# Sonogashira coupling of diethynylsilane and dibromoarene in wet solvent for the formation of poly[(ethynylenearylene)-*co*-(diethynylenesilylenearylene)]

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## Abstract

Copolymerization of diethynylsilane and dibromoarene by Sonogashira coupling was investigated. Polymerization in dry triethylamine gave poly(diethynylsilylenearylene)s, while in wet triethylamine, hydrolytic desilylation competed to afford polymers containing extended ethynylene–arylene units in the backbone. The resulting polymers exhibited hole-transporting properties in the solid state, being applicable to EL device materials.
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## 1. Introduction

Current interest has been focused on organic EL devices. Their brightness and the availability of a wide range of emission allow us to use them for full-color flat panel displays. Many papers concerning synthesis of π-conjugated polymers and their utilities as EL device materials have been published to date [1]. Recently, we have demonstrated that spin-coated films of polymers composed of an alternate arrangement of organosilanylene and π-conjugated units, are useful as efficient hole-transporting materials in multi-layer EL devices [2–4]. In these polymers, electron-donation from the organosilanylene unit is expected to elevate the HOMO energy level of the π conjugated system, leading to improved hole-accepting properties of the system. Well-known

σ–π type conjugation between the silicon σ-orbital and the π-electron system also may be involved [2].

Interestingly, hole-transporting properties of the Si-π alternate polymers, evaluated by performance of the EL devices having the polymer film as the hole-transport, are improved as the π-conjugated system involved in the backbone is extended, in the order of phenylene < biphenylene < naphthylene < diethynyleneanthracene < diethynylenepyrene [4]. However, since monomers with extended π-conjugation usually exhibit low solubility in organic solvents, they are hardly used in the solution-phase polymerization. Although introduction of long alkyl chains is often employed to improve the solubility, it may suppress the intermolecular interaction of the resulting polymers in the solid state, which is important for intermolecular hopping-type carrier-transport. Here, we report a novel method to prepare organosilanylene polymers with extended π-conjugated units in the backbone by Sonogashira coupling [6] of

diethynylsilane ($(HC{\equiv}C)_2 SiR_2$) and dibromoarene ($Br_2Ar$) in wet solvents. In this polymerization, hydrolytic desilylation competed the coupling reactions, leading to the formation of polymers with the structure of $-(C{\equiv}C-Ar)_x-(C{\equiv}C-SiR_2-C{\equiv}C-Ar)_y-$, in which the degree of incorporation of the desilylated units could be controlled by the amount of water added to the reaction medium.

## 2. Results and discussion

### 2.1. Polymer synthesis

When a mixture of 1,4-dibromonaphthalene and dibutyldiethynylsilane was subjected to $PdCl_2(PPh_3)_2$/CuI-catalyzed dehydrohalogenative copolymerization in dry triethylamine, polymer **PN0** having a naphthylene-diethynylenesilylene alternate arrangement (Scheme 1, $x = 0$) was obtained in 71% yield as the orange solids. As shown in Table 1, when similar reactions were carried out in wet triethylamine, hydrolytic desilylation competed the polymerization to afford random copolymers poly[(ethynylenenaphthylene)-*co*-(diethynylenesilylenenaphthylene)]s in good yield (**PN10–PN90**, where numbers in polymer symbols indicate the equiv of water taken for the polymerization).
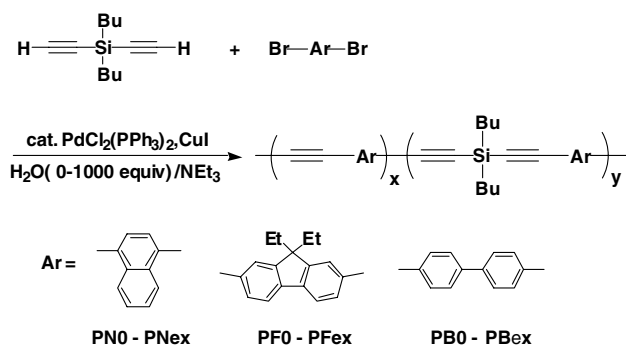
The structures of the polymers were verified by spectrometric analysis. The IR spectrum of **PN0** showed a sharp absorption band due to $C{\equiv}C$ stretching at 2151 cm$^{-1}$, which was broadened and weakened
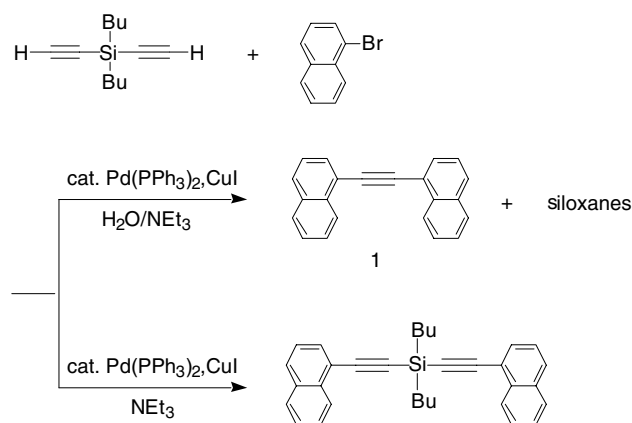


Scheme 1.



