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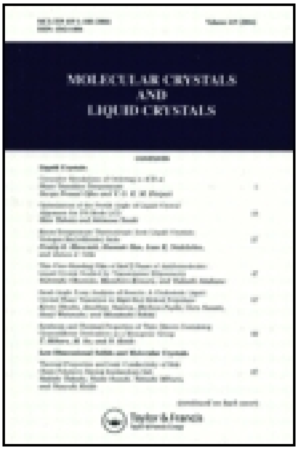

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Synthesis and Properties of Polyacetylene

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Synthesis and Properties of Polyacetylene

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This paper presents an introductory review on synthesis and properties of polyacetylene, a typical semiconducting and conducting organic polymer. Electrical conductivity of polyacetylene can be tailored by an appropriate chemical and/or electrochemical doping with electron accepting or electron donating reagents, spanning the range of insulators (10^{-12} S/cm) and metals (10^5 S/cm).

1. INTRODUCTION

Polyacetylene is the simplest linear synthetic polymer. Fundamental unit consists from one carbon and one hydrogen atoms, as has been called simply $(CH)_x$. Each carbon is σ bonded by sp^2 hybrid orbital to one hydrogen and two adjacent carbon atoms to form a planar chain molecule. The remaining fourth valence electron of the carbon atom is in P_z orbital, π electron, which lies perpendicular to the molecular plane. Thus, the molecule forms a quasi-one-dimensional lattice of the π electrons. Such polymers have been the subject of many theoretical investigators on the electronic structure and bond alternation. According to the simple Hückel model, it was considered that the longer the chain, the bond lengths tend to become equal. If this is true, one would expect that the linear conjugated polymer should provide metallic properties, because the highest occupied level of the π electron band is adjacent to the lowest unoccupied level with zero band gap to form half filled metallic band.

By later theoretical works, however, it was suggested that there is an alternation in carbon-carbon bond length (dimerization) throughout the conjugated chain, even if it becomes infinitely long. As a consequence of the bond alternation, the electronic energy states of the π electrons is separated into two energy bands, the lower band being full and the upper one empty.

Such band structure is the same as those found in inorganic semiconductors such as silicon and germanium. Since the magnitude of the band gap depends on the degree of the bond alternation (dimerization), polyacetylene was expected to be semiconductor to insulator in its electrical property.

Experimentally, this was proved by Hatano *et al.*[1] who studied electrical and magnetic properties of polyacetylene powder in a compressed pellet. Because of its intractability, it remained a material of limited interest only to few polymer scientists. However, a breakthrough was achieved by the formation in the form of flexible silvery films by a direct polymerization of acetylene gas on the surface of concentrated soluble catalyst solution.[2] In 1977, it was found that the semiconducting or insulating silvery films of polyacetylene exhibited a dramatic increase in electrical conductivity when doped with various donors and acceptors.[3-6] The doped polyacetylene has attracted the increasing attention because of its unusual phenomena on the electrical and magnetic properties of the molecular systems.

2. SYNTHESIS OF POLYACETYLENE FILMS

Polyacetylene can be prepared by the catalytic polymerization of acetylene by various kinds of Ziegler-Natta catalysts, such as $TiCl_4$-$Al(C_2H_5)_3$, $TiCl_3$-$Al(C_2H_5)_3$, and $Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$, in which the last combination has been used extensively because it gives a crystalline polymer and it is possible to prepare polyacetylene in the form of lustrous silvery films with thickness varying from 10^{-5} to several mm.

In a typical preparative experiment, the catalyst is prepared in a glass reactor under flow of inert gas by adding 20 ml of toluene (solvent), 3.4 ml (0.01 mol) of $Ti(OC_4H_9)_4$ (titanium tetrabutoxide), and 4.1 ml (0.04 mol) of $Al(C_2H_5)_3$ (triethylaluminium) in this order at Dry Ice temperature (ca. −78°C) with stirring [(a) in Figure 1]. The mixture is aged at room temperature for 30 min and then cooled to Dry Ice temperature and degassed under reduced pressure for several minutes. Polyacetylene films are prepared by wetting the inside wall of the glass reactor with the Ziegler-Natta catalyst solution by rotating the flask (b). Then acetylene gas is admitted in the reaction flask at any pressure below one atmosphere (c). The polymerization of acetylene occurs instantaneously on all surfaces which have been wet by the catalyst solution to form polyacetylene film.

