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Polymerization of 1-(Trimethylsilyl)-1-propyne by Halides of Niobium(V) and Tantalum(V) and Polymer Properties[1]

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ABSTRACT: 1-(Trimethylsilyl)-1-propyne was polymerized by pentahalides of niobium and tantalum to give a new, high-molecular-weight polymer. The polymerization was usually carried out in toluene at 80 °C. Both $TaCl_5$ and $NbCl_5$ quantitatively provided poly[1-(trimethylsilyl)-1-propyne], whose molecular weights were in a range of 10^5–10^6. $TaBr_5$ and $NbBr_5$ behaved similarly as catalysts. Effects of solvents and temperature on the polymerization were studied. The IR and NMR spectra of the polymer supported the structure being $[-C(Me)=C(SiMe_3)-]_n$, while the UV spectrum indicated that the main chain takes a remarkably twisted conformation. Poly[1-(trimethylsilyl)-1-propyne] is a white, amorphous, soluble, air-stable, electrically insulating, nonparamagnetic solid.

Silicon-containing polymers often show interesting characteristics such as high thermal stability, weather resistance, and insulating properties. However, few studies have appeared on the polymers from silicon-containing acetylenes. To our knowledge, only poly(trimethylsilylacetylene) has been studied in some detail.[2,3] This polymer, formed by WCl_6-catalyzed polymerization, is partly insoluble, and its number-average molecular weight ($\bar{M}_n$) is no more than several thousand.[2,4]

We have recently found that pentahalides of niobium (Nb) and tantalum (Ta), group 5 transition metals, polymerize disubstituted hydrocarbon acetylenes.[5,6] These catalysts can generate high-molecular-weight polymers [weight-average molecular weight ($\bar{M}_w$) up to 10^6] from 1-phenyl-1-alkynes and aliphatic disubstituted acetylenes. Further, we have studied the polymerization of 1-(trimethylsilyl)-1-propyne, a silicon-containing disubstituted acetylene, using these Nb and Ta catalysts to find that new, high-molecular-weight, extremely gas-permeable polymer forms in quantitative yield; a preliminary result has been reported.[7]

The present paper deals with a detailed study on the polymerization of 1-(trimethylsilyl)-1-propyne catalyzed by halides of Nb(V) and Ta(V). The structure and properties of the polymer are also described.

Experimental Section

Materials. 1-(Trimethylsilyl)-1-propyne purchased from Petrarch Systems, Inc., was distilled twice from calcium hydride under nitrogen at atmospheric pressure: bp 100 °C (lit. bp 99–100 °C[8]), purity >99.5% [by gas chromatography (GC)]. Halides of Nb and Ta from Alfa, Morton Thiokol Inc., were used without further purification. Toluene as polymerization solvent was washed with 5% sulfuric acid, 10% sodium hydroxide solution, and water, dried over calcium chloride overnight, and then distilled twice from calcium hydride; care was exercised to remove moisture as completely as possible. Other polymerization solvents were similarly purified.

Polymerization. Polymerization was carried out under dry nitrogen since the active species was sensitive to moisture and oxygen. The volume of the polymerizing solution was usually 10 mL, and a 30-mL Erlenmeyer flask equipped with a three-way stopcock was used as reaction vessel.

An example of the procedure is as follows (cf. Table I, no. 6): A monomer solution was prepared by mixing 1-(trimethylsilyl)-1-propyne (1.77 mL, 1.34 g, 12 mmol), chlorobenzene (0.43 mL; as internal standard for GC), and toluene (3.8 mL) and kept at 80 °C. $TaCl_5$ (71.6 mg, 0.20 mmol) was dissolved in toluene (5 mL) at 80 °C for 10 min, which became virtually homogeneous and golden yellow. To this catalyst solution, 5 mL of the above monomer solution was immediately added (the residual monomer solution was used for GC). As reaction proceeded, the polymerization system became brown and solidified. After a given time, polymerization was terminated by adding a mixture (3 mL) of methanol and toluene (1:4 volume ratio) under mingling, which led to decolorization. Monomer consumption (conversion) was determined by measuring the initial and final monomer concentrations by GC (measuring conditions: silicon DC 3 m, 90 °C). The polymer formed was dissolved in toluene (500 mL) with stirring under nitrogen, which was then poured into methanol (5 L). The precipitated polymer was filtered off, washed with methanol, and dried to a constant weight.

