Synthesis and Properties of Organosilicon Polymers Containing 3,4-Benzo-1-silacyclopentene Derivatives

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Anionic ring-opening polymerization of 3,4-[(dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene in the presence of *n*-butyllithium and HMPA in THF at − 78 °C afforded poly[3,4-(dimethylsilylisopropyl)benzo-1,1-dimethyl-1-silapentene]. The characteristic Si-H stretching frequency in the IR is observed at 2100 cm^{-1}. The polycarbosilane has been modified by chloroplatinic acid catalyzed addition of styrene to the polycarbosilane SiH units. Molecular weights and thermal properties of the polymers were compared. The sol-gel polymerization of 3,4-[(dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene in the presence of aqueous HCl or NaOH in THF resulted in a cross-linked polysiloxane. The xerogel has a low surface area of 13-14 m^2/g and is stable up to about 400 °C with only 5% weight loss under a nitrogen atmosphere.

Introduction

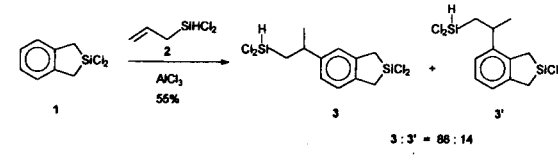
Chlorosilane derivatives have received both academic and industrial attention since the direct synthesis process was developed.[1-3] Recently, novel chlorosilanes such as 3,4-benzo-1,1-dichloro-1-silacyclopentene and allyldichlorosilane were prepared by direct synthesis method.[4,5] 3,4-Benzo-1,1-dimethyl-1-silacyclopentene undergoes an anionic ring-opening polymerization to give a thermally stable polycarbosilane.[6] Friedel-Crafts reaction of aromatic compounds with allyldichlorosilane has been also reported.[7,8] We have previously reported the regioselective Fridel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene as well as the structural confirmation by chemical reaction such as methylation, methoxylation, and reduction.[9,10] Sol-gel polymerization of alkoxysilane has been intensively studied for a wide variety of applications.[11-13]

In this paper we present the synthesis and properties of polymeric materials containing 3,4-benzo-1-silacyclopentene derivatives by anionic ring-opening polymerization of 3,4-[(dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene, followed by polymer modification reaction as well as sol-gel polymerization of 3,4-[(dimethoxysilyl)isopropyl] benzo-1,1-dimethoxy-1-silacyclopentene.

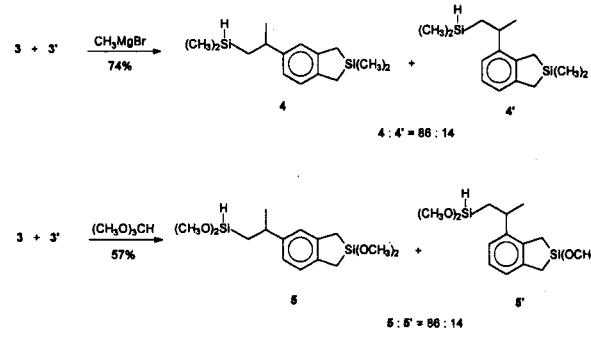
Results and Discussion

Monomer Synthesis. The aromatic benzene ring as well as the chlorine atoms bonded to the silyl center of the silacyclopentene ring are both sites of reactivities of 3,4-benzo-1,1-dichloro-1-silacyclopentene (**1**). Regioselective Friedel-Crafts reaction of allyldichlorosilane (**2**) with **1** in the presence of $AlCl_3$ catalyst gave 3,4-[3'-(dichlorosilyl) isopropyl]benzo-1,1-dichloro-1-silacyclopentene (**3**) along with 3,4-[2'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene (**3'**) in the ratio of 86 : 14 in 55% yield (Scheme 1).[9]

Methylation of the mixture of **3** and **3'** with methylmagnesium bromide afforded an isomeric mixture of 3,4-[3'-(dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene (**4**) and 3,4-[2'-(dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene (**4'**) in a 86 : 14 ratio, respectively. While, methoxylation of the mixture with trimethylorthoformate resulted in also a mixture of 3,4-[3'-(dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene (**5**) and 3,4-[2'-(dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene (**5'**) in a ratio of 86 : 14 (Scheme 2).[9]



Scheme 1.



Scheme 2.

The ratio of isomeric products was in good agreement with that of a mixture of **3** and **3'**. These compounds could be useful monomers for ring-opening polymerization as well as sol-gel polymerization.