Film thickness can be varied by the pressure of acetylene and by the time of acetylene feed. The polymerization can be interrupted by evacuation of acetylene. The films are purified by extensive washing with purified toluene. To avoid oxi-

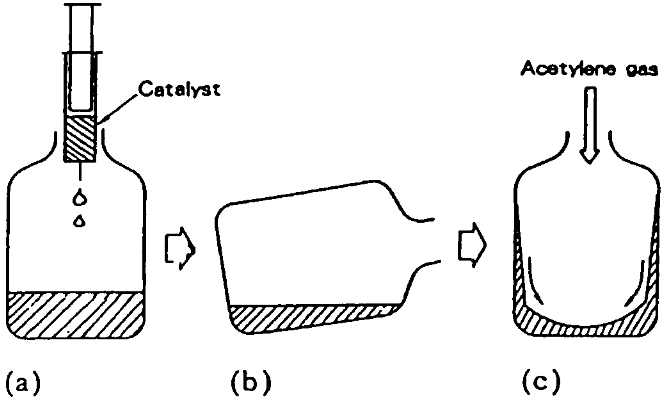

FIGURE 1 Acetylene polymerization for film synthesis.

dation, the films should be stored and treated under highly purified inert gas or under high volume.

3. MOLECULAR STRUCTURE AND PROPERTIES OF POLYACETYLENE

Polyacetylene has two isomeric forms, *trans* and *cis*, as shown in Figure 2, or as a mixture of the two forms depending on the preparative conditions. Thus, if polymerization is carried out at Dry Ice temperature, the film containing more than 85% of *cis* isomer. On the other hand, if a temperature higher than 150°C is used for the polymerization, the film is formed as *trans* isomer. With the intermediate temperature polymerization, the film has a mixture of the two isomers increasing *trans* isomer with increasing temperature.

The *cis* isomer can be converted to the more thermodynamically stable *trans* one on heating to 150–200°C for 30 min under vacuum or inert gas.[7] The films consist of randomly oriented fibrils as shown in Figure 3 (fiber-like crystals, typical diameter of 200 Å) which are highly crystalline extended chain bundles.[2,8] Bulk density is 0.3–0.5 g/cm^3 depending upon the preparative conditions, which is compared with 1.15 g/cm^3 of the fibril density as obtained by flotation method. This shows that the polymer fibrils fill only about one-third of the total volume of the films. Because of its unique solid structure, the film has a quite high surface area of 40–60 m^2/g.

Both *cis* and *trans* polyacetylene films are flexible and *cis* film can be stretched up to 3 times its original length with a combined mechanical and thermal treatment.[8] Since the linear chain of polyacetylene molecules are arranged along the longitu-

