A Novel Synthesis and Extremely High Thermal Stability of Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene]

Masayoshi Itoh,* Masahiko Mitsuzuka,
Kenji Iwata, and Kohji Inoue

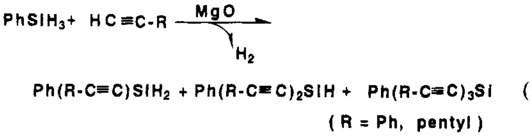
Central Research Laboratory,
Mitsui Toatsu Chemicals, Inc., 1190 Kasama-cho,
Sakae-ku, Yokohama-city 247, Japan

Received June 15, 1994
Revised Manuscript Received September 21, 1994

Introduction

There have been some reports on the dehydrogenative cross-coupling of hydrosilanes with monosubstituted alkynes to produce alkynylsilanes. H_2PtCl_6/LiI, I_2,[1] $IrH_2(SiEt_3)(COD)(AsPh_3)$, iridium catalysts formed by adding triarylarsines or triarylphosphines to $[Ir(OMe)(diolefin)]_2$,[2] $[IrH(H_2O)(bq)L_2]SbF_6$, and $RhClL_3$ (L = PPh_3, bq = 7,8-benzoquinolinato)[3] have been used as catalysts. In these cases, dehydrogenative coupling was found to accompany a hydrosilylation reaction to produce the corresponding alkenylsilanes. Liu, et al. have found that the CuCl/amine catalyst led to the highly selective dehydrogenative coupling of hydrosilanes with alkynes.[4]

We have recently found that the selective dehydrogenative coupling reactions take place on the surface of magnesium oxide and calcium oxide, with no evidence of hydrosilation.[5]



$$PhSiH_3 + HC{\equiv}C\text{-}R \xrightarrow[H_2]{MgO} Ph(R\text{-}C{\equiv}C)SiH_2 + Ph(R\text{-}C{\equiv}C)_2SiH + Ph(R\text{-}C{\equiv}C)_3Si \quad (R = Ph,\ pentyl) \tag{1}$$

Considerable interest has developed in recent years in silicon-containing polymers composed of $[-SiR_2-C{\equiv}C-]$ or $[-SiR_2-SiR_2-C{\equiv}C-]$ (R = alkyl or phenyl) units because of their potential applications in areas such as ceramic precursors, photoresists, and conducting materials.[4,6–11] To our knowledge there are few cases in the literature of a polymer containing the Si-H bond (R = H) in a molecule. Only poly (phenylsilylene)ethynylene-1,3-phenyleneethynylene] $[-Si(Ph)H-C{\equiv}C-C_6H_4-C{\equiv}C-]$,[4] poly[(phenylsilylene)diethynylene] $[-Si(Ph)H-C{\equiv}C-C{\equiv}C-]$,[6] and poly[(methylsilylene)ethynylene] $[-Si(CH_3)H-C{\equiv}C-]$[7] have been prepared, but there was almost no information about the properties of the polymers.

In this paper, we present a new method for the copolymerization of hydrosilanes and alkynes. Dehydrogenative coupling polymerization reactions between phenylsilane and *m*-diethynylbenzene occurred in the presence of alkaline earth metal oxides to give a highly thermally stable polymer, poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene].

Experimental Section

Phenylsilane, *m*-diethynylbenzene (DEB), and benzene were distilled and dried over 3A molecular sieves prior to use. A magnesium oxide or calcium oxide catalyst was obtained by calcining magnesium hydroxide or calcium hydroxide in vacuo or in air at 200–600 °C for 2 h. Silica–alumina (Al_2O_3 12 wt %, commercial SiO_2–Al_2O_3 from Mizusawa Industrial Chemicals Ltd.) was treated at 500 °C for 2 h before use. The size of the particles of all catalysts was 20–60 mesh.

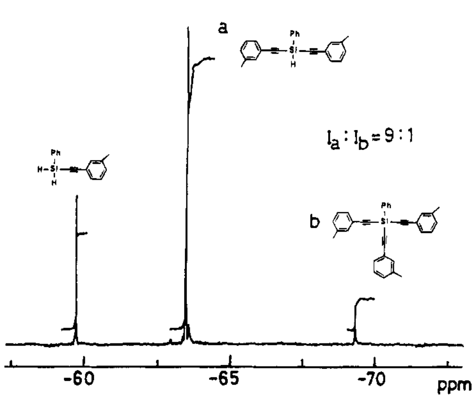


Figure 1. ^{29}Si NMR (non-NOE mode) spectrum of poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (expt no. 5 in Table 1).