Ring-Opening Polymerization and Modification Reaction. A mixture of **4** and **4'** undergoes anionic ring-opening polymerization on treatment with a catalytic amount of *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at − 78 °C to yield poly[3,4-(dimethylsilylisopropyl) benzo-1,1-dimethyl-1-silapentene] (**6**) (Scheme 3). The

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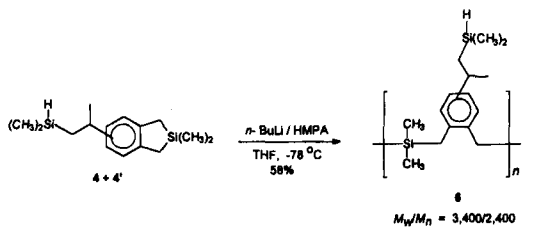
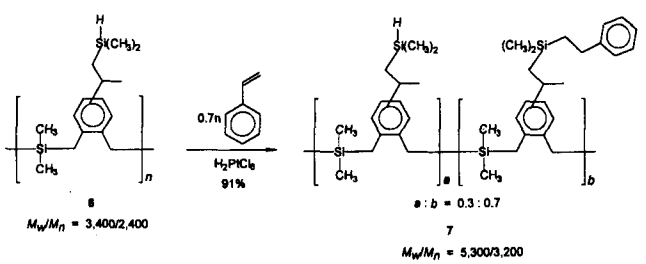


Scheme 3.

molecular weight of **6** is 3,400/2,400 (M_w/M_n). The IR spectrum shows the strong and characteristic Si-H stretching frequency at 2100 cm^{-1}.[14] We believe that this polymerization is initiated by nucleophilic attack of *n*-butyllithium at the silyl center of benzosilacyclopentene **4** or **4'** to form a pentacoordinate cyclic siliconate intermediate.[15] Ring opening of this intermediate leads to a benzylic anion which reacts rapidly with another monomer to form a new anionic siliconate species.

Chemical modification of **6** has been achieved by chloroplatinic acid catalyzed hydrosilylation of the Si-H functional groups with styrene (Scheme 4).[16]

The molecular weight of modified polycarbosilane **7** is 5,300/3,200 (M_w/M_n), which is increased in comparison with **6** due to the graft of styrene. The IR spectrum shows that the intensity of Si-H stretching band at 2100 cm^{-1} of grafted polymer **7** almost disappears, suggesting that the hydrosilylation reaction is almost complete. Based on the area integration of ^1H NMR spectrum, about 70% of Si-H group of polymer **6** had been modified.



Scheme 4.

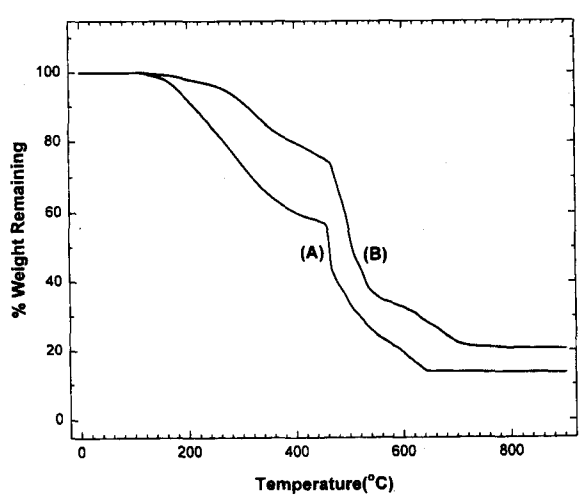


Figure 1. TGA thermograms of polymers **6** (A) and **7** (B) under air atmosphere.

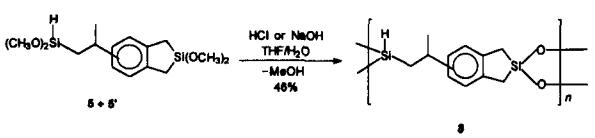
The TGA thermograms under air indicate that the grafted polymer **7** is more thermally stable than **6** (Figure 1).

The polymer **6** is stable to 130 °C under an air atmosphere. When **6** is heated above this temperature, weight loss occurs in two stages. Between 130 and 463 °C, 43% of the initial weight of the sample is lost. Between 463 and 644 °C, an additional 43% weight is lost. When the sample is heated to 900 °C, 14% of residue is obtained. While, the polymer **7** is stable to 161 °C under an air atmosphere. When **7** is heated above this temperature, weight loss occurs also in two stages. Between 161 and 460 °C, 24% of the initial weight of the sample is lost. Between 460 and 550 °C, an additional 40% weight is lost. When the sample is heated to 900 °C, 21% of residue is obtained.