Scheme 2.

Table 1
Preparation of poly[(ethynylenearylene)-*co*-(diethynylenesilylenearylene)]s

| Polym. | Yield (%)[a] | Mw[b] | Mw/Mn[b] | x/y[c] | EL max luminance[d] (cd/m²) |
|---|---|---|---|---|---|
| **PN0** | 71 | 17,600 | 1.9 | | 39 |
| **PN10** | 57 | 18,300 | 2.2 | 1/21 | |
| **PN20** | 34 | 12,000 | 1.4 | 1/8.1 | |
| **PN50** | 46 | 22,400 | 2.6 | 1/4.6 | 57 |
| **PN80** | 48 | 20,600 | 2.5 | 1/4.1 | |
| **PN90** | 66 | 25,200 | 2.5 | 1/4.0 | |
| **PNex** | 19 | 17,500 | 2.3 | 1/4.2 | 279 |
| **PF0** | 52 | 6300 | 1.3 | | 286 |
| **PF10** | 87 | 9600 | 1.6 | 1/131 | |
| **PF20** | 86 | 8400 | 1.4 | 1/13 | |
| **PF50** | 71 | 8700 | 1.6 | 1/11 | 150 |
| **PF80** | 85 | 8600 | 1.5 | 1/3.9 | |
| **PF90** | 25 | 7600 | 1.6 | 1/3.7 | |
| **PFex** | 32 | 10,100 | 1.8 | 1/0.77 | 499 |
| **PB0** | 87 | 11,200 | 1.9 | | 51 |
| **PB20** | 87 | 14,000 | 1.8 | 1/3.1 | |
| **PB50** | 61 | 13,700 | 1.6 | 1/2.5 | 131 |
| **PB80** | 61 | 11,100 | 1.5 | 1/2.1 | |
| **PBex** | 9 | 6500 | 1.2 | 1/1.2 | 360 |

[a] Yield of the polymer soluble in chloroform, after purification by reprecipitation twice from chloroform–ethanol.
[b] Determined by GPC, relative to polystyrene standards.
[c] Determined by $^1$H NMR spectrum.
[d] On a device with the structure of ITO/polymer/Alq3/Mg:Ag.

on going from **PN10** to **PN90**. The incorporation ratios of the desilylated units in the polymers ($x/y$ in Scheme 1) were determined by the integration in ^{1}H NMR spectra. The $x/y$ ratios increased in the order from **PN10** to **PN90** to reach the maximum value of ca. $x/y = 1/4.0$ for **PN90**, as shown in Table 1. However, polymerization in the presence of a large excess of water (1000 equiv.) did not increase the ratio at all, affording polymer **PNex** with $x/y = 1/4.2$. This is probably due to that the introduction of desilylated units to the larger extent led to the less soluble properties of the resulting polymers. In fact, a large amount of insoluble materials that were removed by filtration of the reaction mixture, were formed in the preparation of **PNex**. The rather low yield of soluble **PNex** also resulted from the formation of the insoluble polymers.

We next carried out model reactions of dibutyldiethynylsilane and 1-bromonaphthalene in dry and wet triethylamine as shown in Scheme 2. The reaction in a wet solvent gave dinaphtylacetylene (**1**) in 68% isolated yield, while in a dry solvent, dibutyldi(naphtylethynyl)silane (**2**) was obtained in 92% yield. In the former reaction, a large amount of non volatile oligomers, whose IR spectrum revealed a strong absorption at about 1100 cm$^{-1}$ due to the stretching frequencies of siloxane bonds, were also found to be formed, but no formation of **2** was detected. When polymer **PNex** once separated from the reaction mixture was treated under the same conditions as those of polymerization, no further hydrolysis occurred and the polymer was recovered unchanged. This clearly indicated that hydrolysis of the Si-ethynyl bonds had occurred at the early stage of the polymerization.

