Chem. Mater. **2004,** *16,* 781−785

Facile Preparation of Transparent, Homogeneous, Fluorescent Gel Film Based on $\sigma-\pi$-Conjugated, Hyperbranched Polymer with Siloxane Linkages by Means of Hydrosilylation and Aerial Oxidation

Giseop Kwak,[*,†] Akiko Takagi,[†] Michiya Fujiki,[*,†] and Toshio Masuda[‡]

Graduate School of Materials Science, Nara Institute of Science and Technology,
8916-5 Takayama, Ikoma, Nara 630-0101, Japan, and Department of Polymer Chemistry,
Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

Received November 22, 2003. Revised Manuscript Received December 22, 2003

A new AB$_2$-type monomer, *m*-bis[dimethylsilyl]phenylacetylene (**2**), was obtained by lithiation of *m*-dibromophenylacetylene followed by reaction with chlorodimethylsilane. Rh-catalyzed hydrosilylation and subsequent aerial oxidation of **2** provided a transparent gel film based on hyperbranched poly[(dimethylsilylene)(*m*-phenylene)(*trans*-vinylene)] (**1**) with siloxane linkages. The SEM and EDX analyses of the gel film revealed that the siloxane linkages were uniformly formed in the polymer matrix without any defects such as phase separation and decomposition. The gel film displayed a weak, but clear absorption in a wide range of wavelengths longer than 300 nm, due to the charge-transfer phenomenon. When excited at the charge-transfer absorption wavelength, the gel film emitted quite intense blue light that could be seen by the naked eye. The gel film showed excellent resistance against various organic solvents.

Introduction

Silicon-containing conjugated polymers have shown promise for use in such applications as semiconductors,[1] photo- and electroluminescent materials,[2] and ceramic precursors.[3] Hydrosilylation of hydrosilanes (SiH) with acetylene derivatives by Rh,[4] Pt,[5] and Pd[6] catalysts is available for preparing such $\sigma-\pi$-conjugated polymers containing silylenevinylene moiety as a basic frame of the main chain. Recently, we have reported on synthesis and absorption/emission properties of various regio- and stereoregular poly(silylenearylenevinylene)s which exhibited intense blue emission as well as absorption in the visible region.[4d−4i]

Incorporation of cross-linked structure into a polymer chain is of particular interest from the viewpoint of controlling the chemical, thermal, mechanical, and photophysical properties. Especially, enhanced oxidative, chemical, and thermal stability could be expected for polymers with siloxane (Si−O−Si) cross-linkages.[7] Stoichiometrically, hyperbranched polymers obtained from AB$_X$-type monomers surely leave $X - 1$ equiv of

---

[*] Authors to whom correspondence should be addressed. E-mail: gkwak@ms.aist-nara.ac.jp (G.K.); fujikim@ms.aist-nara.ac.jp (M.F.).

[†] Nara Institute of Science and Technology.

[‡] Kyoto University.

(1) (a) Ishikawa, M.; Hasegawa, Y.; Kunai, A.; Yamanaka, T. *J. Organomet. Chem.* **1990**, *381*, C57. (b) Ishikawa, M.; Sakamoto, H.; Ishii, M.; Ohshita, J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3281. (c) Fang, M. C.; Watanabe, A.; Matsuda, M. *Chem. Lett.* **1994**, 13. (d) Kunai, A.; Toyoda, E.; Horata, K.; Ishikawa, M. *Organometallics* **1995**, *14*, 714. (e) Kunugi, Y.; Harima, Y.; Yamashita, K.; Ohshita, J.; Kunai, A.; Ishikawa, M. *J. Electroanal. Chem.* **1996**, *414*, 135. (f) Harima, Y.; Zhu, L.; Tang, H.; Yamashita, K.; Tanaka, A.; Ohshita, J.; Kunai, A.; Ishikawa, M. *Synth. Met.* **1998**, *98*, 79. (g) Tang, H.; Zhu, L.; Harima, Y.; Yamashita, K.; Ohshita, J.; Kunai, A.; Ishikawa, M. *Electrochim. Acta* **1999**, *44*, 2579.