Table I
Polymerization of 1-(Trimethylsilyl)-1-propyne by Halides of Niobium and Tantalum[a]

		polymer			
no.	catalyst	yield, %	$\bar{M}_w$[b]/10^4	$\bar{M}_n$[b]/10^4	$[\eta]$,[c] dL/g
1	NbF_5	94[d]			
2	$NbCl_5$	100	31	21	0.71
3	$NbBr_5$	100[e]	28	11	0.63
4	NbI_5	0			
5	TaF_5	0			
6	$TaCl_5$	100	73	13	5.43
7	$TaBr_5$	95	41	11	3.80
8	TaI_5	0			

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = 20 mM. [b] Determined by GPC. [c] Measured in toluene at 30 °C. [d] Completely insoluble in toluene. [e] Partly insoluble (~20%) in toluene.

Polymer Characterization. Molecular weight distributions (MWD) of polymers were observed by gel permeation chromatography (GPC) by using a high-performance liquid chromatograph (Jasco Triroter; column: Shodex A802, 804, 806 polystyrene gel; eluent: chloroform). Weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$, respectively) were determined tentatively on the basis of a polystyrene calibration. Intrinsic viscosities ($[\eta]$) of polymers were measured in toluene at 30 °C.

IR spectra (KBr disk) and UV–visible spectra (cyclohexane solution) were recorded on Shimadzu IR435 and UV190 spectrophotometers, respectively. ^1H and ^{13}C NMR spectra were taken with a JEOL FX90Q spectrometer [90 MHz for ^1H; room temperature; concentration: 5 (^1H) and 20 (^{13}C) vol %; accumulation: 10 (^1H) and 5000 (^{13}C) times; reference: CH_2Cl_2 (^1H) and $CDCl_3$ (^{13}C)]. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out with a Shimadzu 20B thermal analyzer (heating rate 10 °C/min). Unless otherwise specified, the polymer prepared with $TaCl_5$ in toluene at 80 °C (Table I, no. 6; see below) was used for studies on the structure and properties of polymer.

Results and Discussion

Polymerization of 1-(Trimethylsilyl)-1-propyne. Table I lists the polymerization of 1-(trimethylsilyl)-1-propyne by Nb and Ta catalysts. Among the halides of Nb(V) and Ta(V), $NbCl_5$, $TaCl_5$, and $TaBr_5$ afforded

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Table II
Solvent Effect on the Polymerization of 1-(Trimethylsilyl)-1-propyne by $NbCl_5$ and $TaCl_5$[a]

	polymer		
solv	yield, %	$\bar{M}_w$[b]/10^4	$\bar{M}_n$[b]/10^4
	$NbCl_5$ Catalyst		
cyclohexane	86	7.8	6.2
heptane	59	30	20
CCl_4	96	13	7.5
$(CH_2Cl)_2$	100[c]		
PhCl	59	35	22
	$TaCl_5$ Catalyst		
cyclohexane	100	95	21
heptane	62	78	17
CCl_4	31	3.8	1.1
$(CH_2Cl)_2$	100	25	3.2
PhCl	62	39	14

[a] Polymerized at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = 20 mM. [b] Determined by GPC. [c] Completely insoluble in toluene.

completely soluble poly[1-(trimethylsilyl)-1-propyne] in virtually quantitative yields. The $\bar{M}_w$'s of polymers were as high as several hundred thousand. The high molecular weights of polymers can be confirmed by their high intrinsic viscosities. $NbBr_5$ provided a partly insoluble polymer, and NbF_5 gave a totally insoluble polymer. None of NbI_5, TaF_5, and TaI_5 polymerized this monomer (no monomer was consumed).

