utilizing these and other synthons will be reported shortly

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Supplementary Material Available: General synthetic procedure, complete spectral data for all compounds synthesized, and a description of the structure determination (3 pages). Ordering information is given on any current masthead page.

Synthesis and Some Properties of Poly(diacetylene) (Polyenyne) Oligomers

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A large family of polymers with a polyenyne backbone is accessible through a solid-state polymerization of suitably substituted diacetylenes as depicted below:

$$\underset{\mathbf{1}}{RC\equiv C{-}C\equiv CR} \xrightarrow{h\nu} \underset{\mathbf{2}}{[{-}C\equiv CC(R){=}C(R){-}]_n} \qquad (1)$$

In this process, a single crystal of a diacetylene is essentially converted to a single crystal of a poly(diacetylene)[1] ("PDA"), a phenomenon observed only in one other case, the preparation of $(SN)_x$.[2] There are no reported procedures for the synthesis of well-characterized polyenyne itself (**2**, R = H).[3] The PDA's (**2**, R = long-chain ester, urethane, etc.) have recently received much attention, not only from a mechanistic point of view (polymerization via a diradical followed by a propagating carbene)[1] but due to potentially important technological aspects such as nonlinear optical properties in the solid state[4] and unusual chromotropic[5] and dichroic[6] effects in solution.

Meanwhile, over the last decade it was shown that practically all polymers possessing an unsaturated, conjugated backbone could be converted to electrical conductors[7] with electrical conductivities on the order of 1 to 10^2 S cm^{-1} (pure, Na-doped poly(acetylene) has a conductivity of 10^3 S cm^{-1}, $S = \Omega^{-1}$). The PDA's are a glaring exception; acceptor doping was found to enhance their conductivity by only a few orders of magnitude and iodine formed only a very weak charge-transfer complex with a PDA containing relatively small R substituents.[8]

In order to (1) make a *direct* comparison between the solid-state properties of nondegernate ground state, conjugated backbone, conducting polymers (e.g., poly-*p*-phenylene, poly(thiophene), etc.) and polyenyne and (2) ascertain what aspect of the above unusual properties of PDA's were intrinsic to their polyenyne backbone, we decided to employ a strategy of modeling the macromolecule (**2**, R = H) with monodisperse, fully characterized oligomers. The ultimate goal is to obtain a monodisperse polyenyne with a 50-carbon atom ("C_{50}") backbone.[9]

Here we report the successful preparation of suitably substituted C_6, C_{10}, C_{14}, C_{22}, and C_{30} polyenyne oligomers[10] and some preliminary, surprising properties. Other properties are currently being determined.[11]

Scheme I

$$(CH_3)_3CC\equiv CZnCl + ICH{=}CHCl \xrightarrow{i} (CH_3)_3CC\equiv CCH{=}CHCl \qquad (2)$$

$$(CH_3)_3CC\equiv CCH{=}CHCl + RC\equiv CMgX \xrightarrow{ii} \underset{C_6,\ R\,=\,t\text{-Bu}}{(CH_3)_3CC\equiv CCH{=}CHC\equiv CR} \qquad (3)$$

$i = (Ph_3P)_2PdCl_2$, ii = dpppNiCl$_2$; R = *t*-Bu orMe$_3$Si

The compounds in Table I were prepared according to Scheme I.

This "universal" scheme shows the preparation of C_6 as a typical example of the sequence of reactions employed for oligomer syntheses. Application of this scheme to the preparation of, for example, C_{14} would require the Grignard reagent of reaction 3 to have R = Me$_3$Si [$(CH_3)_3Si$] followed by removal[12] of this group from the "C_6-Me$_3$Si" product, deprotonation of the alkyne with methyl Grignard, conversion to the alkynyl zinc reagent with $ZnCl_2$, and coupling of two parts of this reagent with one of *trans*-diiodoethylene in the presence of i. Full experimental details are available.[12,13]

As can be seen from the Table, all new compounds were easily characterizable (IR, ^{1}H and ^{13}C NMR, elemental analysis). The only exception was C_{14}, it discolored upon standing and elemental analysis gave poor agreement with expected values.

