Palladium-Catalyzed Cross-Coupling Polycondensation of Bisalkynes with Dihaloarenes Activated by Tetrabutylammonium Hydroxide or Silver(I) Oxide

Atsunori Mori,* Tatsuhiro Kondo, Tsuyoshi Kato, and Yasushi Nishihara
Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta, Yokohama 226-8503

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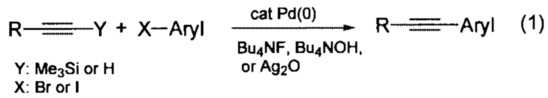
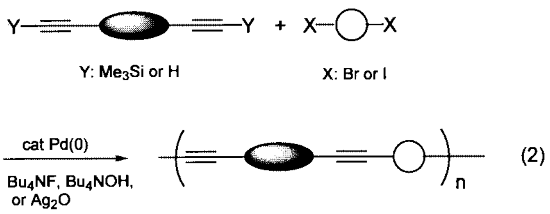
The palladium(0)-catalyzed polycondensation of bis-trimethylsilylethynylated compounds with diiodoarenes to give the polymers bearing arylene-ethynylene moieties is carried out by the use of silver(I) oxide as an activator. Polycondensation of bifunctional terminal alkynes and aryl halides is also accomplished by the palladium-catalyzed cross coupling in the presence of tetrabutylammonium hydroxide (TBAOH), tetrabutylammonium fluoride (TBAF), or silver(I) oxide.

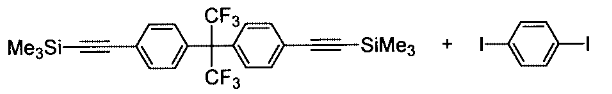
We have recently reported several palladium-catalyzed cross-coupling reactions of a trimethylsilyl or a terminal alkyne with an aryl halide, which are promoted by the use of silver(I) oxide, tetrabutylammonium fluoride (TBAF), or tetrabutylammonium hydroxide (TBAOH) as an activator to give a variety of aryl alkynes (eq 1).[1] We thus envisaged that the new findings would provide a practical method for the synthesis of poly(aryleneethynylene)s by reacting bifunctional alkynes with haloarenes as shown in eq 2.[2] The resulting materials have potential applications as conductive polymers and in light emitting diodes (LED).[3] The modular nature of our method provides a valuable synthetic route to these important materials. Herein, we report new polycondensation reactions, which are available to the reactions of both trimethylsilylated and terminal alkynes with aryl halides.



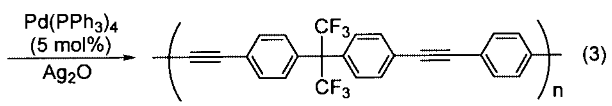


We first performed the polycondensation of bis-trimethylsilylethynylated compounds with aryl halides in the presence of Ag_2O as an activator. A bis-trimethylsilylethynylated compound **1a** was readily prepared form bisphenol AF.[4] As shown in eq 3, the reaction of **1a** with 1,4-diiodobenzene (**2**) was carried out in the presence of 5 mol% of $Pd(PPh_3)_4$ as a catalyst affording the polymer **3a** in 77% yield after stirring at 60 °C for 6 h.[5] The polymer **3a** was isolated by simple filtration of the reaction mixture followed by reprecipitation of the concentrated solution into methanol. A molecular weight (M_w) and molecular weight distribution (M_w/M_n) were found to be 21200 and 2.3, respectively, by measurement of size exclusion chromatography (SEC). Under these conditions cross coupling between Csp–Csp[2] centers was the only condensation reaction observed. The undesired homocoupling to form diyne or bisaryl byproduct did not take place according to analysis of the ^{13}C NMR spectrum of the polymer. The similar polymerization was also carried out using 1,4-bis(trimethylsilyl)-1,3-butadiyne (**1b**) and bis(trimethylsilyl)-ethyne (**1c**). In these reactions, a 2,7-diiodofluorene derivative **4** was employed as a monomer for the purpose to form polymers easily soluble in a common organic solvent. The polycondensation reactions furnished the corresponding polymers bearing ethynyl and butadiynyl moiety **5b** and **5c** in 99% and 91% yields, respectively (eq 4).

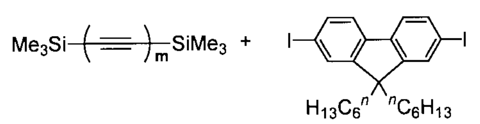
The related polycondensation has also been performed by the Sonogashira-(Hagihara) coupling,[6] the cross coupling of bifunctional aromatic dihalides and terminal alkynes, which have been occasionally synthesized by desilylation of the bis-trimethylsilylated alkynes. Accordingly, the present polycondensation with trimethylsilyl alkyne could be affected by omitting the deprotection procedure. It is also remarkable that the reactions with **1b** and **1c** have been carried out without using gaseous and/or potentially explosive 1,3-butadiyne and ethyne as monomers.