Equimolar mixtures of $MoCl_5$ or WCl_6 with tetraphenyltin (Ph_4Sn) are excellent catalysts for the polymerization of many disubstituted acetylenes such as 1-phenyl-1-propyne, 1-chloro-2-phenylacetylene, and 2-octyne.[4] However, no reaction of 1-(trimethylsilyl)-1-propyne occurred at all with either $MoCl_5$–Ph_4Sn or WCl_6–Ph_4Sn. This seems due to the large steric effect of this monomer. This result implies also that Nb and Ta catalysts are more active toward sterically hindered disubstituted acetylenes than are Mo and W catalysts.

Ti(O-*n*-Bu)$_4$–Et_3Al (1:4) is famous for acetylene polymerization, and iron tris(acetylacetonate)–Et_3Al (1:3) polymerizes both primary and secondary alkylacetylenes. However, like other disubstituted acetylenes examined to date, no 1-(trimethylsilyl)-1-propyne was consumed with these Ziegler catalysts.

Table II shows results for the solvent effect on the $NbCl_5$- and $TaCl_5$-catalyzed polymerizations. In general, good yields were obtained with hydrocarbons and halogenated hydrocarbons. Aromatic hydrocarbons like toluene are optimal polymerization solvents for the following reasons: (i) they dissolve both catalysts and the polymer best; (ii) they keep the propagating species active because of their low coordinating ability and low reactivity toward the propagating species.

The $\bar{M}_w$ of polymer was the highest (7×10^5–1×10^6) when the polymerization was carried out with $TaCl_5$ in hydrocarbons (see Table II). The $\bar{M}_w$'s of polymers obtained with $TaCl_5$ were usually higher than those with $NbCl_5$ in the same solvents. The dispersity ratios ($\bar{M}_w/\bar{M}_n$) of the polymers formed with $NbCl_5$ in various solvents were all smaller than 2, whereas those with $TaCl_5$ were larger than 2.

Table III
Effect of Temperature on the Polymerization of 1-(Trimethylsilyl)-1-propyne by $NbCl_5$ and $TaCl_5$[a]

	polymer			
temp, °C	yield, %	$\bar{M}_w$[b]/10^4	$\bar{M}_n$[b]/10^4	[η],[c] dL/g
		$NbCl_5$ Catalyst		
0	93	32	11	0.80
30	100	38	21	0.81
60	100	25	15	0.67
80	100	31	21	0.71
100	98	34	19	0.98
130	0			
		$TaCl_5$ Catalyst		
0	0			
30	100	45	7.6	3.60
60	100	64	18	4.10
80	100	73	13	5.43
100	100	54	18	3.05
130	95	33	4.7	2.78

[a] Polymerized in toluene (in xylene for 130 °C) for 24 h; $[M]_0$ = 1.0 M, [Cat.] = 20 mM. The catalysts were completely dissolved in advance by heating them at 80 °C for 10 min. [b] Determined by GPC. [c] Measured in toluene at 30 °C.

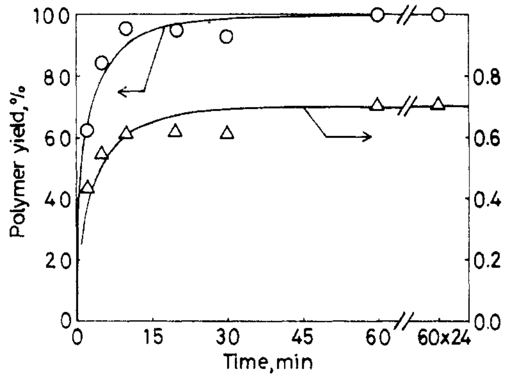


Figure 1. Time dependence of the polymerization of 1-(trimethylsilyl)-1-propyne by $NbCl_5$ (in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = 20 mM).