The choice of *tert*-butyl end groups was based on the very high stability-conferring ability of this residue (as contrasted, for example, with a methyl of phenyl end group) in the preparation of the longest isolable and characterizable polyyne.[14,15] Whereas this moiety could influence the electronic properties of the smaller oligomers, it was not expected to have an important effect on the

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Table I. Properties of Polyenyne Oligomers

t-Bu-$(C{\equiv}C{-}CH{=}CH)_n$-$C{\equiv}C$-t-Bu	$E^n \equiv {}^1C_6$	$E,E^n \equiv {}^2C_{10}$	$E,E,E^n \equiv {}^3C_{14}$	$E,E,E,E,E^n \equiv {}^5C_{22}$	$E,E,E,E,E,E,E^n \equiv {}^7C_{30}$
MP, °C	69–72	118–120	155–156	220 dec	204 dec
^{1}H NMR ($CDCl_3$)	1.14 (s), 5.75 (s)	1.24 (s), 5.98 (s)	1.25 (s), 6.00 (s), 6.09 (s)	CS_2/acetone-d_6, 1.23 (s), 5.92 (s), 6.08 (br), 6.10 (br)	not soluble enough
^{13}C NMR ($CDCl_3$), 300 or 500 mHz	28.06, 30.88, 77.73, 102.33, 120.01	28.24, 30.82, 77.89, 92.22, 104.88, 119.05, 121.84	28.28, 30.78, 77.82, 92.22, 94.22, 105.47, 118.83, 120.65, 122.48	not soluble enough	not soluble enough
mass spectrum	calcd 188, found 188	calcd 238, found 238	calcd 288, found 288	calcd 388, found 388	calcd 488, found 488
UV–vis (hexanes) ($\epsilon \times 10^4$), nm	275 (2.77), 261 (3.07)	333 (5.00), 312 (4.48)	374 (5.53), 347 (6.05)	418 (sh) (4.98), 402 (sh) (6.58), 385 (7.98)	414 (9.10), 436 (sh) (7.44), 454 (sh) (4.87), (benzene)
elemental analysis					
calcd	C, 89.29; H, 10.71	C, 90.70; H, 9.30	C, 91.61; H, 8.39	C, 92.74; H, 7.26	C, 93.40; H, 6.60
found	C, 88.94; H, 10.46	C, 90.58; H, 9.43	C, 90.69; H, 8.45	C, 92.60; H, 7.26	C, 92.64; H, 6.72
IR (KBr), cm^{-1}	3020 w, 2980 s, 2920 m, 2890 m, 2860 m, 2220 m, 2170 w, 1455 m, 1445 m, 1362 m, 1292 m, 1275 m, 1250 m, 1200 m, 935 s	3022 m, 2960 s, 2920 m, 2860 m, 2210 m, 2160 w, 1755 m, 1455 m, 1360 m, 1295 s, 1255 m, 1205 m, 1285 w, 930 s, 845 m	3038 m, 2962 s, 2925 m, 2900 m, 2860 m, 2220 m, 2170 w, 1755 m, 1480 m, 1460 m, 1450 m, 1370 m, 1305 s, 1290 m, 1275 m, 1260 m	3030 m, 2960 m, 2920 m, 2860 w, 2210 w, 2150 w, 1750 m, 1455 m, 1362 m, 1305 m, 1280 m, 1255 m, 1215 m, 1200 m, 930 s	3032 m, 2970 m, 2924 m, 2854 w, 2218 w, 1747 m, 1635 m, 1454 m, 1315 m, 1219 m, 1202 m, 933 s, 698 m

