chains and can be substantial as in the case of poly[bis(4-*tert*-butylphenoxy)phosphazene] with bulky *tert*-butylphenoxy groups, leading to a T_g significantly above room temperature. The ^{31}P NMR results support the suggestion of flexibility and conformational disorder in the backbone of the amorphous phase and the mesophase. The absence of liquid crystalline order below $T(1)$ in the amorphous phase of poly[bis(4-ethylphenoxy)phosphazene] may be ascribed to the geometrical constraints provided by the crystalline phase. No such constraints appear to exist in poly[bis(4-*tert*-butylphenoxy)phosphazene], which is not crystalline, and liquid crystalline order is observed instead throughout the entire temperature range.

To summarize, we have primarily studied the backbone motional and conformational states of polyphosphazenes by selective excitation of ^{31}P nuclei. The chemical shifts of amorphous backbone ^{31}P nuclei move upfield with increasing temperature, which suggests that the amorphous phase becomes more disordered. At first the amorphous line width in poly[bis(4-ethylphenoxy)phosphazene] decreases with temperature, than it increases as the amorphous chains apparently become more tightly constrained by the higher temperature crystalline polymorph, and finally it is sharply reduced as poly[bis(4-ethylphenoxy)phosphazene] moves into the liquid crystalline state. The motional and conformational state of the side groups should yield important information concerning these transitions. A more detailed companion study including the results of solid-state ^{13}C NMR and X-ray diffraction studies will be published elsewhere.

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Polymerization of 3-Silyl-1-hexynes and Polymer Properties[1]

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ABSTRACT: 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne and 3-(dimethylphenylsilyl)-1-hexyne [$HC{\equiv}CCH(SiMe_2R)$-n-C_3H_7; R = n-C_6H_{13}, Ph; new compounds] formed polymers in excellent yields in the presence of Mo and W catalysts. The highest weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of poly[3-(dimethyl-*n*-hexylsilyl)-1-hexyne] were ca. 4 × 10^5 and 2 × 10^5, respectively ($MoCl_5$–Ph_3Sb as catalyst), while the highest $\bar{M}_w$ and $\bar{M}_n$ of the corresponding phenyl-substituted polymer were ca. 2 × 10^5 and 8 × 10^4 (WCl_6–Ph_3Sb). Both of the present polymers were yellow solids, whose structure could be represented as [—$CH{=}C(CHSiMe_2R$-n-$C_3H_7)$—]$_n$. They dissolved in many common organic solvents and could be cast from solution into films. Mechanical, thermal, and some other properties of the polymers are discussed.

Introduction

Recently, many polymers have been synthesized from substituted acetylenes by use of transition metal catalysts.[3] Among the polymers, Si-containing polyacetylenes often exhibit unique properties and functions (e.g., high gas permeability[4]); thus their synthesis is an intriguing subject. One of the simplest Si-containing acetylenes is (trimethylsilyl)acetylene. This monomer, however, usually produces a polymer partly insoluble in common organic solvents,[5] and the molecular weight of its soluble fraction is no more than ca. 1 × 10^4. Monomers in which one of the methyl groups in (trimethylsilyl)acetylene is replaced by other groups such as *n*-hexyl and phenyl also provide only polymers with similar molecular weights.[6]

In a previous paper,[7] 3-(trimethylsilyl)-1-alkynes [$HC{\equiv}CCH(SiMe_3)$-n-alkyl, 1] were employed as another

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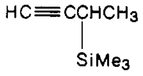
Table I
Polymerization of 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne by Various Catalysts[a]

no.	catalyst	monomer convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
1	$MoCl_5$	100	89	260	140
2	$MoCl_5$–Ph_3Sb	100	93	410	200
3	$MoCl_5$–Ph_3Bi	60	42	130	47
4	$MoCl_5$–Ph_3SiH	100	89	260	120
5	$MoCl_5$–Et_3SiH	100	81	210	87
6	$MoCl_5$–Ph_4Sn	100	92	270	150
7	$MoCl_5$–*n*-Bu_4Sn	100	78	230	100
8	$Mo(CO)_6$–$h\nu$[c]	100	96	200	98
9	WCl_6	100	56	59	18
10	WCl_6–Ph_3Sb	100	80	110	43
11	WCl_6–Ph_3Bi	88	61	47	28
12	WCl_6–Ph_3SiH	100	62	55	16
13	WCl_6–Et_3SiH	100	81	68	23
14	WCl_6–Ph_4Sn	100	88	140	32
15	WCl_6–*n*-Bu_4Sn	100	61	53	16
16	$W(CO)_6$–$h\nu$[c]	100	88	76	13
17	$NbCl_5$	100	56	41	12
18	$NbCl_5$–Ph_3Sb	100	65	100	27
19	$NbCl_5$–Ph_3SiH	100	81	87	40
20	$NbCl_5$–Ph_4Sn	100	52	34	9
21	$TaCl_5$	86	0		
22	$TaCl_5$–Ph_3Sb	32	0		

