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Communications to the Editor

A Novel Cross-Coupling Polycondensation of Alkynylsilanes with Aryl Triflates Catalyzed by CuCl/Pd(PPh_3)$_4$

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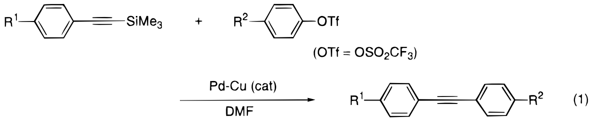
Recently, we have found that the reaction of alkynylsilanes with copper(I) chloride in a polar solvent, DMF, allows the alkynyl groups on silicon to oxidatively homocouple, and the corresponding 1,3-butadiyne derivatives were produced.[1] In addition, we also documented that CuCl/Pd(PPh_3)$_4$ catalyzed the cross-coupling reaction between aryl(ethynyl)silanes and aryl triflates to give unsymmetrical diarylethynes as shown in eq 1.[2]

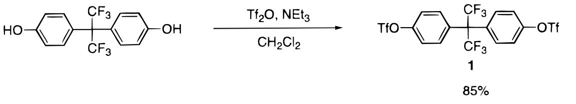


(1)

On the other hand, the Sonogashira–Hagihara reaction, a coupling of a terminal alkyne with an aryl halide, serves as an alternative synthesis of diarylethynes,[3] and the coupling is also applied to polymer synthesis via polycondensation with bifunctional monomers.[4] Concerning the syntheses of the alkyne monomers, however, initial formation of a trimethylsilylated alkyne followed by deprotection of the silyl group has been a general pathway.

Hence, polymerization by the direct coupling using silylated dialkynes would be a facile method for the synthesis of polymers bearing a C≡C bond in the main chain. Herein, we report the cross-coupling polycondensation reactions of alkynylsilanes with aryl triflates as well as preliminary characterizations of the resulting polymers.

The bifunctional aryl triflate as a monomer, 2,2-bis(4-trifluoromethanesulfonylphenyl)hexafluoropropane (**1**), was readily prepared from 2,2-bis(4-hydroxyphenyl)hexafluoropropane[5] according to the procedure as shown in eq 2.[6,7] Although a large number of such fluorine-containing polymers as polycarbonate and polyimide have been prepared to take advantage of their high thermostability,[8] monomer **1** is particularly suitable for the present polymerization because triflates with an electron-withdrawing group undergo the coupling reaction extremely smoothly.[2]



(2)

We first studied the polymerization of **1** with bis(trimethylsilyl)acetylene (**2a**) in DMF at 0.2 M (Table 1, run 1) at 80 °C for 24 h in the presence of 5 mol % of Pd(PPh_3)$_4$ and 10 mol % of CuCl as shown in eq 3. The resulting black DMF solution was poured into a mixture of methanol and 3 M HCl to yield black precipitates, which were collected by filtration. Reprecipitation of the chloroform solution into methanol gave gray precipitates of **3a** in 32% yield. Molecular weights (M_n) of **3a** was found to be 9800 by GPC. The reaction at higher concentration, 0.5 M, slightly improved the yield of polymer **3a** up to 42% (Table 1, run 2). We then carried out the reaction of **1** and **2a** (Table 1, run 3) at 1.0 M and obtained **3a** in 63% yield with the comparable molecular weight. Polymer **3a** isolated herein was gray

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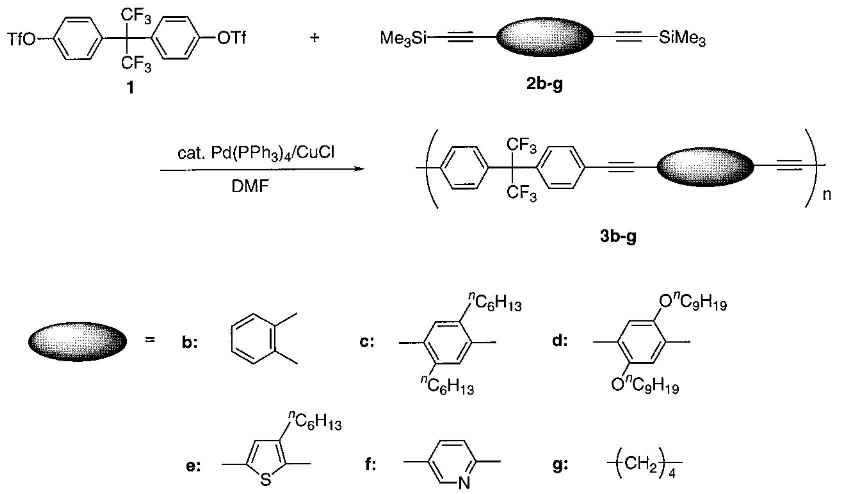
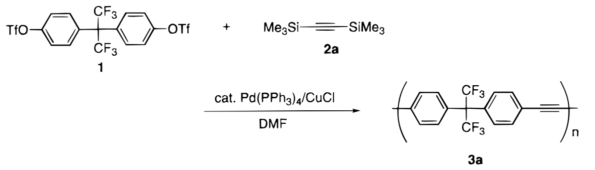
Table 1. Yields and Molecular Weight Data for Polymers 3a–3g[a]



