the scope and limitations of this coupling method (Table 2). Alkoxy-substituted dihalobenzenes successfully polymerized, and **1d** gave a soluble polymer with M_n of 4700 and M_w of 10600 (runs 9, 10). On the other hand, polymerization of dibromobenzenes with a nitro group reached 100% conversion but did not produce methanol-insoluble polymers (runs 11, 12). The heterocyclic dihalides such as dihalopyridine **1g** and dihalothiophene **1h** were also polymerized to give good yields of polymers (runs 13, 14). ^{1}H NMR spectrum[5] indicated that **3h** had a totally random stereostructure; the HT–HT : HT–HH : TT–HT : TT–HH (HT = head-to-tail) ratio was 35 : 19 : 26 : 20, and the HH to HT ratio was approximately 1.0, whereas the polymer prepared with Ni(cod)$_2$ possesses high content of the HH junctions.[1a] Monomers with an ether group, **1i** (run 15), and a carbonyl linkage, **1k** (run 16), also gave the corresponding polymers in good yields.

Table 2. Pd-Catalyzed polymerization of dihaloarenes **1**[a]

Run	Monomer	Polymer			
		3	Yield/%[b]	M_n[c,d]	M_w[c,d]
9	**1c**	**3c**	100	insoluble	
10	**1d**	**3d**	93	4700	10600
11	**1e**	**3e**	0	—	—
12	**1f**	**3f**	0	—	—
13	**1g**	**3g**	88	insoluble	
14	**1h**	**3h**	92	3660	7400
15	**1i**	**3i**	100	insoluble	
16	**1j**	**3j**	83	insoluble	
17	**1k**	**3k**	94	insoluble	
18	**1l**	**3l**	96	14700	35500

[a]Polymerized under the conditions of Run 8 in Table 1. [b]Methanol-insoluble part. [c]THF-soluble part. [d]Estimated by GPC (THF, PSt).

Azobenzene is a well-known photoresponsive chromophore, and its photo-induced and thermal geometric isomerization have been extensively studied over decades.[6] It should be noted that the application of the present method allows the production of azobenzene-containing conjugated polymers,[7] **3k** and **3l**, that are inaccessible by use of Ni(cod)$_2$.[8] Thus, a soluble polymer **3l** whose M_n and M_w values were 14700 and 35500, respectively, was obtained from **1l** bearing alkyl side chains. Polymer **3l** showed the *trans*-to-*cis* isomerization at 20 °C upon irradiation at 300 nm < λ_1 < 400 nm (Figure 1) as well as the *cis*-to-*trans* isomerization either at 20 °C upon irradiation at λ_2 > 450 nm or at 80 °C in the dark.

In conclusion, a new method has been developed for the preparation of poly(arylene)s from various dihaloarenes using bis(pinacolato)diboron **2** as a condensation reagent. With this method, novel azobenzene-based photoresponsive conjugated polymers[7,10] are readily synthesized from the corresponding halides, which is impossible by the Ni(cod)$_2$-promoted polymerization.

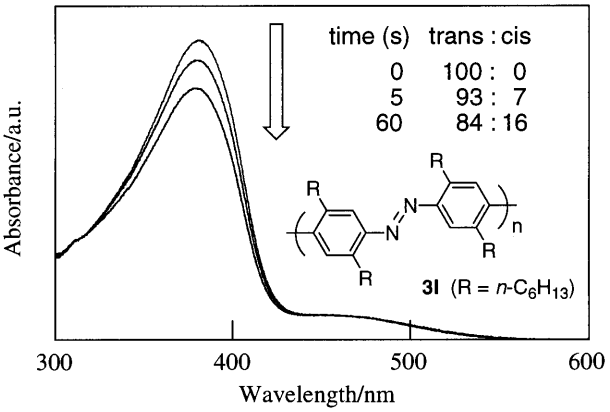

Figure 1. Variation of the UV/vis spectrum of **3l** in toluene at 20 °C upon irradiation at 300 < λ_1 <400 nm.

References and Notes

1 a) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. -H. Zhou, Y. Nakamura, and T. Kanbara, *Macromolecules*, **25**, 1214 (1992). b) T. Yamamoto, *Bull. Chem. Soc. Jpn.*, **72**, 621 (1999).

2 Bis(pinacolato)diboron was purchased from Aldrich and used without further purification.

3 a) T. Ishiyama, N. Matsuda, N. Miyaura, and A. Suzuki, *J. Am. Chem. Soc.*, **115**, 11018 (1993). b) T. Ishiyama, M. Murata, and N. Miyaura, *J. Org. Chem.*, **60**, 7508 (1995). c) A. Giroux, Y. Han, and P. Prasit, *Tetrahedron Lett.*, **38**, 3841 (1997).

4 W. J. Thompson, J. H. Jones, P. A. Lyle, and J. E. Thies, *J. Org. Chem.*, **53**, 2052 (1988).

5 a) R. M. Souto Maior, K. Hinkelmann, H. Eckert, and F. Wudl, *Macromolecules*, **23**, 1268 (1990). b) H. Mao, B. Xu, and S. Holdcroft, *Macromolecules*, **26**, 1163 (1993).

6 a) G. S. Kumar and D. C. Neckers, *Chem. Rev.*, **89**, 1915 (1989). b) A. Natansohn, "Azobenzene-Containing Materials", Wiley, New York (1999).

7 a) M. E. Wright and M. J. Prosch, *Polym. Prepr.*, **39**, 278 (1998). b) M. Teraguchi and T. Masuda, *Macromolecules*, **33**, 240 (2000). c) A. Izumi, M. Teraguchi, R. Nomura, and T. Masuda, *J. Polym. Sci., Polym. Chem.*, **38**, 1057 (2000).

8 Although Ni(cod)$_2$ was reported to be effective for the polymerization of dihaloazobenzene,[9] our attempt failed to synthesize poly(azobenzene)s by using Ni(cod)$_2$.[10]

9 T. Yamamoto, S. -B. Kim, and T. Maruyama, *Chem. Lett.*, **1996**, 413.

10 A. Izumi, M. Teraguchi, R. Nomura, and T. Masuda, *Macromolecules*, in press.