Sol-Gel Polymerization. The sol-gel polymerization of the isomeric mixture of **5** and **5'** in the presence of aqueous HCl or NaOH in THF was employed to afford a new polymeric material of polysiloxane (**8**) as a white powder (Scheme 5).

We believe that the sol-gel polymerization involves the hydrolysis of methoxy groups into silanol groups and subsequent condensation of silanols to form siloxane bonds.[17] The IR spectrum shows that the strong Si-H stretching frequency appears at 2152 cm^{-1}. The xerogel **8** has a relatively low surface area of 13-14 m^2/g in comparison with alkylene-bridged polysilsesquioxanes,[18,19] which might be attributed to the formation of linear ladder type of structure.

The TGA thermogram of polysiloxane **8** prepared in the presence of aqueous NaOH in THF is shown in Figure 2. **8** is stable up to about 400 °C with only 5% weight loss in a nitrogen atmosphere. When 8 is heated above this temperature, additional 28% of weight loss occurs between 400 and 681 °C. When the sample is heated to 900 °C, 64% of the initial weight of **8** is remained.



Schme 5.

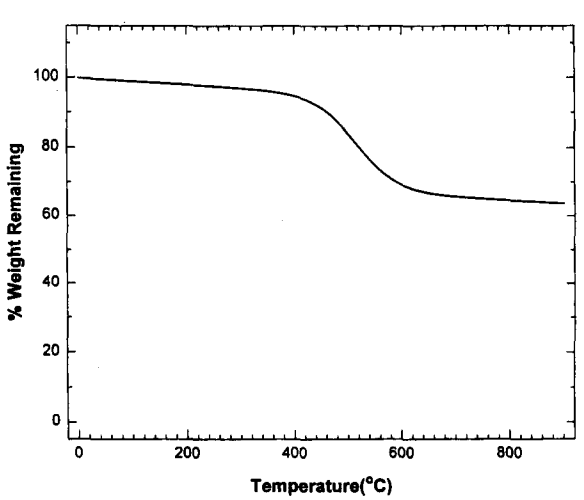


Figure 2. TGA thermogram of polymer **8** under nitrogen atmosphere.

Conclusions

Anionic ring-opening polymerization of 3,4-[(dimethylsilyl)isopropyl]-benzo-1,1-dimethyl-1-silacyclopentene in the presence of *n*-butyllithium and HMPA in THF at −78 °C afforded poly[3,4-(dimethylsilylisopropyl)-benzo-1,1-dimethyl-1-silapentene] **6** with molecular weight of 3,400/2,400 (M_w/M_n). The IR spectrum shows the strong and characteristic Si-H stretching frequency at 2100 cm^{-1}. The partial hydrosilylation of Si-H with styrene using chloroplatinic acid catalyst yielded a grafted polycarbosilane **7** with molecular weight of 5,300/3,200 (M_w/M_n). The TGA thermograms under air atmosphere indicate that the polymer **7** is more thermally stable than **6**.

The sol-gel polymerization of 3,4-[(dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene in the presence of aqueous HCl or NaOH in THF resulted in a new polymeric material of polysiloxane **8** as a white powder. The IR spectrum shows that the strong Si-H stretching frequency appears at 2152 cm^{-1}. The xerogel **8** has a surface area of 13-14 m^2/g. The polysiloxane **8** on TGA thermogram turns out to be very stable up to about 400 °C with only 5% weight loss under a nitrogen atmosphere.

Experimental Section

All chemicals were purchased from Aldrich Chemicals, Inc. or Yakuri Chemical, Inc. Tetrahydrofuran (THF), *n*-hexane, and diethyl ether were distilled from sodium metal and benzophenone ketyl prior to use. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and stored over 4 Å molecular sieves. All glassware was dried overnight in an oven at 120 °C. The apparatus was assembled and was then flamed-dried while being swept with argon.

Reactions were monitored by analytical GLC of Hewlett Packard 5890 Series II equipped with HP-1 capillary column (0.53 mm × 30 m) coated with cross-linked methyl silicone gum and with FID detector. The column was deactivated immediately before use by injection of 50 μL of hexamethyldisilazane.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer. Chemical shifts were measured using tetramethylsilane or the solvents as internal standards. IR spectra were recorded by a Shimadzu IR 430 spectrometer or a Bruker IFS-48 FTIR spectrometer.

Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology, Seoul, Korea. Low resolution mass spectra were measured on Kratos MS 25 REA instrument by EI ionization at 70 eV.

Gel permeation chromatography (GPC) analyses were performed on a Waters Model 510 system equipped with a Waters Styragel HR 3 column and a refractive index detector. The eluting solvent was HPLC grade THF at a flow rate of 1.0 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 580, 3250, 10100, and 28500 whose M_w/M_n are less than 1.2.

Thermogravimetric analysis (TGA) of polymer samples was performed on a TGA-50 Shimadzu thermal analysis system. The temperature program for the analysis was from room temperature with a heating rate of 10 °C/min to 900 °C with nitrogen flow rate of 20 mL/min. The surface area of samples were obtained with a Micrometrics Model ASAP 2010C using nitrogen at liquid nitrogen temperature. The surface area was determined from the calculation of a monolayer using the BET equation in the relative pressure range 0.01-0.25 of N_2 gas.

3,4-[3′-(Dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene (3) was prepared as previously reported procedure by the reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene.[9] Compound **3** had the following spectral properties. ^1H NMR ($CDCl_3$): δ 1.36 (d, J=7.0 Hz, 3H, CH_3), 1.55-1.61 (m, 2H, CH_2), 2.57 (d, J=5.2 Hz, 4H, CH_2), 3.07-3.14 (m, 1H, CH), 5.33 (t, J=2.1 Hz, 1H, SiH), 7.02-7.05 (m, 1H, ArH), 7.11-7.20 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 24.85, 24.89, 25.37, 30.34, 34.60, 125.37, 127.08, 129.32, 135.39, 137.51, 145.67. IR (KBr): ν 3070, 3020, 2960, 2930, 2870, 2200 (Si-H), 1600, 1565, 1500, 1490, 1480, 1450, 1440, 1420, 1380, 1330, 1265, 1235, 1210, 1190, 1130, 1100-1000, 900-750, 600-500 cm^{-1}. MS *m/e* (relative intensity): 344 (M^+, 63), 329 [$(M-CH_3)^+$, 40], 301 (41), 265 (29), 229 [$(M-SiHCl_2CH_2)^+$, 71], 193 (23), 129 (29), 115 (22), 83 (100). Compound **3** was containing 3,4-[2′-(dichlorosilyl)isopropyl] benzo-1,1-dichloro-1-silacyclopentene **3′** in 14% based on the ^1H NMR spectrum.

Synthesis of 3,4-[3′-(Dimethylsilyl)isopropyl] benzo-1,1-dimethyl-1-silacyclopentene (4). In a 100 mL 3-neck round bottom flask equipped with reflux condenser, pressure equalizing dropping funnel, and a Teflon covered magnetic stirring bar were placed 3.0 M methylmagnesium bromide (14.5 mL, 0.043 mol) and diethyl ether (40 mL) under argon atmosphere. The mixture of **3** and **3′** (3.00 g, 8.0 mmol) and diethyl ether (40 mL) was placed in the dropping funnel, and added dropwise to the well stirred solution over 1 h. The reaction mixture was stirred for another 6 h. *n*-Hexane (100 mL) was poured. The organic layer was separated, washed with water (3 × 100 mL) and with saturated NaCl solution, dried over anhydrous magnesium sulfate, and filtered. The volatile solvent was then removed by evaporation under reduced pressure. The residue was fractionally distilled. A fraction with bp 93-95 °C/5 mmHg in 1.7 g, 75% yield, was obtained. ^1H NMR ($CDCl_3$): δ 0.08 (d, J=3.3 Hz, 6H, $Si(CH_3)_2$), 0.26 (s, 6H, $Si(CH_3)_2$), 1.08 (dd, J=3.9 Hz, 4.8 Hz, 2H, CH_2), 1.33 (d, J=6.6 Hz, 3H, CH_3), 2.05 (d, J=5.1 Hz, 4H, CH_2), 2.84-2.91 (m, 1H, CH), 3.86-3.90 (m, 1H, SiH), 6.94-6.97 (m, 1H, ArH), 7.10-7.17 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ −4.17, −3.67, −2.29, 20.72, 21.30, 24.78, 25.48, 36.23, 123.96, 127.29, 129.00, 139.48, 142.10, 146.94. IR (neat): ν 3090, 3060, 3000, 2950, 2900, 2860, 2100 (Si-H), 1600, 1560, 1480, 1460, 1450, 1410, 1400, 1390, 1370, 1325, 1250, 1210, 1190, 1125, 1100, 1045, 1010, 1000, 900, 880, 830, 760, 740, 710, 680 cm^{-1}. MS *m/e* (relative intensity): 262 (M^+, 55), 247 [$(M-CH_3)^+$, 51], 231 [$(M-2(CH_3)-H)^+$, 25], 219 (84), 205 (72), 189 [$(M-(CH_3)_2SiHCH_2)^+$, 89], 173 (61), 159 (36), 145 (51), 131 (28), 115 (27), 100 (26), 73 [$(CH_3)_2SiHCH_2)^+$, 100]. Anal. Cacld for $C_{15}H_{26}Si_2$: C, 68.70; H, 9.92. Found: C, 68.30; H, 9.23. Compound **4** was containing 3,4-[2′-(dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene **4′** in 14% on the base of ^1H NMR spectrum.[9]

