Dehydrogenative cross-coupling reactions between phenylsilane and ethynylbenzene in the presence of metal hydrides

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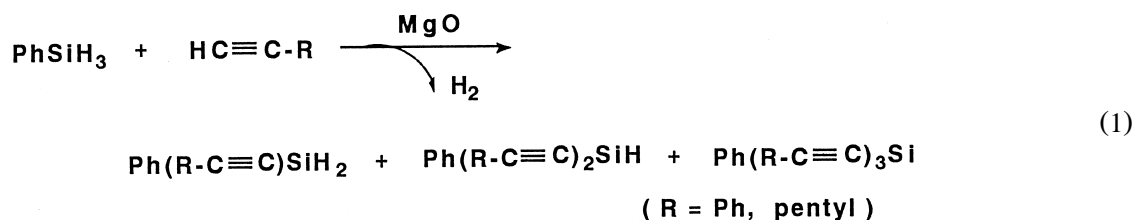Received 5 August 1997; received in revised form 24 September 1997

Abstract

Dehydrogenative cross-coupling reactions occurred between phenylsilane and ethynylbenzene in the presence of the metal hydrides, such as $LiAlH_4$, $NaAlH_4$, $LiBH_4$ and $LiAlH(Ot-Bu)_3$ to produce some ethynyl compounds. Phenylsilane and diethynylbenzene produced a highly thermally stable polymer, poly[(phenylsilylene)ethynylenephenyleneethynylene]. The activities and selectivities of the reactions were discussed on the basis of the mechanism involving the alkynylaluminate anion. © 1998 Elsevier Science S.A.

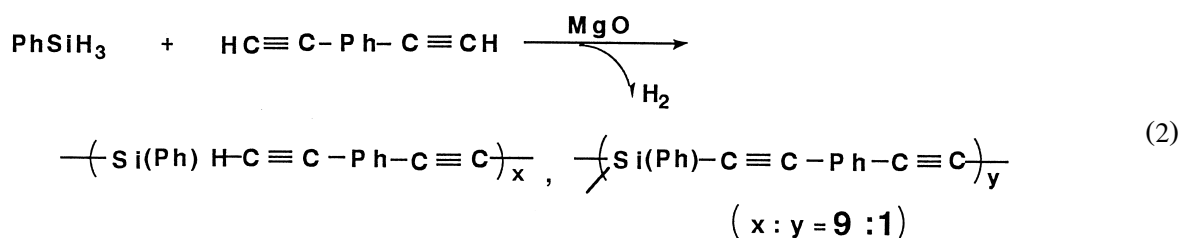*Keywords:* Phenylsilane; Ethynylbenzene; Metal hydrides

1. Introduction

There have been some reports on the dehydrogenative cross-coupling reactions of hydrosilanes with monosubstituted alkynes to produce alkynylsilanes. H_2PtCl_6/LiI, I_2 [1–3], $IrH_2(SiEt_3)(COD)(AsPh_3)$, iridium catalysts formed by adding triarylarsines or triarylphosphines to $[Ir(OMe)(diolefin)]_2$ [4], $[IrH(H_2O)(bp)L_2]SbF_6$, $RhClL_3$ (L = PPh_3, bp = 7, 8-benzoquinolinato) [5] have been used as catalysts. In these cases, the dehydrogenative cross-coupling reactions were found to accompany the significant hydrosilylation reactions to produce corresponding alkenylsilanes. Calas and Bourgeois [6,7] obtained alkynylsilane (n-Bu–C≡C–SiEt$_3$) from Et_3SiH and 1-hexyne using Na or NaH as a catalyst. Liu and Harrod [8] reported that the CuCl/amine catalyst led to the highly selective dehydrogenative cross-coupling reactions of hydrosilanes with alkynes [8]. We have found that the solid bases such as MgO catalyze the same selective dehydrogenative cross-coupling reactions [9].

$$PhSiH_3 \ + \ HC≡C\text{-}R \ \xrightarrow[\ \ \ \ H_2\ \ \ \ ]{MgO}$$

$$Ph(R\text{-}C≡C)SiH_2 \ + \ Ph(R\text{-}C≡C)_2SiH \ + \ Ph(R\text{-}C≡C)_3Si \tag{1}$$

$$(R = Ph, \ pentyl)$$

When we used phenylsilane and *m*-diethynylbenzene as the reactants, a highly heat-resistant and burn-resistant
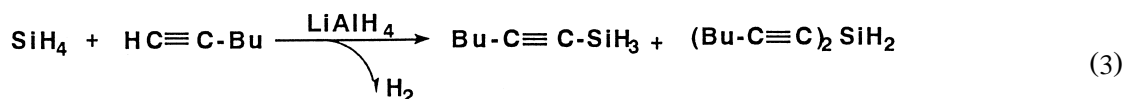
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thermosetting polymer, poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (abbreviated MSP) was obtained [10,11].