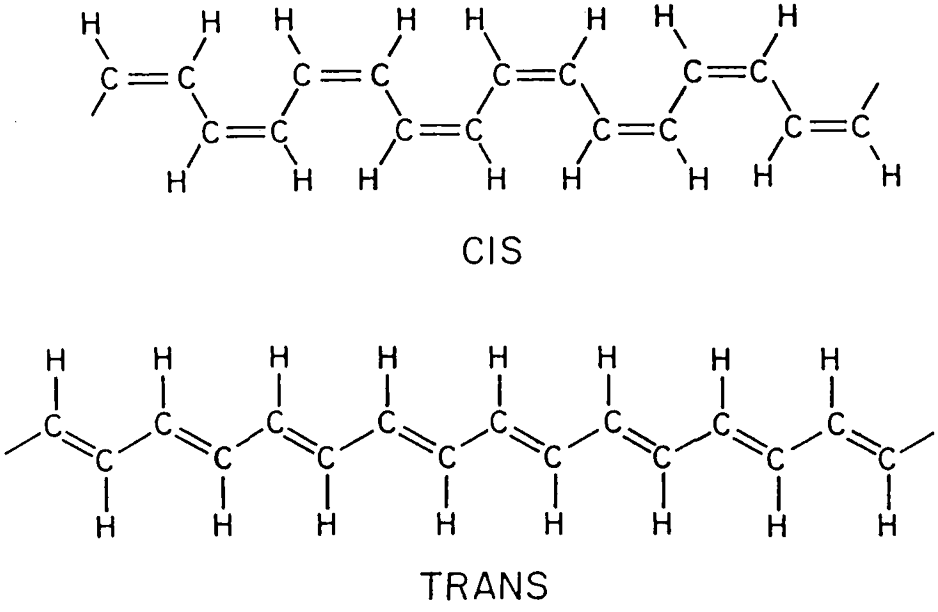

FIGURE 2 Isomeric forms of polyacetylene.

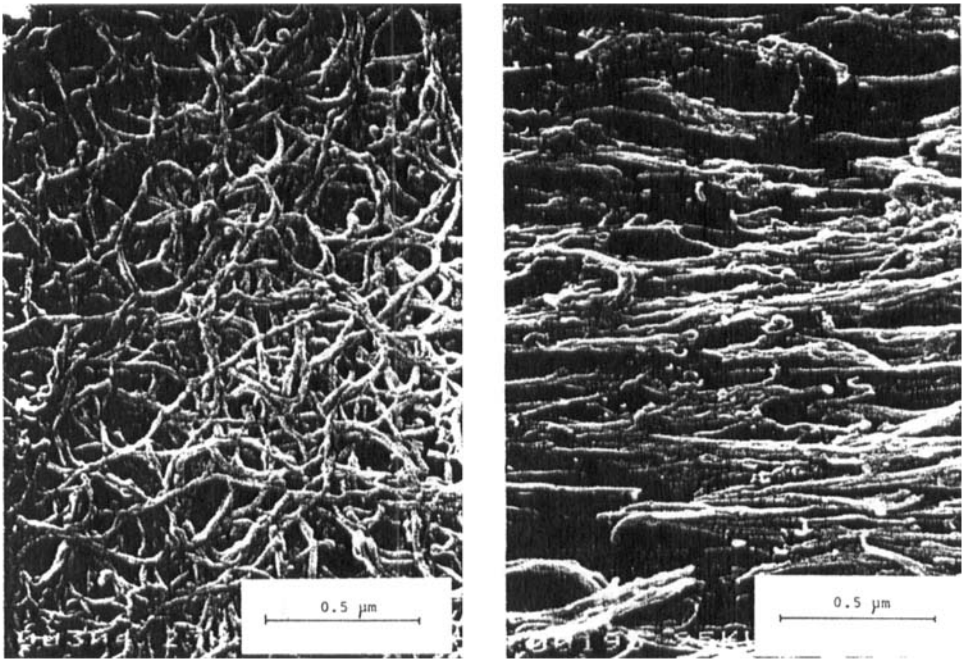

FIGURE 3 Scanning electron micrographs of as-prepared film (left) and stretch-aligned film (right).

dinal direction in the fibrils, partial stretch-alignment of the fibrils results in partial molecular alignment. The stretch-alignment films exhibit considerable electrical,[19] optical[10] and magnetic[11] anisotropy.

The room temperature DC conductivity and the activation energy for electrical conduction of the films depend upon the *cis-trans* contents, varying from 10^{-9} S/cm and 0.5 eV for the *cis* isomer, and 10^{-5} S/cm and 0.3 eV for the *trans* isomer, respectively. From the sign of thermoelectric power, it was concluded that both *cis* and *trans* polyacetylenes are *p*-type.[12,13] In view of the sensitivity of polyacetylene to chemical impurities as demonstrated by chemical doping, which will be described in next section, it appears that the intrinsic conductivity of pure polyacetylene have even lower conductivity. This is supported by the observation that exposure of the *trans* polyacetylene to the vapor of a weak donor such as NH_3, causes the conductivity to fall more than four orders of magnitude without detectable weight increase.[4] This may be due to the reaction (compensation) of NH_3 to the trace amounts of the residual catalyst which act as an acceptor dopant.