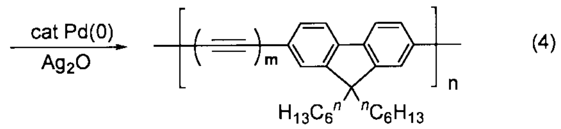
1a **2**



3a: 77%,
M_w=21200, M_w/M_n=2.3



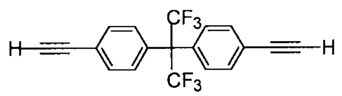
1b (m=2), **1c** (m=1) **4**



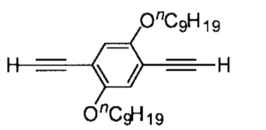
5b (m=2); 99%, M_w=39400, M_w/M_n=2.9
5c (m=1); 91%, M_w=7800, M_w/M_n=1.9

Further, the polycondensation of bifunctional terminal alkynes was examined using a bisphenol AF[4] derivative **6a** or a 1,4-diethynylbenzene derivative substituted with nonyloxy groups **6b**. For the organic electrophiles, 1,4-diiodobenzene (**2**), 1,4-dibromobenzene (**7**), and **4** were employed. In these reactions, TBAOH and TBAF were also used in addition to Ag_2O. Table 1 summarizes the results of the cross-coupling polycondensation.

When the reaction of **6a** with **2** was carried out using 10.0 mol% of Pd(0) and 200 mol% of Ag_2O as an activator in THF, the corresponding polymer was furnished in 96% yield after stirring at 60 °C for 96 h. The obtained polymer was identical with **3a** that was prepared from the reaction of the trimethylsilyl derivative **1a** and **2** and exhibited a molecular weight of 31900 (M_w) with M_w/M_n of 5.7. The polymerization was found to be much faster when TBAOH (240 mol%) was employed as an activator to yield **3a**, after stirring for 6 h with a smaller amount of Pd(0) (2 mol%), in 71% yield (M_w=35400, M_w/M_n=3.5).[7] In order to avoid Pd(0) mediated crosslinking, the reaction had to be run at a concentration of 0.05 M. A significant quantity of insoluble material was obtained when the reaction was carried out at concentrations higher than 0.1 M. The use of TBAF as an activator was equally effective as TBAOH. In contrast that only iodide as an organic electrophile could effect the polycondensation with silylalkynes, the reaction between 1,4-dibromobenzene (**7**) and **6a** could be carried out although considerably longer reaction times (120 h) were needed. Similarly, the dialkyne **6b** was reacted with **2** and **4** to afford highly conjugated polymers in excellent yields.



6a



6b

Table 1. Polycondensation of terminal alkynes[a)]

Diyne	Dihalide	Activator	Time /h	%Yield	M_w $\times 10^{-3\,b}$	M_w/M_n[b]
6a	**2**	Ag_2O	96	86[c]	31.9	5.7
		TBAOH	6	71	35.4	3.5
	7		120	74	34.8	3.7
	2	TBAF	48	91	51.7	3.4
6b	**2**	TBAOH	1.5	>99	30.1	4.3
	4		5	98	135.6	6.0
6a	**2**	Et_3N (excess)[d]	6	68	49.9	2.3
		Et_3N-H_2O[e] (excess)[d]	6	8		

[a]The reaction was carried out as described in ref 7. [b]Estimated by size exclusion chromatography (SEC) with polystyrene standards. [c]$Pd(PPh_3)_4$ (10 mol%) and Ag_2O (200 mol%) was employed. [d]Et_3N (5.0 mL) was used as a solvent. CuI (2 mol%) was employed as a co-catalyst. [e]The amount of water employed was 0.2 mL.

Compared with Sonogashira conditions, which required catalytic Pd(0) and Cu(I) in the presence of large amounts of an amine as solvent or co-solvent,[6,8] the present reactions with bis-trimethylsilyl and bis-terminal alkynes proceeded without using Cu(I). The former is apparently advantageous in use of **1b** and **1c** because of the difficulties in handling of such desilylated derivatives. Although the reaction of **6a** and **2** under the Sonogashira conditions also affords the corresponding polymer **3a** in a comparable yield and molecular weight,[9] the procedural simplicity of the present cross-coupling polycondensation is worthy of note because the use of a large quantities of a high boiling amine can cause serious difficulties in isolation and purification. It should also be pointed out that the reaction with TBAOH could be affected as 40% aqueous solution suggesting potential tolerance of the polymerization to water, while addition of water under Sonogashira conditions considerably reduced the yield of **3a**.