(2) (a) Fang, M. C.; Watanabe, A.; Matsuda, M. *Macromolecules* **1996**, *29*, 6807. (b) Kim, H. K.; Ryu, M. K.; Lee, S. M. *Macromolecules* **1997**, *30*, 1236. (c) Li, H.; Powell, D. R.; Firman, T. K.; West, R. *Macromolecules* **1998**, *31*, 1093. (d) Kim, H. K.; Ryu, M. K.; Kim, K. D.; Lee, S. M.; Cho, S. W.; Park, J. W. *Macromolecules* **1998**, *31*, 1114. (e) Kwak, G.; Masuda, T. *Macromolecules* **2002**, *35*, 4138.

(3) (a) Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym.. Sci., Part A: Polym. Chem.* **1990**, *28*, 955. (b) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485. (c) Pang, Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671. (d) Corriu, R. J. P.; Devylder, N.; Guerin, C.; Henner, B.; Jean, A. *J. Organomet. Chem.* **1996**, *509*, 249. (e) Itoh, M.; Inoue, K.; Iwata, K.; Mitsuzuka, M.; Kakigano, T. *Macromolecules* **1997**, *30*, 694.

(4) (a) Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 11321. (b) Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443. (c) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Macromolecules* **2000**, *33*, 1115. (d) Kwak, G.; Masuda, T. *Macromol. Rapid Commun.* **2001**, *22*, 846. (e) Kwak, G.; Masuda, T. *Macromol. Rapid Commun.* **2001**, *22*, 1233. (f) Kwak, G.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 535. (g) Kwak, G.; Masuda, T. *Macromol. Rapid Commun.* **2002**, *23*, 68. (h) Kwak, G.; Masuda, T. *Kobunshi Ronbunshu* **2002**, *59*, 332. (i) Kwak, G.; Sumiya, K.; Sanda, F.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3615. (j) Cheng, Y.-J.; Hwu, T.-Y.; Hsu, J.-H.; Luh, T.-Y. *Chem. Commun.* **2002**, 1978. (k) Cheng, Y.-J.; Liang, H.; Luh, T.-Y. *Macromolecules* **2003**, *36*, 5912. (l) Hwu, T.-Y.; Basu, S.; Chen, R.-M.; Cheng, Y.-J.; Hsu, J.-H.; Fann, W.; Luh, T.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2218.

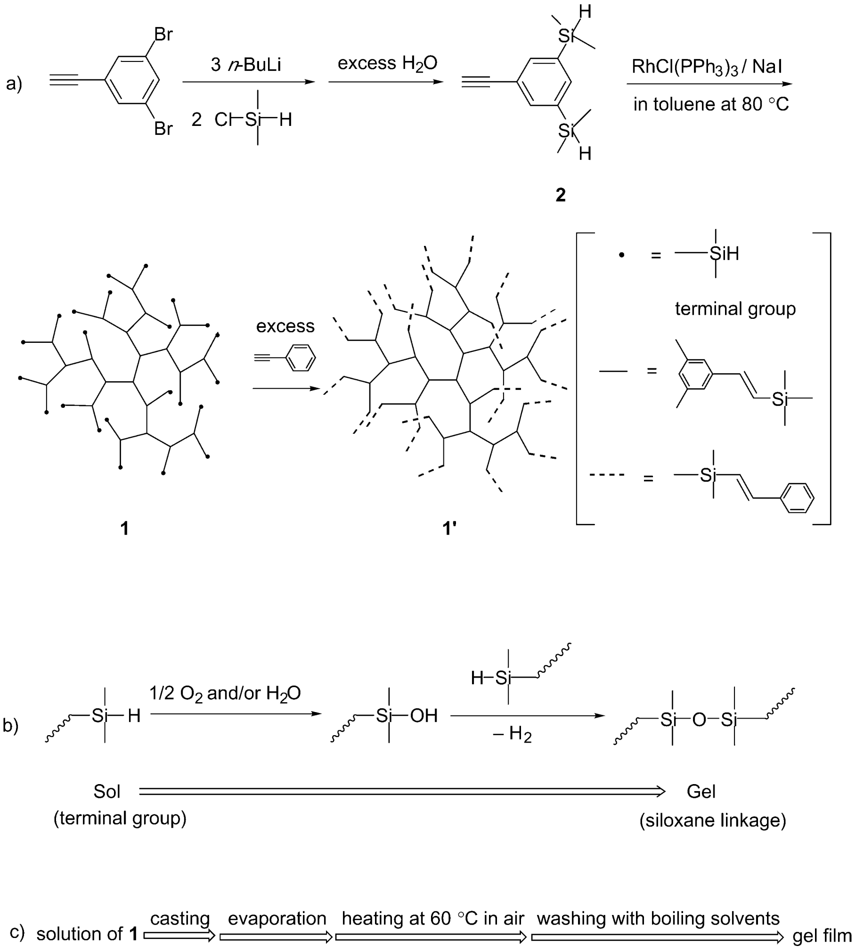
(5) (a) Kim, D. S.; Shim, S. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2933. (b) Gradwell, S. E.; Kepler, C. L. *Macromolecules* **2002**, *35*, 2871. (c) Wang, F.; Kaafarani, B. R.; Neckers, D. C. *Macromolecules* **2003**, *36*, 8225.