Phenylsilane, *m*-diethynylbenzene, benzene as a solvent, and a catalyst were transferred into a 200 mL glass flask, and reactions were carried out at 32–80 °C under nitrogen. Forty milliliters of benzene was used in every experiment. The amounts of the two monomers and the catalyst are shown in Table 1. The polymerization reaction is an easy experiment except that the catalyst surface is very sensitive to moisture. Thus the calcined catalyst must be treated under nitrogen, and monomers and solvent must be dried sufficiently (water content must be 50 ppm or less). On completion of the reaction, the solid catalyst was removed by filtration. Then the amounts of unreacted monomers and the reaction product of phenylsilane with diethynylbenzene $[Ph(H)_2Si-C{\equiv}C-C_6H_4-C{\equiv}CH]$ in the filtration were analyzed by gas chromatography. The filtrate was added to 500 mL of *n*-hexane in a vessel with stirring and polymers were deposited. The polymers were obtained by filtration or decantation, followed by drying at 50 °C in vacuo. Then the amounts of the reaction product of phenylsilane with diethynylbenzene $[Ph(H)_2Si-C{\equiv}C-C_6H_4-C{\equiv}CH]$ in the polymer were analyzed by gas chromatography. In some cases, the polymer was further purified by washing with *n*-hexane several times to remove oligomer, followed by drying.

Infrared, ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were employed to determine the structure of the polymers. Molecular weights were obtained by gel permeation chromatography (GPC) with retention times calibrated against polystylene samples.

Results and Discussion

In Table 1, the results of the polymerization in the presence of various catalysts are shown. The reaction proceeded even at room temperature in the presence of magnesium oxide with the visible evolution of hydrogen, and solid or viscous liquid polymers were obtained. The catalytic activity decreased gradually, since the reaction also produced insoluble cross-linked, high molecular weight polymers, which covered the active sites on the catalyst surface.

Magnesium oxide obtained by calcining magnesium hydroxide at 350 °C exhibited the highest catalytic activity. Magnesium oxide calcined below 300 °C, which has some X-ray diffraction pattern of magnesium hydroxide, had no catalytic activity. A calcining temperature of more than 350 °C gave lower specific surface areas of magnesium oxide and a lower catalytic activity. Calcium oxide, which, like magnesium oxide, is a solid base, also exhibited catalytic activity. Silica–alumina, a typical solid acid, changed from white to black during the reaction and had no activity. Carbonization reaction of diethynylbenzene would have occurred on silica–alumina. A polymerization mechanism which brings together the Si-H and C≡C bonds and the basic site

0024-9297/94/2227-7917$04.50/0

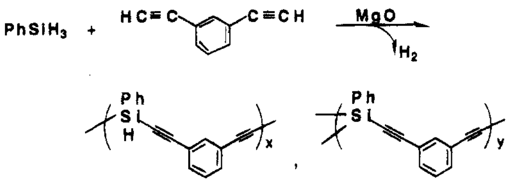
Table 1. **Dehydrogenative Coupling Polymerizations between Phenylsilane and *m*-Diethynylbenzene (DEB)**

expt no.	PHSiH$_3$ (mmol)	DEB (mmol)		cat.[a] (g)	reactn temp (°C)	reactn time (h)	conv PhSiH$_3$ (%)	conv DEB (%)	polymer yield[b] (%)	mol wt[c] M_w	mol wt[c] M_n	mol wt[c] M_w/M_n
1	20	20	MgO	(5.0)	32	27	84	89	73[f]	1120	650	1.7
2	20	20	MgO	(5.0)	80	21	63	72	38[f]	570	440	1.3
3	20	20	MgO	(5.0)	32 → 80	4 → 2	99	97	96[e]	3870	1350	2.9
4	20	20	MgO	(5.0)	32 → 80	4 → 2	95	96	93[e]	3060	1060	2.7
5	48	48	MgO	(5.0)	rt → 80	3 → 40			40[d,e]	2880	1810	1.6
6	20	20	MgO	(5.5)	rt → 50 → 80	18 → 8 → 2			54[d,e]	5400	2620	2.1
7	20	20	MgO	(5.1)	32 → 80	4 → 2	88	95	88[e]	2360	890	2.7
8	20	20	CaO	(5.1)	32 → 80	4 → 2	81	75	55[f]	470	560	1.2
9	20	20	$SiO_2-Al_2O_3$	(5.0)	32 → 80	4 → 2	8	35		299	340	1.1

