(Figure 1A). The number and intensity of cross-peaks, and the resolution apparent in the projection, can be varied by changing the fixed mix time in the pulse sequence. It is frequently useful to be able to select for resonances from, and interactions among, defined populations of spins. There are several clearly resolved cross-peaks in this two-dimensional spin-exchange spectrum despite the large number of labeled nitrogen sites. Correlations for a few cross–peaks have been drawn in the lower half of the contour plot. The indole nitrogen of Trp-26 has a chemical shift of 127 ppm[6] and gives a well-defined cross-peak to 198 ppm, which is most likely from a peptide nitrogen. The resonance at 140 ppm has cross-peaks to resonances at 147 and 187 ppm.

The spectral data become much simpler when the number of labeled sites is decreased. The four valine residues of the fd coat protein are in close proximity in the sequence (Figure 1) and in space (Figure 2). All four sites give resolved resonances in the chemical-shift spectrum (Figure 1D) and the projection (Figure 1E) from the two-dimensional spin-exchange spectrum. Therefore, there is the possibility of detecting the interactions among all the valine peptide nitrogen sites. There is a well-defined cross-peak between the valine ^{15}N resonances at 197 and 165 ppm. The shoulder off the diagonal between the resonances at 197 and 189 ppm is suggestive of a second cross-peak. The cross-peaks due to nitrogens with very similar chemical shifts are difficult to detect because of the width of the diagonal ridge due to T_2 relaxation. The coat protein is almost entirely α-helical and both the ^{15}N chemical shifts and $^{15}N-^{1}H$ dipolar couplings for the valine residues correspond to peptide bonds in an α-helix. Figure 2 shows this segment of protein as an α-helix. Val-30 is only about 2.8 Å from Val-29 or Val-31. The results in Figure 1 are consistent with cross-peaks occuring from Val-30 to Val-29 and Val-31; certainly one of the cross-peaks is present with some doubt about the second. The nitrogens of Val-29 and Val-33 are more than 6 Å apart and are unlikely to give rise to a cross-peak. Spin exchange between the backbones of neighboring protein subunits is unlikely because the distance of closest appraoch is approximately 8 Å.

The simple applications of ^{15}N spin-exchange demonstrated for the coat protein in fd provide distance information with cross-peaks occurring only for nearby sites. In the uniformly labeled virus spectrum in Figure 1C the cross-peak between the Trp-261 ring site and an amide site shows the closeness of a side chain to the backbone. The presence of cross-peaks can be used in making resonance assignments. If there are indeed two cross-peaks off of one nitrogen resonance in Figure 1F, then the resonance at 197 ppm is assigned to Val-30.

Acknowledgment. We thank P. Stewart for help in providing ^{15}N-labeled valine. This research is being supported by a grant from the National Institutes of Health (GM-24266). M.H.F. is supported by a Cell and Molecular Biology Training Grant.

Registry No. Nitrogen-15, 14390-96-6.

Poly[1-(trimethylsilyl)-1-propyne]: A New High Polymer Synthesized with Transition-Metal Catalysts and Characterized by Extremely High Gas Permeability

Toshio Masuda, Eiji Isobe, and Toshinobu Higashimura*

Department of Polymer Chemistry, Kyoto University
Kyoto 606, Japan

Koichi Takada

Technological Research Department
Sanyo Chemical Industry, Ltd., Japan

Received August 1, 1983

Though the polymerization of acetylenes has been attempted by various methods, the products are often not high polymers but linear oligomers and cyclotrimers.[1] It is known that acetylene and monosubstituted acetylenes are selectively cyclotrimerized by the pentachlorides and pentabromides of niobium (Nb) and tantalum (Ta), group 5 transition metals.[2] We have recently found that these metal halides polymerize disubstituted hydrocarbon acetylenes.[3] The present communication reports that 1-(trimethylsilyl)-1-propyne is polymerized by these metal halides to give a new high-molecular-weight polymer. Polymers from aliphatic acetylenes such as *tert*-butylacetylene have been found to exhibit fairly high gas permeabilities.[4] Thus we further examined the permeability of the present polymer to oxygen to observe the highest value among those ever known.