$$PhSiH_3 \quad + \quad HC \equiv C-Ph-C \equiv CH \xrightarrow[\;\;\;\text{MgO}\;\;\;]{} \quad$$

$$\quad \overset{\displaystyle}{\underset{}{}} + Si(Ph)H - C \equiv C - Ph - C \equiv C \xrightarrow{}_x \; , \quad + Si(Ph) - C \equiv C - Ph - C \equiv C \xrightarrow{}_y \quad (2)$$

$$(\, x : y = \mathbf{9 : 1} \,)$$

As MgO is easily separated by filtration from the reaction solution after the completion of the reaction, the polymer is very pure and stable in air. But the catalytic activity of MgO is low, so it needs a large amount of MgO to obtain the product in high yield. We have been searching for a more active catalyst for the dehydrogenative cross-coupling reactions.

We have recently found that $LiAlH_4$ catalyzes the selective dehydrogenative cross-coupling reaction between SiH_4 and 1-hexyne, and briefly reported that phenylsilane and ethynylbenzene also react to produce dehydrogenated products [12].

$$SiH_4 \; + \; HC \equiv C\text{-}Bu \xrightarrow[\;\;\;\text{LiAlH}_4\;\;\;]{} \; Bu\text{-}C \equiv C\text{-}SiH_3 \; + \; (Bu\text{-}C \equiv C)_2 \, SiH_2 \qquad (3)$$

A reaction mechanism involving the alkynylaluminate anion as an intermediate has been proposed [12].

In this paper, we report the details of the dehydrogenative cross-coupling reactions between phenylsilane and monoethynylbenzene in the presence of certain kinds of metal hydride including $LiAlH_4$ as catalysts. Moreover, we present a new method for the dehydrogenative cross-coupling polymerization between phenylsilane and diethynylbenzene to give a highly thermally stable polymer.

2. Experimental

The liquid reactants of phenylsilane, ethynylbenzene (abbreviated EB) and *m*-diethynylbenzene (abbreviated *m*-DEB) were distilled, and dried over 3A molecular sieves prior to use. The solid reactant of *p*-diethynylbenzene (abbreviated *p*-DEB) was purified by recrystallization from toluene, then dissolved in THF and dried over 3A molecular sieves. A solution of diethyl ether containing $LiAlH_4$ was refluxed and the undissolved substance was separated from the solution by filtration. The solution was then dried under reduced pressure at 70°C and white crystals of $LiAlH_4$ were obtained. $NaAlH_4$ was purified like $LiAlH_4$ using THF instead of diethyl ether. $LiBH_4$ and $LiAlH(Ot-Bu)_3$ were used without further purifications. The solvents of THF and diglyme were dried over 3A molecular sieves.

All experiments were carried out in a nitrogen atmosphere. The reactions were performed in a 70-ml autoclave under high pressure, or in a 100-ml glass flask under atmospheric pressure. The prescribed amount of phenylsilane, alkyne, metal hydride and solvent were charged into the autoclave or the glass flask (see Tables 1 and 2) and the reaction was carried out for 20 h at 120°C. After the reactions, the products were taken out and analyzed as follows.

2.1. The reaction products of phenylsilane with EB

After the completion of the reaction, the amounts of the reaction products and unreacted monomers were analyzed by GC using tetradecane as the internal standard. The liquid products were separated by distillation under reduced pressure, and assignments were made based on the GC–MS, IR, and ^1H, ^{13}C and ^{29}Si NMR spectra [10–12].

Table 1
Reaction of phenylsilane with EB

Expt no.	$PhSiH_3$ (mmol)	EB (mmol)	Catalyst	(mmol)	Solvent[a]	Reactn		Conv		Yield (%)[b,j]				
						Temp (°C)	Pressure (kg/cm²abs)	$PhSiH_3$ (%)	EB (%)	1	2	3	4	5
1	52.8	53.4	$LiAlH_4$	2.7[c]	diglyme	120	1	52.8	56.4	41.9	9.2	1.0	1.0	0.5
2	52.4	52.1	$LiAlH_4$	2.7	diglyme	100	1	34.6	35.1	17.3	1.2	0.7	0	0.3
3	51.1	52.5	$LiAlH_4$	2.6	diglyme	80	1	20.8	16.0	12.6	0.6	0.4	0	0
4	50.6	54.2	$LiAlH_4$	2.2	diglyme	120	1	36.5	36.7	29.7	2.4	1.1	0.4	0.5
5	53.6	53.7	$LiAlH_4$	2.7	diglyme	120	14	37.9	66.0	28.2	3.6	3.9	1.8	2.3
6	53.1	52.4	$LiAlH_4$	2.6	THF	120	15	54.1	81.4	17.7	1.1	10.6	5.0	1.9
7	52.7	55.2	$LiAlH_4$	2.6	THF	80	5	31.2	37.9	19.7	1.7	4.0	1.0	0.9
8	52.0	53.1	$NaAlH_4$	2.5	diglyme	120	1	43.5	44.7	30.8	4.6	0.7	0.6	0.2
9	51.6	53.2	$LiBH_4$	3.0	diglyme	120	1	44.4	67.0	17.7	0.5	6.9	3.6	2.0
10[d]	51.6	51.2	$LiAlH(Ot–Bu)_3$	2.5	diglyme	120	1	53.2[d]	56.4	33.5	6.1	1.4	0	0.6
11	51.9	51.3	$LiAl(C≡C–Ph)_4$ .2THF	3.0[c]	diglyme[e]	110	1	33.6	39.6	31.2	7.4	0.3	0.6	0.1
12	51.0	55.2[f]	$LiAl(C≡C–Ph)_4$ .2THF	2.8	diglyme	70	1	6.3	25.4[g]	5.5[h]	0	0	0	0
13[i]	4.9	12.3	MgO	24.8	benzene	80	1	31	−	27	5	0	0	0