[a] Catalysts were calcined in vacuo at 500 °C for 3 h (extp nos. 1, 2, and 7, specific surface are [=SA] 288 m^2/g; expt no. 8, SA = 34 m^2/g; expt no. 9, SA = 350 m^2/g), in vacuo at 500 °C for 2 h (expt nos. 5 and 6, SA 323 m^2/g), in vacuo at 350 °C for 3 h (expt no. 3, SA = 354 m^2/g), and under argon at 350 °C for 8 h (expt no. 4). [b] The amount of the reaction product of phenylsilane with diethynylbenzene [$Ph(H)_2Si-C\equiv C-C_6H_4-C\equiv CH$] was excluded from the polymer. [c] Polystylene equivalents ([$Ph(H)_2Si-C\equiv C-C_6H_4\equiv CH$] was excluded). [d] Polymer was obtained by washing with *n*-hexane several times to remove oligomers. [e] Solid. [f] Viscous liquid.

on the catalytic surface are supposed. More studies of the kinetics and the chemical interaction between hydrosilanes and the solid catalyst surface should help to clarify the reaction mechanism.

The polymer (M_w = 5400, M_n = 2620, M_w/M_n = 2.1; see expt no. 6 in Table 1) was a yellow amorphous solid and was soluble in THF and benzene. Analyses of the infrared, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra of the polymers indicate that the main structure of the polymer is poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [$-Si(Ph)H-C\equiv C-C_6H_4-C\equiv C-$],[4,12] which has some branches.[12,13] The ^{29}Si NMR spectrum is shown in Figure 1.



(2)

A similar polymer was obtained by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene using CuCl/amine as a catalyst.[4] In that case, the polymer had a wider molecular weight distribution, and the Si–H bond was easily hydrolyzed by moisture to make a siloxane bond when the polymer was contaminated with the amine of the catalyst.

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) measurements under argon and air were used to study the thermal properties of the polymer. The glass transition temperature (T_g) of the polymer (M_w = 5400; see expt no. 6 in Table 1) was 52 °C. Though no clear exothermic peak that could be assigned to the melting point was observed, the polymer was fusible and moldable, and it was possible to spin the polymer at 100–150 °C. The polymer changed gradually to black and was cured above 200 °C (curing temperature ca 150–210 °C). The specific gravity of the polymer cured at 150–400 °C was held constant at 1.14. The flexural modulus, bending strength, volume specific resistance, and specific dielectric constant of the polymer heated at 400 °C for 2 h under argon were 5.5 GPa, 16 MPa, 3 × 10^{16} Ω cm, and 3.8, respectively.

TGA–DTA curves of the polymer are shown in Figure 2. The polymer showed a very high thermal stability. There was very little weight loss in thermal cracking under argon. The residue at 1000 °C was 94%, and T_{d_5} (temperature of 5% weight loss, determined by the TGA trace) was 860 °C. These values are much higher than those of polyimide (Kapton; DuPont). T_{d_5} (567 °C) of the polymer under air, which is nearly equal to that of the polyimide, suggests the polymer would be highly incombustible, because the oxygen index (a minimum oxygen concentration for the polymer to continue combustion) of the polyimide is 53.

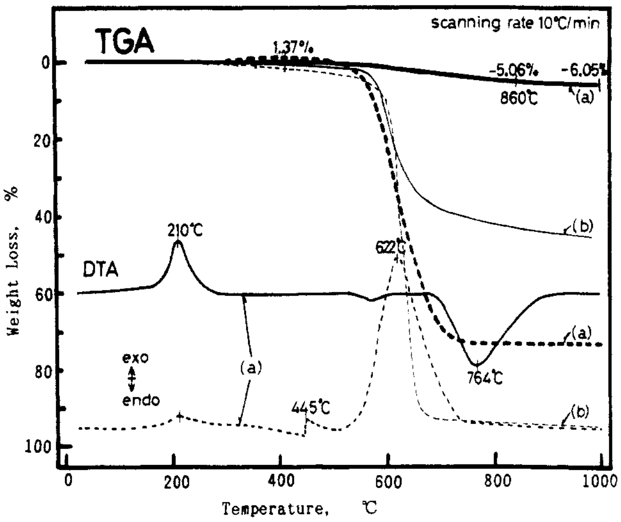


Figure 2. TGA and DTA traces of (a) poly[(phenylsilylene)-ethynylene-1,3-phenyleneethynylene] (expt no. 5 in Table 1) and (b) polyimide (Kapton) under argon (—) and air (- - -).