(6) (a) Yamashita, H.; Uchimaru, Y. *Chem. Commun.* **1999**, 1763. (b) Rao, T. V.; Yamashita, H.; Uchimaru, Y.; Asai, M.; Takeuchi, K. *Chem. Lett.* **2003**, *32*, 580. (c) Yamashita, H.; Leon, M. S.; Channasanon, S.; Suzuki, Y.; Uchimaru, Y.; Takeuchi, K. *Polymer* **2003**, *44*, 7089.

(7) (a) Dvornic, P. R.; Lenz, R. W. *High-Temperature Siloxane Elastomers*; Hüthing & Wepf: Basel, 1990. (b) Lauter, U.; Kantor, S. W.; Schmidt-Rohr, K.; MacKnight, W. J. *Macromolecules* **1999**, *32*, 3426. (c) Kim, S. H.; Woo, H.-G.; Kim, S.-H.; Kim, J.-S.; Kang, H.-G.; Kim, W.-G. *Macromolecules* **1999**, *32*, 6363. (d) Cho, H.-J.; Jung, B.-J.; Cho, N. S.; Lee, J.; Shim, H.-K. *Macromolecules* **2003**, *36*, 6704.

10.1021/cm0352091 CCC: $27.50

Scheme 1. (a) Synthesis of the Monomer, 2, and the Polymers 1, 1′; (b) Proposed Reaction at the Cross-linking Points; (C) Preparation Procedure of the Gel Film of 1



terminal B groups.[8,9] Accordingly, when AB_2-type monomers containing one ethynyl (A) and two SiH (B_2) groups are used for hydrosilylation polymerization, the polymers formed should leave 1 equiv of terminal SiH groups in the polymer chains. Also, since the terminal SiH groups can be readily converted to Si–O–Si linkages at relatively low temperature through aerial oxidation and/or hydrolysis, the polymer should further undergo gelation in air at low temperature.

In addition, SiH group tolerates many reactions compared to chlorosilane (SiCl) and alkoxysilane (SiOR) groups. Furthermore, in the formation of siloxane linkages in polymer matrix, hydrosilanes evolve harmless hydrogen gas, while chloro- and alkoxysilanes necessarily liberate HCl gas and alcohols, respectively, as byproducts, which might lead to a reduced gelation rate and decomposition in the polymer matrix. Thus, siloxane formation from the SiH groups could be more suitable for preparation of a transparent, homogeneous polymer gel with neither phase separation nor decomposition, compared to those from SiCl and SiOR groups.

On the basis of this idea, we synthesized a novel AB_2-type monomer containing one ethynyl (A) and two SiH (B_2) groups. The hydrosilylation and subsequent aerial oxidation of the monomer provided a transparent, homogeneous gel film based on a σ–π-conjugated, hyperbranched polymer with siloxane linkages. The gel film was completely insoluble in a wide range of organic solvents. Surface observation and elemental analysis of the gel film revealed that the siloxane linkages were uniformly formed in the polymer matrix without any defects such as phase separation and decomposition. When excited at the charge-transfer absorption wavelength, the gel film emitted quite intense blue light that could be seen by the naked eye.