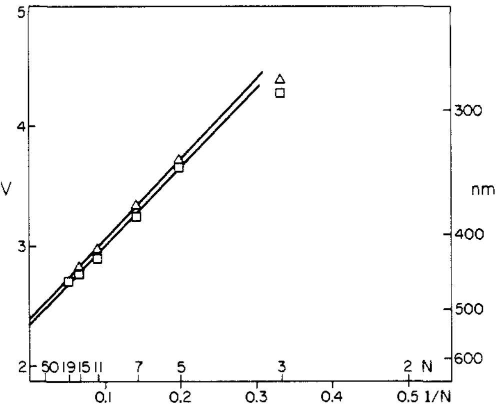

Figure 1. Energy of longest wavelength absorption of polyenyne oligomers as a function of the inverse of the number of unsaturated bonds; (△) in hexane solution; (◇) in benzene solution.

longer chains; its main function is ascribable to steric inhibition of polymerization.

In Figure 1 we depict the electronic properties of the di-*tert*-butyl polyenynes as determined from ultraviolet–visible spectroscopy in solution.[10] The polyenynes are solvatochromic and show a bathochromic shift of ca. 20 nm in going from hexane to benzene or chloroform (see Figure 1). Extrapolation to the infinite chain yields an absorption maximum of 532 nm. Maximum absorption of PDA's is 650 nm, although they also exhibit a peak at 540 nm. If one assumes that the 650-nm peak is due to some unusual solid-state effect,[16] then the extrapolated value of 532 nm is in remarkable agreement with the polymer absorption at 540 nm.

The C_6 and C_{10} oligomers are white, crystalline solids, the C_{14} oligomer is barely perceptibly yellow and the C_{22} and C_{30} oligomers are deep yellow. Surprisingly, with the exception of C_{14} (vide supra), none of the oligomers is unstable to the atmosphere. With the exception of C_{22} and C_{30} the polyenynes have sharp melting points [differential scanning calorimetry (DSC)] and are suluble in all organic solvents. C_{22} and C_{30} can be recrystallized from hot benzene; C_{22} is soluble in cold CS_2 and sparingly soluble in THF and hexane. C_{30} is very sparingly soluble in THF.

The thermal behavior of C_{22} is quite unusual, it undergoes a precipitous exothermic decomposition at 220 °C which corresponds to a weight loss of 38% (a slight excess over loss of two *tert*-butyl groups). The product of this decomposition is a black, electrically insulating solid whose structure has not yet been determined. The C_{30} oligomer exhibits like behavior at 204 °C.

Whereas a C_{22} polyene, carotene, is easily doped with iodine[17] to give infrared and Raman spectra very similar to those of iodine-doped PA, C_{22} does not react with iodine over a period >24 h. Preliminary results showed that attempts to n dope a film of C_{22} with sodium naphthalenide in ether 18-crown-6 did not show an observable[18] decrease in its resistivity, as determined by a two-probe measurement; however, preliminary experiments indicate that direct doping with Cs metal may be possible.[19] The same type of measurement during attempted p doping with AsF_5

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[16] Bloor (Bloor, D., private communication), found that strain effects in the solid state cause the appearance of the long-wavelength absorption of PDA's which normally lack this peak. However, *solutions* of poly-3-BCMU in hexane–chloroform *are blue* and have *a maximum absorption peak at 650 nm*. Therefore, we believe that in this case simple extrapolation as done in Figure 1 is apparently not warranted. Highly sophisticated spectroscopy is currently being done in collaboration with Professor B. Kohler (U.C. Riverside) to shed more light on this problem.

[17] Harada, I.; Furukawa, Y.; Tasumi, N.; Shirakawa, H.; Ikeda, S. *J. Chem. Phys.* **1980**, *73*, 4746.

[18] A film of C_{22} was deposited over two microelectrodes. The resistivity was found to be $>10^6$ Ω cm (the limit of our instrumentation in the drybox); upon dipping into the green reducing solution, the resistivity decreased to 10^4 Ω cm but when the film was lifted out of the solution its resistivity increased to the initial value upon solvent evaporation, implying that the observed decrease in resistivity was due to electrolytic conductance of the sodium naphthalenide.

