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of negative charge by cyano over ester and in terms of the stabilities of the various leaving groups.

Experimental Section

Methods. NMR spectra are recorded with an EM-360 Varian 60-MHz nuclear magnetic resonance spectrometer. The infrared data are obtained from a Perkin-Elmer Model 983 spectrometer. Melting points are measured with a Thomas-Hoover capillary melting point apparatus without any correction. Chemical analyses are performed by MicAnal, Tucson, AZ.

Size exclusion chromatography was carried out with three columns: Du Pont Zorbax PSM 300S and IBM GPC/SEC pore type A column, calibrated with polystyrene standards, chloroform as eluent, and a Spectra Physics detector at 254 nm.

Materials. Dichloromethane was purified by consecutive washing with sulfuric acid, water, aqueous sodium hydroxide, and water and then dried over calcium chloride and distilled from calcium hydride and sodium. Silver *p*-toluenesulfonate and silver trifluoroacetate (Aldrich Chemical Co.) were used without further purification.

All monomers were purified by literature methods.

Representative Synthesis of Initiator. 2,2-Dicyanovinyl chloride (1.12 g, 10 mmol) was added to a solution of silver *p*-toluenesulfonate (2 g, 8 mmol) in 20 mL of dry acetonitrile. The mixture was stirred at 40 °C in the dark for 2 h and cooled. The silver chloride was filtered off, the solvent was evaporated, the residue was dissolved in hot carbon tetrachloride, and the remaining silver chloride was filtered off. On cooling, crude needle-type crystals were obtained. The product was purified by two recrystallizations from carbon tetrachloride.

Polymerization. Polymerizations were performed on a 1-g scale under dry nitrogen in septum-capped polymerization tubes at the required temperature.

The polymers were precipitated from methanol or petroleum ether and dried in vacuo at 50 °C. Yields were determined gravimetrically.

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Registry No. **1**, 97056-16-1; **2**, 97056-16-1; **3**, 108347-13-3; **4**, 108347-14-4; $ClCH{=}C(CN)_2$, 10472-09-0; $4\text{-}MeC_6H_4SO_3Ag$, 16836-95-6; $ClCH{=}CCN(CO_2Me)$, 57337-96-9; F_3CCO_2Ag, 2966-50-9; *N*-vinylcarbazole (homopolymer), 25067-59-8; *p*-methoxystyrene (homopolymer), 24936-44-5; 1,3-dioxolane (homopolymer), 25067-64-5; cyclohexene oxide (homopolymer), 25702-20-9; cyclohexene oxide (SRU), 32146-09-1; poly(oxymethylene), 9002-81-7.

References and Notes

(1) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.

(2) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.

(3) Abdelkader, M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 944.

(4) Abdelkader, M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 949.

(5) Hall, H. K.; Jr.; Rasoul, H. A. A. In *Contemporary Topics in Polymer Science*; Bailey, W. J., Tsuruta, T., Eds.; Plenum: New York, 1984; Vol. 4, p 295.

(6) Padias, A. B.; Hall, H. K., Jr. *Polym. Bull.* **1985**, *13*, 329.

(7) (a) Masuda, T.; Sawamoto, M.; Higashimura, T. *Makromol. Chem.* **1976**, *177*, 2981. (b) Sawamoto, M.; Masuda, T.; Higashimura, T. *Makromol. Chem.* **1976**, *177*, 2995. (c) Sawamoto, M.; Higashimura, T. *Macromolecules* **1978**, *11*, 501. (d) Sawamoto, M.; Higashimura, T. *Macromolecules* **1978**, *11*, 328. (e) Sawamoto, M.; Higashimura, T. *Polym. Bull.* **1978**, *1*, 11. (f) Kunitake, T.; Takarabe, K. *Polym. J.* **1978**, *10*, 105.

(8) (a) Throssel, J. J.; Sood, S. P.; Szwarc, M.; Stannett, V. *J. Am. Chem. Soc.* **1956**, *78*, 1122. (b) Obrecht, W.; Plesch, P. H. *Makromol. Chem.* **1981**, *182*, 1459.

(9) Rappoport, Z.; Topol, A. *J. Chem. Soc., Perkin Trans.* **1972**, *2*, 1823.

(10) Gassman, P. *Acc. Chem. Res.* **1970**, *3*, 26.

Synthesis and Properties of Poly[3-(trimethylsilyl)-1-alkynes][1]

Toshio Masuda,* Hiroshi Tajima, Toshio Yoshimura, and Toshinobu Higashimura*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

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ABSTRACT: 3-(Trimethylsilyl)-1-alkynes [$HC{\equiv}CCH(SiMe_3)R$; R = CH_3, $n\text{-}C_3H_7$, $n\text{-}C_5H_{11}$, and $n\text{-}C_7H_{15}$] were polymerized in high yields with Mo, W, and Nb catalysts to give new high molecular weight polymers. The polymers whose R was CH_3 or $n\text{-}C_3H_7$ were partly or totally insoluble in any organic solvents, whereas those whose R was $n\text{-}C_5H_{11}$ or $n\text{-}C_7H_{15}$ were totally soluble in solvents such as toluene and $CHCl_3$. Maximum weight-average molecular weights of poly[3-(trimethylsilyl)-1-octyne] were 4.5×10^5 with Mo catalysts, 1.6×10^5 with W catalysts, and 1.0×10^5 with Nb catalysts. All the product polymers possessed the structure $-[CH{=}CCH(SiMe_3)R]_n-$ according to spectroscopic analyses and were yellow solids. Poly[3-(trimethylsilyl)-1-octyne] and poly[1-(trimethylsilyl)-1-decyne] were soluble in many low-polarity solvents, film-forming, thermally relatively stable in air, and amorphous. Their electrical conductivities were $\sim 10^{-18}$ S·cm^{-1} and unpaired-electron densities were $<1 \times 10^{15}$ spin·g^{-1}.