Table 1 also summarizes the results of copolymerization of dibutyldiethynylsilane with dibromodiethylfluorene and dibromobiphenyl, from which we obtained polymers **PF0**–**PFex** and **PB0**–**PBex**, respectively. The ^{1}H NMR analyses of polymers **PFex** and **PBex** showed higher $x/y$ ratios than that of **PNex**. The highest degree of incorporation of the desilylated units in the polymer backbone was observed for **PFex** ($x/y = 1/0.77$).

## 2.2. Optical and hole-transporting properties of the polymers

Fig. 1 represents selected UV absorption spectra of the present polymers in THF. As increasing the incorporation ratios of the desilylated units, new absorption bands at lower energies appeared and enhanced. We next examined spin-coated films of the polymers as hole-transports in double layer EL device system. Fig. 2 shows the performance of EL devices with the structure of ITO/polymer/Alq3/Mg:Ag, where Alq3 (tris(8-quinolinolato) aluminum (III)) is used as the electron-transporting-emitter, and ITO (indium–tin-oxide) and Mg:Ag (10:1) are the anode and cathode, respectively. The devices emitted a green light arising from Alq3 emission, when bias voltage exceeded 5–7 V. Among the devices examined, that with **PFex** gave the highest maximum luminance of 499 cd/m$^2$.

The performance of the EL devices based on the naphthylene and biphenylene-containing polymers was improved as increasing the $x/y$ ratios, in accordance with the UV spectral changes depending on the ratios. Both the current densities and the luminances from the devices increased in almost all range of the applied voltage, as increasing $x/y$ ratios. However, the devices with fluorene-containing polymers exhibited no evident changes in the current densities depending on the $x/y$ ratios. The maximum luminances form the devices once decreased on going from **PF0** to **PF50**, but increased when **PFex** was used as the hole-transport. This may be due to other factors than extension of the π-conjugated system,
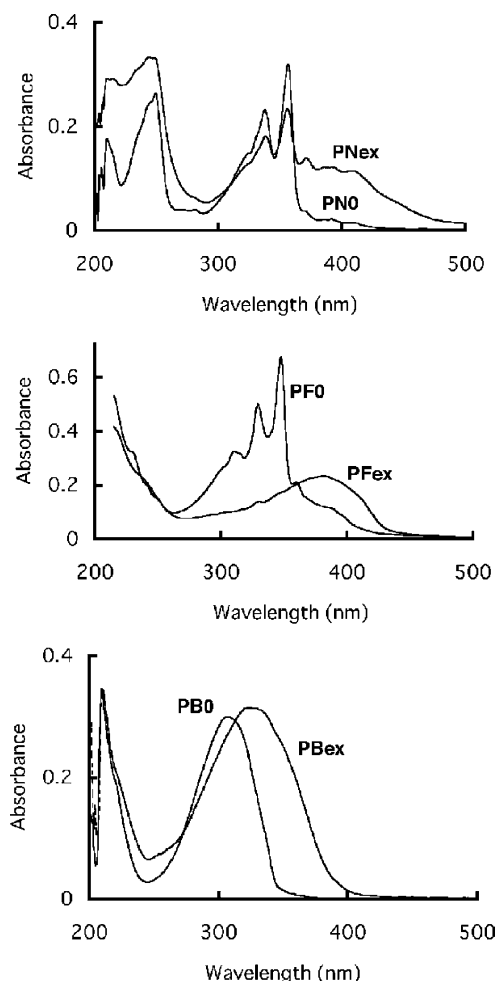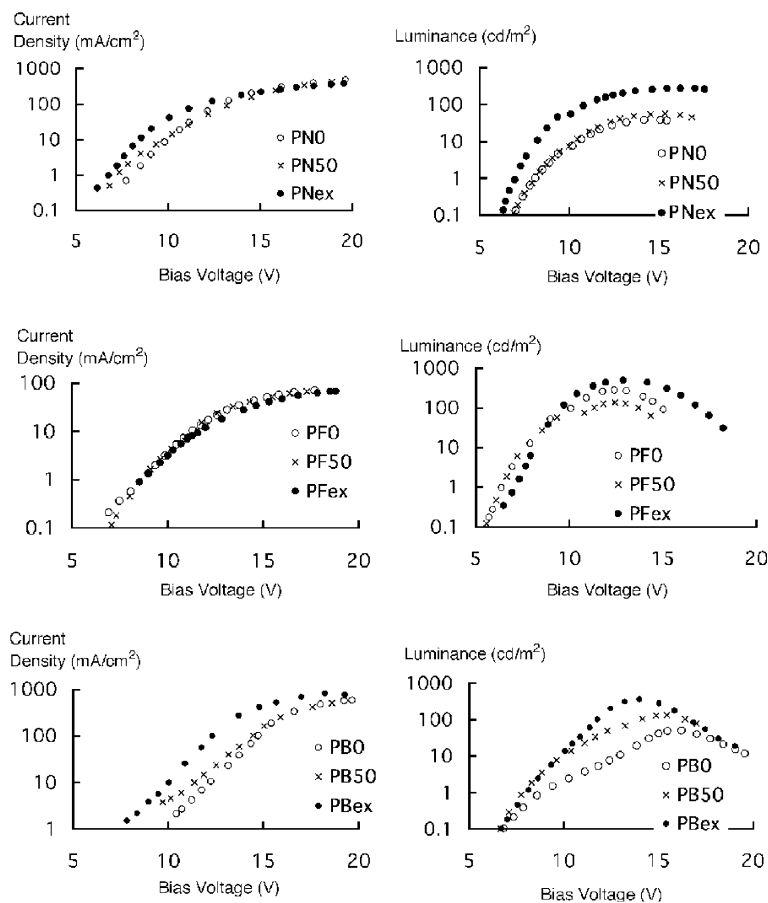