Results and Discussion

Scheme 1a outlines the synthesis of hyperbranched poly[(dimethylsilylene)(*m*-phenylene)(*trans*-vinylene)] (**1**) with terminal SiH groups. Lithiation of *m*-dibromophenylacetylene with 3 equiv of *n*-butyllithium followed by reaction with 2 equiv of chlorodimethylsilane yielded the AB_2-type monomer, *m*-bis[dimethylsilyl]phenylacetylene (**2**), as a clear, colorless liquid in 55% yield. It is well-known that the hydrosilylation with Rh catalysts provides highly regio- and stereochemically controlled polymers.[4] For example, hydrosilylation of bis(dialkylsilyl)arenes with diethynylarenes by $RhCl(PPh_3)_3$/NaI (or $RhI(PPh_3)_3$) at 25 and 80 °C gives polymers containing *all cis*- and *all trans*-vinylene moieties, respectively.[4b] In our previous study, we found that the stereoregularity significantly influences their photophysical

---

(8) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.

(9) For papers on the silicon-containing hyperbranched polymers, see: (a) Yoon, K.; Son, D. Y. *Macromolecules* **1999**, *32*, 5210. (b) Yao, J.; Son, D. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3778. (c) Yao, J.; Son, D. Y. *Organometallics* **1999**, *18*, 1736. (d) Xiao, Y.; Wong, R. A.; Son, D. Y. *Macromolecules* **2000**, *33*, 7232. (e) Xiao, Y.; Son, D. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3383. (f) Rim, C.; Son, D. Y. *Macromolecules* **2003**, *36*, 5580.

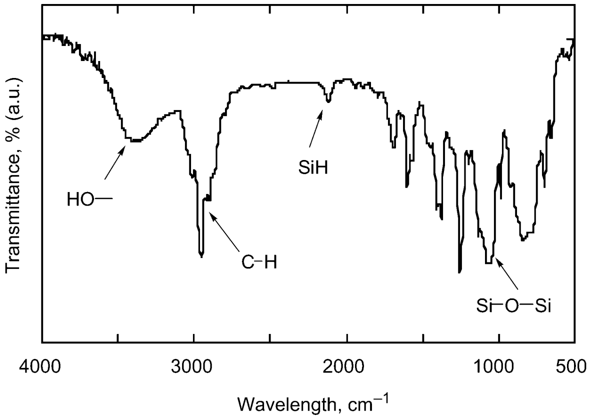


Figure 1. IR spectrum of the gel film of **1**.

properties.[4d,4f] To gain a trans-rich polymer which should be conjugated rather than the corresponding cis-rich polymer, therefore, we conducted the polymerization of **2** in toluene at 80 °C with use of RhCl(PPh$_3$)$_3$/NaI catalyst. This hydrosilylation polymerization gave a clear solution of **1**. As expected, **1** rapidly became completely insoluble after precipitation from methanol. It is because the terminal SiH groups are converted to SiOH groups by aerial oxidation and/or hydrolysis, and then the dehydrocoupling of SiH/SiOH leads to Si−O−Si bondings as cross-linking points (see Scheme 1b). Interestingly, when the toluene solution of **1** was cast as is just after the hydrosilylation, it provided a transparent film which was completely insoluble in a wide range of organic solvents such as toluene, chloroform, tetrahydrofuran, and so on. For further gelation, therefore, the film was heated at 60 °C in air for 10 min and then washed with boiling toluene, acetone, and methanol in turn several times to remove unreacted monomers and catalyst. Scheme 1c shows the preparation procedure of the gel film.

Figure 1 shows the IR spectrum of the gel film. The spectrum exhibited no absorption band at 3300 cm^{-1} due to ethynyl groups of **2**, indicating complete consumption of **2**. As expected, a strong, broad peak due to Si−O−Si bonds was shown in the range of 1000−1200 cm^{-1}, and a weak peak at 2120 cm^{-1} due to the terminal SiH groups was detected. The strong hydroxyl peak around 3400 cm^{-1} indicated conversion of SiH to SiOH groups. These results suggest that a fraction of the terminal SiH groups take part in gelation of **1**, and the other fraction of the SiH groups remain as unreacted or SiOH groups. The regio- and stereoregularity of **1** will be mentioned later with the ^{1}H NMR spectrum of the corresponding soluble polymer (**1′** in Scheme 1a).