[19] Moses, D.; Bitler, S. P., unpublished observations.

showed no decrease in resistivity but a change in color to green and attendant changes in its FTIR spectrum typical of a doped polyene.[16]

Acknowledgment. We are indebted to the National Science Foundation for support of this work through Grant DMR82-15176 from the Polymers Section. We would also like to thank Dr. Hugh Webb for mass spectroscopy and Dr. David Vachon for FT NMR spectroscopy.

Registry No. $t\text{-BuC}\equiv\text{CCH}=\text{CHC}\equiv\text{CBu-}t$, 102745-35-7; $t\text{-Bu(C}\equiv\text{CCH}=\text{CH)}_2\text{C}\equiv\text{CBu-}t$, 102745-36-8; $t\text{-Bu(C}\equiv\text{CCH}=\text{CH)}_3\text{C}\equiv\text{CBu-}t$, 102745-37-9; $t\text{-Bu(C}\equiv\text{CCH}=\text{CH)}_5\text{C}\equiv\text{CBu-}t$, 102745-38-0; $t\text{-Bu(C}\equiv\text{CCH}=\text{CH)}_7\text{C}\equiv\text{CBu-}t$, 102745-39-1.

*Book Reviews**

Solubility Data Series. Volumes 21 and 22. Volume 21: Edited by C. L. Young and P. G. T. Fogg. Volume 22. Edited by T. Mioduski and M. Salomon. Pergamon Press: Oxford and New York. 1985. Volume 21: xvi + 344 pp. $100.00. ISBN 0-08-026177-9. Volume 22: xx + 398 pp. $100.00. ISBN 0-08-030709-4.

In the continuation of this mammoth series of compilations of critically evaluated data on solubilities, Volume 21 reports on ammonia, amines, phosphine, arsine, stibine, silane, germane, and stannane in organic solvents and Volume 22 reports on scandium, yttrium, lanthanum, and lanthanide halides in nonaqueous solvents. Characteristically for the series, not only are numerical data given but much auxiliary information bearing on the reliability of the figures. Source and purity of materials used, and the methods of determination followed, are described, and estimates of errors by the compilers are reported. These volumes will probably remain the last word on the subjects for a long time.

Verzeichnis der Hochschullehrer und Forschungsinstitute für Chemie in der Bundesrepublik Deutschland. By ADUC and GDCh. VCH Verlagsgesellschaft: Weinheim and Deefield Beach, FL. 1985. 350 pp. DM 180.00. ISBN 3-527-26125-7.

The bulk of this book is a listing of chemists in Western Germany, in the style of the "ACS Directory of Graduate Research" and "Chemical Research Faculties, an International Directory". The arrangement is alphabetical according to location, beginning with Aachen. Indexes of individual names and of subject area supplement the main portion. The latter index is especially useful, and the presence of one in the domestic ACS Directory would be a great help to editors. This book differs from the ACS Interntional Directory in having telephone numbers and in listing a few more publications.

Inorganic Chromatographic Analysis. Edited by John C. MacDonald (Fairfield University). John Wiley & Sons: New York. 1985. xiii + 450 pp. $65.00. ISBN 0-471-86263-0.

This book is the latest addition to the prestigious "Chemical Analysis" series of monographs on analytical chemistry and its applications. The book is intended to provide an introduction to modern inorganic chromatographic analyses and to direct the prospective user to the most useful procedures. Throughout the 10 chapters, the knowledge and experience of each contributing author are reflected in a logical and concise treatment. The book is very readable and the references, compiled at the end of each chapter, cover the chemical literature through about 1982.