Introduction

Si-containing polyacetylenes, which possess alternating double bonds along the main chain and Si-containing groups in the side chain, are expected to show properties not seen in conventional polymers because of their unique structure. In fact, poly[1-(trimethylsilyl)-1-propyne], one example of such polymers, is known to be extremely permeable to oxygen.[3]

So far, polymerization of (trimethylsilyl)acetylene[4] and its derivatives[2] ($HC{\equiv}CSiMe_2R$; R = Me, $n\text{-}C_6H_{13}$, CH_2CH_2Ph, CH_2Ph, Ph, and *t*-Bu) as Si-containing monosubstituted acetylenes has been studied. These monomers polymerize in the presence of W catalysts. Though the polymers with flexible R groups (R = $n\text{-}C_6H_{13}$, CH_2CH_2Ph, and CH_2Ph) are soluble, their molecular weights are no more than $\sim 1 \times 10^4$. In contrast, 1-(trimethylsilyl)-1-propyne[5] and its derivatives[6] ($MeC{\equiv}CSiMe_2R$; R = Me, $n\text{-}C_6H_{13}$, Ph, $SiMe_2CH_2SiMe_3$, and $SiMe_2CH_2CH_2SiMe_3$), which are disubstituted acetylenes, produce with Ta catalysts polymers whose molecular weights reach $\sim 1 \times 10^6$.

Such a large difference in the polymerization behavior of mono- and disubstituted Si-containing acetylenes is quite interesting. We sought the reason for this and searched for Si-containing monosubstituted acetylenes that afford soluble, high molecular weight polymers. Eventu-

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Table I
Synthesis and Properties of 3-(Trimethylsilyl)-1-alkyne Monomers

$HC\equiv CC(SiMe_3)HR$ R	yield, %	purity,[a] %	bp, °C (mmHg)	d_4^{20}, g/mL
CH_3	60	90	105 (760)	0.738
n-C_3H_7	70	95	60 (50)[b]	0.768
n-C_5H_{11}	74	96	95 (35)[c]	0.832
n-C_7H_{15}	65	94	105 (15)	0.830

[a] The main impurity was the corresponding 1-(trimethylsilyl)-1-alkyne. [b] Literature[8a] bp 43 °C (15 mmHg). [c] Literature[9] bp 60–61 °C (4 mmHg).

ally, 3-(trimethylsilyl)-1-alkynes, in which the Si atom is bonded to the carbon adjacent to the C≡C bond, proved to be such a monomer.

The present paper reports on the polymerization of 3-(trimethylsilyl)-1-alkynes [$HC\equiv CCH(SiMe_3)R$; R = CH_3, n-C_3H_7, n-C_5H_{11}, and n-C_7H_{15}], especially 3-(trimethylsilyl)-1-octyne, and on properties of the product polymers. It reveals that 3-(trimethylsilyl)-1-octyne and -1-decyne polymerize with Mo and W catalysts to give new, soluble, high molecular weight (1×10^5–4×10^5) polymers.

Experimental Section

Monomers. 1-Alkynes can be 1,3-dilithiated with 2 equiv of n-butyllithium.[7] From the 1,3-dilithiated 1-alkynes, 3-(trimethylsilyl)-1-alkynes had previously been prepared by 3-silylation in ether at low temperature[8] or via 1,3-bis(trimethylsilyl)-1-alkynes.[9] With reference to these methods, we developed an easier method for synthesizing the monomers

$$HC\equiv CCH_2R \xrightarrow[\text{in hexane}]{2n\text{-BuLi}} LiC\equiv CCLiHR \xrightarrow[2.\ H_2O]{1.\ ClSiMe_3} HC\equiv CC(SiMe_3)HR$$

$$R = CH_3,\ n\text{-}C_3H_7,\ n\text{-}C_5H_{11},\ n\text{-}C_7H_{15}$$

As an example, the process for synthesizing 3-(trimethylsilyl)-1-octyne is described: Under nitrogen, a hexane solution of n-butyllithium (0.80 mol, 1.6 M solution, 0.50 L) was added dropwise to a cooled (−10 °C), magnetically stirred mixture of 1-octyne (0.40 mol, 44 g, 59 mL) and hexane (50 mL). The mixture was allowed to warm to 30 °C and stirred for 3 h (the initially formed precipitate completely dissolved). Chlorotrimethylsilane (0.40 mol, 43 g, 51 mL) was added dropwise while keeping the temperature at 0 °C. After the reaction mixture was stirred at room temperature for 24 h, water (50 mL) was added dropwise at 0 °C to decompose the 1-alkynyllithium. The organic phase was washed with dilute hydrochloric acid (3%) and then with water and dried over anhydrous sodium sulfate. After evaporation of hexane at atmospheric pressure, the product was distilled under reduced pressure from calcium hydride.