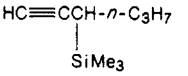
[a] Polymerized in toluene at 0 °C (Mo, W) or 30 °C (Nb, Ta) for 24 h; $[M]_0$ = 0.50 M, [Cat] = [Cocat] = 10 mM. [b] Determined by GPC. [c] Polymerized in CCl_4 at 30 °C.

type of Si-containing monosubstituted acetylenes, and their polymerization was studied. 3-(Trimethylsilyl)-1-



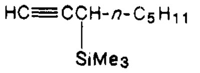
1a

$\mathrm{HC{\equiv}C\underset{SiMe_3}{\underset{|}{C}}HCH_3}$



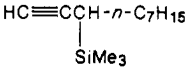
1b

$\mathrm{HC{\equiv}C\underset{SiMe_3}{\underset{|}{C}}H\text{-}\mathit{n}\text{-}C_3H_7}$



1c

$\mathrm{HC{\equiv}C\underset{SiMe_3}{\underset{|}{C}}H\text{-}\mathit{n}\text{-}C_5H_{11}}$

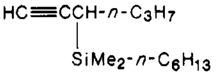


1d

$\mathrm{HC{\equiv}C\underset{SiMe_3}{\underset{|}{C}}H\text{-}\mathit{n}\text{-}C_7H_{15}}$

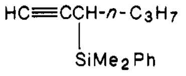
butyne (**1a**) and -1-hexyne (**1b**) polymerized with Mo and W catalysts, but the polymers did not completely dissolve in any solvents. In contrast, 3-(trimethylsilyl)-1-octyne (**1c**) and -1-decyne (**1d**), homologues with longer alkyl chains, gave polymers which were totally soluble in solvents such as toluene and chloroform and had high molecular weights up to ca. 5 × 10^5. Though the insolubility of polymers of **1a** and **1b** is assumed to be due to rather poor flexibility of the side chain, it is not necessarily evident.

We anticipated that soluble, high molecular weight polymers might be obtained if one of the methyl groups on the Si in monomer **1b** is replaced by flexible and/or bulky groups. The present paper reports on the polymerization of 3-(dimethyl-*n*-hexylsilyl)-1-hexyne (**2**) and 3-(dimethylphenylsilyl)-1-hexyne (**3**), both of which are novel compounds belonging to the monomer group of 3-silyl-1-hexynes.



2

$\mathrm{HC{\equiv}C\underset{SiMe_2\text{-}\mathit{n}\text{-}C_6H_{13}}{\underset{|}{C}}H\text{-}\mathit{n}\text{-}C_3H_7}$



3

$\mathrm{HC{\equiv}C\underset{SiMe_2Ph}{\underset{|}{C}}H\text{-}\mathit{n}\text{-}C_3H_7}$

Results and Discussion

Polymerization of 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne (2). The polymerization of this monomer was first examined with various catalysts (Table I). Under the polymerization conditions shown in Table I, the monomer was completely consumed in the presence of the Mo, W, and Nb catalysts, except for the case of Ph_3Bi as cocatalyst. The major products with the Mo, W, and Nb catalysts were methanol-insoluble poly[3-(dimethyl-*n*-hexylsilyl)-1-hexyne]s [poly(**2**)], whose yields were in the range ca. 40–100%.[8] In contrast, the polymer yields with Ta catalysts were zero. It is very interesting that 3-silyl-1-alkynes [**1c**,[7] **1d**,[7] and the present monomers] polymerize in the presence of Nb catalysts when it is taken into account that most monosubstituted acetylenes are selectively cyclotrimerized with Nb and Ta catalysts.[9] The methanol-soluble product in the polymerizations was a mixture of linear oligomers and cyclotrimers according to gel permeation chromatography (GPC) as well as IR and NMR spectra.

Table II
Solvent Effects on the Polymerization of 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne by $MoCl_5$–Ph_3Sb[a]

solvent	monomer convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
toluene	100	91	410	200
anisole	100	57	270	110
PhCl	100	60	130	45
CCl_4	100	52	230	89
$(CH_2Cl)_2$	70	0		

[a] Polymerized at 0 °C for 24 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = $[Ph_3Sb]$ = 10 mM. [b] Determined by GPC.

The weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of poly(**2**) obtained with $MoCl_5$–Ph_3Sb (Table I, no. 2) were 41 × 10^4 and 20 × 10^4, respectively, being the highest among the values in the table.[8] It is noted that not only polymer yield but also molecular weight is rather low with $MoCl_5$–Ph_3Bi, though Ph_3Bi is a Group 5 organometallic compound like Ph_3Sb. The molecular weight of polymer was usually lower when W and Nb catalysts were used instead of Mo catalysts.

As compared with $MoCl_5$ alone, catalysts composed of $MoCl_5$ and an organometallic cocatalyst more or less changed the polymerization rate, polymer yield, and molecular weight. For instance, the polymerization by $MoCl_5$ alone was finished after several hours, whereas the one by $MoCl_5$–Ph_3Sb was completed within 1 h. It is obvious in Table I that use of Ph_3Sb as cocatalyst increases the polymer molecular weight. As seen in Table I, the $Mo(CO)_6$–$h\nu$ catalyst is as effective as $MoCl_5$-based catalysts. Similar tendencies are observed also with WCl_6–cocatalyst and $W(CO)_6$–$h\nu$ systems.

