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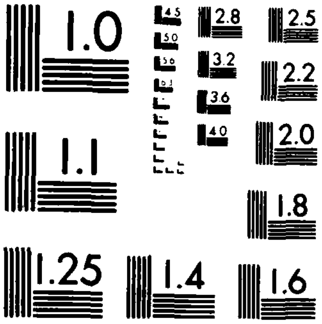

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The dimer of 1,11 dodecadiyne is representative of a family of diacetylene monomers which can be crystallized and then polymerized into semiconducting polymers. These materials possess sheet-like structures containing parallel polyacetylene and polydiacetylene chains bridged by methylene units. Polymeric forms of these coupled diynes have also been prepared and crosspolymerized. Structural studies of these materials have been performed.

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CONDUCTION IN POLYMERIZED POLYFUNCTIONAL DIACETYLENES

by

Robert P. Grasso, Mrinal K. Thakur, and Jerome B. Lando

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CONDUCTION IN POLYMERIZED POLYFUNCTIONAL DIACETYLENES

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Abstract The dimer of ~~1,11~~ 1,11 dodecadiyne is representative of a family of diacetylene monomers which can be crystallized and then polymerized into semiconducting polymers. These materials possess sheet-like structures containing parallel polyacetylene and polydiacetylene chains bridged by methylene units. Polymeric forms of these coupled diynes have also been prepared and crosspolymerized. Structural studies of these materials have been performed.

The dimer of 1,11 dodecadiyne was prepared in a unique manner which eliminates the possibility of contamination by oligomeric impurities that hinder crystallization. Microscopic single crystals of the dimer, obtained from hexane solution, were used in a structure analysis by electron diffraction. These results were compared to the structure of the fully polymerized crystal which was determined by X-ray analysis.

Originator-supplied keywords include: Polydiacetylenes, and Conductivity.

INTRODUCTION

The solid state polymerization of diacetylene monomers, which form materials with interesting optical and electronic properties, has been the subject of a great deal of research in the past few years[1,2]. The unique characteristic of these polymerizations is that they can result in large, nearly defect-free, single crystals consisting of fully extended conjugated backbones[3]. These polymer crystals are obtained by first crystallizing the monomer and then exposing the crystals to high energy irradiation (γ-rays, ultraviolet) or thermal annealing in order to initiate polymerization. The propagation occurs by way of a 1,4 addition reaction in the crystalline phase. The general diacetylene reaction is shown in Figure 1 and illustrates the two mesomeric structures of the

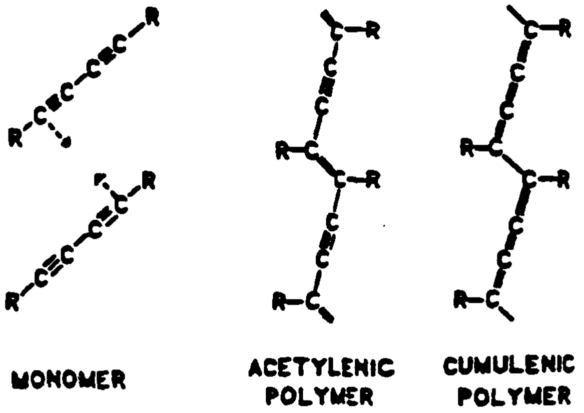


Figure 1. Generalized diacetylene reaction scheme.

polymer backbone. The acetylenic form is energetically more stable and as a result is observed more frequently[4]. However, the cumulenic form is observed in some cases where it is favored by the nature or packing of the side groups[5].

The polymerization of the diacetylene monomers $\leftarrow (CH_2)_n - C \equiv C - C \equiv C \rightarrow_x$ (n = 5,6,8) has been reported earlier[6-8]. These macromonomers were synthesized by a modified Glaser coupling reaction[7,9,10] performed on the appropriate α,ω diyne starting material. The work presented here will describe the synthesis and polymerization of the polyfunctional diacetylene material:

$$HC \equiv C\ (CH_2)_8\ C \equiv C - C \equiv C\ (CH_2)_8\ C \equiv CH \qquad (1)$$

In addition to the central diacetylene unit, the polymerization of the terminal acetylene groups will be studied utilizing comparative structural analysis.