T_{d_5} values of some polymers under argon and air are shown in Figure 3. T_{d_5} of poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [$-Si(Ph)H-C\equiv C-C_6H_4-C\equiv C-$] under argon is much higher than those of poly[(diphenylsilylene)ethynylene-1,3-phenyleneethynylene] [$-Si(Ph)_2-C\equiv C-C_6H_4-C\equiv C-$] ($T_{d_5}$ = 547 °C), which has no Si-H bond, poly[(methylsilylene)-1,4-phenylene] [$-Si(CH_3)H-C_6H_4-$] (T_{d_5} = 320 °C),[14] and poly(silylene-1,4-phenylene) [$-SiH_2-C_6H_4-$] (T_{d_5} = 355 °C),[15] which have no C≡C bond. The polymer [$-Si(Ph)H-C\equiv C-C_6H_4-C\equiv C-$] had an exothermic peak at 210 °C in the DTA curve as shown in Figure 2. The infrared absorption bands characteristic of the Si–H and C≡C bonds of the polymer [$-S(Ph)H-C\equiv C-C_6H_4-C\equiv C-$] were reduced to half the initial absorption band when the polymer was treated at 240 °C for 4 h.[16] These facts suggest a cross-linking reaction involving the Si-H and C≡C bonds might have occurred to form a highly thermally stable structure. Further study will be needed to clarify the mechanism of the reaction and the resulting thermal stability.

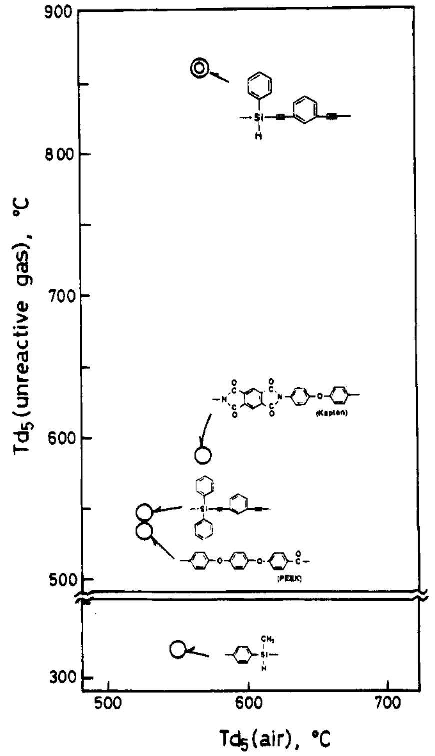


Figure 3. T_{d_5} (temperature of 5% weight loss) of some polymers under argon and air.

All peaks of the infrared, ^{13}C NMR, and ^{29}Si NMR spectra disappeared in the range 500–600 °C. A black glassy material was obtained (specific gravity 1.49) when poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] was heated at 1000 °C under argon. Free carbon and SiC were found upon analysis (peaks assigned to α-SiC were observed in the X-ray diffraction pattern). Poly(diethynylbenzene) also undergoes pyrolytic transformation to glassy carbon with only a small weight loss (Td_{10} values under argon and air were 870 and 420 °C, respectively, which were lower than those of poly(phenylsilylene)ethynylene-1,3-phenyleneethynylene].[17]

This report offers a new economical process for the dehydrogenative coupling polymerization reaction of hydrosilanes with alkynes to produce an extremely thermally stable silicon-containing polymer.

Acknowledgment. This work was performed by Mitsui Toatsu Chemicals, Inc., under the management of the Japan High Polymer Center as part of the Industrial Science and Technology Frontier Program supported by the New Energy and Industrial Technology Development Organization.

References and Notes

(1) (a) Voronkov, M. G.; Druzhdzh, P. V., Pukhnarevich, V. B. *Zh. Obshch. Khim.* **1980**, *50*, 1662. (b) Voronkov, M. G.; Ushakova, N. I.; Tsykhanskaya, I. I.; Pukhnarevich, V. B. *J. Organomet. Chem.* **1984**, *264*, 39. (c) Voronkov, M. G; Pukhnarevich, V. B.; Ushakova, N. L.; Tsykhanskaya, I. I.; Albnov, A. L.; Vikovskii, V. Yu. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1985**, *55*, 80.

