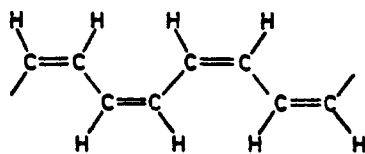


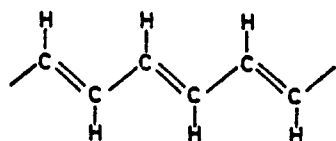
Table I. Conductivity of Polycrystalline Polyacetylene and Derivatives (As-Grown Films)

Material	Conductivity, σ (Ω^{-1} cm $^{-1}$) (25 °C)
<i>cis</i> -(CH) $_x$ ^{a,b}	1.7×10^{-9}
<i>trans</i> -(CH) $_x$ ^{a,b}	4.4×10^{-5}
<i>trans</i> -[(CH)(HBr) $_{0.04}$] $_x$	7×10^{-4}
<i>trans</i> -(CHCl $_{0.02}$) $_x$	1×10^{-4}
<i>trans</i> -(CHBr $_{0.05}$) $_x$ ^c	5×10^{-1}
<i>trans</i> -(CHBr $_{0.23}$) $_x$ ^{b,c}	4×10^{-1}
<i>cis</i> -[CH(ICI) $_{0.14}$] $_x$	5.0×10^1
<i>cis</i> -(CHI $_{0.25}$) $_x$	3.6×10^2
<i>trans</i> -(CHI $_{0.22}$) $_x$ ^{b,c}	3.0×10^1
<i>trans</i> -(CHI $_{0.20}$) $_x$ ^b	1.6×10^2
<i>cis</i> -[CH(I $_{0.15}$) $_x$]	4.0×10^2
<i>trans</i> -[CH(I $_{0.12}$) $_x$]	1.2×10^2
<i>trans</i> -[CH(AsF $_5$) $_{0.03}$] $_x$	7×10^1
<i>trans</i> -[CH(AsF $_5$) $_{0.10}$] $_x$ ^b	4.0×10^2
<i>cis</i> -[CH(AsF $_5$) $_{0.14}$] $_x$	5.6×10^2
<i>trans</i> -[Na $_{0.28}$ (CH)] $_x$	8×10^1

^a H. Shirakawa, T. Ito, and S. Ikeda, unpublished results; see ref 1-3. ^b Composition obtained by chemical analysis from Galbraith Laboratories, Inc. (sum of all elements is ~ 99.8 -100.1%). ^c See ref 1-3.



(1)



(2)

(CH) $_x$ (2) polymer were doped with controlled amounts of electron-attracting species such as chlorine, bromine, iodine, or AsF $_5$, their electrical conductivity could be systematically and controllably varied over a wide range, with up to 10^{11} overall increase in conductivity. The most highly conducting films exhibited a conductivity at room temperature of several hundred Ω^{-1} cm $^{-1}$ —by far the highest conductivity observed for any covalent organic polymer. The (CH) $_x$ polymer films used in the studies were prepared using the techniques developed previously by Shirakawa et al.⁴

We wish to report that this doping phenomenon, previously studied primarily with *trans*-(CH) $_x$, also occurs, possibly to an even greater extent, with *cis*-(CH) $_x$, and that for both isomers significantly higher conductivities than those previously observed can now be obtained (Table I). New electron-attracting dopants which give remarkably high conductivities with both isomers have been identified and studied (Table I). In addition, we have succeeded in making conducting films with an electron donor such as sodium as dopant.

Four platinum wires were attached to films of *cis*- or *trans*-(CH) $_x$ by means of Electrodag and were connected to an apparatus for measuring their dc conductivity by the four-probe method. The films were then treated with the vapor of the dopant at room temperature in vacuo for 3-4 h, and their resistance was monitored at intervals. Final compositions of

Table II. Conductivity, σ (Ω^{-1} cm $^{-1}$), at Room Temperature

Compd	Polycrystalline (compressed pellets), σ_{av} of $\sigma_{ }$ and σ_{\perp}	Single crystal
(SN) $_x$	~ 20	$\sigma_{ } = 3.7 \times 10^3$
(SNBr $_{0.4}$) $_x$	~ 30 -300	$\sigma_{ } = 3.8 \times 10^4$
(TTF)(TCNQ)	~ 10	$\sigma \sim 3$ - 7×10^2
<i>cis</i> -[CH(AsF $_5$) $_{0.14}$] $_x$	5.6×10^2 (as-grown film)	Unknown

the doped (CH) $_x$ were determined either by the elemental analysis of a piece of reference film placed just below the film whose conductivity was being measured and/or by the increase in weight of the reference film during doping. The Na-doped films were prepared by treating the polymers with a solution of sodium naphthalide, Na $^+$ (C $_{10}$ H $_8$) $^-$, in THF, whereupon electron transfer from the naphthalide radical anion to the (CH) $_x$ occurred. The results of a number of experiments are given in Table I.