SYNTHESIS OF DIACETYLENE

The diacetylene monomer Eq. (1) for this study was originally prepared by controlling the kinetics of the Glaser coupling reaction of 1,11-dodecadiyne[11]. Originally, it was incorrectly believed that the oligomeric impurities present in the product mixture were negligible in quantity relative to the desired dimer material. This assumption was based on the gel permeation chromatography (GPC) results shown

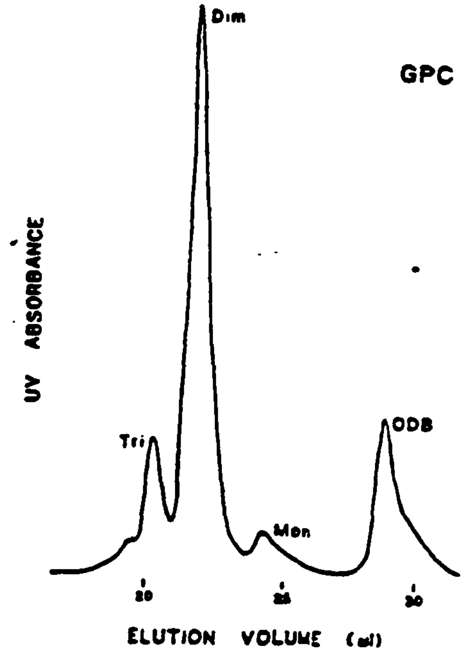
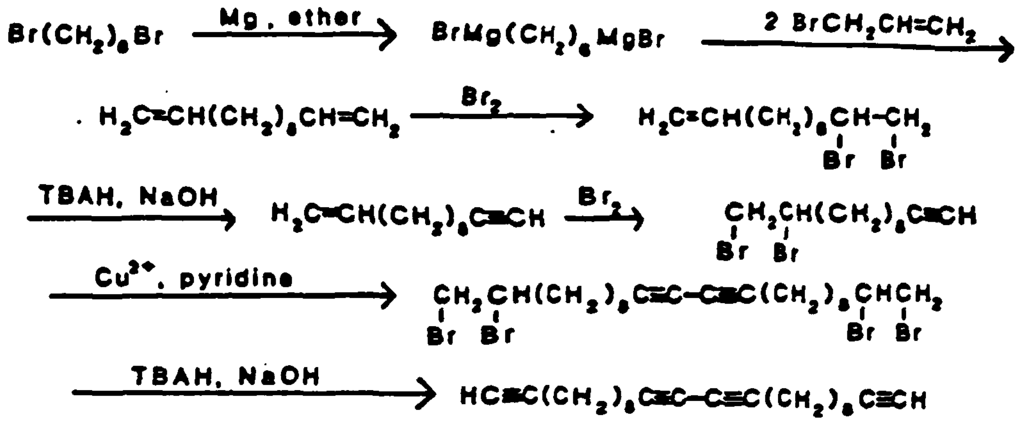


Figure 2. Gel permeation chromatography trace of the oligomeric product mixture obtained from coupling 1,11-dodecadiyne. Orthodichlorobenzene (ODB) is used as a standard.

in Figure 2. Peak area was used as a relative means of estimating composition. However, since the dimer tends to remain dissolved in the monomer present, and since the isolation of the dimer from the oligomers is difficult due to similarities in physical constants, the crystallization of the diacetylene dimer was very difficult[12].

In order to overcome these problems, we developed a direct synthesis of the dimer[13] which would yield no oligomeric impurities. This synthesis is shown in Scheme 1. The scheme still makes use of the modified Glaser reaction; but, in addition, a protective dibromo group was utilized. Once the material was coupled using the Cu^{2+}/ pyridine catalyst, the terminal groups were dehydrobrominated to form the acetylenic groups. Changes in functional groups were monitored using IR and NMR analyses. A GPC chromatogram of the multistep product (Figure 3) shows that diacetylene product is not contaminated with oligomeric impurities.



Scheme 1. Multistep synthetic pathway used to obtain the dimer.

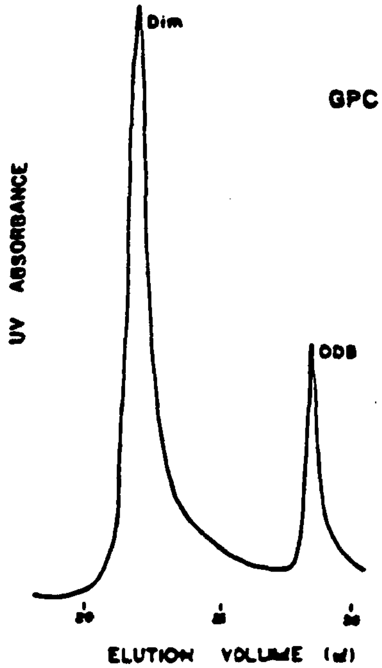


Figure 3. Gel permeation chromatography trace of the product mixture obtained from the multistep synthetic pathway.