run	monomer	polymer	[M]	temp/°C	time/h	yield[b]/%	M_n[c]	M_w[c]	M_w/M_n[c]	DP[d]
1	**1**, **2a**	**3a**	0.2	80	24	32	9900	12500	1.27	61
2			0.5	80	22	42	9800	12100	1.22	60
3			1.0	80	16	63	9700	12900	1.33	59
4	**1**, **2b**	**3b**	0.5	120	72	52	6000	7300	1.21	28
5	**1**, **2c**	**3c**	1.0	120	2	80	6200	8900	1.44	21
6	**1**, **2d**	**3d**	0.5	80	5	90	7800	11100	1.42	20
7	**1**, **2e**	**3e**	0.5	80	1	58	5000	7100	1.43	19
8	**1**, **2f**	**3f**	0.5	80	6	43	11700	15000	1.28	55
9	**1**, **2g**	**3g**	0.5	80	37	48	8900	12000	1.35	42

[a] Polymerizations were carried out in the presence of 5 mol % tetrakis(triphenylphosphine)palladium and 10 mol % copper(I) chloride in DMF. [b] Isolated yield by reprecipitation. [c] Determined by GPC with THF as an eluent relative to polystyrene standards. [d] DP = 2*n*.

solids and soluble in chloroform and THF but insoluble in methanol.



(3)

We next examined the polycondensation of **1** with various bifunctional alkynylsilanes **2b**–**2g**. The yields and molecular weights of the corresponding polymers **3b**–**3g** are also summarized in Table 1. Rather low yields of polymers **3e**–**3g** are ascribed to the formation of chloroform-insoluble polymers, whereas methanol-soluble oligomers were formed in the reaction with **2b**. The produced polymers **3a**–**3g** from these cross-coupling reactions were well characterized with the ^1H and ^{13}C NMR spectra.[9]

Although undesirable homocoupling are reported to occur in several Sonogashira polycondensation reactions as a side reaction,[4] it is remarkable that the amount of such homocoupled segment was found hardly detectable in the polymerization of a bifunctional alkynylsilane and a bifunctional aryl triflate. A measurement of ^{13}C NMR spectrum of **3d**, for example, shows characteristic signals assignable to $C\equiv C$ at 87.7 and 93.7 ppm, whereas the signal assignable to $C\equiv C-C\equiv C$ (79.8 ppm)[10] of the corresponding authentic polymer was trace or not detectable. The ^{13}C NMR spectra of diarylated butadiynes that we synthesized previously[1] as well as polymers bearing a diyne moiety prepared by Sonogashira polycondensation[11] also suggest that the corresponding signals appear in the range 74–82 ppm. However, no significant amount of such signals has also been observed in other polymers **3a**–**3g** (see also Supporting Information).

Table 2. UV–vis, Fluorescence, and Excitation Spectra of Polymers 3a–3g[a]

polymer	λ_{max}/nm	Em_{max}/nm[b]	Ex_{max}/nm[c]
3a	292, 300, 313	316, 329, 339	293, 301, 312
3b	281, 303, 318	350, 366, 375	282, 307, 315
3c	318, 336, 354	366, 400	318, 337, 357
3d	311, 375	414, 437	313, 376
3e	362, 380^{sh}	399, 420	364, 380^{sh}
3f	333, 352^{sh}	363, 398	333, 352^{sh}
3g	262	*d*	

[a] In $CHCl_3$. [b] Wavelength of maximum fluorescence emission. [c] Wavelength of maximum fluorescence excitation. [d] No fluorescence was observed.