Synthesis of 3,4-[3'-(Dimethoxysilyl)isopropyl] benzo-1,1-dimethoxy-1-silacyclopentene (5). In a 100 mL 3-neck round bottom flask equipped with reflux condenser, $CaCl_2$ drying tube, and a Teflon covered magnetic stirring bar were placed The mixture of **3** and **3'** (3.44 g, 10.0 mmol) and trimethylorthoformate (10.94 g, 100 mmol). The reaction mixture was stirred at 60 °C for 3 h. After reaction was completed, the volatile solvent was removed by evaporation under reduced pressure. The residue was fractionally distilled. Compound 3 in 1.86 g, 57% yield, was obtained. ^{1}H NMR ($CDCl_3$): δ 1.04 (dd, J=4.3 Hz, 5.6 Hz, 2H, CH_2), 1.29 (d, J=7.0 Hz, 3H, CH_3), 2.02 (d, J=6.9 Hz, 4H, CH_2), 2.95 (m, 1H, CH), 3.48 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 3.56 (s, 6H, OCH_3), 4.42 (t, J=1.3 Hz, 1H, SiH), 6.94-6.97 (m, 1H, ArH), 7.08-7.15 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 15.01, 15.59, 22.78, 24.99, 34.09, 50.76, 50.98, 51.04, 124.19, 127.24, 129.15, 136.68, 139.17, 146.68. IR (neat): ν 3030, 2950, 2800, 2170 (vs, Si-H), 1605, 1560, 1480, 1450, 1190, 1100 (br), 955, 835 (br), 795, 660 cm^{-1}. MS *m/e* (relative intensity): 326 (M^+, 69), 309 (34), 294 [$(M-CH_3OH)^+$, 48], 283 (35), 276 (52), 262 (37), 247 (34), 221 [$(M-SiH(OMe)_2CH_2)^+$, 71], 204 (40), 189 (79), 162 (37), 129 (29), 121 (92), 91 [$SiH(OMe)_2^+$, 85], 83 (100), 79 (29). Anal. Cacld for $C_{15}H_{26}Si_2O_4$: C, 55.19; H, 8.03. Found: C, 55.40; H, 8.11. Compound **5** was containing 3,4-[2'-(dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene **5'** in 14% on the base of ^{1}H NMR spectrum.[9]

Synthesis of Poly[3,4-(dimethylsilylisopropyl) benzo-1,1-dimethyl-1-silapentene] (6). In a flame-dried 100 mL Schlenk flask equipped with a Teflon covered magnetic stirring bar under argon was placed a mixture of **4** and **4'** (1.0 g, 3.8 mmol), dry THF (20 mL) and five drops of HMPA. The flask was sealed with a rubber septum and was cooled to −78 °C in a dry ice/acetone bath. To the well stirred reaction mixture was slowly added *n*-butyllithium (0.12 mL, 0.19 mmol) via a syringe. The reaction was allowed to stir at −78 °C for 3 h. It was then quenched by addition of saturated aqueous ammonium chloride (10 mL). 50 mL of THF was added, and the organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and the solvents were removed by evaporation under reduced pressure. The residue was taken up in THF and the polymer **6** was precipitated by addition of methanol (M_w/M_n=3,400/2,400). In this way, 0.60 g, 60% yield of viscous polymer **6** was obtained. ^{1}H NMR ($CDCl_3$): δ −0.14 (s, 6H, $Si(CH_3)_2$), −0.11~−0.07 (m, 6H, $Si(CH_3)_2$), 0.92-0.96 (m, 2H, CH_2), 1.24 (d, J=7.1 Hz, 3H, CH_3), 1.96 (s, 4H, CH_2), 2.75 (m, 1H, CH), 3.78 (m, 1H, SiH), 6.70 (m, 1H, ArH), 6.76 (m, 2H, ArH). IR (KBr): ν 3060, 3030, 2950, 2900, 2100 (Si-H), 1600, 1560, 1500, 1490, 1480, 1460, 1450, 1420, 1410, 1290, 1250, 1190, 1070, 990, 900, 880, 830, 760, 700, 630 cm^{-1}. Anal. Cacld for $(C_{15}H_{26}Si_2)_n$: C, 68.70; H, 9.92. Found: C, 68.30; H, 10.50.