UNPOLYMERIZED DIACETYLENE STRUCTURE

Microscopic single crystals of the dimer were obtained from a dilute hexane solution at 4°C. Electron diffraction patterns from these crystals were recorded at various orientations in order to determine the unit cell constants. A photograph of the b^*c^* lattice net is shown in Figure 4. The unit cell constants were calculated using

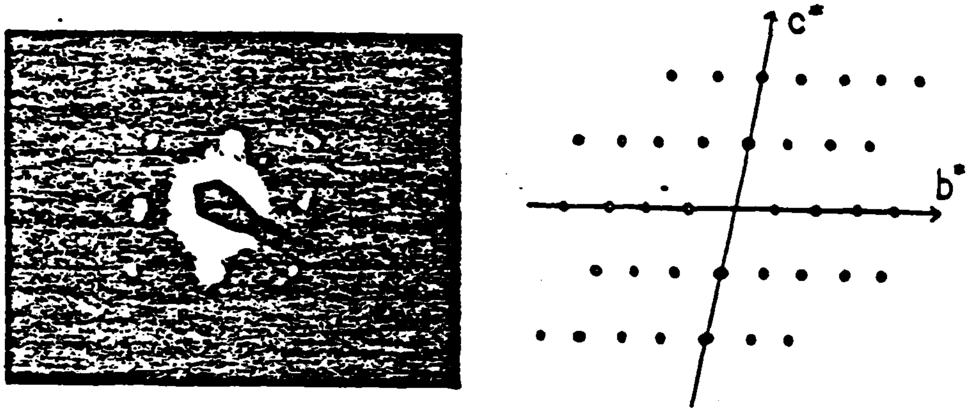


Figure 4. Electron diffraction photograph of the b^*c^* lattice net. Observed and absent reflections are schematized.

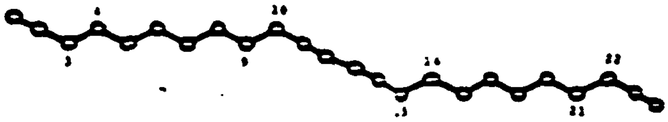
platinum as a standard. It should be mentioned that the dimer's monoclinic unit cell, space group P $2_1/b$, has the a-axis as its unique axis. As a result, the diacetylene and acetylene polymer backbones will be oriented along the c-axis. Unit cell data on the a^*-axis were obtained by tilting the dimer crystal in the electron beam. However, the intensities of reflections in the a^* nets were not acceptable for the structure analysis. Dynamic scattering effects were ignored since the crystals were less than 300 Å and composed of low mass atoms (carbon and hydrogen). It should be noted that the nonorthogonal axes b and c and the angle γ are changed from those reported earlier[11] for convience in the structure determination.

The structure of the unpolymerized material was solved essentially by a trial method. Information derived from the structure of the polymerized material, which was solved earlier by this group[11], was helpful in the initial steps of refinement. Since we obtained only 19 unique reflections, the structure refinement was carried out using the linked atom least-squares (LALS) program originally developed by Arnott and co-workers[14]. The linked atom description of the molecule defines interatomic relationships in terms of bond lengths, bond angles and dihedral angles. The LALS program applies various geometrical restraints on the molecule and can then refine only conformational parameters. This greatly increases the ratio of data to parameters refined and thereby, allows a structure analysis to be reliably undertaken. The agreement between the observed and the calculated structure factors was characterized by the reliability index or residual:

$$R = \frac{\Sigma \left| |F_o| - |F_c| \right|}{\Sigma |F_o|}$$

Density calculations were used to determine that there are 2 molecules per unit cell (4 assymetric units). This offers four possibilities for the locations of the molecules within the unit cell. Each of these cases was refined using LALS and it was found that on the basis of both interatomic contacts and the structure factor residual, the two molecules should be centered at the fractional coordinates 0,0,0 and 1/2,1/2,0.