Fig. 1. UV spectra of the polymers.

Fig. 2. *I–V* and *L–V* plots of EL devices with the structure of ITO/polymer/Alq3/Mg:Ag.

such as film morphology, although we have no data to support this.

## 3. Conclusions

On the basis of the results mentioned above, we demonstrated that Sonogashira coupling of diethynylsilane and dibromoarene in wet solvent, competing hydrolytic cleavage of Si-ethynyl bonds, led to the formation of poly[(ethynylenearylene)-co-(diethynylenesilylenearylene)]s in good yield. The ratios of the incorporation of desilylated ethynylenearylene units in the polymer backbone, which significantly affected the polymer properties, could be controlled by the amount of water added into the reaction medium. Although the EL device performance based on the present polymers was not so good as that of a similar double layer device with a spin-coated film of poly(vinylcarbazol) that is known as a typical hole-transporting material (ITO/poly(vinyl-carbazol)/Alq3/Mg:Ag), from which the luminance as high as 8000 cd/m$^2$ was obtained at a bias voltage of 16 V [4b,4c], the present studies would provide a novel synthetic route to organosilicon polymers with extended π-conjugated units.

## 4. Experimental

### 4.1. General methods

All reactions were carried out under an inert atmosphere. Triethylamine used as the reaction solvent was distilled from KOH just before use. NMR spectra were recorded on a JEOL Model JNM-EX270 spectrometer. IR spectra were measured on a Shimadzu FT-IR Model 8700 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrophotometer. Molecular weights of the polymers were determined by gel-permeation chromatography relative to polystyrene standards, using Shodex 806 and 804 columns that were connected in series, and eluting with THF.

### 4.2. Polymerization

In a 50 mL two necked flask fitted with a reflux condenser and a magnetic starrier was placed 0.168 g (0.875 mmol) of dibutyldiethynylsilane, 0.250 g (0.875 mmol) of 1,4-dibromonaphthalene, 0.050 g of PdCl$_2$ (PPh$_3$)$_2$, 0.015 g of CuI, and 15 mL of triethylamine and the flask was heated at 50 °C for 34 h. After filtration

of the resulting precipitates, the solvent was evaporated from the filtrate and the residue was reprecipitated twice from chloroform–ethanol to give 0.195 g (71% yield) of **PN0**. $^1$H NMR (CDCl$_3$) $\delta$ 0.90–1.06 (m, 10H), 1.42–1.68 (m, 8H), 7.59 (dd, $^3J$ = 6.3 Hz, $^4J$ = 3.3 Hz, 2H), 7.71 (s, 2H), 8.42 (dd, $^3J$ = 6.3 Hz, $^4J$ = 3.3 Hz, 2H). $^{13}$C NMR (CDCl$_3$) $\delta$ 13.84, 14.60, 25.86, 26.15, 96.80, 104.53, 121.58 126.63, 127.46, 130.31, 133.21. IR 2151 cm$^{-1}$ ($v_{C\equiv C}$).