Solvent effect on the polymerization was studied by using $MoCl_5$–Ph_3Sb which proved to be one of the most useful catalysts (Table II). Although the monomer was quantitatively consumed not only in toluene but also in anisole and halogen-containing solvents, the polymer yield in toluene was the highest (>90%). The $\bar{M}_w$ of poly(**2**) became the highest in toluene among the solvents examined.

Figure 1 shows the effect of temperature on the polymerization by $MoCl_5$–Ph_3Sb in toluene. The monomer conversion at 0 °C and above was quantitative under the conditions in Figure 1. The polymer yield was about 90% in the range 0–60 °C, while it was lower at −20 °C. The $\bar{M}_w$ of poly(**2**) exhibited a maximum around 0 °C. Therefore, 0 °C is suitable to obtain a high molecular weight polymer in high yield.

When this polymerization was carried out with $MoCl_5$–Ph_3Sb in toluene at 0 °C, all of monomer **2** was virtually consumed after 1 h, and at that point the yield of methanol-insoluble polymer reached about 90% (Figure 2). Then the $\bar{M}_w$ of the poly(**2**) was as high as ca. 4 × 10^5; even though the polymerization was continued over 24 h, the molecular weight did not change, indicating that no polymer degradation occurred.

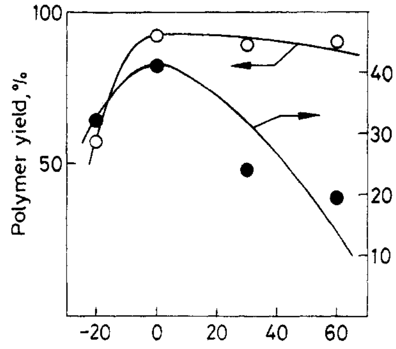


Figure 1. Effects of temperature on the polymerization of 3-(dimethyl-*n*-hexylsilyl)-1-hexyne by $MoCl_5$–Ph_3Sb (in toluene, 24 h, $[M]_0$ = 0.50 M, $[MoCl_5]$ = $[Ph_3Sb]$ = 10 mM).

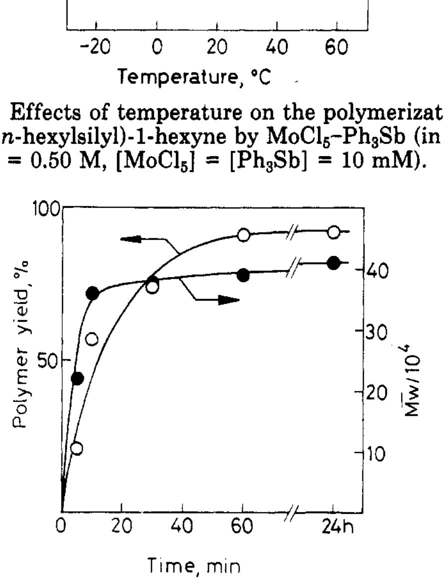


Figure 2. Time course of the polymerization of 3-(dimethyl-*n*-hexylsilyl)-1-hexyne by $MoCl_5$–Ph_3Sb (in toluene, 0 °C, $[M]_0$ = 0.50 M, $[MoCl_5]$ = $[Ph_3Sb]$ = 10 mM).

Table III
Polymerization of 3-(Dimethylphenylsilyl)-1-hexyne by Various Catalysts[a]

no.	catalyst	monomer convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_w/10^3$ [b]
1	$MoCl_5$	28	20	46	22
2	$MoCl_5$–Ph_3Sb	49	43	76	33
3	$MoCl_5$–Ph_3Bi	0	0		
4	$MoCl_5$–Ph_3SiH	92	80	110	60
5	$MoCl_5$–Et_3SiH	94	91	180	72
6	$MoCl_5$–Ph_4Sn	77	73	120	45
7	$MoCl_5$–*n*-Bu_4Sn	36	17	56	29
8	$Mo(CO)_6$–$h\nu$[c]	100	87	62	25
9	WCl_6	100	87	170	64
10	WCl_6–Ph_3Sb	100	98	210	82
11	WCl_6–Ph_3Bi	44	21	27	13
12	WCl_6–Ph_3SiH	94	86	140	39
13	WCl_6–Et_3SiH	100	91	160	54
14	WCl_6–Ph_4Sn	96	92	170	67
15	WCl_6–*n*-Bu_4Sn	97	88	170	56
16	$W(CO)_6$–$h\nu$[c]	97	84	50	24
17	$NbCl_5$	100	55	27	13
18	$NbCl_5$–Ph_3Sb	100	21	18	7
19	$NbCl_5$–Ph_3SiH	100	53	24	14
20	$NbCl_5$–Ph_4Sn	100	62	19	9
21	$TaCl_5$	73	4		
22	$TaCl_5$–Ph_3Sb	80	8		

[a] Polymerized in toluene at 0 °C (Mo, W) or 30 °C (Nb, Ta) for 24 h; $[M]_0$ = 0.50 M, [Cat] = [Cocat] = 10 mM. [b] Determined by GPC. [c] Polymerized in CCl_4 at 30 °C.

