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SUBSTITUTED POLYACETYLENES BY CYCLOPOLYMERIZATION: POLY(1,6-HEPTADIYNE) AND POLY(PROPIOLIC ANHYDRIDE)


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Résumé - Deux polyacétylènes substitués, le poly (1,6-heptadiyne) et le poly (propiolic anhydride), ont été synthétisés par cyclopolymérisation de précurseurs diacétyléniques. Le premier polymère a été examiné en détail. Dans des conditions adéquates, il peut être dopé jusqu'à ~ 1 s/cm. Il présente un certain nombre de propriétés, morphologie, cristallinité et résonance électronique, qui contrastent avec celles du polyacétylène. Le poly (propiolic anhydride) a été examiné de manière succincte ; toutefois, ce système offre la possibilité de générer toute une gamme de substituants par une modification aisée du monomère de départ ou du polymère produit. La cyclopolymérisation est une voie pratique pour la synthèse de toute une famille de polymères conducteurs.

Abstract - Two substituted polyacetylenes, poly(1,6-heptadiyne) and poly(propiolic anhydride), have been synthesized by cyclopolymerization of diacetylenic precursors. The former polymer has been examined in some detail. Under suitable conditions, it can be doped to a conductivity(0) of ~ 1 s/cm. It displays a number of contrasts to polyacetylene in its morphology, lack of crystallinity, and electron spin resonance behavior. Poly(propiolic anhydride) has been examined only in a preliminary manner; however, this system offers the possibility for generation of a range of substituents by facile modification of the starting monomer or the product polymer. Cyclopolymerization is a feasible route for synthesis of a family of conducting polymers.

INTRODUCTION

Over the past twenty-five years electrically conductive polymers have been the subject of sporadic interest to chemists and physicists /1,2/ because of the intriguing prospect of being able to combine in a single material the electrical properties of a metal (high conductivity, greater than 1 s/cm) or semiconductor (moderate conductivity, 10^-1 to 1 s/cm) with those of a polymer (mechanical strength, flexibility, lighter weight, low preparation and fabrication costs, etc.).

Polyacetylene, the prototypical conducting polymer, has been known since 1958 /3/. It had been oxidized with Lewis acids (doped) to relatively high conductivity. /4/ But the field was relatively dormant until the late 1970's when two significant events occurred. First, Ito, Shirakawa and Ikeda reported the synthesis of continuous free-standing polyacetylene films using a very concentrated catalyst. /5/ Second, this discovery came to the attention of an interdisciplinary team of chemists and physicists, who produced metallic conductivity in polyacetylene films by oxidation or reduction (p- or n-doping) with suitable Lewis acids or bases. /6/
As with any prospective new application of polymers, we reasoned that optimization of physical and chemical properties would be required in order to generate practically useful materials. We were concerned about mechanical properties, flexibility, conductivity levels, solubility, processability, oxidative stability, etc. Based upon the perceived requirement of a conjugated polyene structure, substituted polyacetylenes were the obvious way to tailor these characteristics.

Unfortunately the literature provided ample evidence of the sluggish nature of substituted polyacetylenes toward polymerization. /7/ However, we were aware of the utility of cyclopolymerization in the area of polyolefins /8/ and also were aware of the work of Stille and Frey on the cyclopolymerization of 1,6-heptadiyne to a soluble polymer of proposed structure 1 using a heterogeneous Ziegler-Natta catalyst. /9/ With the initial objective of determining if a substituted polyacetylenes could be polymerized to free-standing films and b. then converted to a highly conductive state, we began our investigation of this cyclopolymerization in early 1979.

**DISCUSSION**

A. Poly(1,6-heptadiyne)

Free-standing films of poly(1,6-heptadiyne) can indeed be prepared in situ using a number of homogeneous Ziegler-Natta catalysts. Spectroscopic studies (infrared, nuclear magnetic resonance) using model monomers and the polymer film prepared from 1,6-heptadiyne-1,7-d2 supported structure 1 for the polymer. As reported by Stille and Frey for the soluble polymer, /9/ the insoluble "poly-1,6" also underwent a thermal rearrangement which converted it from a lustrous golden-green opaque film to a transparent red-orange film. Again by spectroscopic studies using model compounds, structure 2 was indicated for the rearranged polymer.