Figure 2a shows the scanning electron microscope (SEM) image of the surface of the gel film. It really appeared to be a homogeneous glasslike matrix at the micro or nano level. Furthermore, as shown in Figure 2b, the energy-dispersive X-ray spectroscopy (EDX) revealed that the gel film consists only of carbon, oxygen, and silicon atoms, whose average contents were determined to be 72, 18, and 10 wt %, respectively. Also, a highly uniform distribution of each atom was readily

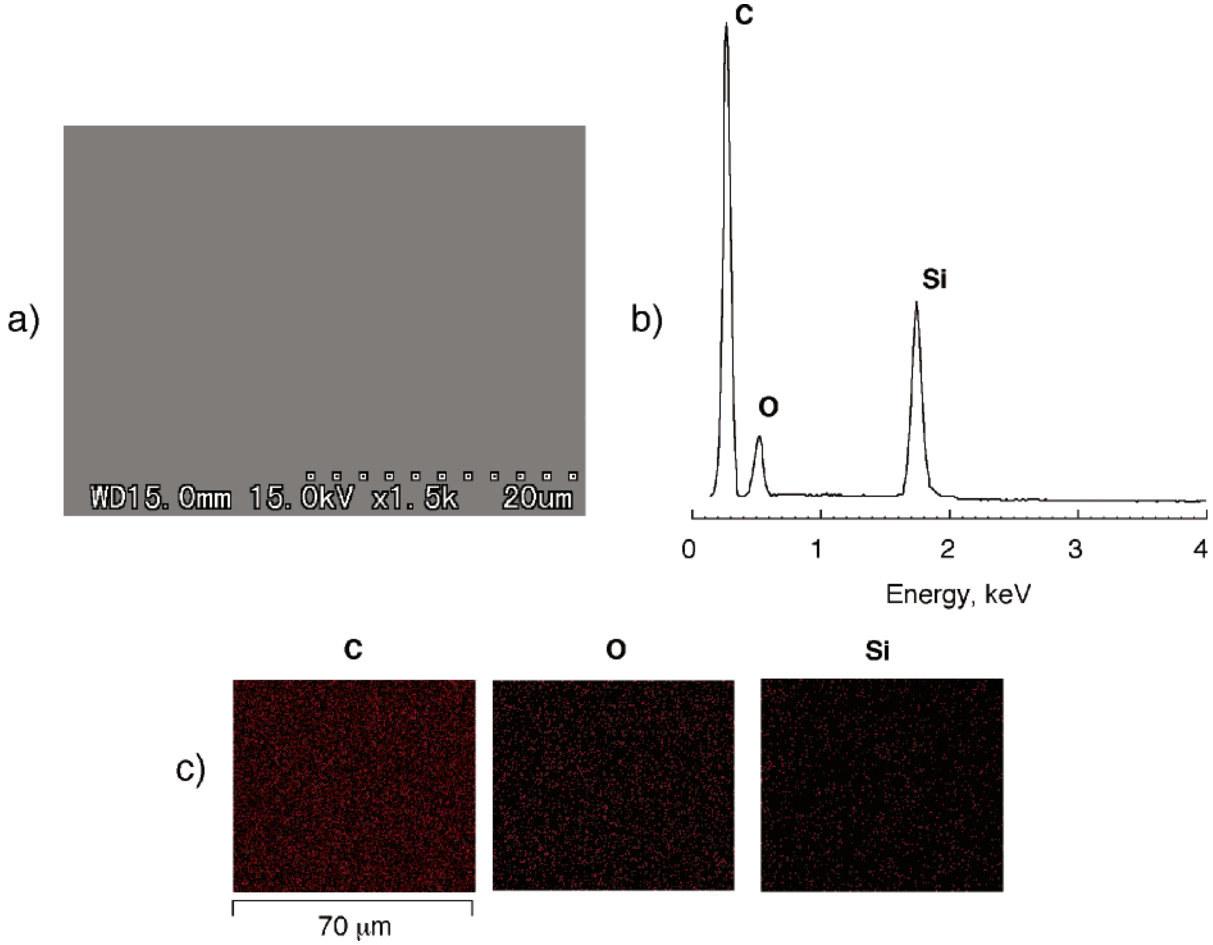


Figure 2. (a) SEM image, (b) EDX spectra, and (c) X-ray elemental maps of the gel film of **1**.