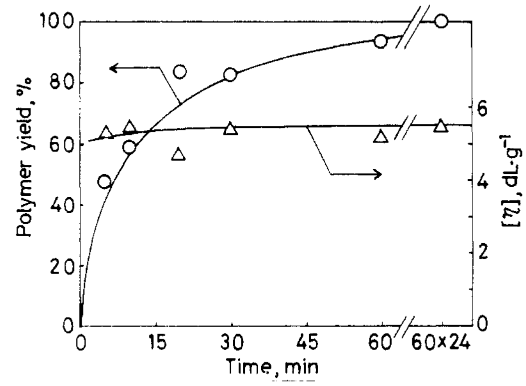


Figure 2. Time dependence of the polymerization of 1-(trimethylsilyl)-1-propyne by $TaCl_5$ (in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = 20 mM).

Effects of temperature on the polymerizations by $NbCl_5$ and $TaCl_5$ in toluene were examined (Table III). Poly[1-(trimethylsilyl)-1-propyne] can be virtually quantitatively obtained in a temperature range of 30–100 °C with both $NbCl_5$ and $TaCl_5$. The $\bar{M}_w$ of polymer did not change very much with temperature in the case of $NbCl_5$ (ca. 3×10^5), while it showed a maximum of about 7×10^5 at 80 °C with $TaCl_5$. Polymerization below 0 °C is unfavorable because of the low solubility and activity of the catalysts at such temperature. The active species appears to partly or totally deactivate at 130 °C or above. Since one must heat the catalyst solution around 80 °C to completely dissolve 20 mM of $NbCl_5$ or $TaCl_5$ in toluene, the polymerization at 80 °C is the most practical.

Figures 1 and 2 show the time dependences of polymer yield and intrinsic viscosity in the polymerizations by $NbCl_5$ and $TaCl_5$, respectively, in toluene at 80 °C. The

Table IV
Effects of Monomer and Catalyst Concentrations on the Polymerization of 1-(Trimethylsilyl)-1-propyne by $NbCl_5$ and $TaCl_5$[a]

no.	$[M]_0$, M	[Cat.], mM	$[M]_0$/[Cat.]	polymer yield, %	polymer $\bar{M}_w$[b]/10^4	polymer $\bar{M}_n$[b]/10^4	polymer $[\eta]$,[c] dL/g
			$NbCl_5$ Catalyst				
1	0.25	20	12.5	74	35	23	0.73
2	0.50	20	25	87	34	19	0.65
3	1.0	20	50	100	31	21	0.71
4	1.0	10	100	100	32	22	0.63
			$TaCl_5$ catalyst				
5	0.25	20	12.5	100	25	7.6	1.45
6	0.50	20	25	100	29	5.8	2.30
7	1.0	20	50	100	73	13	5.43
8	1.0	10	100	98	84	19	6.15
9	1.0	5	200	77	91	33	6.80

[a] Polymerized in toluene at 80 °C for 24 h. [b] Determined by GPC. [c] Measured in toluene at 30 °C.

polymerization by $NbCl_5$ reached the quantitative polymer yield in 1 h, at which the intrinsic viscosity of polymer was ~0.7 dL/g. Even if the polymerization was continued as long as 24 h, the intrinsic viscosity of ~0.7 dL/g did not decrease; that is, no polymer degradation occurred. The polymerization by $TaCl_5$ also approached 100% yield in 1 h. The intrinsic viscosity was almost constant at 5.0–5.5 dL/g over a long range of polymerization time from those corresponding to low polymer yields to 24 h.

Effects of monomer and catalyst concentrations were studied for the polymerization in toluene at 80 °C for 24 h (Table IV). When $NbCl_5$ was used as catalyst, polymer yield reached 100% at a monomer concentration of 1.0 M, but not a lower monomer concentrations; thus, the yield apparently increased with an increase in the monomer to catalyst ratio, $[M]_0$/[Cat.]. The molecular weights and intrinsic viscosity of the polymer appear to be independent of $[M]_0$/[Cat.]. On the other hand, in the case of $TaCl_5$ as catalyst, polymer yield tended to decrease and molecular weights and intrinsic viscosity increased with increasing $[M]_0$/[Cat.]. Eventually, the conditions that $[M]_0$ = 1.0 M and [Cat.] = 20 mM seem best to prepare high-molecular-weight poly[1-(trimethylsilyl)-1-propyne] quantitatively with both $NbCl_5$ and $TaCl_5$.

