

SHORT COMMUNICATION

Synthesis of Novel Poly(tetramethyl-2,7-silpyrenylenesiloxane) and Its Thermal and Optical Properties

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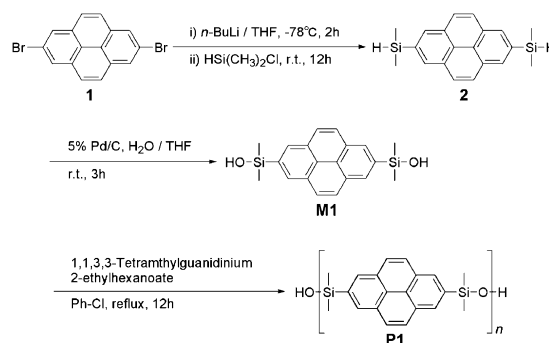
Pyrene has been well-known to exhibit the good fluorescence property¹ and the unique emission based on its excited dimer in the fluorescence spectrum of the solution at a relatively high concentration (*ca.* 10^{-3} mol/L) and/or of the solid state. Thus, various pyrene derivatives have been used for the emission moiety as an emitting fluorescence probe for biological analyst, electronics and photonics materials such as organic light-emitting diodes (OLEDs) and organic transistor, and so on.² In addition, the incorporation of silyl substituents onto aromatic species has been reported to result in the high fluorescence quantum yield as well as in the red-shift of maximum absorption wavelength.³ If the silyl substituent is incorporated onto pyrene, the development of the highly efficient fluorophore is presumably promised.³

On the other hand, polysiloxanes having fluorophore moiety in the main chain have been reported to be obtained as oil products up to now.⁴ Thus, the use of polysiloxane derivatives as polymeric OLED materials seems to be inadequate because of their low glass transition temperature (T_g)^{5,6} inducing the formation of aggregates, even though the other properties of polysiloxanes such as good thermostability and stability against atomic oxygen^{5,6} seem to be appropriate for the polymeric OLED materials. One of the methods for raising T_g is incorporation of bulky and rigid moieties into the main chain.⁷ For example, the T_g of poly(dimethylsiloxane) has been reported to be -123°C ;⁵ however, those of a series of poly(tetramethylsilyarylenesiloxane) derivatives to be in the range from -52°C to 156°C depending on the arylene moiety introduced.⁷⁻⁹

From these points of view, we report here the synthesis of poly(tetramethyl-2,7-silpyrenylenesiloxane) (**P1**) via solution polycondensation of 2,7-bis(dimethylhydroxysilyl)pyrene (**M1**), as shown in Scheme 1. **M1** was prepared by the hydrolysis of 2,7-bis(dimethylsilyl)pyrene (**2**), which had been obtained by the lithiation reaction of 2,7-dibromopyrene (**1**)¹⁰ at -78°C followed by the addition of chlorodimethylsilane. **M1** underwent polycondensation in chlorobenzene under reflux for 12 h to afford **P1**. The reaction solution was poured into acetone to isolate **P1** as yellow precipitates. The structure of **P1** was confirmed by ^1H and ^{13}C NMR spectroscopy, where each signal was consistently assigned (Figure S1).

P1 is soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, and toluene. The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of **P1** were estimated to be 43000 and 1.38, respectively, by the measurement of size-exclusion chromatography (SEC) of **P1** in tetrahydrofuran (THF) eluent using polystyrene standards. The SEC profile of **P1** indicated that the obtained polymer was unimodal and that the low-molecular-weight species as a cyclic dimer or trimer were almost completely removed by reprecipitation in acetone.

The thermal characterization of **P1** was carried out by differential scanning calorimetry (DSC) as well as thermogravimetry (TG). The DSC measurement of **P1** indicated that the melting temperature (T_m) of **P1** was 286°C ; however, the glass transition temperature (T_g) was not clearly



Scheme 1. Synthetic pathways for **P1**.