4. CHEMICAL DOPING

Polyacetylene, either *cis* or *trans* isomer, can be doped chemically or electrochemically with a variety of electron accepting reagents (acceptors) and electron donating reagents (donors) to form *p*- and *n*-type semiconductors;

$$(CH)_x + xyA \rightarrow [(CH)^{y-}(A^+)_y]_x$$

$$(CH)_x + xyD \rightarrow [(D^+)_y(CH)^{y+}]_x$$

where A and D represent acceptor and donor dopant species, respectively, and y is the dopant concentration. The electrical conductivity increases with increasing the dopant concentration over twelve orders of magnitude. Figure 4 and 5 show the electrical conductivity of iodine doped *cis* polyacetylene films as a function of doping time under various iodine vapor pressure, and iodine concentration, respectively. Raman,[14-16] ESCA,[17] and Mössbauer[18] studies indicate that I_3^- and I_5^- ions are present in the iodine doped polyacetylene. This is consistent with charge transfer from polyacetylene to iodine.

Figure 5 shows that logarithm of the conductivity increases linearly with increasing logarithm of dopant concentration. Transport studies, however, indicate that qualitative changes occur in temperature dependence of the conductivity, thermoelectric power,[19] and optical absorption[4] at $y_c \simeq 0.01-0.02$. Thus, the activation energy for conduction of the undoped *trans* polyacetylene is $\Delta E_a = 0.3$ eV. Above y_c, ΔE_a becomes small (ca. 20 meV) and nearly independent of the dopant concentration, that is, the conductivity is no longer activated in heavily doped poly-

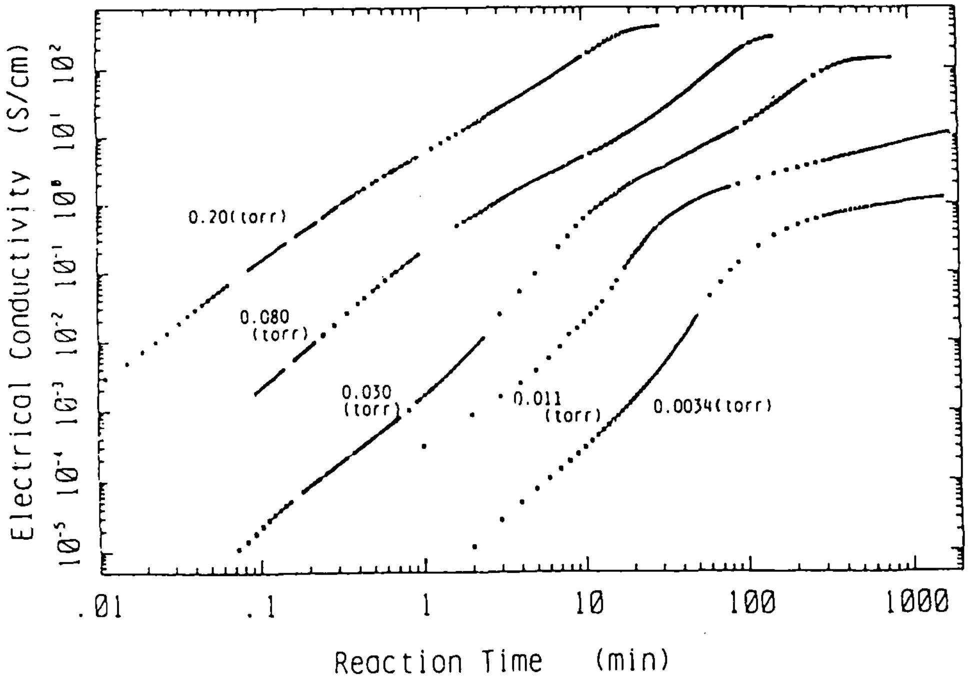

FIGURE 4 Electrical conductivity of iodine doped *cis* polyacetylene as a function of doping time under various iodine vapor pressures.

