

Synthesis and Properties of Poly(methylphenylsilane) Containing Anthracene Units

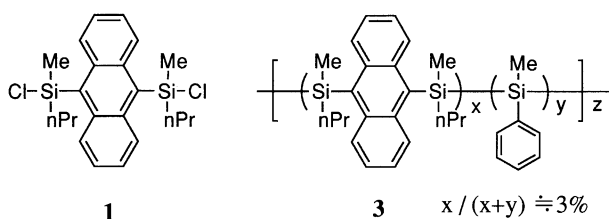
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A poly(methylphenylsilane) containing anthracene units in the polymer backbone was synthesized by the Wurtz-type reaction of 9,10-bis(methylpropylchlorosilyl)anthracene and methylphenyldichlorosilane. This polymer exhibited light blue photoluminescence with 87% quantum efficiency. The excitation spectrum suggested that energy transfer occurred intramolecularly from the polysilane chain to anthracene in the excited state.

Polysilanes are an intriguing class of macromolecules which possess peculiar photo-electronic properties.¹ This behavior is attributed to delocalized electronic states derived from σ -conjugated silicon-silicon bonds in the polymer backbone. The electronic structure and spectral properties of polysilanes more closely resemble those of conjugated π -systems such as polyacetylenes. There have been several reports regarding charge transfer from the Si-Si σ bond to the aromatic moiety in the excited state.²⁻⁴ On the other hand, 9,10-disilylanthracenes have photoluminescence around 450 nm with high quantum efficiency, which suggests activation of the π -systems by the silyl groups.⁵ Polysilanes containing anthracene units will attract much attention as σ - π conjugated organosilicon polymers, which have a possible application as electroluminescence materials, because these polysilanes will be regarded as organic semiconductors with high photoluminescence quantum efficiency. Here we report the synthesis and photo-electronic properties of the poly(methylphenylsilane) containing anthracene units in the polymer backbone (**3**).

A polymer **3**, which consists of about 3% (mol/mol) of anthracene units, was synthesized by the Wurtz-type reaction of 9,10-bis(methylpropylchlorosilyl)anthracene (**1**)⁶ with methylphenyldichlorosilane (**2**) [**1**/**2** (mol/mol) = 0.04].



At reflux temperature under argon, 4.6 g (200 mmol) of sodium was dispersed in 140.0 mL of toluene. To this dispersion, a solution of 1.05 g (2.5 mmol) of **1** and 8.05 g (60 mmol) of **2** in 10.0 mL toluene was slowly added within 15 min. After stirring for 3 h at reflux temperature, the reaction mixture was cooled and filtered to remove the salts. The organic layer was added to excess methanol (1500 mL) with stirring to precipitate the yellow solid polymer. The product was obtained in 48.2% yield after dried in a vacuum oven (ca. 133 Pa) at 50 °C for 20 h. The obtained polymer was analyzed by using gel permeation chromatography (GPC).

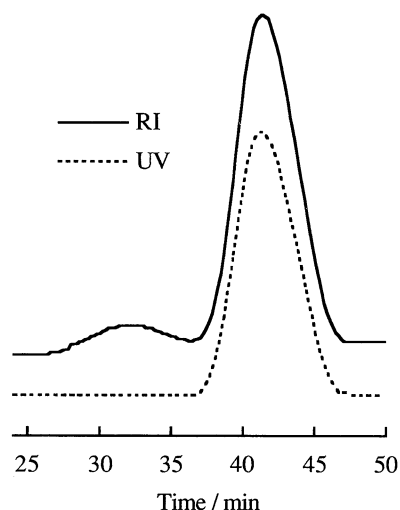


Figure 1. GPC profile of the obtained polymer (THF eluent).

The RI analysis of the GPC (Figure 1) showed that the obtained polymer had a bimodal molecular weight distribution with higher ($M_n = 361000$, $M_w = 954000$) and lower ($M_n = 6500$, $M_w = 11600$) portions, which was similar to the common polysilanes formed by the Wurtz coupling reactions.⁸ On the other hand, the UV(400nm) detector exhibited only the lower portions. These results revealed that the lower weight polymers contained some anthracene units and few anthracene units were introduced to the higher weight polymers, since poly(methylphenylsilane) (PMPS) does not have any UV absorption at longer wavelength than 400 nm. In order to investigate the photo-properties of the polysilane containing anthracene units, we have isolated the lower molecular weight polymer (**3**) by fractional reprecipitation using a THF-acetone (1:1) system. A characterization of polymer **3** was performed by using UV and photoluminescence (PL) spectroscopies.

The UV absorption spectrum of **3** compared with that of common poly(methylphenylsilane) (PMPS) is shown in Figure 2. The polymer **3** exhibited a weak broad absorption maximum around 420 nm ($\epsilon = 2.3 \text{ Lg}^{-1}\text{cm}^{-1}$) due to the anthracene units and a strong absorption at 335 nm due to the Si-Si σ -bond conjugation, which indicated that polymer **3** consisted of a polysilane chain and anthracene units. The content of the anthracene units in polymer **3** was determined to be 2.9% by using the UV absorbance at 420 nm in the polymer **3** and $M_n (= 6500)$ by GPC, where the molar absorptivity of an anthracene unit was assumed to be the same as that of 9,10-bis(trimethylsilyl)anthracene (BTSA) ($\epsilon = 10100 \text{ Lmol}^{-1}\text{cm}^{-1}$); it was impossible to determine the content by NMR.