The book begins with a brief introduction of the different chromatographies, which include adsorption, partition, size exclusion, and ion-exchange chromatography. Chapter 2 discusses the theory of chromatography and factors influencing the distribution of solute molecules between the mobile and stationary phases. Basic instrumentation for gas chromatography and high-performance liquid chromatography are presented in Chapters 3 and 4, respectively. The following three chapters are devoted to separations of inorganic and organometallic compounds using gas chromatography, high-performance liquid chromatography, and thin-layer chromatography. Ion exchange in radiochemistry and ion chromatography are covered in Chapters 8 and 9. The remaining chapter deals with computer online database literature searching and includes examples of computer printouts of literature searches in inorganic chromatography.

This book contains many of the recent advances in inorganic chromatographic analysis. It is a valuable addition to every analytical chemist's library and a useful reference book for a graduate course on chemical separations.

William E. Acree, Jr., *Kent State University*

Chromatography, The State of the Art. Volumes I and II. Edited by H. Kalász and L. S. Ettre. Adadémiai Kiadó: Budapest. 1985. xi + 903 pp. $75.00. Volumes I and II: ISBN 963-05-4081-9.

Proceedings of the Budapest Chromatography Conference, Budapest, Hungary, 1983. In English. Two volumes containing 60 typescript papers by leading chromatographers and biochemists of Eastern Europe and many other countries. Many of the papers report research in biochemistry in which chromatography has played an important part. More than a dozen describe separation of proteins and peptides. Five papers are on separation of amines and amino acids and eight are on drugs and metabolites. Papers on chromatography itself give an interesting picture of the state of the art in Eastern Europe. Eight papers cover GC. Many kinds of column liquid chromatography, including ion, precipitation chromatography, and capillary LC, are reported. There are several advanced applications of thin-layer chromatography, as might be expected, since Hungary is a center for sophisticated overpressure TLC apparatus. Although the range of subjects is very broad, readers with a special interest can scan the subject or author index to find theirs. Titles in the table of contents are also grouped by general category. References to Eastern European literature will be useful to some. These volumes will be valuable additions to chromatography and biochemistry libraries.

J. G. Atwood, *The Perkin-Elmer Corp.*

An Introduction To Macromolecules. By Leo Mandelkern (Florida State University). Springer-Verlag: New York. 1983. xi + 162 pp. $18.90. ISBN 0-387-90796-3 (hardcover); 0-540-90796-3 (paperback).

Polymer chemistry is fast becoming recognized as one of the most important areas of modern chemistry for both its practical considerations (about half of all chemists work in this field) and the biological, medical, and theoretical aspects of this realm of human endeavor. This excellent book by Professor Mandelkern brings some of these important considerations into sharper focus. There are many polymer textbooks available today, but this small book meets an important need. Most polymer texts are aimed at the organic chemistry areas, with almost no consideration of the physical aspects of the macromolecules. Some other texts are geared more toward the engineers, with very little organic chemistry presented. In actual fact, a polymer chemist needs to know much about both aspects concerning macromolecules. Although it is true that there are specialized books available in almost every conceivable area involving macromolecules, most of these are far too detailed for use in an introductory polymer chemistry course. Professor Mandelkern's book makes no attempt to span all these areas but concentrates on an excellent overview of the physical chemistry of polymers and then explains how these molecular properties exert their effect on living systems in the last third of the book. Obviously many details are not covered, but this was not the purpose of the book. In my opinion, this book should be a valuable supplementary text for other polymer books which tend to omit the areas covered. It should also prove useful as an optional text for the basic courses in organic, physical, and biological chemistry.

Charles G. Gebelein, *Youngstown State University*

Free-Electron Lasers. By Thomas C. Marshall (Columbia University). Macmillan Publishing Company: New York. 1985. xii + 191 pp. $24.95. ISBN 0-02-948620-3.

Since the first stimulated-scattering experiments at Stanford only 10 years ago, the conceptual and practical development of the free-electron laser as a powerful source of electromagnetic radiation has been extremely rapid. Within the next few years, chemists will begin to acquire access to these devices for spectroscopic and photochemical research. The optical power and tunability of FELs in the far-infrared and soft X-ray regions is truly unique, while their efficiency and power in the ultraviolet

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*Unsigned book reviews are by the Book Review Editor.