(2) Fernandez, M. J.; Oro, L. A.; Manzano, B. R. *J. Mol. Catal.* **1988**, *45*, 7.

(3) Jun, C. H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

(4) Liu, H. Q.; Harrod, J. F. *Can. J. Chem.* **1990**, *68*, 1100.

(5) Itoh, M.; Mitsuzuka, M.; Tetsura, U.; Iwata, K.; Inoue, K. *J. Organomet. Chem.* **1994**, *476*, C30.

(6) Brefort, J. L.; Corriu, R. J. P.; Gerbier, Ph.; Guerin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, Th.; Garnier, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500.

(7) Seyferth, D.; Yu, Y. F. U S Patent 772375, 1986.

(8) (a) Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Jean, A.; Mutin, P. H. *Organometallics* **1992**, *11*, 2507. (b) Corriu, R. J. P.; Douglas, W. E.; Yang, Z. *J. Polym. Sci., Part C* **1990**, *28*, 431. (c) Maghsoodi, S. I.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A* **1990**, *28*, 955. (d) Cirriu, R. J. P.; Guerin, C.; Henner, B.; Kuhlmann, T.; Jean, A.; Garnier, F.; Yassar, A. *Chem. Mater.* **1990**, *2*, 351.

(9) Nate, K.; Inoue, T.; Sugiyama, H.; Ishikawa, M. *J. Appl. Polym. Sci.* **1987**, *34*, 2445.

(10) (a) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604. (b) Ohshita, J.; Matsugguchi, A.; Furumori, K.; Hong, R. F.; Ishikawa, M.; Yamanaka, T.; Koike, T.; Shioya, J. *Macromolecules* **1992**, *25*, 2134. (c) Barton, T. J.; Ijadi-Maghsoodi, S.; Pang, Y. *Macromolecules* **1991**, *24*, 1257. (d) Chicart, P.; Corriu, R. J. P.; Moreau, J. J. E.; Garnier, F.; Yassar, A. *Chem. Mater.* **1991**, *3*, 8.

(11) For example: (a) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106. (b) Iwahara, M.; Hayase, S. H.; West, R. *Macromolecules* **1990**, *23*, 1298. (c) Corriu, R. J. P.; Douglas, W. E.; Yang, Z. *J. Organomet. Chem.* **1993**, *455*, 69. (d) Corriu, R. J. P; Gerbier, Ph.; Guerin, C.; Henner, B. *J. Organomet. Chem.* **1993**, *449*, 111. (e) Hu, S.; Weber, W. P. *Polym. Bull.* **1989**, *22*, 133. (f) Kotani, S.; Shiina, K.; *Appl. Organomet. Chem.* **1991**, *5*, 417.

(12) Spectral data for poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene]: IR (neat) ν(Si–H, C≡C) 2159, δ(Si–H) 800 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS) δ 3.07 (s, C≡CH), 4.71 (s, (Ph)SiH_2), 5.11 (s, (Ph)SiH), 7.3–7.9 (m, PhH); ^{13}C NMR ($CDCl_3$/TMS) δ 78.2 (C≡CH), 82.4 (C≡CH), 86.6 (C≡C–C_6H_4–), 107.2 (C≡C–C_6H_4–), 123–136 (Ph); ^{29}Si NMR ($CDCl_3$/TMS) δ −59.7 ((Ph)SiH_2), −63.5 ((Ph)SiH), −69.3 ((Ph)Si≡).

(13) ^{29}Si NMR ($CDCl_3$/TMS) spectra of three model compounds were obtained. Ph–C≡C–Si(Ph)H_2, δ −59.6; (Ph–C≡C)$_2$-Si(Ph)H, −63.6; (Ph–C≡C)$_3$SiPh, −69.3. "Off-resonance spectra" were also used for the assignment of signals of the polymer (*J*(SiH) = 233 Hz, *J*(SiH_2) = 216 Hz).

(14) Ohshita, J.; Ishii, M.; Ueno, Y.; Ishikawa, M. Unpublished data.

(15) Tanaka, M.; Sakakura, T. Unpublished data.

(16) The polymer [–Si(Ph)D–C≡C–C_6H_4–C≡C–] was synthesized, and IR absorption bands characteristic of the Si–D bond (590 cm^{-1}) and C≡C bond (2159 cm^{-1}) were measured.

(17) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* **1988**, *21*, 3528.