Other 3-(trimethylsilyl)-1-alkynes were also prepared in a similar way. The yields and properties of 3-(trimethylsilyl)-1-alkynes are given in Table I. While 3-(trimethylsilyl)-1-hexyne and -1-octyne are known compounds, others are new. According to ^{13}C NMR and gas chromatography (GC), the main impurity in the product was the corresponding 1-(trimethylsilyl)-1-alkyne, which is known to be inactive in the polymerization.[6b]

Polymerization. Polymerization procedures were carried out under dry nitrogen. Catalysts composed of equimolar metal chloride (MCl_n) and organometallic cocatalyst (e.g., $MoCl_5$–Et_3SiH) were allowed to stand (aged) in toluene solution at 30 °C for 15 min before use. Catalysts based on metal carbonyls [$M(CO)_6$s] were irradiated with UV light (200-W) high-pressure Hg lamp, distance 5 cm) in CCl_4 solution at 30 °C for 1 h before use. Unless otherwise stated, polymerizations were carried out in toluene (MCl_n-based catalysts) or in CCl_4 [$M(CO)_6$-based catalysts] at $[M]_0$ = 0.50 M and [cat.] = 10 mM.

A typical example of polymerization is described (cf. Table III, no. 2): A 30-mL baked flask was charged with toluene (4.3 mL), 3-(trimethylsilyl)-1-octyne (6.0 mmol, 1.1 g, 1.3 mL), and bromobenzene (internal standard of GC, 0.4 mL) via syringe, and 1.0 mL of the solution was taken off to use for GC measurement. $MoCl_5$ (0.20 mmol, 55 mg) was dissolved in toluene (10 mL), triethylsilane (0.20 mmol, 23 mg) was added, and the solution was allowed to stand (aged) at 30 °C for 15 min. Then 5 mL of this catalyst solution was added to the above monomer solution at 30 °C, and polymerization was continued for 24 h. The reaction was then terminated by adding a mixture of toluene and methanol (5 mL, 4:1 volume ratio). Monomer conversion was determined by GC (silicone DC 3 m, 140 °C) to be 100%. The reaction mixture was diluted with toluene (100 mL), and the polymer was precipitated into methanol (2 L), filtered off, and dried (the methanol-insoluble fraction of reaction product is referred to as "polymer" in this paper). The polymer yield was determined by gravimetry to be 90%.

Table II
Polymerization of 3-(Trimethylsilyl)-1-alkynes by $MoCl_5$ and WCl_6[a]

no.	$HC\equiv CC(SiMe_3)HR$ R	catalyst	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
1	CH_3	$MoCl_5$	80[c]		
2	CH_3	WCl_6	70[c]		
3	n-C_3H_7	$MoCl_5$	82[c]		
4	n-C_3H_7	WCl_6	74[c]		
5	n-C_5H_{11}	$MoCl_5$	77	180[d]	41
6	n-C_5H_{11}	WCl_6	72	42	15
7	n-C_7H_{15}	$MoCl_5$	82	170	56
8	n-C_7H_{15}	WCl_6	80	55	19

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 0.50 M, [cat.] = 10 mM; the monomer conversions were all 100%. [b] Determin by GPC. [c] Partly insoluble in toluene. [d] $[\eta]$ = 1.23 $dL\cdot g^{-1}$.

Polymer Characterization. Weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$, respectively) of polymers were measured by gel permeation chromatography (GPC) on a Jasco Trirotar liquid chromatograph [eluent, $CHCl_3$; columns, Shodex A804, A806, and A807 (Showa Denko, Co., Jpn); polystyrene calibration]. Intrinsic viscosities ($[\eta]$s) were determined in toluene solution at 30 °C.

IR spectra (KBr pellet) and UV-visible spectra (CCl_4 solution) of the polymer were recorded with Shimadzu IR435 and UV190 spectrophotometers, respectively. ^1H and ^{13}C NMR spectra of the polymers were observed on a JEOL FX90Q spectrometer (90 MHz for ^1H, $CDCl_3$ solution). Thermogravimetric analysis (TGA) was carried out with a Shimadzu 20B thermal analyzer (in air, heating rate 10 °C/min). Other analyses were performed as described before.[5,6]

Results and Discussion

Polymerization of 3-(Trimethylsilyl)-1-alkynes. Table II shows results on the polymerization of 3-(trimethylsilyl)-1-alkynes by $MoCl_5$ or WCl_6 alone. Every monomer produced a polymer in high yields of 70–80% under the conditions shown in Table II. The polymer yield with $MoCl_5$ was slightly higher than that with WCl_6 for any monomers. Poly[3-(trimethylsilyl)-1-butyne] and poly[3-(trimethylsilyl)-1-hexyne] were partly or totally insoluble in any of a variety of organic solvents examined. In contrast, poly[3-(trimethylsilyl)-1-octyne] and poly[3-(trimethylsilyl)-1-decyne] completely dissolved in solvents such as toluene and $CHCl_3$. Their $\bar{M}_w$s were in the range 4×10^4–18×10^4, and $MoCl_5$ achieved higher $\bar{M}_w$ than did WCl_6. Polymerization of 3-(trimethylsilyl)-1-octyne and -1-decyne, which proved to give totally soluble polymers, was studied in more detail.

