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.

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(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.

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(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,