Table I. Polymerization of 1-(Trimethylsilyl)-1-propyne by Halides of Nb and Ta[a]

run	catalyst	polymer yield, %	"$\overline{M}_n$"[b]/ 10^4	"$\overline{M}_w$"[b]/ 10^4	[η],[c] dL/g
1	$NbCl_5$	100	23	32	0.99
2	$NbBr_5$	100	13	27	0.63
3	$TaCl_5$	100	61	85	5.43
4	$TaBr_5$	95	26	61	3.60

[a] Polymerized under dry nitrogen in toluene at 80 °C for 24 h: $[M]_0 = 1.0$ M, [Cat] = 20 mM. [b] Number- and weight-average molecular weights ("$\overline{M}_n$" and "$\overline{M}_w$", respectively) determined by gel permeation chromatography using a calibration curve for polystyrene. [c] Measured in toluene at 30 °C.

Table II. Gas Permeability of Poly[1-(trimethylsilyl)-1-propyne][a]

polymer sample[b]	P_{O_2}[c]	P_{N_2}[c]	P_{O_2}/P_{N_2}
1	72×10^{-8}	42×10^{-8}	1.7
2	83×10^{-8}	49×10^{-8}	1.7
3	61×10^{-8}	34×10^{-8}	1.8
4	63×10^{-8}	37×10^{-8}	1.7

[a] Measured at 25 °C. [b] Corresponding to the run numbers in Table I. [c] In units of cm^3 (STP)/cm/(cm^2 s cmHg).

Under the conditions shown in Table I, the chlorides and bromides of Nb(V) and Ta(V) yielded poly[1-(trimethylsilyl)-1-propyne] virtually quantitatively. The molecular weights of the polymers, determined tentatively by gel permeation chromatography, ranged from 1×10^5 to 1×10^6. The high molecular weights are endorsed by the high intrinsic viscosities, [η]. This polymerization proceeded in hydrocarbons (toluene, cyclohexane, etc.) and halogenated hydrocarbons [CCl_4, $(CH_2Cl)_2$, etc.] but not in oxygen-containing solvents (anisole, acetophenone, etc.). Similarly, some homologues such as 1-(dimethylpropylsilyl)-1-propyne and 1-(dimethyl-*n*-butylsilyl)-1-propyne polymerized with $NbCl_5$ and $TaCl_5$.

The fluorides and iodides of Nb(V) and Ta(V) did not polymerize 1-(trimethylsilyl)-1-propyne at all. $MoCl_5-Ph_4Sn$ (1:1) and WCl_6-Ph_4Sn (1:1) work as effective polymerization catalysts for mono- and disubstituted acetylenes,[5] Fe(III) complexes–Et_3Al (1:3) for monosubstituted acetylenes,[6] and Ti(O-*n*-Bu)$_4$–Et_3Al (1:4) for acetylene.[7] None of these catalysts, however, polymerized 1-(trimethylsilyl)-1-propyne. Thus the high efficiency toward disubstituted acetylenes with large steric hindrance is a characteristic of the Nb and Ta catalysts.

---

(1) For reviews, see: (a) Simionescu, C. I.; Percec, V. *Prog. Polym. Sci.* **1982**, *8*, 133. (b) Chauser, M. G.; Rodionov, Yu. M.; Misin. V. M.; Cherkashin, M. E. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 348; *Usp. Khim.* **1976**, *45*, 695.

(2) (a) Dändliker, G. *Helv. Chim. Acta* **1969**, *52*, 1482. (b) Masuda, T.; Mouri, T.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1152. (c) Masuda, T.; Deng, Y.-X.; Higashimura, T. *Ibid.* **1983**, *56*, 2798.

(3) Masuda, T.; Takahashi, T.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1982**, 1297.

(4) Higashimura, T.; Masuda, T.; Okada, M. *Polymn. Bull.* **1983**, *10*, 114.

(5) Masuda, T.; Higashimura, T. *Acc. Chem. Res.*, in press.

(6) (a) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *7*, 179. (b) Kern, R. J. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 621.

(7) (a) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.

0002-7863/83/1505-7473$01.50/0

Well-characterized Nb and Ta complexes, which contain a transition-metal carbon double bond and catalyze olefin metathesis, have been reported.[8] Therefore it is very likely that metal carbenes and metallacyclobutenes formed from them and the acetylene mediate the present polymerization. A similar mechanism has been proposed for the W- and Mo-catalyzed polymerization of acetylenes.[5,9]

The data of combustion analysis and spectroscopies of the polymer formed[10] support a conjugated polyene structure, $\{C(Me){=}C(SiMe_3)\}_n$. The UV spectrum,[11] however, indicates that the main chain, being sterically crowded, takes a twisted conformation. This is supported by the low values of electrical conductivity ($\sigma = 1 \times 10^{-17}$ S cm^{-1}) and unpaired-electron density (<15 spin g^{-1}).