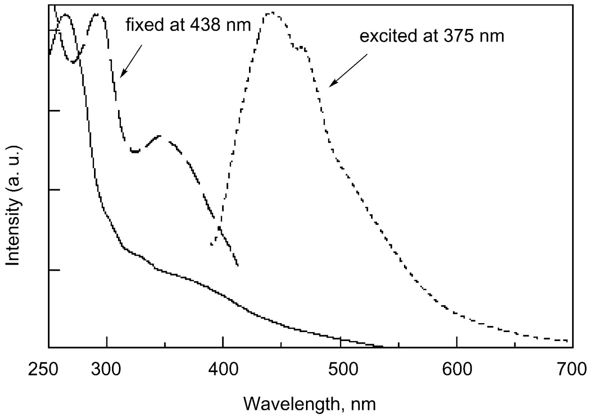


Figure 3. UV–vis absorption (—), excitation (– –), and emission (- - -) spectra of the gel film of **1**.

seen from an X-ray elemental map as shown in Figure 2c. It is thus confirmed that the siloxane linkages are uniformly formed in the polymer matrix without any defects such as phase separation, decomposition, and aggregation.

Figure 3 shows the UV–vis absorption, excitation, and emission spectra of the gel film. It is noted that the film displayed a weak, but clear absorption in a wide range of wavelengths longer than 300 nm as well as the intense absorption due to the $\pi-\pi^*$ transitions of the phenylenevinylene moiety around 265 nm. In previous papers, it has already been reported that some silicon-containing hyperbranched polymers composed of 2,5-silylenethienylene[9c] or silylene-1,4-phenylenevinylene[4g] moiety in the main chain show weak π-to-σ charge-transfer absorptions in the range 300–330 nm. Generally, the charge-transfer absorption is considered to be based on a through-space interaction.[10] Thus, the longer wavelength absorption is probably ascribed to the charge-transfer phenomenon because of the following reasons: the present polymer is structurally compact and hence favorable to the through-space interaction of π moieties, due to the hyperbranching structure.

When excited at the charge-transfer absorption wavelength (>300 nm), the gel film emitted quite intense blue light that was seen by the naked eye. In accordance with the blue light emission, the emission spectrum exhibited a broad band with a maximum at 438 nm. When the emission slit was fixed at 438 nm, the excitation spectrum exhibited a band with two maxima around 295 and 345 nm which is far from the excited state of the localized π electrons within the phenylenevinylene moiety. This implies that the blue light emission of the film mainly originates from the charge-transfer excited state but not from the locally excited π^* state.

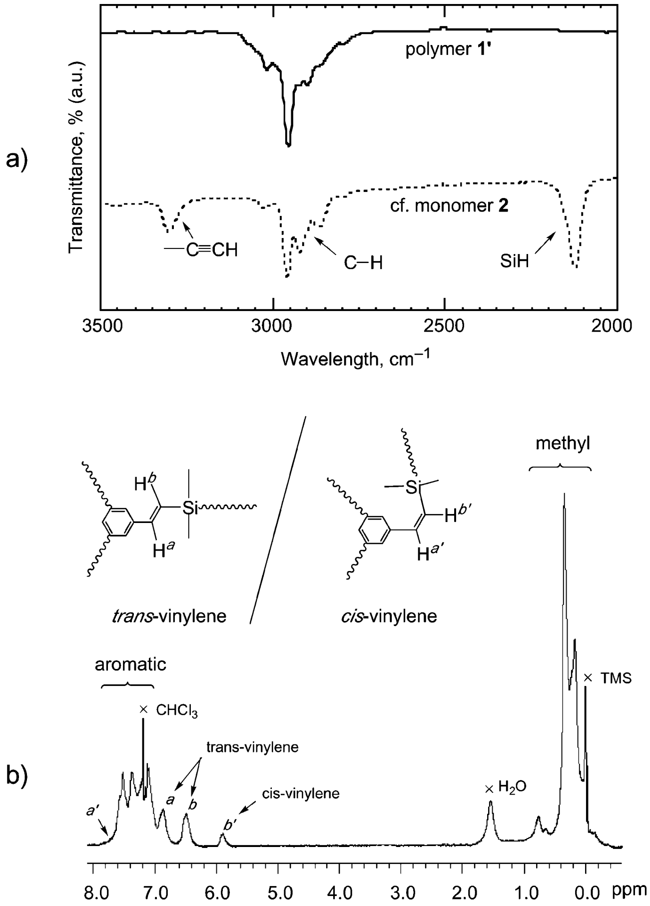


Figure 4. (a) IR and (b) ^{1}H NMR spectra of polymer **1′** (IR determined in KBr pellet; NMR in $CDCl_3$).