The more recent iodination experiments involving *trans*-(CH) $_x$ yield significantly improved electrical properties ($\sigma = 160 \Omega^{-1}$ cm $^{-1}$) as compared with earlier results ($\sigma = 30 \Omega^{-1}$ cm $^{-1}$). This increase may be related to a slower rate of iodination which might be expected to lead to more uniform doping throughout the films. Detailed studies of the effects of film thickness, reaction rate, etc., are underway.

The conductivity of iodinated films is electronic. No evidence of any significant increase in the resistance of a film was observed even after passing enough current through the sample over a time period such that the integrated charge exceeded by a factor of 10 the amount needed to cause complete polarization, if conduction were by an ionic mechanism. Preliminary experiments indicate no significant change in the conductivity of the two films tested to date, [(CH)I $_{0.19}$] $_x$ and [CH(AsF $_5$) $_{0.10}$] $_x$, when they were held in vacuum at room temperature for 1 week. The conductivity of films decreases in air during several days.

Electrical and optical studies² indicate that (CH) $_x$ films can be chemically doped with electron-attracting (acceptor) or electron-donating (donor) species in a manner analogous to that found for simple classical semiconductors such as silicon. The conductivity progressively increases with doping. With certain dopants, e.g., I $_2$, AsF $_5$, etc., a semiconductor-metal transition occurs at a few mole percent dopant concentration to give flexible films of organic metals having a very high room temperature conductivity (Table I).²

As a result of the extreme sensitivity of "pure" (CH) $_x$ to impurities, we expect that the intrinsic conductivity of both the *cis* and *trans* isomers is probably considerably smaller than the values given in Table I. This is supported by the observation that exposure of *trans*-(CH) $_x$ to vapor of the donor, NH $_3$, causes the conductivity to fall more than four orders of magnitude (to $< 10^{-9} \Omega^{-1}$ cm $^{-1}$) without detectable weight increase. Subsequent reaction of the compensated film with AsF $_5$ brings the conductivity back up to metallic levels.

It has been known for some time that treatment of a fairly wide variety of compounds such as (CH) $_x$ powder,⁵ polyphenylacetylene,⁶ polycyclic hydrocarbons,⁷ glyoximate,⁸ and phthalocyanine⁹ metal complexes, (SN) $_x$,¹⁰ etc., with an electron-withdrawing species, usually iodine, may result in an increase of conductivity of many orders of magnitude, but the final room temperature conductivity obtained with most single crystals and with all polycrystalline material, with the exception of (SN) $_x$ derivatives, is still very small. From Table I it can be seen that, when (CH) $_x$ is doped with a number of different species, extraordinarily large increases in conductivity

Table III. Conductivity Adjusted for Density

Material	Density, d (g cm ⁻³)	Conductivity (vol), σ (Ω^{-1} cm ⁻¹) (25 °C)	Conductivity (wt), σ/d (cm ² Ω^{-1} -(g ⁻¹)) (25 °C)
Cu	8.92	5.8×10^5	6.5×10^4
Au	19.3	4.1×10^5	2.1×10^4
(SNBr _{0.4}) _x	2.67	3.8×10^4	1.4×10^4
Fe	7.86	1.0×10^5	1.3×10^4
(SN) _x	2.30	3.7×10^3	1.6×10^3
Hg	13.6	1.0×10^4	7.4×10^2
<i>cis</i> -[(CH)(AsF ₅) _{0.14}] _x	0.8	5.6×10^2	7.0×10^2

are observed in certain cases—ca. 10^{11} increase when *cis*-(CH)_x is converted to *cis*-[(CH)(AsF₅)_{0.14}]_x. Furthermore, *surprisingly large room temperature conductivities are obtained with several dopants*. Some of the (CH)_x derivatives, even in the form of polycrystalline, uncompressed, nonaligned films, have an electrical conductivity much greater than polycrystalline compressed pellets of (SN)_x,¹¹ (TTF)-(TCNQ),¹² etc. (Table II). Indeed, the conductivity of *cis*-[(CH)(AsF₅)_{0.14}]_x is identical with that commonly found for single crystals of (TTF)(TCNQ) (Table II). This strongly suggests that aligned films of (CH)_x derivatives should have still higher conductivities.

The highly conducting polymers formed from (CH)_x and electron-withdrawing species may be charge-transfer π complexes of the type believed to be formed during the halogenation of olefins. Stable colored compounds which may be charge-transfer and/or carbonium ion complexes of this type have been obtained by the action of bromine on certain substituted ethylenes.¹³ These latter observations suggest that the substances formed from (CH)_x and electron-attracting species may consist of a positively charged (CH)_x chain acting as a polycation with appropriate halogen, etc., anions situated at intervals adjacent to the chain.

Although the resistivity (ρ) of a material is usually defined on a volume basis, it can also be defined on a mass basis (ρd) where d is the density. Since the bulk density of the (CH)_x derivatives obtained from the dimensions and weight of a film is considerably smaller (~ 0.5 – 1 g cm⁻³) than that of most metals, the conductivity adjusted for density of a material such as *cis*-[(CH)(AsF₅)_{0.14}]_x is comparable with that of many metals (Table III).