[a] Some 10 ml of the solvent was used in each experiment.
[b] The percent ratio of the product vs. the charged $PhSiH_3$. [**1**: $Ph–C≡CSi(Ph)H_2$, **2**: $(Ph–C≡C)_2Si(Ph)H$, **3**: $Ph–CH=CHSi(Ph)H_2$, **4**: $Ph–CH(SiPhH_2)–CH_2Si(Ph)H_2$, **5**: $Ph–C≡CSi(Ph)(CH=CH–Ph)H$].
[c] 102 mg.
[d] Some alkoxysilanes [$PhSi(Ot–Bu)H_2$; yield 1.9%, $PhSi(Ot–Bu)_2H$; yield 1.2%, $Ph–C≡CSi(Ph)(Ot–Bu)H$; yield 3.7%, $Ph–C≡CSi(Ph)(Ot–Bu)$; yield 0.9%, which were assigned using GC–MS, were also produced.
[e] 10 ml of diglyme and 3 ml of THF were used as solvents.
[f] 1-Hexyne was used instead of EB.
[g] 1-Hexyne.
[h] n-$BuC≡CSi(Ph)H_2$, identified by GC–MS ($C_4H_9C≡CSi(Ph)H_2$:MS (m/z)(EI-mode) 105 (base peak), 146, 145, 131, 188 (M+)). EB (yield 15.2%) and **1** (yield 0.1) were also produced.
[i] 100 mg of MgO was used and the reaction was carried out for 4 h [9].
[j] Styrene were also produced with 5, 6 and 13% yields in expt nos. 5, 6 and 9, respectively.

Table 2
Reaction of phenylsilane with *m*-DEB)

Expt no.	PhSiH$_3$ (mmol)	*m*-DEB (mmol)	LiAlH$_4$ (mmol)	Solvent[a]	Reactn		Conv		Polymer[b,d] yield (%)	Adduct[c] yield (%)	Mol. wt[d]		
					Temp. (°C)	Pressure (kg/cm^{2}abs)	PhSiH$_3$ (%)	*m*-DEB (%)			Mw	Mn	Mw/Mn
1	52	53	2.7	diglyme	120	1	51	56	26	15	853	566	1.5
2	55	55	2.6	diglyme	120	18	45	70	36	12	1430	670	2.2
3	53	53	2.6	THF	120	32	76	92	56	9	2880	970	3.0
4	52	53[e]	2.6	diglyme[f]	120	1	65	73	41	14	1390	710	1.9
5	52	51[e]	2.6	THF	120	21	51	78	41	15	1330	730	1.8

[a] Some 10 ml of the solvent was used in each experiment.
[b] The percent ratio of the polymer weight vs. the total weight of the two charged monomers.
[c] The reaction product of PhSiH$_3$ with DEB [HC≡C–Ph–C≡CSi(Ph)H$_2$].
[d] The adduct was excluded.
[e] *p*-DEB was used instead of *m*-DEB.
[f] Some 19 ml of the solvent was used.

2.2. The polymerization reaction products of phenylsilane with DEB

The reaction products and unreacted monomers were analyzed by GC and gel permeation chromatography (GPC). The reacted solution was then added to 20 ml of toluene and 20 ml of 1N HCl aq. in a vessel with stirring, and separated into two layers (I and II). The under layer (II) was added to 5 ml more of toluene and the layer of the toluene solution (III) was separated. The upper layer (I) was added to above the toluene solution (III), and washed with water three times. The upper layer (I) was then dried over calcium sulfate and evacuated for 50 h at 60°C to give the liquid or solid polymer. IR, and ^{1}H, ^{13}C and ^{29}Si NMR spectra were employed to determine the structure of the polymers [10,11]. Molecular weights were obtained by GPC with retention times calibrated against polystyrene samples.