Polymerization of 3-(Dimethylphenylsilyl)-1-hexyne (3). The polymerization of 3 was examined with various catalysts (Table III). In the case of this monomer, W catalysts usually achieved higher yields and higher $\bar{M}_w$'s than did the corresponding Mo catalysts. Eventually, WCl_6–Ph_3Sb provided virtually quantitatively poly[3-(dimethylphenylsilyl)-1-hexyne] [poly(3)] having the highest $\bar{M}_w$ (21×10^4) and $\bar{M}_n$ (8×10^4). It proves that the effect of cocatalyst is different depending on the kinds of catalyst (WCl_6 and $MoCl_5$); e.g., Ph_3Sb is very effective when combined with WCl_6, while it is not as effective with $MoCl_5$. As in the case of monomer 2, Nb catalysts were useful to some extent in effecting polymerization, whereas Ta catalysts hardly produced poly(3).

Table IV
Solvent Effects on the Polymerization of 3-(Dimethylphenylsilyl)-1-hexyne by WCl_6-Ph_3Sb[a]

solvent	monomer convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
toluene	100	98	210	82
anisole	100	56	19	9.9
PhCl	100	59	12	6.2
CCl_4	100	60	25	11
$(CH_2Cl)_2$	81	30	6.6	4.5

[a] Polymerized at 0 °C for 24 h; $[M]_0$ = 0.50 M, $[WCl_6]$ = $[Ph_3Sb]$ = 10 mM. [b] Determined by GPC.

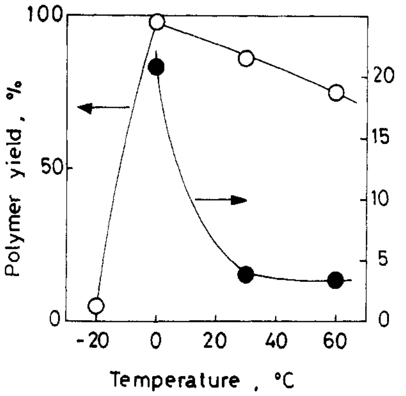


Figure 3. Effects of temperature on the polymerization of 3-(dimethylphenylsilyl)-1-hexyne by WCl_6–Ph_3Sb (in toluene, 24 h, $[M]_0$ = 0.50 M, $[WCl_6]$ = $[Ph_3Sb]$ = 10 mM).

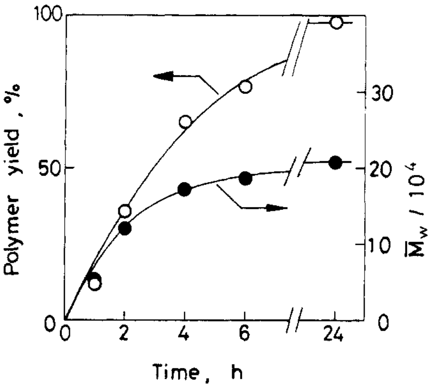


Figure 4. Time course of the polymerization of 3-(dimethylphenylsilyl)-1-hexyne by WCl_6–Ph_3Sb (in toluene, 0 °C, $[M]_0$ = 0.50 M, $[WCl_6]$ = $[Ph_3Sb]$ = 10 mM).

Though the polymerization of monomer 3 by WCl_6–Ph_3Sb proceeded in solvents other than toluene, the polymer yield considerably decreased, and the $\bar{M}_w$ reduced to about 1/10 the value with toluene (Table IV). As shown in Figure 3, the polymerization by WCl_6–Ph_3Sb in toluene exhibited the highest values for both yield and $\bar{M}_w$ of polymer at 0 °C; the $\bar{M}_w$ decreased sharply with increasing temperature. Thus, the selection of an appropriate temperature is very important in this polymerization. The polymerization of monomer 3 by WCl_6–Ph_3Sb was not completed within a few hours (Figure 4), being slower than the polymerization of monomer 2 by $MoCl_5$–Ph_3Sb. The $\bar{M}_w$ of polymer increased with polym-

Table V
Polymerization of 3-(Trimethylsilyl)-1-hexyne[a]

no.	catalyst	polymer yield, %
1	$MoCl_5$	92
2	$MoCl_5$–Ph_3Sb	96
3	WCl_6	83
4	WCl_6–Ph_3Sb	84

[a] Polymerized in toluene at 0 °C for 24 h; $[M]_0 = 0.50$ M, [Cat] = [Cocat] = 10 mM; the monomer conversions were all 100%.

erization time to reach ca. 2×10^5 after 24 h. The increase of $\bar{M}_w$ with increasing polymer yield suggests the presence of long-lived propagating species.