The LALS program was then used to refine the Eulerian angles which define the relative orientation of the molecule with respect to the unit cell. Several conformational parameters which would bring about a minimum in both the potential energy and structure factor residual were also varied. The diacetylene molecule, omitting hydrogens for clarity, is shown below:



The initial bond lengths, bond angles and dihedral angles, were taken from standard tables and model compounds. The conformational parameters that were varied include the bond angles 10 (= 15) and 3 (= 22), and the dihedral angles about carbons 9-10(= 15-16) and 3-4(= 21-22). The minimum residual obtained from this refinement was 8%.

The following changes were observed in the refined structure. Bond angles 10 and 15, which were initialized at 112.5°, increased 12.2 to 124.7°. This was expected since this angle would initially be larger than the standard sp^3 carbon bond angle. The dihedral angle around carbons 9-10 (identical by symmetry to the one between carbons 15-16) was found to change 4.2° from its original 180° setting. This was determined to be a significant modification through the use of Hamilton statistics[15]. The bond angles 3 and 22 as well as the dihedral angles around carbons 3-4 and 21-22 were allowed to vary but no significant change was observed. Finally, the relative orientation of the molecule, which is determined by the Eulerian angles, can be visualized in the *ab* and *bc* projections. These are shown in Figures 5 and 6 respectively. It should be noted here that the methylene chains are 7.0° from their original positions, which were parallel to the *a*-axis.

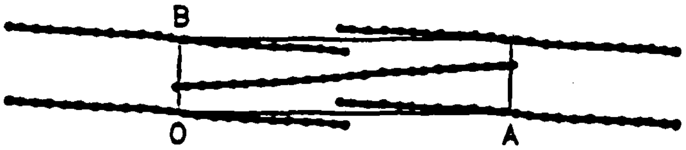


Figure 5. The *ab* projection of unpolymerized dimer structure. Only carbon atoms are shown for clarity.

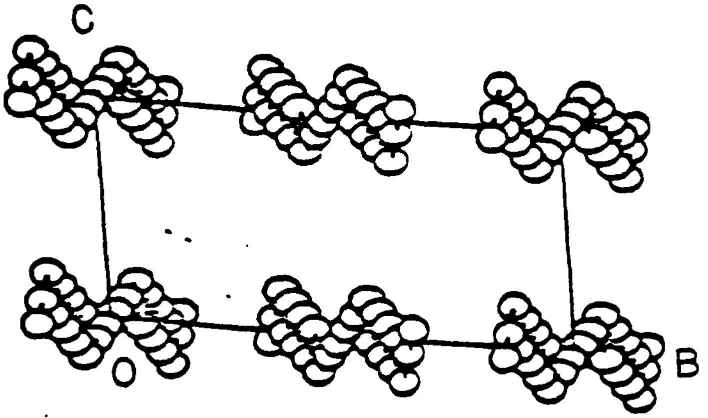


Figure 6. The *bc* projection of unpolymerized dimer structure. Hydrogens have been omitted for clarity.

POLYMERIZED DIACETYLENE STRUCTURE

A large plate-like polymerized crystal of the dimer was selected for the X-ray structure analysis, which was reported earlier[11]. The final structure is composed of sheets of two-dimensional networks of polydiacetylene and polyacetylene chains interconnected by eight methylene units. There are two of these sheets per unit cell. If we designate the origin of one sheet to be at a corner (fractional coordinates 0,0,0), then the origin of the second sheet would be at the fractional coordinates: 1/2,1/2,0. A portion of one of these sheets can be visualized in the *ac* section shown in Figure 7. The interplanar spacing between these sheets is approximately 4 Å.

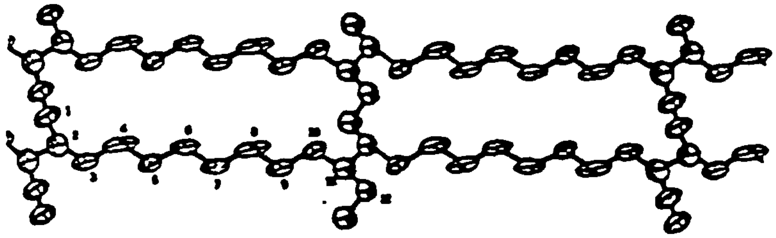


Figure 7. The *ac* section of the polymerized dimer structure. The carbons in one assymetric unit are numbered and acetylenic hydrogens have been omitted.