Other polymers were prepared as above in the absence or presence of water. Incorporation ratios of desilylated units ($x/y$ in Scheme 1) in the polymers were determined by integration of the $^1$H NMR signals. Typical data are as follows. Data for **PF0**: $^1$H NMR (CDCl$_3$) $\delta$ 0.28 (t, $J$ = 7.6 Hz, 6H, Et), 0.70–1.00 (m, 10H, Bu), 1.39–1.66 (m, 8H, Bu), 2.01 (q, $J$ = 7.6 Hz, 4H, Et), 7.47 (s, 2H), 7.50 (d, $J$ = 8.1 Hz, 2H), 7.62 (d, $J$ = 8.1 Hz, 2H). $^{13}$C NMR (CDCl$_3$) $\delta$ 8.38, 13.80, 14.72, 25.99, 26.13, 32.60, 56.34, 89.78, 107.53, 119.84, 121.71, 126.63, 131.52, 141.46, 150.19. IR 2153 cm$^{-1}$ ($v_{C\equiv C}$). Data for **PB0**: $^1$H NMR (CDCl$_3$) $\delta$ 0.80–0.96 (m, 10H), 1.41–1.61 (m, 8H), 7.54 (d, $J$ = 8.0 Hz, 4H), 7.58 (d, $J$ = 8.0 Hz, 4H). $^{13}$C NMR (CDCl$_3$) $\delta$ 13.80, 14.58, 25.95, 26.06, 90.57, 106.36, 122.19, 126.77, 132.69, 140.47. IR 2157 cm$^{-1}$ ($v_{C\equiv C}$). Data for **PNex**: $^1$H NMR (CDCl$_3$) $\delta$ 0.88–1.00 (m, 8.08H), 1.26–1.69 (m, 6.46H), 7.60–7.90 (m, 2H), 8.30–8.52 (m, 2H), 8.52–8.68 (m, 2H). IR 2144 cm$^{-1}$ ($v_{C\equiv C}$). Data for **PFex**: $^1$H NMR (CDCl$_3$) $\delta$ 0.28 (br t, $J$ = 7.6 Hz, 6H), 0.70–1.00 (m, 4.35H) 1.39–1.66( m, 3.48H) 2.01 (br q, $J$ = 7.6 Hz, 4H), 7.43–7.52 (m, 6H), 7.38–7.69 (m, 6H). IR 2149 cm$^{-1}$ ($v_{C\equiv C}$). Data for **PBex**: $^1$H NMR (CDCl$_3$) $\delta$ 0.79–0.97 (m, 5.45H), 1.38–1.61 (m, 4.36H), 7.54–7.63 (m, 8H). IR 2157 cm$^{-1}$ ($v_{C\equiv C}$).

### 4.3. Model reactions

In a 100 mL two necked flask fitted with a reflux condenser and a magnetic stirrer was placed 0.576 g (3.00 mmol) of dibutyldiethynylsilane, 1.24 g (6.00 mmol) of 1-bromonaphthalene, 0.100 g of PdCl$_2$(PPh$_3$)$_2$, 0.030 g of CuI, and 30 mL of triethylamine and the flask was heated at 50 °C for 48 h. After filtration of the resulting precipitates, the solvent was evaporated from the filtrate and the residue was chromatographed on a silica gel column eluting with hexane to give 1.23 g (92% yield) of compound **2**. MS $m/z$ 444 (M$^+$). $^1$H NMR (CDCl$_3$) $\delta$ 0.96–1.07 (m, 10H), 1.66–1.74 (m, 8H), 7.40–7.59 (m, 4H), 7.76–7.86 (m, 4H), 8.42–8.45 (m, 6H). $^{13}$C NMR (CDCl$_3$) $\delta$ 13.86, 14.79, 26.15, 26.20, 94.86, 104.78, 120.52, 125.09, 126.27, 126.43, 126.94, 128.27, 129.29, 131.16, 133.08, 133.55. $^{29}$Si NMR (CDCl$_3$) $\delta$ −33.89. IR 2145 cm$^{-1}$ ($v_{C\equiv C}$). *Anal*. Calc. for C$_{32}$H$_{32}$Si: C, 86.46; H, 7.21. Found: C, 86.59; H, 7.29%.

A similar reaction in the presence of 1000 equiv. of water was carried out under the same conditions to give compound **1** in 68% yield. All spectral data for **1** was identical with those reported in the literature [7].

### 4.4. Fabrication of EL devices

A film of the polymer with an approximate thickness of 50 nm was prepared by spin-coating (2000 rpm) from a solution of polymer in chloroform (5 g/L) on an anode, ITO coated on a glass substrate (Nippon Sheet Glass Co.). An electron-transporting-emitting layer with a thickness of 50 nm was then prepared by vacuum deposition of Alq3 at $1 \times 10^{-5}$ torr on the polymer film. Finally a layer of Mg:Ag alloy with an atomic ratio of 10:1 was deposited on the Alq3 layer as a cathode at $1 \times 10^{-5}$ torr.

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