Polymerization of 3-(Trimethylsilyl)-1-octyne. Polymerization of 3-(trimethylsilyl)-1-octyne was tried by using various Mo and W catalysts (Table III). As compared with $MoCl_5$ alone, a catalyst composed of an equimolar mixture of $MoCl_5$ and Et_3SiH increased both yield and molecular weight of polymer; thus the yield reached 90% and $\bar{M}_w$ about 3×10^5. A catalyst obtained by UV irradiation of CCl_4 solution of $Mo(CO)_6$ [$Mo(CO)_6$–CCl_4–$h\nu$] was effective similarly to $MoCl_5$–Et_3SiH. The

Table III
Polymerization of 3-(Trimethylsilyl)-1-octyne by Mo and W Catalysts[a]

		polymer		
no.	catalyst	yield, %	$\bar{M}_w/10^3$[b]	$\bar{M}_n/10^3$[b]
1	$MoCl_5$	77	180	41
2	$MoCl_5$–Et_3SiH	90	320[d]	94
3	$Mo(CO)_6$–CCl_4–$h\nu$[c]	88	300	105
4	WCl_6	72	42	15
5	WCl_6–Et_3SiH	75	100	26
6	$W(CO)_6$–CCl_4–$h\nu$[c]	81	160	53

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 0.50 M, [cat.] = [cocat] = 10 mM; the monomer conversions were all 100%. [b] Determined by GPC. [c] Polymerized in CCl_4 at 30 °C for 24 h after irradiation of the CCl_4 solution of $M(CO)_6$ with UV light at 30 °C for 1 h. [d] $[\eta]$ = 1.85 dL·g^{-1}.

Table IV
Effects of Organometallic Cocatalysts on the Polymerization of 3-(Trimethylsilyl)-1-octyne by $MoCl_5$[a]

	monomer	polymer		
cocat	convn, %	yield, %	$\bar{M}_w/10^3$[b]	$\bar{M}_n/10^3$[b]
none	100	77	98	22
Et_3SiH	100	90	320	94
Ph_3SiH	100	90	320	104
n-Bu_4Sn	100	85	210[b]	70
Ph_4Sn	100	80	130	34
Ph_3Bi	100	80	190	59
n-BuLi	11	0		
Et_3Al	8	0		

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 0.50 M, [cat.] = [cocat] = 10 mM. The catalyst solutions were aged by keeping at 30 °C for 15 min. [b] $[\eta]$ = 1.31 dL·g^{-1}.

Table V
Effects of Solvent and Time on the Polymerization of 3-(Trimethylsilyl)-1-octyne by $MoCl_5$–Et_3SiH[a]

		monomer	polymer		
solvent	time, h	convn, %	yield, %	$\bar{M}_w/10^3$[b]	$\bar{M}_n/10^3$[b]
toluene	24	100	90	320	94
hexane	24	100	79	130[c]	51
cyclohexane	24	100	83	230	71
anisole	24	100	80	90	21
$(CH_2Cl)_2$	24	100	72	45[d]	17
toluene	1/6	91	75	300	90
toluene	1	97	83	330	105

[a] Polymerized at 30 °C; $[M]_0$ = 0.50 M, [cat.] = [cocat] = 10 mM. [b] Determined by GPC. [c] $[\eta]$ = 0.85 dL·g^{-1}. [d] $[\eta]$ = 0.33 dL·g^{-1}.

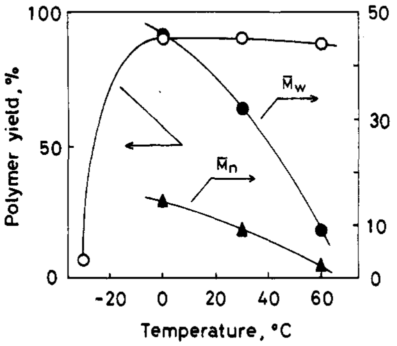

Figure 1. Temperature effect on the polymerization of 3-(trimethylsilyl)-1-octyne by $MoCl_5$–Et_3SiH (in toluene, 24 h, $[M]_0$ = 0.50 M, $[MoCl_5]$ = $[Et_3SiH]$ = 10 mM).

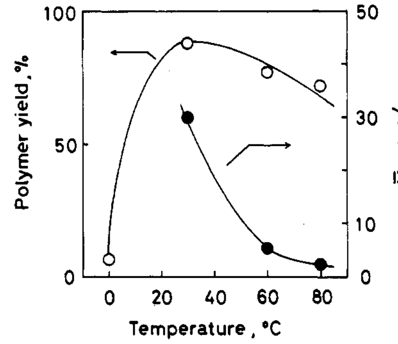

Figure 2. Temperature effect on the polymerization of 3-(trimethylsilyl)-1-octyne by $Mo(CO)_6$–CCl_4–$h\nu$ (in CCl_4, 24 h, $[M]_0$ = 0.50 M, $[Mo(CO)_6]$ = 10 mM).

three corresponding W catalysts in Table III were somewhat less active; that is, the yield and molecular weight of polymer were lower than those with their Mo counterparts. Eventually various Mo and W catalysts, especially Mo catalysts, were found to be effective in the polymerization of 3-(trimethylsilyl)-1-octyne.

Table IV shows effects of organometallic cocatalysts on the polymerization by $MoCl_5$. Organometallics containing group 4 and 5 main-group metals (Si, Sn, Bi, etc.) are thought to reduce and/or alkylate $MoCl_5$ and WCl_6 moderately. When they were employed as cocatalysts, both the yield and the molecular weight of the polymer increased. Especially hydrosilanes (Et_3SiH and Ph_3SiH) increased the polymer yield to 90% and the $\bar{M}_w$ by about 3 times. In contrast, organometallics with a stronger reducing ability like n-BuLi and Et_3Al rather deactivated the catalyst.

This polymerization proceeded not only in toluene but also in aliphatic hydrocarbons (hexane and cyclohexane), anisole, and 1,2-dichloroethane (Table V). In somewhat polar solvents like anisole and 1,2-dichloroethane, the polymer yields remained fairly high (70–80%), but the $\bar{M}_w$s reduced to below 1 × 10^5.