Some examples have been reported showing that metal carbenes are formed by the reactions of early transition metals with coordinating acetylenes.[9] Further, Schrock and co-workers have isolated many carbene complexes of Nb and Ta.[10] Katz and co-workers support metal carbene mechanisms for the acetylene polymerization by W-based catalysts.[11] From these results, we infer that the present polymerization proceeds via metal carbenes and metallacyclobutenes like the W- and Mo-catalyzed polymerization of acetylenes.[4,12]

On the basis of the above results on polymerization, one can reach the following conclusions: (i) Chlorides and bromides of Nb(V) and Ta(V) are unique and excellent catalysts for the polymerization of 1-(trimethylsilyl)-1-propyne; (ii) an optimal polymerization procedure to obtain a completely soluble, high-molecular-weight polymer in high yield is the one using $TaCl_5$ in toluene at 80 °C as shown by the experiment in Table I, no. 6.

Polymer Structure. The data for the elemental analysis of polymer (sample: Table I, no. 6) is as follows. Calcd for $(C_6H_{12}Si)_n$: C, 64.20; H, 10.78. Found: C, 64.11; H, 10.97. These data and those for polymers made under other polymerization conditions alike agreed well with the theoretical values.

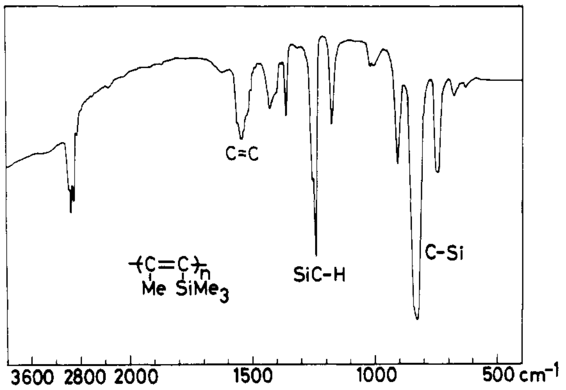


Figure 3. IR spectrum of poly[1-(trimethylsilyl)-1-propyne] (sample: Table I, no. 6).

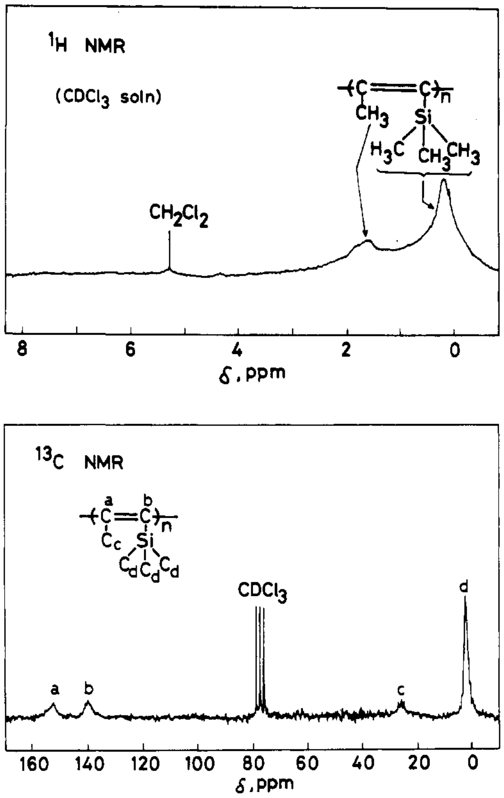


Figure 4. ^{1}H and ^{13}C NMR spectra of poly[1-(trimethylsilyl)-1-propyne] (sample: Table IV, no. 5; measured in $CDCl_3$).