Poly-1,6 is distinct from polyacetylene in its morphology. The latter is very porous, being comprised of fibrils of 100-800 Å diameter, /10/ and has an apparent density /6/ of about 0.4 g/cm³. Poly-1,6 has very little void space and displays a number of morphologies depending upon polymerization conditions. While polyacetylene prepared by the Shirakawa catalyst is 80-90% crystalline, /11/ poly-1,6 displays no crystallinity to x-ray diffraction, although differential scanning calorimetry of some samples shows a sharp transition (endotherm) in the range 164-184°C, perhaps indicative of small crystalline domains.

With these contrasts in molecular structure, morphology and crystallinity between poly-1,6 and polyacetylene, we undertook a study of the oxidation (doping) of poly-1,6 to a conductive state. Indeed, exposure to iodine vapor in vacuo at room temperature successfully raised the conductivity from an initial value of $10^{-6}$ to $10^{-1}$ (s/cm) over the period of one hour, (Figure 1) a rate similar to that for polyacetylene. However, the conductivity-time curve proceeded through this maximum value and then decreased by about a factor of 10 before leveling (Figure 1). If the iodine source were removed at the maximum, the conductivity decreased by only a factor of about four. This was hypothesized to be due to iodine catalyzed rearrangement of 1 to 2, resulting in loss of conjugation. To test this hypothesis, the "doping" was carried out at -78°C in toluene saturated with iodine; a value of 0.4 s/cm was reached after ten days with no sign of loss of conductivity, until the temperature was raised (Figure 2). This corresponds to a room temperature value of 5 to 10
s/cm based upon the activation energy of 3 kcal/mole (0.1eV). This value may be compared to the 10-20 s/cm we observed for iodine treatment of polyacetylene. AsF₅ treatment of poly-1,6 led to a conductivity of 10⁻² s/cm at 25°C, in comparison to a reported value of 10⁻¹ s/cm for polyacetylene. /6/

Iodine content on an I atom per double bond basis is the same (0.50) for poly-1,6 and polyacetylene prior to vacuum treatment. Vacuum treatment (26 hrs., 25°C, 10⁻⁶ Torr) leaves only 0.11 I atoms per double bond, compared to 0.30 for polyacetylene. Similarly poly-1,6 after vacuum treatment retains 0.11 mole AsF₅ per double bond as compared to 0.28 for polyacetylene.

The oxidation (doping) process in the case of iodine has been monitored by electron spin resonance (esr) and infrared and optical spectroscopies. Esr reveals a narrowing of the initially broad (ΔH ≈ 20G vs. 9G for cis- and 0.8G for trans-polyacetylene) to ~10G upon iodine vapor treatment. The number of spins increases with first order kinetics. By contrast with polyacetylene there is no change in linewidth and the radical population decreases with first order kinetics. /12/ In the infrared spectra three broad features at 750, 1100 and 1370 cm⁻¹ appear (Figure 3), whereas in polyacetylene sharp lines appear at 900 and 1370 cm⁻¹. Optically, oxidation with iodine causes the peak at 2eV (cf. 1.9 for polyacetylene) /6/ to completely disappear and a new peak to appear at 0.9eV (Figure 4) (cf. 0.8eV for polyacetylene). /6/

These results are consistent with the following explanation. In both systems removal of π-electrons of double bonds by the acceptor (iodine) can lead to radical cations (polarons). In polyacetylene due to symmetry there is no barrier to radical coupling to reform a bond and leave two cations (positive solitons), whereas due to the asymmetry of poly-1,6, non-degenerate radical cation (polaron) structures result and there is a finite barrier to such a process. This is manifested by a buildup of spins in the esr spectra of poly-1,6 similar in mechanism and rate to the loss of spins in polyacetylene. The optical transition in poly-1,6 is most likely then due to a transition between the radical state and the empty π-orbital of the radical cation (polaron), while that in polyacetylene is a transition from the valence band to the empty free-radical (soliton) orbital midway between valence and conduction bands. /6/