As seen in Table V, the monomer conversion in toluene is almost quantitative within 1 h, and it may not be necessary to continue polymerization for so long a period as 24 h. Neither degradation nor cross-linking for the formed polymer, however, took place during the 24-h polymerization (no significant change in $\bar{M}_w$ or $\bar{M}_n$). Therefore, polymerization time can be chosen fairly arbitrarily.

In general, temperature greatly affects polymerization. In the polymerization by $MoCl_5$–Et_3SiH, polymer yield was negligible at −30 °C, whereas it reached approximately 90% at 0 °C and above (Figure 1). The $\bar{M}_w$ at 0 °C was as high as 4.5 × 10^5 ($[\eta]$ = 2.33 dL·g^{-1}). The $\bar{M}_w$ and $\bar{M}_n$ values decreased with increasing temperature of polymerization.

The $M(CO)_6$-based catalysts generally show lower activity but often achieve higher polymer molecular weight in the polymerization of substituted acetylenes than do the corresponding MCl_n-based catalysts.[10] In the case of 3-(trimethylsilyl)-1-octyne, the $Mo(CO)_6$–CCl_4–$h\nu$ catalyst provided a polymer in fair yields at 30 °C or above (Figure 2). The $\bar{M}_w$ was ca. 3 × 10^5 at 30 °C and decreased drastically with increasing temperature. Thus the maximum $\bar{M}_w$ with $Mo(CO)_6$–CCl_4–$h\nu$ was not higher than that with $MoCl_5$–Et_3SiH.

Interestingly, 3-(trimethylsilyl)-1-octyne polymerized in the presence of $NbCl_5$, a group 5 transition-metal chloride (Table VI). It had been shown before that monosubstituted acetylenes are selectively cyclotrimerized with $NbCl_5$ and $TaCl_5$ and undergo no other reactions.[10] Hence, this is the first example of polymer formation from a monosubstituted acetylene with $NbCl_5$. Use of cocatalysts hardly changed polymer yield, but somewhat decreased both $\bar{M}_w$ and $\bar{M}_n$. When $TaCl_5$ was used as catalyst, almost all of the product was cyclotrimers (1,2,4- and 1,3,5-trisubstituted benzenes), which is close to the general trend

Table VI
Polymerization of 3-(Trimethylsilyl)-1-octyne by Nb and Ta Catalysts[a]

catalyst	monomer convn, %	polymer		
		yield, %	$\bar{M}_w/10^3$ [b]	$\bar{M}_n/10^3$ [b]
$NbCl_5$	100	80	100	39
$NbCl_5$–Et_3SiH	100	88	70[c]	27
$NbCl_5$–Ph_4Sn	100	84	62	25
$NbCl_5$–Ph_3Bi	85	60	55	27
$TaCl_5$	76[d]	3		
$TaCl_5$–Et_3SiH	100[d]	4		

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 0.50$ M, [cat.] = [cocat] = 10 mM. The catalyst solutions were aged in advance by heating at 80 °C for 15 min. [b] Determined by GPC. [c] $[\eta] = 0.33$ dL·g^{-1}. [d] The main product was cyclotrimers.

for monosubstituted acetylenes. The reason why the present acetylene produces a polymer with $NbCl_5$ is not clear at present, but a large steric effect of the monomer seems to be associated.

Polymerization of 3-(Trimethylsilyl)-1-decyne. Polymerization of 3-(trimethylsilyl)-1-decyne, which also gives a soluble polymer, was studied using various group 5 and 6 transition-metal catalysts (Table VII). Though this monomer appeared slightly less reactive than 3-(trimethylsilyl)-1-octyne, the polymer yields after 24 h reached 80–90% with all of Mo and W catalysts. Like the case of 3-(trimethylsilyl)-1-octyne, $NbCl_5$ afforded a polymer, while $TaCl_5$ gave only cyclotrimers. The $\bar{M}_w$s of poly[3-(trimethylsilyl)-1-decyne] obtained with Mo catalysts were higher than those with the corresponding W and Nb catalysts. A maximum $\bar{M}_w$ of 2.4×10^5 was achieved with $MoCl_5$–Ph_3SiH.

Polymer Structure. The structure of the poly[3-(trimethylsilyl)-1-octyne] (sample no. 2, Table III) was studied in detail. The elemental analysis values agreed well with the theoretical values for the polymerization product: Anal. Calcd for $(C_{11}H_{22}Si)_n$: C, 72.44; H, 12.16. Found: C, 71.91; H, 12.26.

In the IR spectrum, a weak absorption due to C=C stretching is observed at ~1600 cm^{-1} (Figure 3). Since the Si atom is not directly bonded to the main chain, this bond is weak and appears at the ordinary position (1650–1600 cm^{-1}) (cf. $\nu_{C=C}$ 1540 cm^{-1} (m) in poly[1-(trimethylsilyl)-1-propyne][4b]). The presence of the Si atom is confirmed by SiC–H deformation (1250 cm^{-1}) and Si–C stretching (830 cm^{-1}).

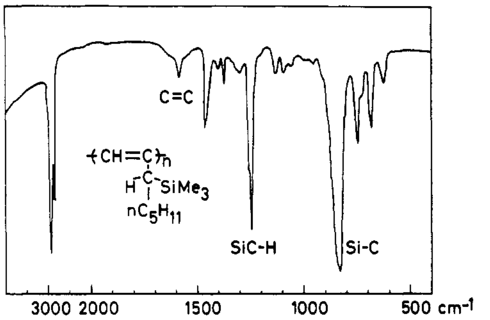

Figure 3. IR spectrum of poly[3-(trimethylsilyl)-1-octyne] (sample no. 2, Table III; KBr pellet).

