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, $\lbrack C(Me){=}C(SiMe_3)\rbrack_n$. 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,

131.5, 130.8, 130.6, 128.7, 128.3, 127.9, 126.8, 126.6, 126.3, 105.7, 105.2, 93.2, 93.0, 90.9, 89.3.

Dynamics of Micellized Radical Pairs. Measurement of Micellar Exit Rates of Benzylic Radicals by Time-Resolved Flash CIDNP and Optical Spectroscopy [*J. Am. Chem. Soc.* **1983**, *105*, 6347–6349]. NICHOLAS J. TURRO,* MATTHEW B. ZIMMT, and IAN R. GOULD

Page 6348, column 2, first paragraph, line 4: the extrapolated values for k_{obsd} should read $(2.4 \pm 0.4) \times 10^5$ rather than $(2.4 \pm 0.4) \times 10^6$.

*Book Reviews**

Macromolecular Syntheses. Volume 8. Edited by Eli M. Pearce (Polytechnic Institute of New York). John Wiley & Sons, New York. 1982. ix + 112 pp. $32.50.

This volume maintains the same high quality of previous volumes of the series. It has lucid, detailed experimental procedures and reaction schemes, accompanied by copious cautionary notes, and contains syntheses covering a wide breadth of polymerization mechanisms and types, including both classical and novel examples of step-growth, condensation, and chain-growth addition. There are examples of anionic living polymerization and cyclopolymerizations, and solution polycondensation and interfacial polymerization techniques are described. The preparation of block, alternating, and graft copolymers using both free radical and anionic initiators, poly(imides), poly(amideimides), phosphazines, poly(L-lactide), and several polymer derivatives are presented. An interesting and useful procedure is the preparation of macroreticular polystyrene beads. This timely addition to the series can be highly recommended to anyone interested in polymer synthesis.

Richard D. Gilbert, *North Carolina State University*

Raman Spectroscopy in Biology: Principles and Applications. By Anthony T. Tu. John Wiley and Sons, New York. 1982. xvi + 448 pp. $65.00.

This book reviews and illustrates applications of Raman spectroscopy in numerous areas of biological investigation. Included are reviews of Raman studies of proteins, nucleic acids, lipids, carbohydrates, visual pigments, iron–sulfur proteins, and heme–proteins. These reviews are organized in separate chapters and clearly illustrate the biological information available from Raman spectral measurements. Each area has an introductory section which clearly describes the molecular vibrations which are studied and describes the sensitivity of the vibrations to environment and molecular structure and conformation. The various empirical relationships which have been used to quantitate the molecular structure dependence of Raman frequencies and intensities are also described.

This book will serve as a valuable introduction to biological Raman studies for the novice and can be used by the practicing Raman spectroscopist as a review of the recent results in a diverse series of biological systems. A nice feature of this book is the brief introductory section included in each chapter which clearly describes the biological problems under study. Chapters 1 and 2, which serve as the introduction to Raman theory and instrumentation, utilize a pictorial approach which is quite effective in describing the Raman polarizability tensor.

A weakness of the book is that it does not treat Raman fundamentals and theory in any depth and only rarely critically assesses the structural conclusions which derive from the Raman studies. A book which covers the biological aspects of Raman spectroscopy so well should have placed more stress on the fundamentals so the reader would have a better understanding of the information available from Raman scattering as well as its limitations.

Sanford A. Asher, *University of Pittsburgh*

Molecular Light Scattering and Optical Activity. By Lawrence D. Barron (University of Glasgow). Cambridge University Press, New York. 1983. xv + 408 pp. $69.50.

This book provides a unified theoretical treatment of processes originating in asymmetric response of bulk samples to left and right circularly polarized light; it covers not only natural optical rotation, circular dichroism, the Faraday effect, and magnetic circular dichroism but also Rayleigh and Raman optical activity (natural or induced by external electric or magnetic fields) and infrared vibrational optical activity.

The theory is formulated directly from a molecular light scattering model, by considering a light beam of arbitrary azimuth, ellipticity, and degree of polarization incident upon a lamina of the molecular medium, deriving expressions for the infinitesimal changes in intensity and polarization of the beam in terms of molecular response tensors, and then integrating over a finite path. A strong feature of this approach is the common framework provided for the discussion of different processes; for example, in the section on polarization phenomena in Rayleigh and Raman scattered light, the expressions given for the Stokes parameters of the scattered wave can be used to "derive explicit expressions, in terms of dynamic molecular property tensors, for the intensity and polarization of light scattered into any direction from an incident beam of arbitrary polarization by a gaseous, liquid, or solid medium, which can be transparent or absorbing, oriented or isotropic, and also optically active". The expressions are then specialized to particular cases of interest. In several cases (e.g., for natural optical rotation and circular dichroism) a complementary theoretical treatment based on calculation of the induced polarization and magnetization of the medium is also presented. A second strong feature of the book is the emphasis on symmetry arguments, beginning in the first chapter with a short section on spatial symmetry and optical activity and continuing with a 90-page chapter devoted primarily to parity, time reversal, and the behavior of molecular property tensors under these operations. The latter chapter also includes a discussion of the irreducible representations of the permutation group of *n* objects (ligands) and requirements for qualitative completeness of chirality functions.

The book is well organized and very well written. The first chapter provides a survey of different optical activity phenomena, starting with Arago's 1811 observation of colors in sunlight passed along the optic axis of a quartz crystal placed between crossed polarizers, and running through the observation of electric Rayleigh optical activity in gaseous methyl chloride (Buckingham and Shatwell, 1980) and magnetic-field induced infrared circular dichroism (Keiderling, 1981). In the second chapter, the necessary background material from electrodynamics, classical optics, and molecular quantum mechanics is presented; this chapter treats Maxwell's equations, static and dynamic multipole fields, the characterization of polarized light, the Hamiltonian for a molecule in an external field, perturbation theory for molecular polarizability tensors $\alpha_{\alpha\beta}$, electric-dipole magnetic-dipole polarizabilities $G_{\alpha\beta}$, and dipole–quadrupole polarizabilities $A_{\alpha,\beta\gamma}$, Placzek's theory, and the Herzberg–Teller approximation. In the third chapter, the explicit general expressions for the polarization and intensity of light scattered by a collection of molecules are derived; this development is followed by the chapter on symmetry operations and property tensors. The last four chapters are then devoted to specific applications of the general theory to natural electronic optical activity, magnetic electronic optical activity, natural vibrational optical activity, and magnetic Raman optical activity. Chapter 5 includes a discussion of static and dynamic coupling models of optical activity, with a section on exciton coupling, and the inherently chiral chromophore model. As stated in the preface, the illustrations (e.g., in Chapter 5, sections on the carbonyl chromophore and the quadrant and octant rules, the Co^{3+} chromophore, and hexahelicene) are used primarily to "illuminate the theory rather than to give an exhaustive explanation of the optical activity of any particular system".

Consistent with the author's description of the book as a "personal view of the theory of optical activity and related polarized light scattering effects", there are certain limitations in the scope of the work. For a discussion of experimental apparatus and of the experimental challenges encountered in obtaining the spectra, the reader must turn to the references provided. The Kerr effect falls naturally within the theoretical framework developed and it is included in the discussion; but circular polarization of luminescence is treated only briefly. Correlation functions are not used in the analysis.

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*Unsigned book reviews are by the Book Review Editor.