While the monomer, 1-(trimethylsilyl)-1-propyne, shows a band at 2170 cm^{-1} due to C≡C stretching in its IR spectrum, this band is absent and a band at 1540 cm^{-1} attributable to C=C stretching is present in the polymer (Figure 3). For both monomer and polymer of 1-(trimethylsilyl)-1-propyne, a band characteristic of SiC–H deformation is observed at 1240 cm^{-1}, and those due to C–Si stretching are seen at 820 and 740 cm^{-1}.

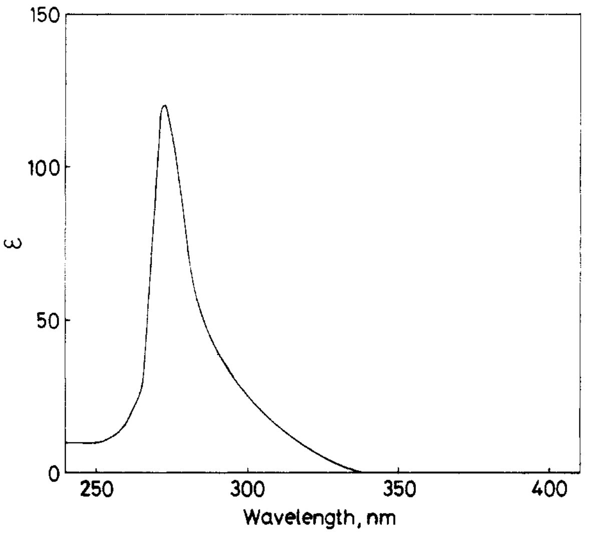
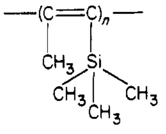


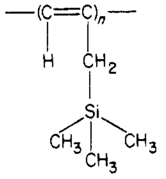
Figure 5. UV–visible spectrum of poly[1-(trimethylsilyl)-1-propyne] (sample: Table I, no. 6; measured in cyclohexane).

Figure 4 shows ^{1}H and ^{13}C NMR spectra. A polymer having a relatively low molecular weight (sample: Table IV, no. 5) was employed to keep the viscosity of polymer solutions low. Two rather broad signals are seen at approximately 1:3 peak ratio in the ^{1}H NMR spectrum, and four signals (due to two olefinic carbons and two kinds of methyl carbons) in the ^{13}C NMR. These numbers of signals and their chemical shifts clearly indicate that the polymer consists of only structure 1, and does not contain any structure 2 which might be formed if monomer isomerization occurs before polymerization.



$-(\underset{CH_3}{C}=\underset{Si(CH_3)_3}{C})_n-$

1



$-(\underset{H}{C}=\underset{CH_2Si(CH_3)_3}{C})_n-$

2

Head-to-head addition is unlikely because of large steric repulsion for two trimethylsilyl groups on adjacent carbon atoms. From the above spectra, no information could be obtained regarding the geometric structure of double bonds along the main chain; the geometric isomerism of the present polymer remains as a future problem like any polymers from other disubstituted acetylene monomers (e.g., ref 6).

The UV–visible spectrum of poly[1-(trimethylsilyl)-1-propyne] shows only a very small absorption at the UV region (λ_{max} 273 nm, ϵ_{max} 120) and none above 340 nm (Figure 5). It is interesting to compare this UV absorption with the following λ_{max} (ϵ_{max}) data:[13] 1,3,5-hexatriene, 268 (34 000); 1,3,5,7-octatetraene, 304 (64 000); 1,3,5,7,9-decapentaene, 334 (121 000). These data enable the following discussion: (i) the λ_{max} of poly[1-(trimethylsilyl)-1-propyne] is close to that of 1,3,5-hexatriene, indicating that any planar conjugated conformation involves only about three double bonds; (ii) the extremely small value of ϵ_{max} for poly[1-(trimethylsilyl)-1-propyne] as compared with low-molecular-weight unsubstituted polyenes means that there are very few such conjugated sequences in the polymer; (iii) the most reasonable explanation for the short λ_{max} and small ϵ_{max} is the steric effect due to the presence of methyl and trimethylsilyl substituents on every repeating unit.