In order to study the reaction mechanism, the aluminum acetylide [LiAl(C≡C–Ph)$_4$ · 2THF], which was synthesized by the reaction between LiAlH$_4$ and EB for 6 h at 64°C in THF as a solvent [13], was used as the catalyst.
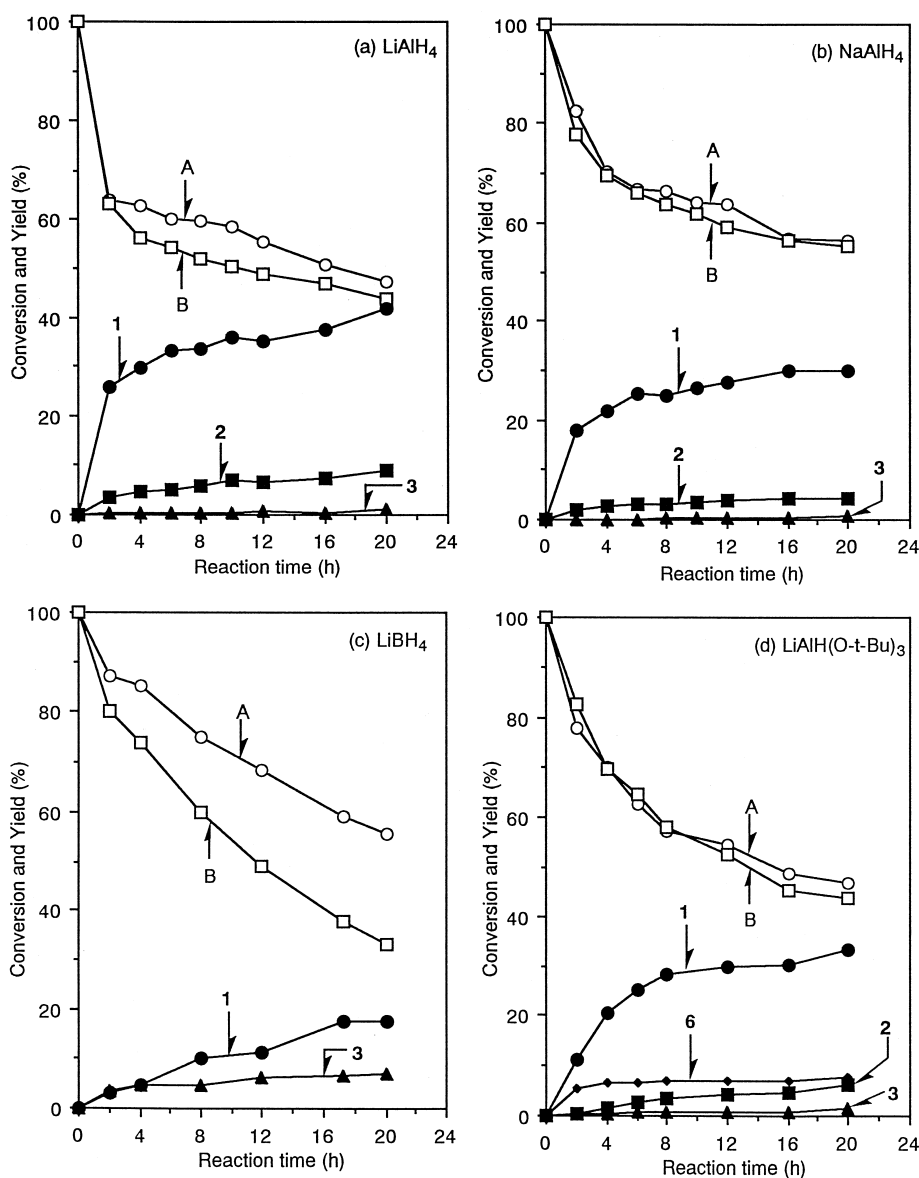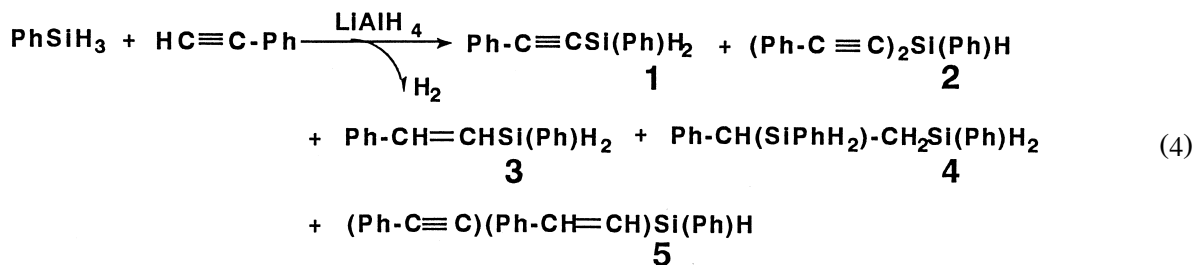