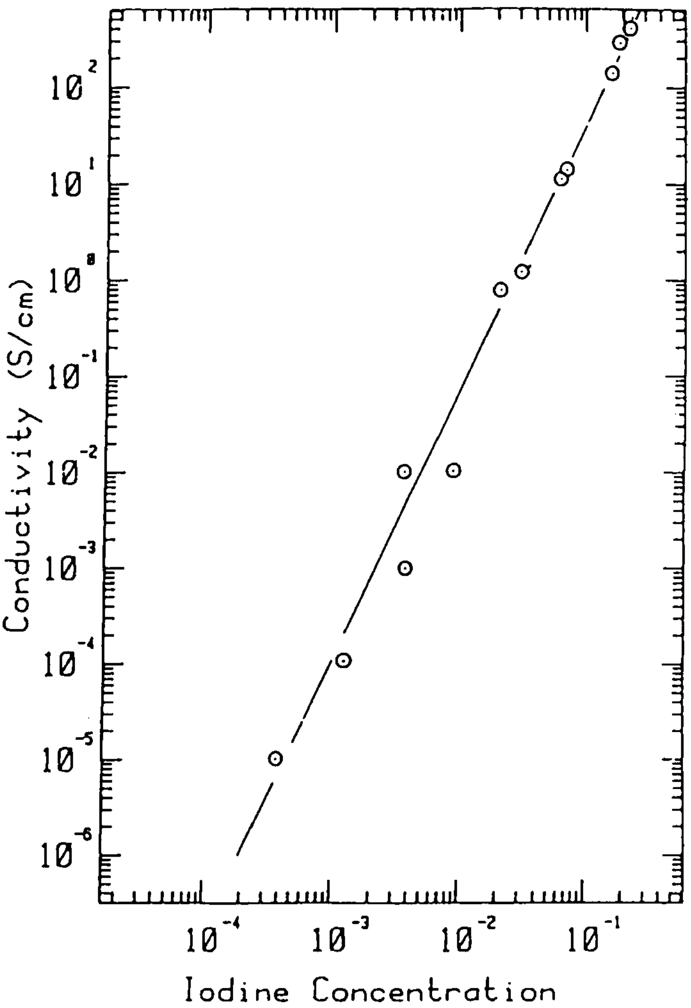

FIGURE 5 Electrical conductivity of iodine doped *cis* polyacetylene as a function of iodine concentration (y) in $(CHI_y)_x$.

acetylene. The thermoelectric power also decreases from 900 mV/K for the undoped *trans* polyacetylene to 10 μV/K at the concentration above y_c. The magnitude and temperature dependence of thermoelectric power are characteristic of a degenerate electron gas and are indicative of intrinsic metallic behavior at molecular level.

The transport mechanism in the doped polyacetylene has remained controversial. It has been proposed that there are at least three dopant regimes[19]:

1. $y < 0.001$; the transport is via carrier hopping, mobility is small and activated.
2. $0.001 \leqslant y \leqslant 0.01$; the transitional region.
3. $y > 0.01$; the metallic state

5. SYNTHESIS OF HIGHLY ORIENTED POLYACETYLENE FILMS

As described in section 3, *cis* polyacetylene film can be stretched up to 3 times its original length with a combined mechanical and thermal treatment. Highly stretchable *cis* polyacetylene films were prepared by a modified polymerization method in which the catalyst system was aged at high temperature combined with a novel nonsolvent polymerization method. Catalyst solution for the polymerization was prepared by adding $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$ into cumene solvent and subsequently it was aged at 150°C for 3 to 5 hours. The polymerization was carried out at −78°C under the condition where solvent was evaporated completely through dynamic pumping just before introduction of acetylene gas. The films thus prepared have not only high density of more than 1.0 g/cm^3 but also high mechanical strengths. Tensile strength and Young's modulus of *trans* films drawn by 7 to 8 times are 0.9 and 100 GPa,[20] respectively, comparable to those of well-known engineering plastics, e.g., Kevlar (3.9 and 132 GPa, respectively). Profound potentiality of the present films was also exemplified in their electrical properties to give high conductivities of more than 2.0×10^4 S/cm upon iodine doping.