Poly[1-(trimethylsilyl)-1-propyne] is the first example of the high-molecular-weight polymer obtained from a silicon-containing acetylene.[12] This polymer is strikingly different in properties from polyacetylene; it is (i) white and amorphous, (ii) stable to air (neither molecular-weight decrease nor oxidation in air at room temperature after a period of 1 month), and (iii) soluble in nonpolar solvents such as toluene, cyclohexane, and carbon tetrachloride to give a tough film by solution casting. Its softening point is in a range of 330–345 °C.[13] No exo- or endothermic peak was observed below 250 °C, and weight loss occurred only above 300 °C in air. Thus this polymer possesses a fairly high thermal stability.

Membranes for oxygen enrichment have recently been the subject of intensive research.[14] Poly(dimethylsiloxane) has the highest permeability coefficient [P; cm^3(STP) cm/(cm^2 s cmHg)] to oxygen among the polymers so far examined ($P_{O_2} = 6.0 \times 10^{-8}$, $P_{N_2} = 3.1 \times 10^{-8}$, $P_{O_2}/P_{N_2} = 1.9$). This good permeability has been attributed to the flexible backbone and in turn the large free volume of the rubbery polymer.

Very interestingly, the P_{O_2} values of poly[1-(trimethylsilyl)-1-propyne] are ca. 60×10^{-8}–80×10^{-8}, about 10 times larger than that of poly(dimethylsiloxane) (see Table II).[15] The ratios P_{O_2}/P_{N_2} are smaller than that of poly(dimethylsiloxane), which is in agreement with a general trend that the higher the permeability of a polymer, the lower the permselectivity of the polymer. As evidenced with CPK molecular models and by exponent a in the viscosity–$\bar{M}_w$ relationship,[16] the present polymer is fairly rigid because the main chain contains alternating double bonds, and two substituents exist in every repeating unit. Therefore, it is of great interest that such a rigid polymer exhibits an unexpectedly high gas permeability.

Registry No. Niobium pentachloride, 10026-12-7; niobium pentabromide, 13478-45-0; tantalum pentachloride, 7721-01-9; tantalum pentabromide, 13451-11-1; oxygen, 7782-44-7; nitrogen, 7727-37-9; 1-(trimethylsilyl)propyne homopolymer, 87842-32-8.

---

(8) (a) Schrock, R. R. *Science (Washington, D.C.)* **1983**, *219*, 13. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(9) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(10) Anal. Calcd for $(C_6H_{12}Si)_n$: C, 64.20; H, 10.78. Found: C, 64.11; H, 10.97. ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 151.5 (C$_2$), 139.0 (C$_1$), 25.8 (C$_3$), 2.4 (SiMe$_3$). ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.5 (br s, 3, CMe), 0.2 (br s, 9, SiMe$_3$). IR (KBr) 2950 (m), 2900 (m), 1620 (w), 1540 (m), 1430 (m), 1360 (m), 1240 (s), 1180 (m), 910 (m), 830 (s), 750 (m) cm^{-1}.

(11) UV λ_{max} (cyclohexane) 273 nm (ϵ 120); no absorption above 325 nm.

(12) The polymerization of (trimethylsilyl)acetylene has been attempted using WCl$_6$-based catalysts to yield only a partly insoluble oligomer; the number-average molecular weight of the soluble fraction is ~7000: (a) Okano, Y.; Masuda, T.; Higashimura, T. *Polym. Prepr. Jpn.* **1982**, *31* (6), 1189. (b) 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. Like monosubstituted hydrocarbon acetylenes, (trimethylsilyl)acetylene yielded only cyclotrimer in the presence of NbCl$_5$ or TaCl$_5$.

(13) The result of dynamic viscoelastic measurement showed no glass transition between −150 and +200 °C. The glass-transition temperature is considered to be higher than 200 °C.

(14) For reviews, see: (a) Lonsdale, H. K. *J. Membrane Sci.* **1982**, *10*, 81. (b) Pusch, W.; Walch, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 660. (c) Strathmann, H. *J. Membrane Sci.* **1981**, *9*, 121.