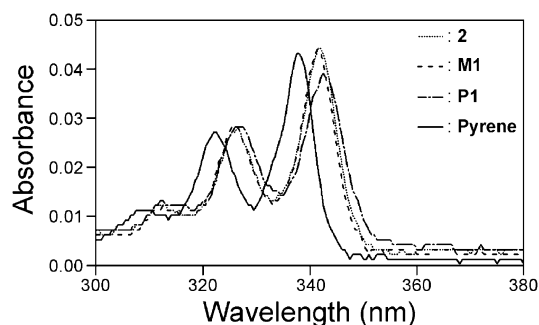


Figure 1. Absorption spectra of **2**, **M1**, **P1**, and pyrene at ambient temperature (Solvent: CHCl_3 , Concentration: 1.0×10^{-6} mol/L).

observed, presumably owing to the high degree of crystallization of **P1**.^{9,11} The TG analysis of **P1** (Figure S2) revealed that the temperature at 5% weight loss (T_{d5}) of **P1** was 519°C , indicating the excellent thermostability of **P1** among a series of poly(tetramethylsilyarylenesiloxane) derivatives.⁹

On the other hand, the optical properties of the obtained pyrene derivatives were also investigated. The absorption spectra of **2**, **M1** and **P1** as well as of pyrene are shown in Figure 1. The introduction of silyl substituent onto pyrene was found to induce the red-shift of maximum absorption wavelength, presumably because of $\sigma^*-\pi^*$ interactions³ between the silyl groups and the pyrenylene moiety. The π -stacking between pyrenylene moieties in **P1** would presumably occur as the transition moments of pyrenylene moieties offsets each other to result in a little smaller molar extinction coefficient of **P1** than those of **M1** and **2**.

Figure 2 depicts the fluorescence spectra of **2**, **M1** and **P1** as well as of pyrene. The increase in emission intensity was observed in the fluorescence

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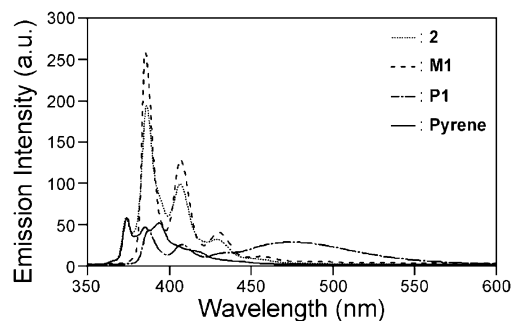


Figure 2. Emission spectra of **2**, **M1**, **P1**, and pyrene at ambient temperature (Solvent: CHCl_3 , Concentration: 1.0×10^{-6} mol/L, $\lambda_{\text{ex}} = 338$ nm).

Table I. Fluorescence characterization of pyrene and 2,7-pyrenylene derivatives

Compound	λ_{em} (nm)	Fluorescence Quantum Yield ^{a)} (Φ_{F})
Pyrene	374, 385, 394	0.19
2	374, 386, 407, 429	0.34
M1	385, 407, 431	0.49
P1	387, 408, 476	0.39

a) Fluorescence Quantum Yield (Φ_{F}) determined in CHCl_3 solution (concentration: 1.0×10^{-6} mol/L, $\lambda_{\text{ex}} = 338$ nm) using a HAMAMATSU PHOTONICS absolute PL quantum yield measurement system C9920-02.¹²

spectra of **2**, **M1** and **P1** compared with that of pyrene, that is, the introduction of silyl substituent onto pyrene induced the increase in emission intensity. A broad emission (λ_{em} between 425 and 550 nm) was observed in the case of **P1**. This broad emission would be due to the formation of excimer, which was resulted from the intra- and/or intermolecular interactions between pyrenylene moieties in **P1**. The maximum emission wavelength and the fluorescence quantum yield (Φ_{F}) of **2**, **M1** and **P1** as well as of pyrene are summarized in Table I.

The quantum yield of **M1** was higher than those of **P1** and **2**, which would be owing to the suppression of π -stacking between pyrenylene moieties by hydrogen bonding between the hydroxy moieties of **M1**.

In summary, we achieved the synthesis of novel poly(tetramethyl-2,7-silpyrenylenesiloxane) (**P1**) by polycondensation of 2,7-bis(dimethylhydroxysilyl)pyrene (**M1**). **M1** as well as **P1** exhibited the good photoluminescence property. **P1** also exhibited the excellent thermostability, indicating that **P1** would be a new heat-resistant polysiloxane derivative and one of promising candidates for OLED materials.

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Electronic Supporting Information Available. Experimental, Figures S1, and S2. These materials are available via the Internet at <http://www.spsj.or.jp/c5/pj/pj.htm>.

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