Comparison of Polymerization of Various 3-Silyl-1-alkynes. When monomers **2** and **3** are compared with each other concerning their polymerization behavior, the following can be pointed out on the basis of the above-stated results: (i) **2** is more reactive than **3** according to the dependences on temperature and time; (ii) the highest $\bar{M}_w$'s differ (poly(**2**) 41×10^4; poly(**3**) 21×10^4); (iii) the kinds of catalysts which attain the highest $\bar{M}_w$'s differ ($MoCl_5$–Ph_3Sb for **2**; WCl_6–Ph_3Sb for **3**).

In a previous paper,[7] polymers partly insoluble in toluene were obtained in the polymerization of monomer **1b** by $MoCl_5$ and WCl_6 in toluene at 30 °C. For the sake of comparison, a few polymerizations of this monomer were carried out under the same conditions as in Tables I and III. As seen in Table V, methanol-insoluble poly[3-(trimethylsilyl)-1-hexyne] [poly(**1b**)] was obtained in high yields. The yields of poly(**1b**) were somewhat higher with Mo catalysts than with the W counterparts. The effect of Ph_3Sb as cocatalyst on the polymer yield was negligible. All of the poly(**1b**) in Table V was only partly soluble in common solvents such as toluene and $CHCl_3$.

In the polymerization of monomer **1c**,[7] Mo catalysts produce poly[3-(trimethylsilyl)-1-octyne] [poly(**1c**)] with higher molecular weight in better yields than W catalysts do; especially, $MoCl_5$–Et_3SiH affords poly(**1c**) in ca. 90% yield with $\bar{M}_w$ of 45×10^4. These results resemble those for monomer **2**. The fact that monomer **3** behaves somewhat differently seems due to the steric effect of the phenyl group.

It was confirmed in the present study that 3-silyl-1-alkynes produce polymers with higher molecular weight than do silylacetylenes. It is presumed that the silyl group directly bonded to the acetylenic carbon is more or less reactive to participate in the chain transfer in the polymerization of silylacetylenes.

Polymer Structure. Unless otherwise specified, the structure and properties of polymers were investigated with use of sample 2 of Table I for poly(**2**), sample 10 of Table III for [poly(**3**)], and sample 2 of Table V for poly(**1b**).

The elemental analysis data of the present polymers agreed well with the theoretical values for the polymerization products: Anal. Poly(**2**) Calcd for $(C_{14}H_{28}Si)_n$: C, 74.91; H, 12.57. Found: C, 74.78; H, 12.79. Poly(**3**) Calcd for $(C_{14}H_{20}Si)_n$: C, 77.71; H, 9.32. Found: C, 76.69; H, 9.28.

Figure 5 gives IR spectra of polymers. The absorption band at 1580 cm^{-1} in every polymer is assignable to C=C stretching. Though the absorption is not strong, it appears clearly unlike the case of the polymers from symmetrically disubstituted acetylenes. In these polymers are seen no signals characteristic of the C≡C (~2150 cm^{-1}) and ≡C—H (~3300 cm^{-1}) bonds which appear in their monomers. Absorptions indicating the presence of Si atom are seen at 1250 cm^{-1} (SiC–H deformation) and in the range 800–700 cm^{-1} (Si–C stretching).

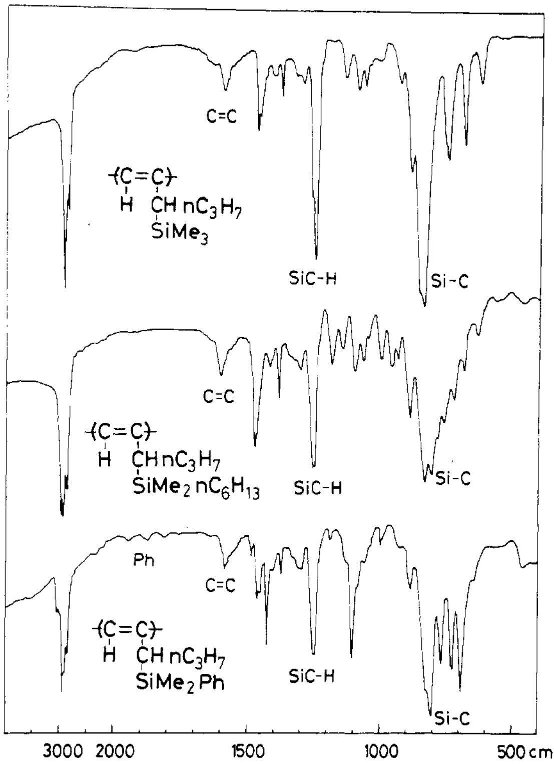


Figure 5. IR spectra of poly(3-silyl-1-hexynes) (KBr pellet; samples from Table I, no. 2, Table III, no. 10, and Table V, no. 2).