Thus, the above spectra lead to a conclusion that the backbone of poly[1-(trimethylsilyl)-1-propyne] comprises alternating double bonds, which are, however, little conjugated with one another because the polymer has mainly twisted conformation.

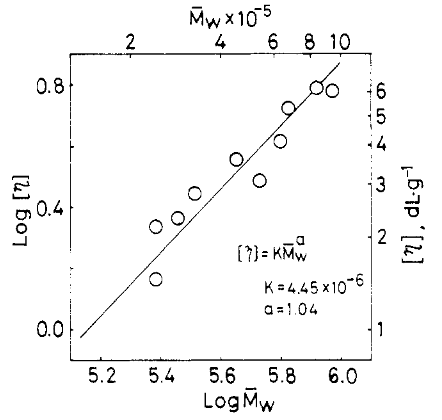


Figure 6. Relationship between the intrinsic viscosity and weight-average molecular weight of poly[1-(trimethylsilyl)-1-propyne] (for samples obtained with $TaCl_5$).

Polymer Properties. Poly[1-(trimethylsilyl)-1-propyne] is a white solid, and amorphous according to the X-ray diffraction analysis of powdery samples: e.g., sample from Table I, no. 6; $2\theta = 9.5°$, $\Delta 2\theta / 2\theta = 0.389$.

The polymer prepared with $TaCl_5$ is soluble in toluene, xylene, benzene, cyclohexane, hexane, heptane, carbon tetrachloride, chloroform, and tetrahydrofurn, but is insoluble in 1,2-dichloroethane, 1,4-dioxane, anisole, diethyl ether, ethyl acetate, acetone, acetic acid, aniline, nitrobenzene, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. The polymer obtained with $NbCl_5$ had similar solubility properties except that hexane and heptane are nonsolvents. The reason for this difference is not clear, but may be due to the geometric structure of the main chain. In comparison with insoluble polyacetylene the solubility of this polymer may be attributed to the interaction between substituents and solvent, which is enhanced by different bulkiness of the methyl group and the trimethylsilyl group (see ref 6, regarding the solubility of polymers of disubstituted acetylenes). Casting the polymer solution on a horizontal glass plate provides a colorless, uniform, tough film.

Figure 6 shows a linear relationship between log [η] and "apparent" weight-average molecular weight obtained by GPC for polymers formed with $TaCl_5$. All the polymers made with $TaCl_5$ have similar MWD's. Therefore, the slope in Figure 6 should be the same as the one that will be obtained by using "true" $\bar{M}_w$. The value of slope a in Figure 6 is determined to be 1.04, which is larger than those (a = ~0.5–~0.8) for most vinyl polymers; this indicates that poly[1-(trimethylsilyl)-1-propyne] is stiffer than ordinary vinyl polymers.

Dynamic viscoelastic measurement showed that the glass transition temperature of this polymer is above 200 °C and that β-dispersion exists around 20 °C.[14] The following values were obtained from the stress–strain curve observed at a constant rate of stretching of 86%/min at room temperature: Young's modulus (E) 190 MPa; tensile strength (σ_B) 8.0 MPa; ultimate elongation (γ_B) 11%.[14] As seen from its β-dispersion and ultimate elongation, this glassy polymer is slightly ductile.