Fig. 1. Reaction of phenylsilane with EB in the presence of (a) LiAlH$_4$ (expt. no. 1 in Table 1), (b) NaAlH$_4$, (c) LiBH$_4$ and (d) LiAlH(Ot–Bu)$_3$. **A**: PhSiH$_3$, **B**: Ph–C≡CH, **1**: Ph–C≡CSi(Ph)H$_2$, **2**: (Ph–C≡C)$_2$Si(Ph)H, **3**: Ph–CH=CHSi(Ph)H$_2$, **6**: PhSiH$_{3-x}$ (Ot–Bu)$_x$.

3. Results

3.1. The reaction of phenylsilane with EB

In Table 1, the results of the reactions in the presence of various catalysts are shown. $LiAlH_4$ catalyzed the dehydrogenative cross-coupling reaction at above 80°C in diglyme and some dehydrogenated products (**1**, **2**) were obtained with high selectivity (expt. nos. 1–3 in Table 1). When the reactions were carried out in the autoclave under high pressure in THF or diglyme as a solvent (expt. nos. 5–7 in Table 1), some amount of hydrosilylated products (**3**, **4**, **5**) were also detected.

$$PhSiH_3 + HC{\equiv}C\text{-}Ph \xrightarrow[H_2]{LiAlH_4} Ph\text{-}C{\equiv}CSi(Ph)H_2 + (Ph\text{-}C{\equiv}C)_2Si(Ph)H$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

$$+ \; Ph\text{-}CH{=}CHSi(Ph)H_2 \;+\; Ph\text{-}CH(SiPhH_2)\text{-}CH_2Si(Ph)H_2 \qquad (4)$$
$$\mathbf{3} \qquad\qquad\qquad\qquad \mathbf{4}$$

$$+ \; (Ph\text{-}C{\equiv}C)(Ph\text{-}CH{=}CH)Si(Ph)H$$
$$\mathbf{5}$$

$NaAlH_4$ also catalyzed the dehydrogenative cross-coupling reaction in a similar manner as $LiAlH_4$ (compare expt. no. 10 with 1 in Table 1). $LiBH_4$ also showed the catalytic activity against the reaction, but the selectivity toward the dehydrogenation was lower than that of $LiAlH_4$ and a considerable amount of styrene was produced, which would be caused by the hydrogenation reaction of EB. In the case of $LiAlH_4$, the reaction proceeded faster during the early stage of the reaction than using $LiBH_4$ as shown in Fig. 1a and b. $LiAlH(Ot{-}Bu)_3$ and $LiAl(C{\equiv}C{-}Ph)_4 \cdot 2THF$ also showed catalytic activities against the dehydrogenation reaction to give the same products as $LiAlH_4$, but in the case of $LiAlH(Ot{-}Bu)_3$, some alkoxysilane compounds were produced (expt. no. 10. 11 in Table 1, and Fig. 1d).

A small amount of the products, which molecular weights were larger than that of product (**5**) and could not be analyzed by GC, were detected by GPC. These would be highly dehydrogenated and/or hydrosilylated products, such as $(Ph{-}C{\equiv}C)_3SiPh$, $(Ph{-}C{\equiv}C)_2(Ph{-}CH{=}CH)SiPh$ and $Ph{-}CH(SiPhH_2){-}CH_2Si(Ph{-}CH{=}CH)(Ph)H$, and they would be easily produced in the reactions which gave high conversions of the reactants or high yields of the
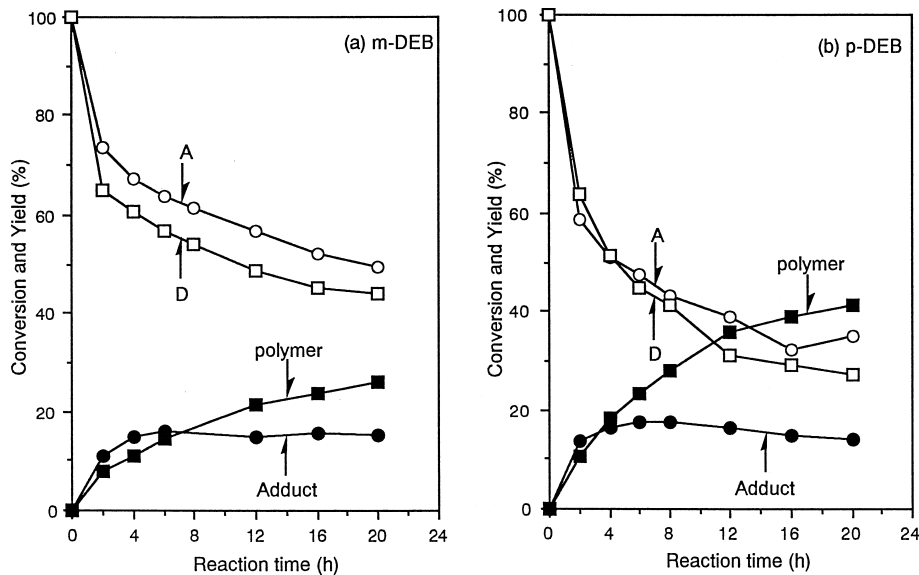