(15) Membrane samples were prepared by casting toluene solution over a glass plate and extending with a doctor knife: membrane thickness 20–50 μm. The permeability coefficients were determined on a K-315-N gas permeability apparatus (Rikaseiki Co. Japan) equipped with a MKS Baratron detector.

(16) $a = 1.0$ in $[\eta] = K\bar{M}_w{}^a$ with polymer samples obtained with TaCl$_5$ in toluene; this value indicates that the polymer is more rigid than most vinyl polymers (a = 0.5–0.8).

Additions and Corrections

Structure and Tunneling Dynamics of Malonaldehyde. A Theoretical Study [*J. Am. Chem. Soc.* **1983**, *105*, 2550]. JOZEF BICERANO, HENRY F. SCHAEFER III, and WILLIAM H. MILLER*

In a recent paper,[1] we commented on an apparent discrepancy between earlier malonaldehyde results (Del Bene and Kochenour)[2] and those of Buoma, Vincent, and Radom.[3] However, there is no discrepancy between these two studies. Del Bene and Kochenour reported fully optimized Hartree–Fock STO-3G geometries for the C_s and C_{2v} forms of malonaldehyde and their relative energy. Later, Radom confirmed these results at the same level of theory.[3] Thus, the correct Hartree–Fock STO-3G value for the increased stability of the C_s form of malonaldehyde relative to the C_{2v} form is 6.6 kcal/mol, and not 10.3 kcal/mol, as stated in ref 1. The 10.3-kcal/mol value, from ref 3, is the increased stability of the C_s form computed with the split-valence 4-31G basis set at optimized STO-3G geometries, and does not represent a difference due to geometry optimization at the STO-3G level.

---

(1) Bicerano, J.; Schaefer, H. F., III; Miller, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 2550.

(2) Del Bene, J. E.; Kochenour, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 2041.

(3) Bouma, W. J.; Vincent, M. A.; Radom, L. *Int. J. Quantum Chem.* **1978**, *14*, 767.

Migration of Tricarbonylchromium Groups in Phenylanthracenes [*J. Am. Chem. Soc.* **1983**, *105*, 3724]. SCOTT D. CUNNINGHAM, KARL ÖFELE,* and BENNETT R. WILLEFORD*

Pages 3724 and 3725, footnotes 5 and 6: The ^{1}H NMR and ^{13}C NMR data given in footnote 5 should be in footnote 6. Also, the ^{1}H NMR, ^{13}C NMR, and IR data given in footnote 6 should be in footnote 5. Thus, the corrected footnotes should read as follows:

(5) Anal. Calcd for $C_{23}H_{14}CrO_3$: C, 70.77; H, 3.61; O, 12.30. Found: C, 70.57; H, 3.56; O, 12.52. Mass spectrum, m/z 390 (M$^+$), 334 [(M − 2CO)$^+$] 306 [(M − 3CO)$^+$], 254 [(M − Cr − 3CO)$^+$], 52 (Cr$^+$, base peak), 28 (CO$^+$); ^{1}H NMR (60 MHz, CD$_2$Cl$_2$) δ 9.45 (m, 1 H), 8.65 (s, 1 H), 8.1 and 7.6 (m, 7 H), 5.75 (m, 5 H); ^{13}C NMR (50.31 MHz, CD$_2$Cl$_2$) δ 131.8, 131.0, 130.8, 129.0, 128.5, 128.1, 127.9, 126.1, 125.3, 125.0, 124.6, 108.6 (Cl′), 99.0 (C3′, C5′), 93.5 (C4′), 90.7 (C2′, C6′); IR (Et$_2$O) 1969, 1900 cm^{-1}.

(6) Anal. Calcd for $C_{23}H_{14}CrO_3$: C, 70.77; H, 3.61; Cr, 13.32. Found: C, 70.48; H, 3.68; Cr, 13.30. Mass spectrum, m/z 390 (M$^+$), 362 [(M − CO)$^+$], 334 [(M − 2CO)$^+$], 306 [(M − 3CO)$^+$], 254 [(M − Cr − 3CO)$^+$], 52 (Cr$^+$); ^{1}H NMR (60 MHz, CD$_2$Cl$_2$) δ 8.32 (s, 1 H), 7.60 (m, 9 H), 6.58 (m, 1 H), 6.15 (m, 1 H), 5.73 (m, 2 H); ^{13}C NMR (50.31 MHz, CD$_2$Cl$_2$) δ 138.4, 136.1, 133.2,