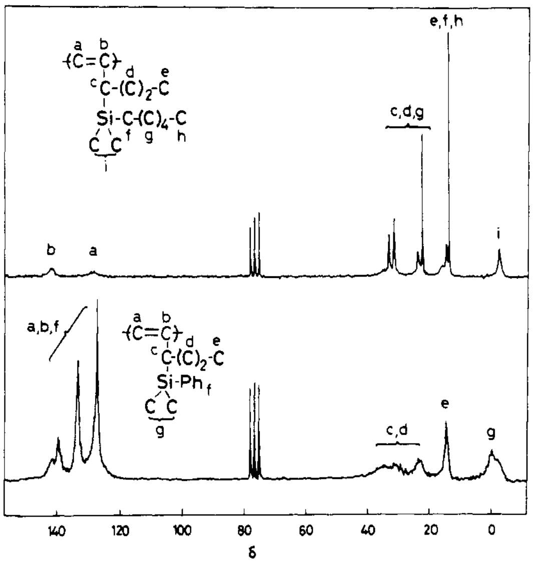


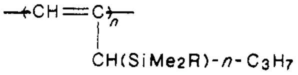
Figure 6. ^{13}C NMR spectra of poly(3-silyl-1-hexynes). ($CDCl_3$ solution; samples from Table I, no. 2, and Table III, no. 10).

The ^{13}C NMR spectrum of poly(**2**) shows two peaks at δ 143 and 128 due to olefinic carbons (Figure 6). In the spectrum of poly(**3**), the peaks of olefinic carbons overlap with those of phenyl carbons. In both polymers, the signals of alkyl carbons appear in the range δ 40–0, among which the methyl carbons bonded to Si are just at δ 0. Acetylenic carbons which should appear between δ 90 and 65 are not seen in these polymers.

The data of UV–visible spectra of the polymers measured in cyclohexane are as follows: poly(**2**) UV$_{max}$ 351 nm (ε 3900) (absorption $\lesssim$486 nm); poly(**3**) UV$_{max}$ 350 nm (ε 2800) (absorption $\lesssim$480 nm). Corresponding to the UV–visible spectra, both polymers were yellow solids.

It will be reasonable to conclude from the above data that the present polymers possess the alternating double bond structure, [—CH=C(CHSiMe$_2$R-n-C$_3$H$_7$)—]$_n$, which assumes appreciably twisted conformations. These data

Table VI
Solubility Properties of Poly(3-silyl-1-hexynes)[a]

 $-\!\!(CH{=}C)_n\!\!-$ with $CH(SiMe_2R)\text{-}n\text{-}C_3H_7$	R: n-C_6H_{13}	R: Ph
hexane	sol[b]	insol[b]
cyclohexane	sol	sol
toluene	sol	sol
CCl_4	sol	sol
$CHCl_3$	sol	sol
$(CH_2Cl)_2$	insol	sol
1,4-dioxane	insol	sol
diethyl ether	sol	sol
THF[c]	sol	sol
anisole	ptly sol[b]	sol
ethyl acetate	insol	sol
methyl benzoate	insol	sol

[a] Samples from Table I, no. 2, and Table III no. 10. [b] Sol, soluble; ptly sol, partly soluble; insol, insoluble. [c] THF, tetrahydrofuran.

and conclusions are analogous with those for poly(**1c**) reported in a previous paper.[7]

Polymer Properties. Whereas poly(**1b**) is partly insoluble in toluene and chloroform,[7] the present polymers completely dissolve in these solvents. The flexible and/or bulky groups of *n*-hexyl and phenyl are able to interact with the solvent effectively, which should have made these polymers soluble, unlike poly(**1b**). At the same time, the idea that the insolubility of poly(**1b**) stems from cross-linking can be denied. As shown in Table VI, there is a considerable difference in the kind of solvents used for poly(**2**) and poly(**3**). For instance, poly(**2**) dissolves in hexane, an alkane, but does not dissolve in ethyl acetate, a fairly polar solvent, whereas the opposite is the case with poly(**3**).

When the mechanical properties of poly(**2**) and poly(**3**) are compared (Table VII), the former polymer has a lower Young's modulus, a smaller tensile strength, and a larger elongation at break. This is explainable in terms of the difference in the nature of substituents *n*-hexyl and phenyl. It turns out that poly(**1c**) is close to poly(**3**) in mechanical properties, rather than to poly(**2**). Roughly talking, all these polymers are somewhat soft and ductile among various substituted polyacetylenes owing to the presence of relatively long alkyl groups.[10]

Most of the substituted polyacetylenes possess high glass transition temperatures (*Tg*) around 200 °C.[10] Among substituted polyacetylenes, poly(**2**) has a relatively low T_g (Table VII), which is attributable to the presence of a flexible *n*-hexyl group. In contrast, poly(**3**), which does not have such a long alkyl group, exhibits a high T_g. By a similar reason, the softening points of these polymers are pretty different from each other. The T_g and softening point of poly(**1c**) are again closer to those of poly(**3**) than to those of poly(**2**).

The weight loss of the present two polymers in the thermogravimetric analysis (TGA) in air starts in the vicinity of 200 °C (Table VII). This means that the thermal stability of these polymers is medium and not very high among various substituted polyacetylenes.[11] The presence of an allylic proton in these polymers seems responsible for this. When these polymers are heat-treated in air at 120 °C for 20 h, they suffer moderate decreases of molecular weight (Table VII) among substituted polyacetylenes.[11] This also leads to a conclusion similar to that for TGA. The $\bar{M}_w/\bar{M}_n$ ratio after the heat treatment is relatively close to two, which indicates that virtually only polymer degradation takes place, and cross-linking is negligible.