Fig. 2. Polymerization reaction of phenylsilane with (a) *m*-DEB (expt. no. 1 in Table 2) and (b) *p*-DEB (expt. no. 5 in Table 2) in the presence of $LiAlH_4$. **A**: $PhSiH_3$, **D**: $HC{\equiv}C{-}Ph{-}C{\equiv}CH$, **Adduct**: $HC{\equiv}C{-}Ph{-}C{\equiv}CSi(Ph)H_2$.

hydrosilylated products (**3, 4, 5**). The large differences between the conversions of the reactants and the total yields of the products (**1–5**) in expt. nos. 5, 6, 9 and 10 in Table 1 would be caused by these products.

3.2. The polymerization reaction of phenylsilane with DEB

These results are shown in Table 2 and Fig. 2. Solid or viscous liquid polymers were obtained. The polymer in expt. no. 3 in Table 2 was fractionated using GPC and the polymer with a high molecular weight (Mw = 11000, Mn = 4940, abbreviated polymer (**a**)) was obtained. The ^{13}C and ^{29}Si NMR spectral data of the polymer (**a**) are shown in Fig. 3. The spectral data of the IR and NMR were the same as those of MSP, which was obtained by the dehydrogenative cross-coupling polymerization reaction using the same monomers in the presence of MgO as a
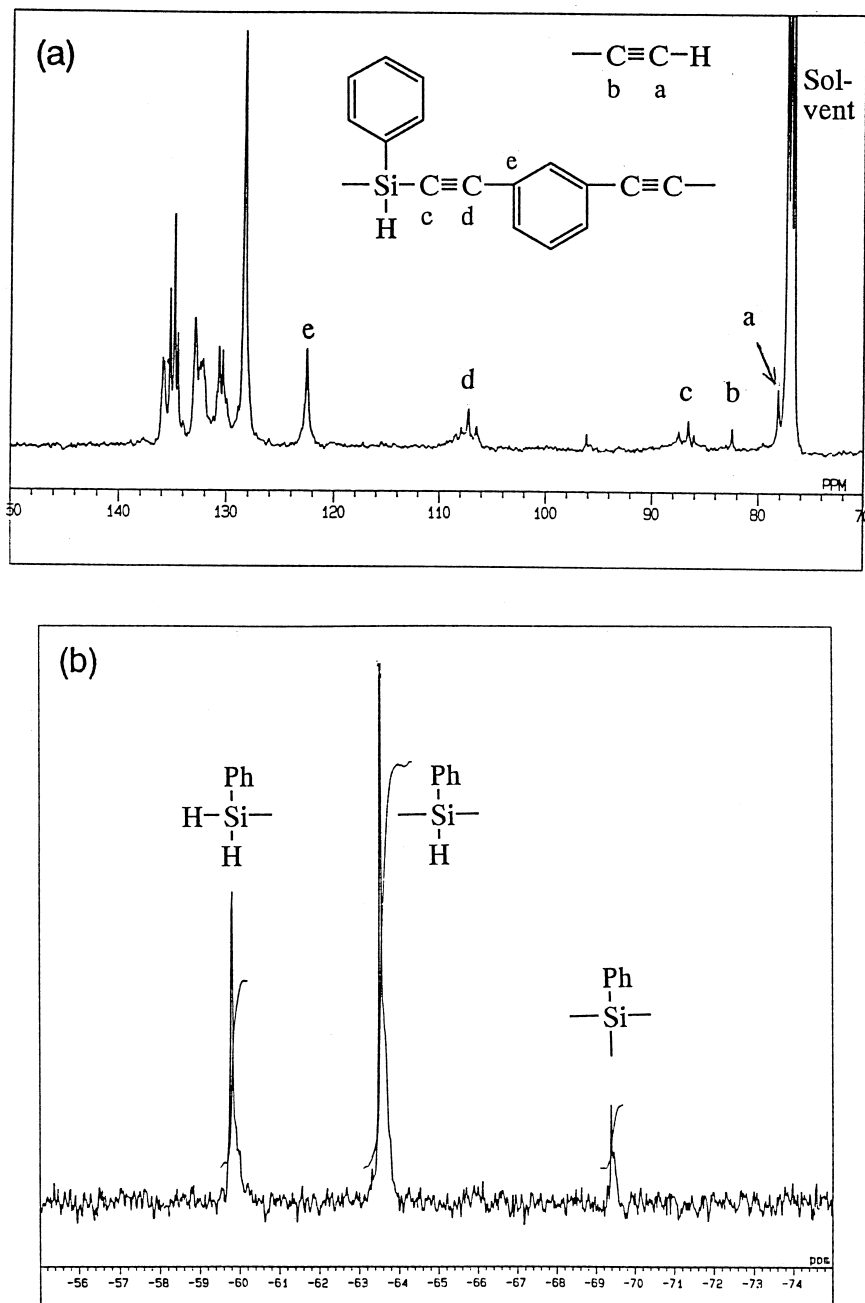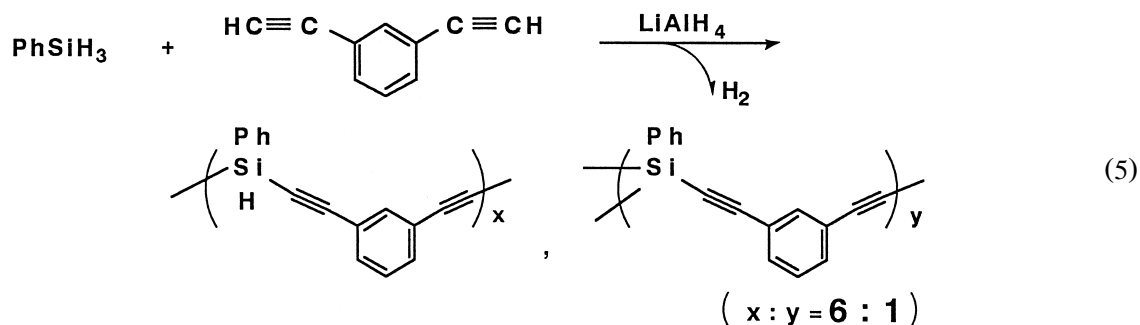