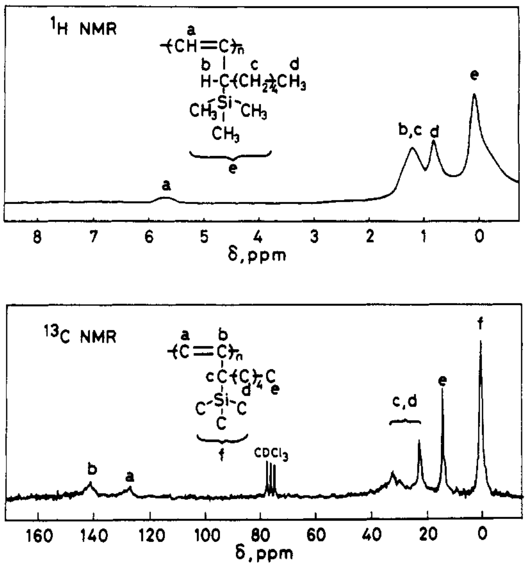

Figure 4. ^{1}H and ^{13}C NMR spectra of poly[3-(trimethylsilyl)-1-octyne] (sample no. 2, Table III; $CDCl_3$ solution).

The ^{1}H NMR spectrum consists of four rather broad peaks, which can be assigned from downfield to an olefinic proton, methine and methylene protons, methyl protons at the alkyl end, and trimethylsilyl protons, respectively (Figure 4). In the ^{13}C NMR spectrum, two kinds of olefinic carbons in the main chain are observed in reasonable positions, and the trimethylsilyl carbons just at δ 0 (Figure 4).

As shown in Figure 5, the UV–visible spectrum exhibits an absorption maximum in the UV region (λ_{max} 353 nm, ϵ_{max} 3800), the absorption continuing up to ~475 nm.

These IR and NMR spectra support that the polymer formed has the alternating double bond structure shown in Figures 3 and 4. The UV–visible spectrum, however, indicates that the extent of conjugation of alternating double bonds is not very high; that is, the main chain is considerably twisted. No information on the geometric structure of the main chain could be obtained from these spectral data. These spectra of the polymer did not differ

Table VII
Polymerization of 3-(Trimethylsilyl)-1-decyne by Group 5 and 6 Transition-Metal Catalysts[a]

no.	catalyst	monomer convn, %	polymer			
			yield, %	$\bar{M}_w/10^3$ [b]	$\bar{M}_n/10^3$ [b]	$[\eta]$, dL·g^{-1} [c]
1	$MoCl_5$	100	82	170	56	0.86
2	$MoCl_5$–Et_3SiH	100	87	220	79	1.17
3	$MoCl_5$–Ph_3SiH	100	85	240	80	1.20
4	$MoCl_5$–n-Bu_4Sn	100	87	130	50	0.77
5	$Mo(CO)_6$–CCl_4–$h\nu$[d]	98	84	200	85	1.15
6	WCl_6	100	80	55	19	0.41
7	WCl_6–Et_oSiH	100	85	150	54	
8	$W(CO)_6$–CCl_4–$h\nu$[d]	97	80	130	47	0.64
9	$NbCl_5$	79	60	51	23	0.26
10	$TaCl_5$	72[e]	0			

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 0.50$ M, [cat.] = [cocat] = 10 mM. [b] Determined by GPC. [c] Measured in toluene at 30 °C. [d] Polymerized in CCl_4 at 30 °C for 24 h after irradiation of the CCl_4 solution of $M(CO)_6$ with UV light at 30 °C for 1 h. [e] The main product was cyclotrimers.

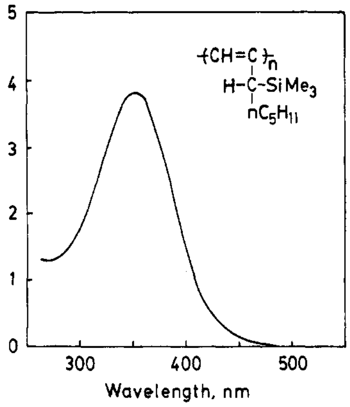

Figure 5. UV-visible spectrum of poly[3-(trimethylsilyl)-1-octyne] (sample no. 2, Table III; CCl$_4$ solution).

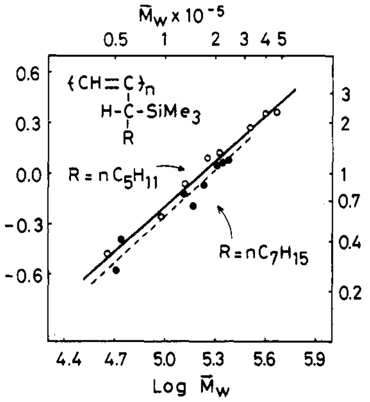

Figure 6. Relationships between the [η] and $\bar{M}_w$ of poly[3-(trimethylsilyl)-1-octyne] and poly[3-(trimethylsilyl)-1-decyne].

even though polymerization conditions were changed.

Other poly[3-(trimethylsilyl)-1-alkynes] showed analogous IR spectra, and the ^{1}H and ^{13}C NMR spectra of poly[3-(trimethylsilyl)-1-decyne] resembled those of poly[3-(trimethylsilyl)-1-octyne]. Hence it can be concluded that all these polymers have the same structure of $-[\mathrm{CH{=}CCH(SiMe_3)R}]_n-$.