The solvent resistance of the gel film was estimated by means of solvent extraction experiments. Even after the gel film was kept in boiling solvents such as toluene, THF, and chloroform for 1 h, no weight reduction was seen in the error range of 0.1 wt %. Furthermore, the UV–vis spectra of the extracts showed no absorption due to the polymer. This indicates the excellent solvent-resistant property of the gel film. In the differential scanning calorimetry (DSC) of the gel film in the range from −50 to 200 °C, a significant peak due to the glass transition temperature was seen at a relatively high temperature of 80 °C, but neither melting point nor decomposition temperature was observed, indicating good thermal stability in addition to appropriate mechanical strength.

In addition, treatment of **1** with excess phenylacetylene quantitatively provided the fully hydrosilylated polymer (**1′** in Scheme 1a) which dissolved well in organic solvents even after precipitation from methanol whereas **1** became completely insoluble after the precipitation. The apparent molecular weight (M_w) of **1′** evaluated by gel permeation chromatography (GPC, eluent THF, polystyrene calibration) was 70 × 10^3 ($M_w/M_n = 2.0$). Figure 4 shows the IR and ^{1}H NMR spectra of **1′**. The IR spectrum exhibits no absorptions around 3300 cm^{-1} ($\nu_{H-C\equiv}$) and 2120 cm^{-1} (υ_{SiH}), indicating the full hydrosilylation of the terminal SiH groups. Although the selectivities of polymerization and end capping with phenylacetylene might be different, the ^{1}H NMR spectrum exhibits fairly high regio- and stereoregularity of **1′**; the two doublet signals around 6.6 (a) and 6.9 (b) ppm were characteristic of *trans*-vinylene, and the signal around 5.9 (b′) ppm was attributable to *cis*-vinylene proton adjacent to the silicon atom whereas the other *cis*-vinylene proton (a′) adjacent to the phenylene proton overlapped with the signals of phenylene protons. From the peak ratio of *trans*- to *cis*-vinylenes, the trans content of **1′** was calculated at about 90%. Additionally, no vinyl protons based on α-addition-

---

(10) Van Walree, C. A.; Roest, M. R.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395.

type hydrosilylation were found. The NMR spectrum of **1′** also tells us the stereochemical structure of the insoluble polymer, **1**. In some hyperbranched polymers, it is possible to confirm the branched nature of the polymer from the degree of branching (DB) estimated by NMR spectra.[9] Unfortunately, ^{29}Si, ^{1}H NMR spectra of **1′** provided no information about the DB because all silicon atoms in **1′** have the same type of branching points, leading to virtually the same chemical shifts.

Conclusion

We successfully prepared a glasslike gel film based on a $\sigma-\pi$-conjugated, hyperbranched polymer through hydrosilylation, subsequent aerial oxidation of AB_2-type monomer containing two hydrosilane groups. The IR, SEM, and EDX studies verified that siloxane linkages are uniformly formed in the polymer matrix without any defects such as phase separation, decomposition, and aggregation. The gel film exhibited intense blue emission due to the charge-transfer phenomenon. This facile synthetic method of a transparent, homogeneous, fluorescent gel film may be available for development of new photonic/electronic device materials and optical sensors with chemical and thermal resistance.