Partial Hydrosilylation Reaction of the Polymer 6 with Styrene. In a flame-dried 20 mL round bottom flask equipped with a Teflon covered magnetic stirring bar under argon was placed polymer **6** (0.68 g, 2.6 mmol based on SiH group of **6**) and styrene (0.19 g, 1.8 mmol). To the well stirred reaction mixture were added five drops of a solution of H_2PtCl_6 in propan-2-ol (0.1 M) at 0 °C by ice-water bath. Stirring was continued for 4 h at 0 °C, then for 4 h at ambient temperature. 20 mL of THF was added, and the organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and the solvents were removed by evaporation under reduced pressure. The residue was taken up in THF and the grafted polymer **7** was precipitated by addition of methanol (M_w/M_n=5,300/3,200). In this way, 0.79 g, 91% yield of viscous polymer **7** was obtained. ^{1}H NMR ($CDCl_3$): δ −0.17 (s, $Si(CH_3)_2$), −0.12~−0.06 (m, $Si(CH_3)_2$), 0.83-0.88 (m, CH_2), 1.20 (s, CH_3), 1.57 (s, CH_2), 1.86-1.92 (m, CH_2), 2.73 (m, 0.7H, CH), 3.75 (m, 0.3H, SiH), 6.70 (m, ArH), 6.78 (m, ArH). IR (KBr): ν 3060, 3000, 2950, 2900, 1635, 1580, 1500, 1465, 1420, 1385, 1255, 1165, 1130, 1090, 1030, 1000, 960, 915, 845, 785, 705 cm^{-1}.

Sol-Gel Polymerization; Polysiloxane (8). In a 25 mL volumetric flask was placed the mixture of **5** and **5'** (3.26 g, 10 mmol) with 10-12 mL of THF and the solution was throughly mixed. The aqueous HCl catalyst (1.08 mL of 1 N HCl, 10.8 mol%) with 10 mL of THF was added, and then additional THF was added to achieve a final volume equal to 25 mL. The reaction mixture was vigorously shaken to ensure mixing, and poured into a 50 mL of bottle. The bottle was capped, sealed with septum, and allowed to stand undisturbed for 2 weeks at room temperature. The gel was slightly blue. After aging for additional 48 h at room temperature, the formed gel was processed by immersing the gel into a series of solvent: THF, chloroform, diethyl ether, and carbon tetrachloride and then by washing with the same series of solvents. The processed gel was allowed to air dry for 24 h followed by crushing and drying intact under vacuum. In this way, 1.5 g, 46% yield of white powder type of polysiloxane **8** was obtained. IR (KBr): ν 3030, 2958, 2900, 2152 (Si-H), 1605, 1487, 1480, 1068, 880, 786, 665 cm^{-1}. N_2 surface area: 13-14 m^2/g.