Polymer Properties. Properties of the four kinds of poly[3-(trimethylsilyl)-1-alkynes], especially of poly[3-(trimethylsilyl)-1-octyne] (sample no. 2, Table III) and poly[3-(trimethylsilyl)-1-decyne] (sample no. 2, Table VII) were examined. These polymers are all yellow solids; there is no practical difference of color among these polymers.

As mentioned before, poly[3-(trimethylsilyl)-1-butyne] and poly[3-(trimethylsilyl)-1-hexyne] are partly insoluble in any solvents. This insolubility might be attributed to the short, bulky, rather stiff side chains. On the other hand, poly[3-(trimethylsilyl)-1-octyne] and poly[3-(trimethylsilyl)-1-decyne] are totally soluble in toluene. The solubility properties of these two polymers are as follows: soluble in toluene, hexane, cyclohexane, CCl$_4$, CHCl$_3$, tetrahydrofuran, diethyl ether, etc. but insoluble in (CH$_2$Cl)$_2$, 1,4-dioxane, anisole, ethyl acetate, methyl benzoate, acetone, acetophenone, nitrobenzene, acetonitrile, *N,N*-dimethylformamide, dimethyl sulfoxide, etc. Casting of toluene solutions of these polymers on a glass plate gave yellow, transparent, free-standing films.

The logarithmic plots of [η] vs. $\bar{M}_w$ for poly[3-(trimethylsilyl)-1-octyne] and poly[3-(trimethylsilyl)-1-decyne] gave good linear relationships (Figure 6). By the least-squares treatment of these plots, values for the exponent a and coefficient K in the equation $[\eta] = K\bar{M}_w{}^a$ were obtained, which are shown in Table VIII. The values for the exponent a in Table VIII are close to unity like those for other substituted polyacetylenes.[10] This contrasts with those (a = 0.5–0.8) for most vinyl polymers. It means that these substituted polyacetylenes take more extended conformations in solution than do vinyl polymers. The rather stiff polymer chain due to the alternating double bonds in the main chain as well as the bulky side group seems responsible.

Table VIII
Several Properties of Poly[3-(Trimethylsilyl)-1-alkynes]^a
$-(\mathrm{CH{=}C[CH(SiMe_3)R]}_n-$

parameter	R: CH$_3$	R: *n*-C$_3$H$_7$	R: *n*-C$_5$H$_{11}$	R: *n*-C$_7$H$_{15}$
$[\eta] = K\bar{M}_w{}^a$				
K			2.11×10^{-5}	9.78×10^{-6}
a			0.896	0.950
softening point, °C	260–270	310–320	290–300	215–220
E,^{b} MPa			630^c	530^c
γ,^{d} %			11^c	90^c
T_g,^{e} °C			170^c	150^c
2θ $(\Delta 2\theta/2\theta)^f$	9.5° (0.22)	9.2° (0.17)	8.0° (0.21)	7.1° (shoulder)
	17.2° (0.17)	17.2° (0.18)	17.4° (0.26)	17.6° (0.28)
σ,^{g} S·cm^{-1}			3×10^{-18}	1×10^{-18}
spin density,^{h} g^{-1}			$<1 \times 10^{15}$	$<1 \times 10^{15}$

[a] Samples: Table I, no. 1 (R = CH$_3$); Table I, no. 3 (R = *n*-C$_3$H$_7$); Table III, no. 2 (R = *n*-C$_5$H$_{11}$); Table VII, no. 2 (R = *n*-C$_7$H$_{15}$). [b] E is Young's modulus. [c] Data from ref 11. [d] γ is the elongation at break. [e] T_g is the glass transition temperature. [f] Wide-angle X-ray diffraction data (Cu Kα radiation); 2θ, diffraction angle; $\Delta 2\theta$, half-height width. [g] σ is the electrical conductivity (25 °C). [h] Unpaired-electron density measured by electron spin resonance (ESR) at 25 °C.

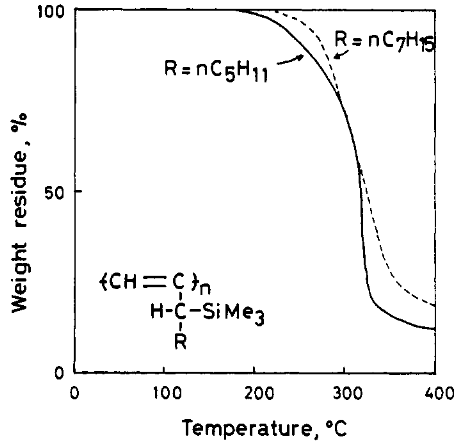

Figure 7. TGA curves of poly[3-(trimethylsilyl)-1-octyne] (sample no. 2, Table III and poly[3-(trimethylsilyl)-1-decyne] (sample no. 2, Table VII) (in air, heating rate 10 °C/min).

As shown in Table VIII, the present polymers have appreciably high softening points among monosubstituted acetylene polymers [cf. poly(1-hexyne), which is less than room temperature and poly(*tert*-butylacetylene) ~250 °C[10]]. It is obvious that the bulkiness and flexibility of the substituent greatly affect the softening points of the polymers. When poly[3-(trimethylsilyl)-1-octyne] was heat-treated in air at 100 °C for 20 h, its $\bar{M}_w$ decreased from 320 × 10^3 to 170 × 10^3 and $\bar{M}_n$ from 94 × 10^3 to 48 × 10^3. This polymer, however, hardly suffered any change in molecular weight and showed no change in the IR spectrum even when it had been left in air at room temperature over 1 month. These results indicate that the polymer is relatively thermally stable among various substituted polyacetylenes.[10] Figure 7 shows that the weight loss of poly[3-(trimethylsilyl)-1-octyne] and poly[3-(trimethylsilyl)-1-decyne] starts around 200 °C in TGA in air; this result also indicates that these polymers are thermally relatively stable.