An alternative preparative method of highly aligned films which we have developed is a liquid crystal method. Several nematic liquid crystals such as 4-(*trans*-4-*n*-propylcyclohexyl)butoxybenzene and 4-(*trans*-4-*n*-propylcyclohexyl) ethoxybenzene were used for this purpose as ordered matrix solvents. Thus, polymerization of acetylene was carried out in the liquid crystal solvent into which a $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$ catalyst system was dissolved and aligned by gravity flow of the solution or by applying magnetic field higher than 5 kG. Characterization of these films were carried out through SEM observation and measurements of polarized visible and infrared absorption spectroscopies. Results indicated that as-prepared films were highly oriented.[21]

6. SUMMARY

In summary, the chemistry and physics of polyacetylene will open an extensive area for further researches of fundamental scientific interest.

References

1. H. Hatano, S. Kambara and S. Okamoto, *J. Polym. Sci.*, **51**, s26 (1961).
2. T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci. Polym. Chem. Ed.*, **2**, 11 (1974).
3. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *JCS Chem. Commun.*, 578 (1977).
4. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. MacDiarmid, *Phys. Rev. Lett.*, **93**, 1098 (1977).
5. C. K. Chiang, M. A Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park and H. Shirakawa, *J. Am. Chem. Soc.*, **100**, 1013 (1978).
6. C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis and A. G. MacDiarmid, *J. Chem. Phys.*, **69**, 5098 (1978).
7. T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1943 (1975).

8. H. Shirakawa and S. Ikeda, *Synthetic Metals*, **1**, 177 (1980).
9. Y. W. Park, M. A. Druy, C. K. Chiang, A. G. MacDiarmid, A. J. Heeger, H. Shirakawa and S. Ikeda, *J. Poly. Sci. Polym. Lett. Ed.*, **17**, 195 (1979).
10. C. R. Fincher, Jr., D. L. Peebles, A. J. Heeger, M. A. Druy, Y. Matsumura, A. G. MacDiarmid, H. Shirakawa and S. Ikeda, *Solid State Commun.*, **27**, 489 (1978).
11. S. Kuroda, M. Tokumoto, N. Kinoshita and H. Shirakawa, *Phys. Soc. Jpn.*, **51**, 693 (1982).
12. F. D. Kleist and N. R. Byrd, *J. Polym. Sci.*, **A-1 7**, 3419 (1969).
13. D. J. Berets and D. S. Smith, *Trans. Faraday Soc.*, **64**, 823 (1968).
14. H. Shirakawa, T. Sasaki and S. Ikeda, *Chem. Lett.*, 1113 (1978).
15. I. Harada, M. Tasumi, H. Shirakawa and S. Ikeda, *Chem. Lett.*, 1411 (1978).
16. I. Harada, Y. Furukawa, M. Tasumi, H. Shirakawa and S. Ikeda, *J. Chem. Phys.*, **73**, 4746 (1980).
17. I. Ikemoto, M. Sakairi, T. Tsutsumi, H. Kuroda, I. Harada, M. Tasumi, H. Shirakawa and S. Ikeda, *Chem. Lett.*, 1189 (1979).
18. T. Matsuyama, H. Sakai, H. Yamaoka, Y. Maeda and H. Shirakawa, *Solid State Commun.*, **40**, 563 (1981).
19. Y. W. Park, A. J. Heeger, M. A Druy and A. G. MacDiarmid, *J. Chem. Phys.*, **73**, 946 (1980).
20. H. Kyotani, M. Shimomura, Y. Tanabe, Y. Watanabe, M. Suezaki, T. Kasai, K. Akagi and H. Shirakawa, *Rep. Prog. Polym. Phys. Jpn.*, **31**, 265 (1988).
21. H. Shirakawa, K. Akagi, S. Katayama, K. Araya, A. Mukoh andT. Narahara, *J. Macromol. Sci. Chem.*, **A25**, 643 (1988).