Fig. 3. NMR spectra of the polymer (**a**) obtained by the reaction between phenylsilane and *m*-DEB in the presence of LiAlH$_4$ subscript (expt. no. 3 in Table 2). (a) ^{13}C NMR (b) ^{29}Si NMR.

catalyst [10,11]. These results show the dehydrogenative cross-coupling polymerization reaction occurred in the presence of $LiAlH_4$.



$$(x : y = 6 : 1) \tag{5}$$

From the ^{29}Si NMR spectrum in Fig. 3b, the ratio of the branched structure ($= x/y$) of the polymer (**a**) was 6/1. The present polymer is higher branched in comparison with MSP ($x/y = 9/1$, Eq. (2)). The end structure of the polymer (**a**) was $-Si(Ph)H_2$ or $-C\equiv CH$ (see Fig. 3a and b); the ratio of $-Si(Ph)H_2$ to $-C\equiv CH$, which was determined by ^1H NMR spectral data, was nearly 1.

The polymer (Mw = 2880, Mn = 970, Mw/Mn = 3.0; expt. no. 3 in Table 2) was a yellow amorphous solid, soluble in THF and benzene, fusible and moldable at 100–150°C. The polymer was cured at 150–210°C and showed a high thermal stability [Td_5 (temperature of 5% weight loss) in helium = 760°C] similar to MSP (Td_5 = 860°C) [10,11].

4. Discussion

As we mentioned in previous reports, the reactions between SiH_4 and a monosubstituted alkyne [12] or alkenes [14] were studied. The dehydrogenative cross-coupling reaction between hydrosilane and an alkyne would proceed via the alkynylaluminate anion as shown in Eq. (6), and the hydrosilylation reaction would proceed via the alkenylaluminate anion as shown in Eq. (7).

$$(6)$$

$$(7)$$
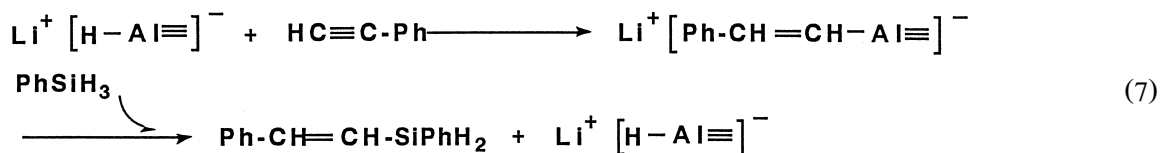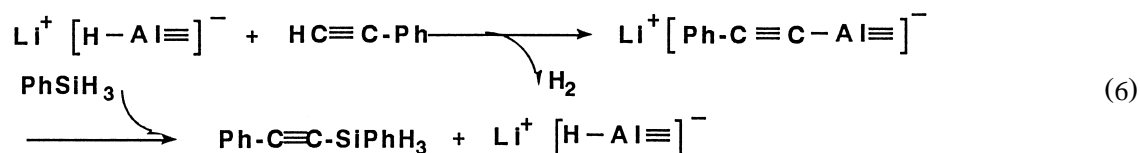
The dehydrogenative cross-coupling reaction would begin with the coupling reaction between the basic hydrogen of the metal hydride and the acidic hydrogen of the ethynyl compound.