Poly[3-(trimethylsilyl)-1-octyne] is a somewhat hard and brittle polymer according to its reported Young's modulus and elongation at break (see Table VIII).[11] In contrast, poly[3-(trimethylsilyl)-1-decyne] is slightly softer and more ductile, which is explained in terms of the presence of the longer alkyl group. The glass transition temperatures of these polymers are 150 °C or higher,[11] indicating that the polymers are glassy at room temperature (see below for morphology).

Table VIII includes data for the X-ray diffraction analysis of the present polymers. Because the peaks in the diffraction patterns are all broad, the ratios of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) are all greater than 0.15. In general, crystalline diffraction peaks are sharp, and hence their values of $\Delta 2\theta/2\theta$ are usually smaller than 0.05.[10] Consequently it can be said that the present polymers are amorphous.

The electrical conductivities of poly[3-(trimethylsilyl)-1-octyne] and poly[3-(trimethylsilyl)-1-decyne] were in the insulator range (see Table VIII). The unpaired-electron densities of these polymers were below the usual detection limit of 1×10^{15} spin·g^{-1}. These values for electrical conductivity and unpaired-electron density support the idea that only several alternating double bonds in the main chain can conjugate simultaneously.

Conclusions

No high molecular weight polymer has been obtained from monosubstituted acetylenes having the Si atom directly bonded to the acetylene carbon (e.g., $HC\equiv CSiMe_3$). The present study has revealed that monosubstituted acetylenes in which the Si atom is bonded to the carbon adjacent to the $C\equiv C$ bond [$HC\equiv CCH(SiMe_3)$—n-C_5H_{11} and $HC\equiv CCH(SiMe_3)$—n-C_7H_{15}] produce soluble, high molecular weight polymers. As well as poly(*tert*-butylacetylene)[10] and poly[*o*-(trifluoromethyl)phenylacetylene],[12] these polymers provide rare examples of thermally stable, film-forming, monosubstituted acetylene polymers. Studies on the function of these polymers such as separation of gas or liquid mixtures are now under way.

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Registry No. $HC\equiv CCH(SiMe_3)CH_3$, 14583-73-4; $HC\equiv CCH(SiMe_3)C_3H_7$, 74289-55-7; $HC\equiv (SiMe_3)C_5H_{11}$, 91118-21-7; $HC\equiv CCH(SiMe_3)C_7H_{15}$, 100858-81-9; $HC\equiv C(CH_2)_5CH_3$, 629-05-0; BuLi, 109-72-8; $LiC\equiv CCHLi(CH_2)_4CH_3$, 55988-36-8; $ClSiMe_3$, 75-77-4; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; $Mo(CO)_6$, 13939-06-5; Et_3SiH, 617-86-7; Ph_3SiH, 789-25-3; $NbCl_5$, 10026-12-7; $W(CO)_6$, 14040-11-0; Bu_4Sn, 1461-25-2; Ph_4Sn, 595-90-4; Ph_3Bi, 603-33-8; $TaCl_5$, 7721-01-9; poly(3-(trimethylsilyl)-1-octyne, 100858-80-8; poly(3-(trimethylsilyl)-1-butyne), 107985-73-9; poly(3-(trimethylsilyl)-1-hexyne), 107985-74-0; poly(3-(trimethylsilyl)-1-decyne), 100858-82-0; 3-(trimethyl)-1-octyne cyclotrimer, 107942-60-9.

References and Notes

(1) Part 7 of "Polymerization of Si-Containing Acetylenes". See ref 2 for Part 6.

(2) Tajima, H.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(3) (a) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473. (b) Takada, K.; Matsuya, H.; Masuda, T.; Higashimura, T. *J. Appl. Polym. Sci.* **1985**, *30*, 1605.

(4) (a) Voronkov, M. G.; Pukhnarevich, V. B.; Sushchinskaya, S. P.; Annenkova, V. Z.; Annenkova, V. M.; Andreeva, N. J. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 53. (b) Okano, Y.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1603. (c) Zeigler, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*(2), 223. (d) Liaw, D. J.; Soum, A.; Fontanille, M.; Parlier, A.; Rudler, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 309.

(5) (a) Masuda, T.; Isobe, E.; Higashimura, T. *Macromolecules* **1985**, *18*, 841. (b) Masuda, T.; Isobe, E.; Hamano, T.; Higashimura, T. *Macromolecules*, **1986**, *19*, 2448.

(6) (a) Isobe, E.; Masuda, T.; Higashimura, T.; Yamamoto, A. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1839. (b) Masuda, T.; Isobe, E.; Hamano, T.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(7) (a) Sagar, J. G.; Scheinmann, F. *Synthesis* **1976**, 321. (b) Quillinan, A. J.; Scheinmann, F. *Org. Syn.* **1978**, *58*, 1.

(8) (a) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 113. (b) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981; p 52.

(9) Rajagopalan, S.; Zweifel, G. *Synthesis* **1984**, 111.

(10) For reviews, see: (a) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121. (b) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51.

(11) Masuda, T.; Tang, B.-Z.; Tanaka, A.; Higashimura, T. *Macromolecules* **1986**, *19*, 1459.

(12) Muramatsu, H.; Ueda, T.; Ito, K. *Macromolecules* **1985**, *18*, 1634.