The electrical conductivities of poly(**2**) and poly(**3**) measured in the dark at 25 °C with dc current are 9×10^{-18} and 7×10^{-18} S·cm^{-1}, respectively. These values are indicative of typical insulators. The unpaired electrons in the present polymers were undetectable by the electron spin resonance measured at 25 °C in bulk. Therefore, their unpaired electron levels should be lower than 1×10^{15} spin·g^{-1}. These electrical and magnetic data mean that the double bonds in the present polymers are conjugated only in a limited extent. The insulating and nonparamagnetic properties are common in many of the polyacetylenes with bulky substituents.[3a]

Both the oxygen permeability coefficients (P_{O_2}) and the separation factor of oxygen to nitrogen (P_{O_2}/P_{N_2}) of poly(**2**) and poly(**3**) at 25 °C are intermediate in magnitude among those of various substituted polyacetylenes,[3a] as seen from the following data: poly(**2**), P_{O_2} = 19 barrer, P_{O_2}/P_{N_2} = 3.0; poly(**3**), P_{O_2} = 41 barrer, P_{O_2}/P_{N_2} = 2.9. These P_{O_2} values are not as large as that of poly[1-(trimethylsilyl)-1-propyne]. This agrees with the general trend that the presence of a long *n*-alkyl group or phenyl group reduces the oxygen permeability of substituted polyacetylenes.[4b]

Experimental Section

Monomer Synthesis. Monomers **2** and **3** were prepared with reference to the literature methods for synthesizing 3-(trimethylsilyl)-1-alkynes[7,12] according to the following scheme:

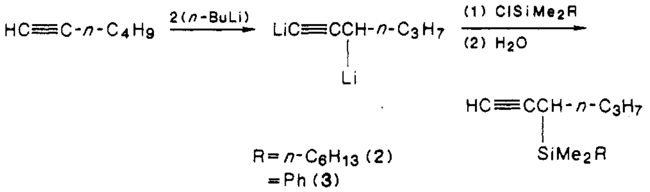
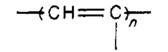
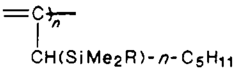


Table VII
Mechanical and Thermal Properties of Soluble, Film-Forming Poly(3-silyl-1-alkynes)[a]

	 $-\!\!(CH{=}C)_n\!\!-$ with $CH(SiMe_2R)\text{-}n\text{-}C_3H_7$; R = n-C_6H_{13} [poly(**2**)]	R = Ph [poly(**3**)]	 $-\!\!(CH{=}C)_n\!\!-$ with $CH(SiMe_2R)\text{-}n\text{-}C_5H_{11}$ [poly(**1c**)]
E,[b] MPa	210	660	630
σ_B,[c] MPa	6	22	27
γ_B,[d] %	65	40	11
T_g,[e] °C	~60	~200	~170
softening pt,[f] °C	185	310	290
wt loss,[g] °C			
start/10%/50%	200/240/300	180/280/330	190/240/320
heat treatment[h]			
$\bar{M}_w/10^3$	410 → 85	210 → 80	400 → 90
$\bar{M}_n/10^3$	200 → 36	82 → 33	170 → 40

[a] Samples from Table I, no. 2, and Table III, no. 10. [b] Young's modulus.[10b] [c] Tensile strength.[10b] [d] Elongation at break.[10b] [e] Glass transition temperature measured by dynamic viscoelasticity.[10b] [f] Heating rate 10 °C/min. [g] Measured by thermogravimetric analysis (in air; heating rate 10 °C/min). [h] Heat-treated in air at 120 °C for 20 h.

Dimethyl-*n*-hexylsilyl chloride, a starting compound, was prepared according to ref 4b. Monomer **2** was prepared as follows: Under nitrogen, a flask was charged with a hexane solution (263 mL) of *n*-BuLi (0.42 mol). With ice cooling, a mixture of 1-hexyne (23.0 mL, 0.20 mol) and hexane (40 mL) was added dropwise; after the completion of addition, the mixture was stirred at room temperature for 2 h. A mixture of dimethyl-*n*-hexylsilyl chloride (42.3 mL, 0.20 mol) and hexane (80 mL) was added dropwise, while the flask was kept at −30 °C; then the reaction was completed by stirring the mixture at 60 °C for 2 h. Water was added dropwise at 0 °C to decompose residual organo-Li compounds. The reaction mixture was washed with aqueous NH_4Cl solution and water. The hexane solution was dried over anhydrous sodium sulfate. Hexane was evaporated, and the crude product was distilled twice at reduced pressure from calcium hydride. Yield 55%; bp 75 °C (3 mmHg); purity 96% [gas chromatography (GC); the main impurity was the corresponding 1-silyl-1-hexyne (byproduct)]. IR (neat) 3300 (s, $\nu_{\equiv C-H}$). 2950 (s), 2850 (m), 2080 (m, $\nu_{C\equiv C}$), 1470 (m), 1250 (s, δ_{SiC-H}), 830 (s, ν_{Si-C}), 625 (m), 590 (m) cm^{-1}. ^{13}C NMR ($CDCl_3$) δ 86.6 (C_2), 68.4 (C_1), 33.3, 31.6, 23.7, 22.6, 18.5, 13.7, −4.9 (2Me–Si).