Thus a number of contrasts exist between poly-1,6 and polyacetylene: morphology, crystallinity, undoubtedly molecular weight, the dopant content and the final state after doping. Yet in the absence of the rearrangement poly-1,6 is capable of similar conductivities, albeit at higher activation energy (0.1eV vs. 0.04eV /6/) than polyacetylene. Thus one may question whether these features of polyacetylene are prerequisites for its high conductivity.

B. Poly(propio1ic Anhydride)

In an attempt to alleviate the oxidative problem encountered with polyacetylene /14/ and poly-1,6, /15/ we have examined the cyclopolymerization of propionic anhydride (3) to polymer (4). This process was reported to yield polymer of molecular weight up to 25000 (200 double bonds) by anionic cyclopolymerization using mild nucleophiles such as I, CNS⁻, Cl⁻ in dimethylformamide (DMF) /16/ and by coordination polymerization using PdCl₂ in DMF. /17/
Our preliminary investigation shows that it is possible to prepare insoluble, crosslinked polymer or soluble uncrosslinked cyclopolymer by control of the initiator: monomer ratio. In DMF at 78°C using KI as the initiator, the molecular weight by end group analysis is 4600-6000 (37-50 double bonds), regardless of initiator/monomer ratio.

The value of cyclopolymerization is demonstrated by the fact that neither ethyl propiolate (5) nor propiolic acid (6) yield any polymer under these conditions.

![Chemical Structure](image)

The polymer prepared by this process contains DMF as solvent and probably also in the form of structure 7 formed from 4 via decarbonylation of a formyl anhydride intermediate. This side reaction precludes meaningful doping studies of this system in view of the potential for reaction of the carboxyl and amide functionalities. Nonetheless, treatment with iodine or AsF₅ at 25°C raised the conductivity of pressed pellets from 2x10⁻¹⁴ to 5x10⁻¹⁴ and 2x10⁻¹⁵ s/cm, respectively. Moreover, as anticipated the undoped polymer was stable in dry air.

Hydrolysis of the polymer with aqueous NaOH at 25°C was accompanied by decarboxylation to yield a copolymer (8) of acetylene and propiolic acid. This polymer after fractionation had MW 5400 (90 double bonds). Upon doping it gave conductivity values comparable to polymer 4.

These preliminary results and the possibility for facile modification of the starting diacetylene and the resultant cyclopolymers make this system attractive for further investigation.

**CONCLUSIONS**

1. Substituted polyacetylenes can be prepared effectively by cyclopolymerization of suitable diacetylenes.

2. Such substituted polyacetylenes can be oxidized (and presumably reduced) (doped) to high electrical conductivity.
1. Conductivity of poly(1,6-heptadiyne) versus exposure time to iodine vapor in vacuo at 25° C. Top curve is for sample continuously exposed to iodine. Bottom curve results when iodine source was removed at indicated point.

2. Conductivity (at -78° C) of poly(1,6-heptadiyne) versus exposure time to a saturated solution of iodine in toluene at -78° C. Note precipitous drop in conductivity when temperature was raised to 0° C and then to 25° C.

3. Infrared spectra of poly(1,6-heptadiyne) film before (top curve) and after iodine treatment on an argon stream to yield a conductivity of $10^{-3}$ s/cm. (bottom curve).

4. Reflectance spectra of poly(1,6-heptadiyne) before (full curve) and after iodine treatment to yield a conductivity of $10^{-3}$ s/cm (broken curve).
REFERENCES

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18. We thank Dr. JOHN SPIEWAK of these laboratories for pointing this possibility out.