We have shown that Ag_2O, TBAOH, and TBAF serve as new activators for the cross-coupling polycondensations of bis-trimethysilylated and -terminal alkynes with dihaloarenes for the synthesis of poly(aryleneethynylene)s. This method is a valuable alternative to the Sonogashira coupling, which employs a catalytic amount of Pd(0)/Cu(I) in the presence of excess amine. Furthermore, we have previously reported that polycondensation of bis-trimethylsilylated alkynes with ditriflates can be catalyzed by Pd(0)/CuCl.[10] Thus, the described palladium-catalyzed polymerization of dihaloarenes and alkynes expands the scope of the polymer synthesis to include either phenols or aryl halides as starting materials. This new method further enhances the flexibility of synthetic design of these important polymeric materials.

References and Notes

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4 2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane. The authors thank Central Glass Co. Ltd. for kind donation of the sample.

5 The reaction of bis-trimethylsilylated alkyne **1a** and **2** with Ag_2O: To a solution of **1a** (0.128 g, 0.25 mmol) in THF (2 mL) were added Ag_2O (0.5 mmol), **2** (0.083 g, 0.25 mmol), and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) under an argon atmosphere. The resulting suspension was heated at 60 °C for 5 h. After cooling to room temperature the mixture was passed through a Celite pad to remove the silver residue. The pad was washed with 20 mL of THF. The combined organic solution was concentrated into 10 mL. The resulting residual liquid was poured into a mixture of 300 mL of methanol and 50 mL of 3 M hydrochloric acid to form a precipitate, which was collected by filtration. The solid was dissolved in a minimum amount of chloroform and the dark brown solution was subjected to reprecipitation into 300 mL of methanol. The formed solid was separated by filtration to give 0.082 g of **3a** (77% yield). M_w = 21200, M_w/M_n = 2.3. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, J = 8.4 Hz, 4 H), 7.53 (s, 4 H), 7.39 (d, J = 8.4 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 64.5 (sept, J = 24 Hz), 90.1, 90.7, 123.0, 123.9 (q, J = 284 Hz), 124.1, 130.2, 131.4, 131.7. IR (KBr) 3044, 2217, 1609, 1520, 1483, 1252, 1207, 1175, 828 cm^{-1}.

6 K. Sonogashira, "Metal-Catalyzed Cross-Coupling Reactions," ed. by F. Diederich and P. J. Stang, Wiley-VCH, Weinheim (1998), Chap. 5, pp. 203–229.

7 The reaction of bis-terminal alkyne **6a** and 1,4-diiodobenzene (**2**) with TBAOH: To a mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (5.2 mg, 0.005 mmol), PPh_3 (5.3 mg, 0.02 mmol), and **6a** (0.176 g, 0.5 mmol) in THF under an argon atmosphere were added **2** (0.105 g, 0.5 mmol) and TBAOH (0.08 mL of 40% aqueous solution, 1.2 mmol). The resulting mixture was heated at 60 °C for 6 h. Then, the mixture was cooled to room temperature and poured into a mixed solution of methanol (300 mL) and 3 M hydrochloric acid (50 mL) to form a precipitate, which was collected by filtration. The solid was dissolved in a minimum amount of chloroform and the dark brown solution was subjected to reprecipitation into 300 mL of methanol. The formed solid was separated by filtration to give 0.24 g of **3a** (71% yield). M_w = 31900, M_w/M_n = 3.5.

8 a) T. Yamamoto, K. Honda, N. Ooba, and S. Tomaru., *Macromolecules*, **31**, 7 (1998). b) Y. Pang, J. Li, B. Hu, and F. E. Karasz, *Macromolecules*, **31**, 6730 (1998). c) T. Sato, D.-L. Jiang, and T. Aida, *J. Am. Chem. Soc.*, **121**, 10658 (1999). d) J. M. Hong, H. N. Cho, D. Y. Kim, and C. Y. Kim, *Synth. Met.*, **102**, 933 (1999) e) R. W. Wagner, T. E. Johnson, J. S. Lindsey, *J. Am. Chem. Soc.*, **118**, 11166 (1996) and references cited therein.

9 The reaction with 2 mol% of $PdCl_2(PPh_3)_2$ and 2 mol % of CuI in Et_3N–THF at 60 °C for 6 h afforded 68% of **3a** (M_w = 49900, M_w/M_n = 2.3).

10 Y. Nishihara, J. Ando, T. Kato, A. Mori, and T. Hiyama, *Macromolecules*, **33**, 2780 (2000).