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References

1. Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.
2. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.
3. Noll, W. *Chemistry and Technology of Silicons*; Academic Press: New York, 1968.
4. Jung, I. N.; Yeon, S. H.; Han, J. S. *Bull. Korean Chem. Soc.* **1993**, *14*, 315.
5. Yeon, S. H.; Lee, B. W.; Kim, S. I.; Jung, I. N. *Organometallics* **1993**, *12*, 4887.
6. Park, Y. T.; Zhou, Q.; Weber, W. P. *Polym. Bulletin* **1989**, *22*, 349.
7. Nametkin, N. S.; Vdovin, V. M.; Finkelshtein, E. Sh.; Oppengeim, V. D.; Chekalina, N. A. *Izv. Akad. Nauk*

SSSR, Ser. Khim. **1966**, *11*, 1998.
8. Lee, B. W.; Yoo, B. Y.; Kim, S. I.; Jung, I. N. *Organometallics* **1994**, *13*, 1312.
9. Park, Y. T.; Park, S. U.; Kim, H. C. *Bull. Korean Chem. Soc.* **1995**, *16*, 1208.
10. Park, Y. T.; Kim, S. O. *Bull. Korean Chem. Soc.* **1997**, *18*, 232.
11. Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.
12. Chambers, R. C.; Jones, W. E. Jr.; Haruvy, Y.; Webber, S. E.; Fox, M. A. *Chem. Mater.* **1993**, *5*, 1481.
13. Loy, D. A.; Shea, K. *J. Chem. Rev.* **1995**, *95*, 1431.
14. Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Chapman and Hall: London, 1975.
15. Weber, W. P.; Park, Y. T.; Zhou, S. Q. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 259.
16. Marciniec, B.; Gulinski, J.; Urbaniak, W.; Kornetka, Z. W. In *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon Press: Oxford, U.K., 1992.
17. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, 1st ed.; Academic Press: San Diego, 1990; p 908.
18. Oviatt, H. W. Jr.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993**, *5*, 943.
19. Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Myers, S. A.; Assink, R. A.; Shea, K. J. *Chem. Mater.* **1996**, *8*, 656.

Synthesis of PPV-PTV Alternating Copolymer and EL Devices Using the Polymer

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An alternating copolymer of PPV and PTV, poly[2-methoxy-5-(3,7-dimethyl)octyloxy-1,4-phenylenevinylene-alt-2,5-thienylenevinylene] (DAPPV-PTV) has been synthesized and light-emitting properties of the polymer have been studied. A single layer EL device using DAPPV-PTV as an emitting layer between ITO and Al electrodes (ITO/DAPPV-PTV/Al) has been fabricated, and light emission of the device becomes visible at 3 V. The EL emission maximum of the device is about 620 nm. Double layer EL device using DAPPV-PTV and Alq_3 (ITO/DAPPV-PTV/Alq_3/Al) has also been fabricated. The double layer EL device shows two-color emission depending on the applied voltage. The device emits a pale green color from 8 V, and then the color turns to red at about 18 V.

Introduction

Electroluminescent (EL) devices based on organic materials have attracted much attention in the past ten years due to their potential applicability in display technology. Organic and polymer LEDs have many advantages for the development of a large-area visible light-emitting display, such as the good processibility, low operation voltage, fast response time and color tunability over the full visible range by control of the HOMO-LUMO bandgap of the emissive layer.[1-3] Conjugated polymers such as poly(1,4-phenylenevinylene) (PPV),[1,3,4] polythiophene,[5] polyfluorene,[6] poly(*p*-phenylene) (PPP)[7] derivatives have been most widely used as the emissive layer for the light-emitting diodes. EL devices using polymer blends,[8-10] molecular doping[11] and organic or polymer multilayer structure[12-14] have been extensively investigated in order to improve the quantum efficiency and stability of the device.

Recently we have synthesized an alternating copolymer of dialkoxyphenylenevinylene (DAPV) and thienylenevinylene (TV) units, poly[2-methoxy-5-(3,7-dimethyl)octyloxy-1,4-phenylenevinylene-alt-2,5-thienylenevinylene] (DAPPV-PTV), and fabricated single and multilayer EL devices using the polymer in order to obtain a pure red light emission. Dialkoxy-PPV such as MEH-PPV shows an efficient electroluminescece, good processiblity and good mechanical property, but the EL emission from the dialkoxy-PPV corresponds to orange red region.[3] By the way, poly(thienylenevinylene) (PTV) shows an EL emission in pure red region but luminescence efficiency of PTV is very low.[15] So we synthesized an alternating copolymer of dialkoxy-PPV and PTV in order to obtain an efficient pure red light emission. Here we report the synthesis and properties of DAPPV-PTV, and characteristics of the single and multilayer EL devices using the polymer. Synthetic route of the DAPPV-PTV is shown in Scheme 1.

Experimental

Synthesis of 2,5-bis(dibromomethyl)thiophene (1). Compound **1** was prepared by reacting 5.0 g (44.6 mmol) of 2,5-dimetylthiophene with 15.9 g (89.2 mmol) of