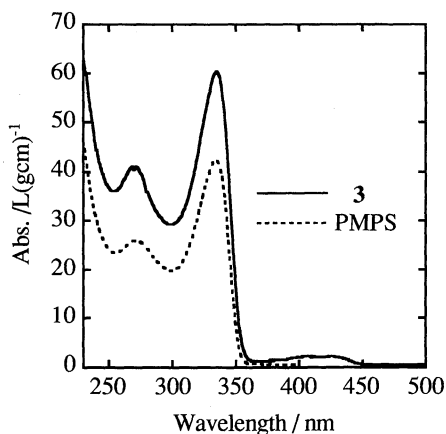


Figure 2. UV absorption spectra of polymer **3** and PMPS in THF.

The PL spectrum of **3** exhibited two emission maxima (Figure 3). The weak luminescence at 350 nm was due to the poly(methylphenylsilane) chain.^{9,10} The strong luminescence around 500 nm, which was red-shifted about 50 nm as compared to that of BTSA, gave light blue PL with 87% quantum efficiency.

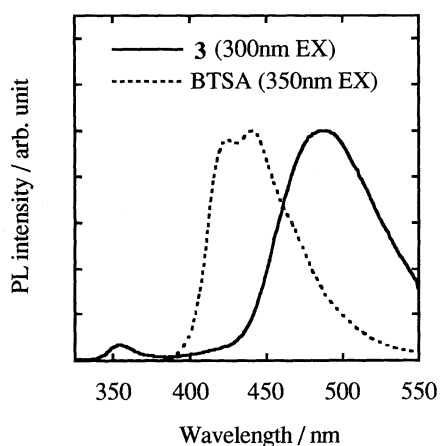


Figure 3. PL spectra of **3** and BTSA in THF.

The excitation spectrum of **3**, which was obtained by monitoring emission at 500 nm, is shown in Figure 4. Three excitation maxima were observed around 420 and 350-250 nm due to the anthracene unit and the poly(methylphenylsilane) chain, respectively. These results suggested that energy transfer occurred in the polymer **3** from the Si-Si σ orbitals to anthracene in the excited state.

The polysilane **3** was soluble in common solvents such as benzene, toluene, xylene, CHCl_3 , and THF and was able to form

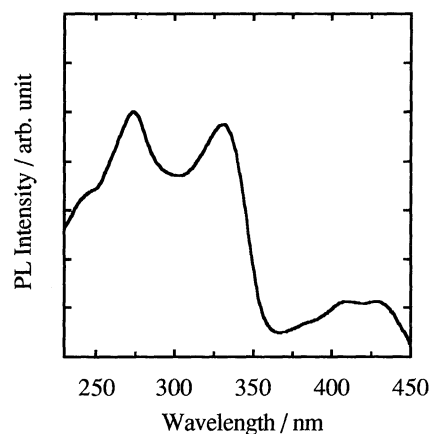


Figure 4. Excitation spectrum of **3** obtained by monitoring emission at 500 nm in THF.

a thin film by casting or spin-coating. Further investigations of the electroluminescence materials are now in progress.

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References and Notes

- 1 R. D. Miller and J. Michl, *J. Chem. Rev.*, **89**, 1359 (1989).
- 2 H. Sakurai, H. Sugiyama, and M. Kira, *J. Phys. Chem.*, **94**, 1837 (1990).
- 3 D. Declercq, F. C. De Schryver, and R. D. Miller, *Chem. Phys. Lett.*, **186**, 467 (1991).
- 4 D. Declercq, E. Hermans, F. C. De Schryver, and R. D. Miller, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **105**, 451 (1993).
- 5 M. Ikarugi, S. Kyushin, H. Matsumoto, and M. Goto, presented at the 67th Annual Meetings of the Chemical Society of Japan, Tokyo (1994), Abstr., 352.
- 6 To a mixture of 10 mL of anhydrous diethyl ether and 20.0 g (128 mmol) of methylpropyldichlorosilane was added 9,10-dilithioanthracene⁷ (100 mL of a 0.3 molL⁻¹ solution, 30 mmol) dropwise at 20 °C. After stirring for 20 h, the reaction mixture was filtered to remove the salts. The organic solvent was removed under reduced pressure. The residue was reprecipitated from pentane to give 6.55 g (52.1%) of a yellow solid. **1**: ¹H NMR (CDCl_3) δ 8.47 (dd, 4, Ar-H), 7.46 (dd, 4, Ar-H), 1.54 (m, 8, Si-CH₂CH₂), 1.09 (s, 6, Si-CH₃), 1.03 (t, 6, CH₂CH₂-CH₃). Anal. Found: C, 62.75; H, 6.71%. Calcd: C, 62.97; H, 6.74%.
- 7 B. F. Duerr, Y.-S. Chung, and A. W. Czarnik *J. Org. Chem.* **53**, 2120 (1988).
- 8 R. West, *J. Organomet. Chem.*, **300**, 327 (1986).
- 9 L.A. Harrah and J. M. Zeigler, *Macromolecules*, **20**, 601 (1987).
- 10 J. M. Zeigler, *Chem. Phys. Lett.*, **145**, 75 (1988).