Experimental Section

Synthesis of *m*-Bis[dimethylsilyl]phenylacetylene, 2. A 200-mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. *m*-Dibromophenylacetylene (8.0 g, 30.6 mmol) and dry THF (100 mL) were placed in the flask at −75 °C. At the same temperature, a hexane solution of *n*-butyllithium (58.0 mL, 1.56 M, 92.0 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. A solution of dimethylchlorosilane (5.8 g, 61.3 mmol) in dry THF (30 mL) was added dropwise, and it was allowed to warm to room temperature slowly and kept overnight. After excess water was added to the reaction mixture, the stirring was continued for 1 h. The mixture was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (Merck, silica gel 60; eluent, hexane) to give the desired product (yield 3.5 g, 55%) as a colorless liquid. IR (KBr): 3300, 2957, 2923, 2861, 2120, 1572, 1373, 1250, 1133, 880, 838, 763, 640 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.67 (s, 2H, aromatic), 7.50 (s, 1H, aromatic), 4.42 (heptet, 2H, Si*H*), 3.08 (s, 1H, ethynyl), 0.34 (d, 12H, $Si(CH_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, δ): 138.4, 132.9, 127.9, 121.6, 84.2, 77.6, −3.8 ppm. ^{29}Si NMR ($CDCl_3$, δ): −16.5 ppm. Anal. Calcd for $C_{12}H_{18}Si_2$: C, 65.98; H, 8.31. Found: C, 65.90; H, 8.21.

Synthesis of Hyperbranched Poly[(dimethylsilylene)-(*m*-phenylene)(*trans*-vinylene)], 1. To a solution of **2** (80 mg, 0.38 mmol) in dry toluene (2.5 mL) at 25 °C under nitrogen, a solution of $RhCl(PPh_3)_3$ (1.2 mg, 1.3 μmol) and NaI (0.2 mg, 1.3 μmol) in dry toluene (1.0 mL) was added. The mixture was kept at 80 °C for 2 h to give a solution of **1**, which was then used as is in further functionalization reactions.

Preparation of Gel Film. The solution of **1** prepared from the hydrosilylation of **2** in toluene (0.38 mmol/1 mL) was cast on a quartz or glass plate. After evaporation of the solvent at room temperature in air, the obtained film was heated at 60 °C for 10 min and then washed with boiling toluene, acetone, and methanol in turn several times to remove unreacted monomers and catalyst.

Synthesis of Polymer 1′. To the solution of **1** prepared from the hydrosilylation of **2** in toluene (0.38 mmol/1 mL), 2 equiv of phenylacetylene (30 mg, 0.76 mmol) in 0.7 mL of toluene was added. The mixture was stirred at 80 °C for 4 h and then poured into a large excess of dry methanol to precipitate polymer, **1′**. Polymer **1′** was filtered with a sintered glass (G3) and dried in a vacuum for several hours. This polymer was quantitatively obtained as a brownish yellow solid. IR (KBr): 3020, 2950, 2902, 1600, 1373, 1250, 1072, 982, 845, 770, 694 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.70−7.05 (br, 8H, aromatic), 6.90 (d, 2H, *trans*-vinylene), 6.60 (d, 2H, *trans*-vinylene), 5.90 (d, 0.2H, *cis*-vinylene), 0.5−0.1 (br, 12H, methyl) ppm. ^{29}Si NMR ($CDCl_3$, δ): −10.1 ppm.

Solvent Extraction Experiments. The following procedure is exemplary: After the gel film (1.70 mg) was immersed in boiling THF (4.0 mL) for 1 h and then dried under highly reduced pressure of less than 3 mmHg, the weight was 1.70 mg. The weight of the sample before and after the extraction was measured on a METTLER TOLEDO AX205 analytic balance with readability up to 0.01 mg. The UV−vis spectra of the extract were measured without further dilution.

Measurements. The ^{1}H (400 MHz) NMR spectrum was measured in $CDCl_3$ solution at 25 °C on a JEOL EX-400 spectrometer. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymers were evaluated using gel permeation chromatography (Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column and HPLC-grade tetrahydrofuran as eluent at 40 °C), based on a calibration with polystyrene standards. DSC analysis was performed under nitrogen at a heating rate of 10 °C/min from −50 to 200 °C using a Seiko EXSTRA6000/DSC6200 apparatus. IR, UV−vis, and emission spectra were measured on Horiba FT-730, JASCO UV-550, and JASCO FP-6500 spectrophotometers, respectively. The SEM image was recorded on an Hitachi S-3500N scanning electron microscope using an accelerating voltage of 20 kV. Elemental analysis was determined using a Horiba EX-400 energy-dispersive X-ray (EDX) spectrometer attached to the microscope.

Acknowledgment. The authors thank Dr. D.-J. Byun for helpful discussions and are also grateful to Dr. S. Ogata, Mr. T. Kawai, and Ms. A. Takeuchi for technical assistance.

CM0352091