Since dimethylphenylsilyl chloride was less reactive than dimethyl-*n*-hexylsilyl chloride, the synthesis of monomer **3** was carried out in a mixture of hexane and diethyl ether instead of hexane alone: Under nitrogen, a hexane solution (263 mL) of *n*-BuLi (0.42 mol) was placed in a flask, and a part of the hexane (ca. 100 mL) was removed by evaporation with an aspirator. The concentrated solution of *n*-BuLi was diluted slowly with diethyl ether (200 mL) at −50 °C. 1-Hexyne (23.0 mL, 0.20 mol) was added dropwise while keeping the flask at −30 °C; after the addition, the mixture was gradually heated and refluxed at ca. 35 °C for 2 h. At −10 °C, dimethylphenylsilyl chloride (Shin-Etsu Silicone, Japan; 33.1 mL, 0.20 mol) was added dropwise; then the mixture was stirred at ambient temperature for 2 h. Water was added at 0 °C, and the reaction was worked up similarly to the case of monomer **2**. Yield 45%; bp 95 °C (5 mmHg); purity 95% (GC). IR (neat) 3300 (s; $\nu_{\equiv C-H}$), 3050 (m), 2950 (s), 2860 (m), 2100 (m; $\nu_{C\equiv C}$), 1430 (m), 1250 (s, δ_{SiC-H}), 1105 (s), 820 (s; ν_{Si-C}), 790 (m), 725 (m), 700 (m), 630 (m) cm^{-1}. ^{13}C NMR ($CDCl_3$) δ 136.8 (C_{sp^2}–Si) 133.9 ($2C_o$), 129.2 (C_p), 127.7 ($2C_m$), 86.2 (C_2), 69.0 (C_1), 31.2 (C_4), 22.4 (C_5), 19.0 (C_3), 13.5 (C_6), −4.4 (Me–Si), −5.2 (Me′–Si).

Catalysts and Solvents. Mo, W, and organometallic compounds were commercially obtained, stored in sealed small ampules to protect from moisture and air, and used without further purification. Toluene as polymerization solvent was washed by a standard method and distilled twice from calcium hydride. Other solvents were purified in similar manners.

Polymerization. Polymerizations were carried out in a dry nitrogen atmosphere. The procedure for the polymerization of sample 2 of Table I is exemplary: A monomer solution (6.3 mL) composed of monomer **2** (1.49 mL, 1.18 g, 5.25 mmol), bromobenzene (0.81 mL; internal standard of GC), and toluene (4.0 mL) was prepared in an Erlenmeyer flask. In another flask were placed $MoCl_5$ (27.3 mg, 0.10 mmol), Ph_3Sb (35.3 mg, 0.10 mmol), and toluene (4.0 mL), and the mixture was left to stand at 30 °C for 15 min to mature the catalyst. At 30 °C the monomer solution (6.0 mL) was added to the catalyst solution. After 24 h the polymerization reaction was terminated by adding a mixture (4 mL) of toluene and methanol (volume ratio 4:1). The monomer consumption was determined by GC (silicone DC 3 m, 160 °C). The reaction mixture was diluted with toluene and poured into a large amount of methanol to isolate the formed polymer. The polymer was filtered off and dried.

Polymer Analyses. Molecular weight distributions of polymers were observed with a Jasco Trirotar liquid chromatograph equipped with three series of polystyrene gel columns, Shodex A802, A804, and A806; eluent $CHCl_3$. The $\bar{M}_w$ and $\bar{M}_n$ values were calculated on the basis of a polystyrene calibration. Other analyses were carried out in the same manner as described previously.[7]

Acknowledgment. The authors are grateful to Dr. T. Kawamura for the measurement of ESR spectra. Thanks are also due to Mr. H. Tajima for his experimental assistance. The partial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. C61550676) is gratefully acknowledged.

Registry No. **2**, 117439-31-3; **2** (homopolymer), 117439-33-5; **3**, 117439-32-4; **3** (homopolymer), 117439-34-6; O_2, 7782-44-7; N_2, 7727-37-9; $HC{\equiv}C(CH_2)_3CH_3$, 693-02-7; BuLi, 109-72-8; $MoCl_5$, 10241-05-1; Ph_3Sb, 603-36-1; Ph_3Bi, 603-33-8; Ph_3SiH, 789-25-3; Et_3SiH, 617-86-7; Ph_4Sn, 595-90-4; Bu_4Sn, 1461-25-2; $Mo(CO)_6$, 13939-06-5; WCl_6, 13283-01-7; $NbCl_5$, 10026-12-7; $TaCl_5$, 7721-01-9; dimethylhexylsilyl chloride, 3634-59-1; dimethylphenylsilyl chloride, 768-33-2.

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