Films of *cis*-(CH)_x doped with AsF₅ have been used as substitute "wires" in simple electrical circuits. For example, such films with contacts ~ 1 cm apart having a weight of ~ 10 mg will carry sufficient current to cause a flashlight bulb to glow brightly when connected to two 1.5-V flashlight batteries.

Considering possible polyacetylene derivatives, replacement of some or all of the hydrogen atoms in (CH)_x with organic or inorganic groups, copolymerization of acetylene with other acetylenes or olefins, and the use of different dopants should lead to the development of a large new class of conducting organic polymers with electrical properties that can be controlled over the full range from insulator to semiconductor to metal.

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References and Notes

- H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
- C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).
- M. Akhtar, C. K. Chiang, M. J. Cohen, J. Kleppinger, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, J. Milliken, M. J. Moran, D. L. Peebles, and H. Shirakawa, *Ann. N.Y. Acad. Sci.*, in press.
- H. Shirakawa and S. Ikeda, *Polym. J.*, **2**, 231 (1971). H. Shirakawa, T. Ito and S. Ikeda, *ibid.*, **4**, 460 (1973). T. Ito, H. Shirakawa, and S. Ikeda, *J.*

- Polym. Sci., Polym. Chem.*, **12**, 11 (1974); **13**, 1943 (1975). See also M. Hatano, S. Kambara, and S. Okamoto, *J. Polym. Sci.*, **51**, S-26 (1961).
- D. J. Berets and D. S. Smith, *Trans. Faraday Soc.*, **64**, 823 (1968).
- G. M. Holob and P. Ehrlich, *J. Polym. Sci., Polym. Phys.*, **15**, 627 (1977).
- S. B. Mainthia, P. L. Kronick, H. U. E. F. Chapman, and M. M. Labes, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **4**, No. 1 (1963); H. Akamatu, H. Inokuchi, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **29**, 213 (1956); H. Akamatu, Y. Matsunaga, and H. Kuroda, *ibid.*, **30**, 618 (1957); T. Uchida and H. Akamatu, *ibid.*, **34**, 1015 (1961); J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).
- H. Endres, H. J. Keller, and R. Lehmann, *Inorg. Nucl. Chem. Lett.*, **11**, 769 (1975); J. S. Miller and C. H. Griffiths, *J. Am. Chem. Soc.*, **99**, 749 (1977); A. S. Foust and R. H. Soderberg, *ibid.*, **89**, 5507 (1967); A. E. Underhill, D. M. Watkins, and R. Pethig, *Inorg. Nucl. Chem. Lett.*, **9**, 1269 (1973); T. J. Marks, D. F. Webster, S. L. Ruby, and S. Schultz, *J. Chem. Soc., Chem. Commun.*, 444 (1976); A. Gleizes, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 3545 (1975).
- J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, *J. Am. Chem. Soc.*, **99**, 286 (1977); T. J. Marks, *Ann. N.Y. Acad. Sci.*, in press.
- C. K. Chiang, M. J. Cohen, D. L. Peebles, A. J. Heeger, M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, and M. J. Moran, *Solid State Commun.*, **23**, 607 (1977); W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Lett.*, **38**, 1305 (1977).
- M. M. Labes, *Pure Appl. Chem.*, **12**, 275 (1966).
- L. B. Coleman, Ph.D. Thesis, University of Pennsylvania, 1975.
- R. E. Buckles and N. A. Meinhardt, *J. Am. Chem. Soc.*, **74**, 1171 (1952); R. E. Buckles and W. D. Womer, *ibid.*, **80**, 5058 (1958).
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Protonation and Ionization of 4-Chlorocyclohexene in Superacid. A Fast 1,2-Hydride Shift in the 4-Cyclohexenyl Cation

Sir:

Recently we reported the ring contraction of the 3-cyclohexenyl cation (**1**), generated from 3-chlorocyclohexene (**2**), to the 1-methylcyclopentenyl cation (**3**) and measured the rate of this transformation in FSO₃H-SbF₅ (4:1)-SO₂FCl solution.¹ It is conceivable that the first step of this reaction is the formation of the 4-cyclohexenyl cation (**4**) from **1**, by a 1,2-hydride shift. This same transformation is involved in the isotope scrambling observed in a sample of **1** labeled with deuterium.² The scrambling occurred at a temperature (-65 °C) much lower than that at which the rate of ring contraction (**1** \rightarrow **3**) becomes reasonably fast (-20 °C); by extrapolation it was estimated that $k_{-1} \approx 10^4 k_2$ (Scheme I). At the same time, since none of the homoallylic ion **4** was ever evidenced¹⁻³ in equilibrium with **1**, it follows that, in Scheme I, $k_{-1} \gg k_1$.

Generation of the 4-cyclohexenyl cation (**4**) from various precursors (**5**) in superacid solutions has been attempted before.³ In each case, the ring-contracted isomer **3** was the only

Scheme I