$$M^{\delta+}-H^{\delta-} + H^{\delta+}-C^{\delta-}\equiv C-Ph \rightarrow M^{\delta+}-C^{\delta-}\equiv C-Ph + H_2 \uparrow$$

$$\times (M{:}Al,B) \tag{8}$$
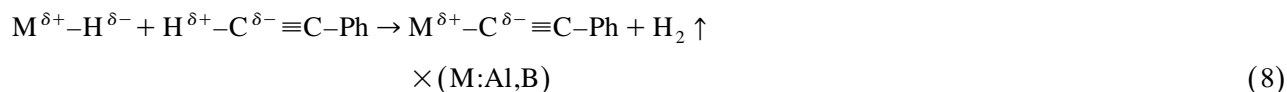
As the aluminum atom has a lower electronegativity than the boron atom, the hydrogen of $LiAlH_4$ is more basic than that of $LiBH_4$, and the catalytic activity of $LiAlH_4$ against the coupling of the two hydrogens would be higher than that of $LiBH_4$. Diglyme is more polar than THF, so it would support the polarization of the two hydrogens of the alkyne and $LiAlH_4$, which would promote the coupling of the two hydrogens.

$LiAlH(On-Bu)_3$ gave some alkoxysilane compounds together with the dehydrogenated products. This suggests that

$LiAlH(On-Bu)_3$ would be changed into a more active hydride as shown in Eq. (9), and catalyze the dehydrogenative cross-coupling reaction.

$$PhSih_3 + LiAlH(Ot-Bu)_3 \rightarrow LiAlH_{1+x}(Ot-Bu)_{3-x} + PhSiH_{3-x}(Ot-Bu)_x \tag{9}$$

$LiAl(C\equiv C-Ph)_4 \cdot 2THF$ also catalyzed the dehydrogenative cross-coupling reactions of phenylsilane with EB to give the same products as $LiAlH_4$. When 1-hexyne was used instead of EB, a dehydrogenated product [n-BuC$\equiv$CSi(Ph)H$_2$] was produced with a larger conversion of 1-hexyne than that of phenylsilane (expt. no. 12 in Table 1). The exchange reaction as shown in Eq. (10) would occur. These facts support the mechanism of the dehydrogenation reaction shown in Eq. (6).

$$LiAl(C\equiv C-Ph)_4 + x\,HC\equiv C-C_4H_9 \rightarrow LiAl(C\equiv C-Ph)_{4-x}(C\equiv C-C_4H_9)_x + x\,HC\equiv C-Ph \tag{10}$$
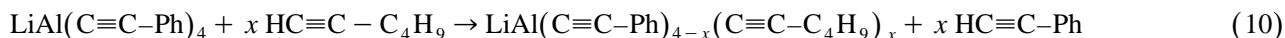
The reaction under atmospheric pressure is more selective against the dehydrogenative cross-coupling reaction than that at high pressure based on the equilibrium consideration (compare expt. no. 1 with 5 in Table 1). In expt. nos. 5, 6 (reaction under closed system) and 9 (reaction under $LiBH_4$) in Table 1, a small amount of styrene was also produced by the hydrogenation of EB, and the conversion of EB was larger than that of phenylsilane.

As expected, the polymers of [poly(phenylsilylene)ethynylene-1,3-phenylene ethynylene] and [poly(phenylsilylene)ethynylene-1,4-phenyleneethynylene] were obtained by the reaction of phenylsilane with *m*-DEB and *p*-DEB, respectively. Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] showed slightly less thermal stability than MSP when prepared using the MgO catalyst [10,11]. The polymer prepared using $LiAlH_4$ would contain some C=C bonds in the molecule, which would be synthesized by the hydrosilylation reaction, though no peak assigned to the C=C bond was observed in the spectra. The advantage of using $LiAlH_4$ as the catalyst is lower amount of catalyst is needed than when using MgO [9] (expt. no. 13 in Table 1). Further studies will be needed to determine which process is more industrially advantageous.

R_3Si-H could be activated by transition metal complexes (MLn) to make Si–M and M–H bonds ($R_3Si-M(Ln)-H$). We have shown that ionic compounds such as $LiAlH_4$ and MgO catalyze the reactions concerning hydrosilanes. This might suggest that the Si–H bond could be more easily polarized and activated to make an ionic state than the C–H bond. We are now making an effort to study other reactions catalyzed by an ionic catalyst and other new ionic catalysts.

Acknowledgements

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