Poly[1-(trimethylsilyl)-1-propyne] exhibited a sharp softening point in a temperature range of 326–345 °C, e.g., 345 ($TaCl_5$), 331 ($TaBr_5$), 326 ($NbCl_5$), 330 ($NbBr_5$) °C (the samples obtained in Table I were used). This softening point is only an apparent one, because air oxidation and thermal decomposition may participate. Figure 7 shows

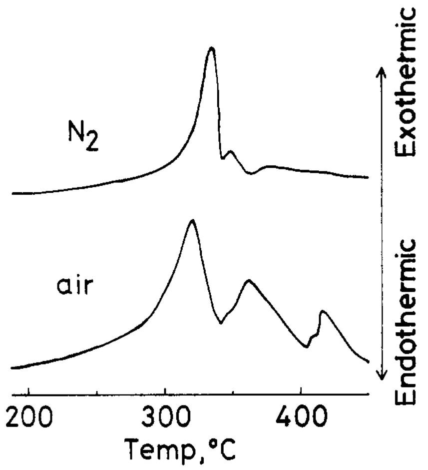


Figure 7. DTA curves of poly[1-(trimethylsilyl)-1-propyne] (sample: Table I, no. 6).

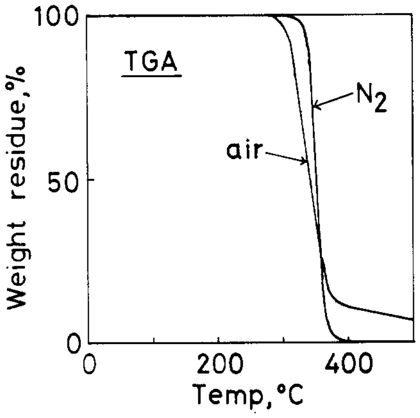


Figure 8. TGA curves of poly[1-(trimethylsilyl)-1-propyne] (sample: Table I, no. 6).

DTA curves of the polymer. There is neither exotherm nor endotherm below 200 °C irrespective of the presence or absence of oxygen. Under nitrogen, an exothermic peak due to geometric isomerization and/or decomposition appears in a relatively narrow temperature range of ca. 300–370 °C; an endothermic peak due to softening is overlapping at 345 °C. In air, exothermic oxidation makes the DTA curve complicated. The weight loss of poly[1-(trimethylsilyl)-1-propyne] started at 280 °C in air, and at 330 °C under nitrogen (see Figure 8). The polymer completely changed into volatile materials at 400 °C under nitrogen, while polymer residues remained at that temperature in air which is likely to be SiO_2. When this polymer was heated in air at 100 °C for 20 h, neither oxidation (no C=O in the IR spectrum) nor molecular-weight decrease occurred.[15] Further, the molecular weight of the polymer was unchanged after 3 months in air at room temperature. Consequently, it can be said that poly[1-(trimethylsilyl)-1-propyne] has a higher air stability and a higher thermal stability than many other polyacetylenes.

The electrical conductivity of poly[1-(trimethylsilyl)-1-propyne] was 1×10^{-17} S·cm^{-1}, being in the insulator range ($<10^{-9}$ S·cm^{-1}). The detection limit of unpaired electrons in ESR was $\sim 10^{15}$ spin·g^{-1}, and the unpaired electron density of this polymer was lower than the limit. These small values of conductivity and unpaired electron density can be attributed to the twisted conformation of the main chain.

The permeability coefficient of a poly[1-(trimethylsilyl)-1-propyne] film to oxygen (P_{O_2}; 25 °C) is ca. 4×10^{-7} cm^3(STP)·cm/(cm^2·s·cmHg), and its permselectivity of oxygen to nitrogen is ca. 2.[7,16] It is worthy of noting that this P_{O_2} value is about 10 times as large as that of a poly(dimethylsiloxane) film which so far possessed higher oxygen permeability than any other polymer films. Detailed studies on the gas permeability of the present polymer are reported elsewhere.[16]

In conclusion, poly[1-(trimethylsilyl)-1-propyne] is white, amorphous, soluble, air stable, electrically insulating, and nonparamagnetic owing to the presence of the substituents, which are in striking contrast to polyacetylene. Poly[1-(trimethylsilyl)-1-propyne] is a new polymer and the first example of the high-molecular-weight polymer from a silicon-containing acetylene. We expect that this unique polymer will find many applications as speciality polymer.

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