Use of a sterically hindered bifunctional acetylene, 1,2-bis(trimethylsilylethynyl)benzene (**2b**), required high reaction temperature (120 °C) and prolonged reaction time (72 h), and polymer **3b** was obtained with an M_n value of 6000 and M_w/M_n of 1.21 (Table 1, run 4). Reactions of **1** with 1,4-bis[(trimethylsilyl)ethynyl)]-2,5-dihexylbenzene (**2c**) and 1,4-bis(trimethylsilyl)ethynyl-2,5-bis(nonyloxy)benzene (**2d**) gave polymers **3c** and **3d** in 80 and 90% yield, respectively (Table 1, runs 5 and 6). Monomer **2e** containing a thiophene ring in place of a benzene ring was subjected to the polymerization with **1**. The yield of the resulting polymer **3e** was 58% (Table 1, run 7). Molecular weights (M_n) of **3f** derived from the reaction of **1** and 2,5-bis[(trimethylsilyl)ethynyl]pyridine (**2f**) at 0.5 M were 11 700 (Table 1, run 8), the highest value among the polymers prepared.

UV–vis absorption and fluorescence data of polymers **3a**–**3g** are listed in Table 2. Polymer **3d** showed strong UV absorption at 375 nm, about a 30 nm red shift from that of monomer **2d**. This is probably due to the π-conjugation between the aromatic rings and the

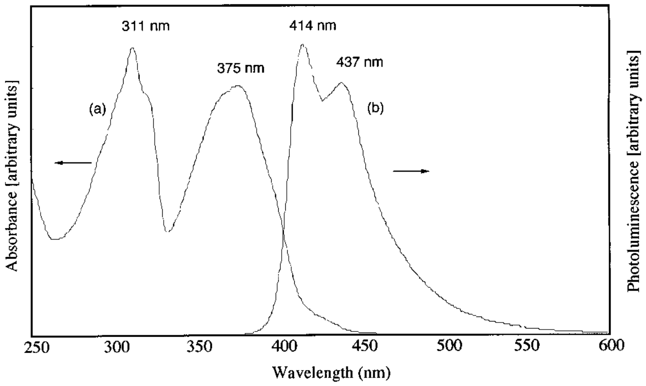


Figure 1. (a) Absorption spectrum of **3d** in $CHCl_3$. (b) Fluorescence spectrum of **3d** (1×10^{-4} g/L) in $CHCl_3$ with excitation wavelength at 311 nm. Excitation at 375 nm gave essentially the same spectrum.

Table 3. Thermal Characterization of Polymers[a]

polymer	T_{d}^{5}/°C[b]	T_{d}^{10}/°C[c]	char yield/%[d]
3a	387	497	51
3b	392	501	62
3c	354	389	42
3d	327	345	39
3e	389	447	51
3f	367	477	58
3g	362	427	46

[a] Measured in a nitrogen atmosphere with a heating rate of 10 °C/min. [b] Temperature at 5% weight loss. [c] Temperature at 10% weight loss. [d] Percent mass remaining at 1000 °C.

acetylenic unit, whereas polymer **3g** with an alkylene main chain had $\lambda_{\max}$ at a shorter wavelength, since there is no π-conjugation along the main chain of the polymer. Polymer **3d** exhibited a dual fluorescence spectrum as shown in Figure 1. Strong fluorescence maxima at 414 and 437 nm (the blue light region) for **3d** indicate that it is a possible candidate for emissive components in electroluminescent devices.[12]

We examined thermal properties of polymers **3a**−**3g** with thermogravimetric analyses (TGA) in temperatures ranging from 20 to 1000 °C under an atmosphere of nitrogen. The results are summarized in Table 3. The TGA profiles for **3a**−**3g** were essentially similar, showing no significant weight loss until 300 °C. When polymer **3c** is compared with **3d**, the thermal decomposition of **3c** occurred at higher temperature and gave higher char yield at 1000 °C than those of **3d**. The origin of the higher thermal stability for polymers **3a**−**3g** is probably due to the strong carbon−fluorine bond as well as a high degree of conjugation in the main chain.

In conclusion, we have applied the Cu(I)/Pd(0)-catalyzed cross-coupling reaction of alkynylsilanes and aryl triflates to the synthesis of polymers containing diarylethyne moieties with M_{n} values as high as 11 700. The polymers were shown to be possible new materials with high thermal stability. Efforts for improvement of polymer yield as well as studies on other chemical and physical properties of the polymers are currently underway.

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Supporting Information Available: Experimental methods for monomer synthesis. Spectroscopic and analytical data of monomers and polymers and the ^{13}C NMR spectra of polymers **3a**−**3g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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