POLYMERIZATION MECHANISM

By comparing the structures of the unpolymerized and polymerized dimer material (see Figure 8) as well as applying the principle of least motion[16,17], we can rationalize the mechanism of polymerization in the following manner. First, the diacetylene rod must tilt

$P2_1/b$		$P2/n$	
a = 28.25 Å	α = 100.8°	a = 26.78 Å	γ = 119.6°
b = 8.50		b = 8.25	
c = 5.24		c = 4.91	
ρ = 0.866		ρ = 1.134	

Figure. 8. Space group and unit cell parameters for a) the unpolymerized dimer and, b) the polymerized dimer.

by an angle of about 60° and is simultaneously translated by 0
along the c-axis. This is in accordance with the translationa
direction invariant motion as is described by Baughman[18]. Sec
the two methylene chains swing 7° so as to bring the terminal
acetylenic groups into position so that they can react to form
polyacetylene chains. We cannot be certain whether this secon
step occurs before, during or after the diacetylene polymeriza
However, it is unlikely that it occurs before, due to the fact
the least motion principle does not favor the acetylene polyme
tion to be the initial one. Furthermore, if the acetylene pol
zation occurs after the diacetylene reaction, then the latter
be very difficult to induce. This can be estimated by Baughma
root-mean-square displacement (RMSD) parameter. Judging by th
ease of polymerization, a concerted mechanism seems to be the
likely candidate. Finally, the resulting two-dimensional netw
can then slide along each other into a van der Waals potential
in order to minimize the potential energy of the structure.

CONDUCTING PROPERTIES

Conductivity measurements were carried out using a digital ele
eter with a range of 10^{-12} to 10^{-1} amp as the current source a
digital Keithley multimeter to measure the voltage. The condu
was found to decrease with decreasing temperature. At room te
ture, a two-point resistivity measurement carried out on a sin
crystal of the polymerized dimer yielded a conductivity calcul
of at least $10^{-2}\ \Omega^{-1}\ cm^{-1}$ along the chain direction[illegible]. This
measurement should be compared to values of about $10^{-8}\ \Omega^{-1}\ cm^{-}$
is typical of most other polydiacetylenes and $10^{-4}\ \Omega^{-1}\ cm^{-1}$ fo
trans-polyacetylene.

Since the electrical properties of a crystalline material
ultimately depend upon its chemical structure, an explanation
this unusually high conductivity must be based on the structur
the dimer crystal. As was previously mentioned, the polymeriz

dimer is composed of sheets of alternating polyacetylene and polydiacetylene chains. These sheets are staggered by *a*/2 and as a result, polyacetylene and polydiacetylene chains are only about 4 Å apart along the *b* direction. One explanation, given earlier by this group to rationalize these unique electrical properties, was based on the overlap and coupling of π electron orbitals between interchain atoms.

A more recent explanation suggests the possibility of self doping. This is based on partial charge calculations and theoretical band structures which appear to agree with the spectroscopic data[19]. Thus the assignment of several peaks in the absorption spectrum correspond to gaps in the band structure of the polymerized dimer (see figure 9).

OPTICAL SPECTRUM OF POLYDIACETYLENE DIMER (PDD)

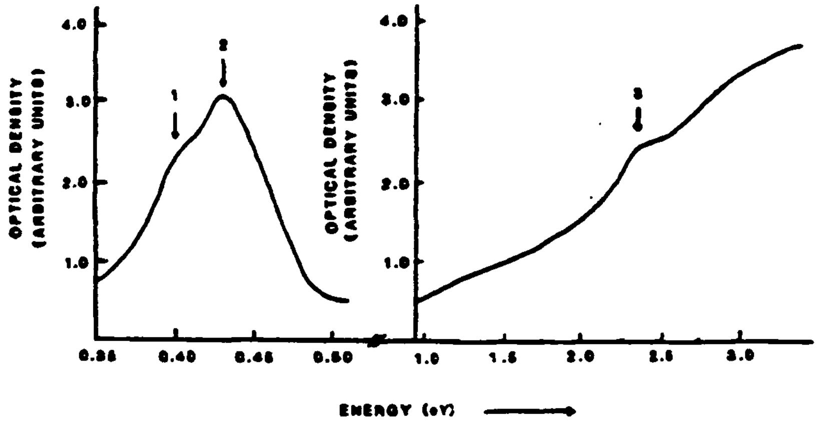


Figure 9. Absorption spectrum of the polymerized dimer obtained from a Nicolet FTIR (left) and a Cary UV/visible spectrometer (right).

Finally, a study of the temperature dependence of resistivity was carried out and a linear relationship between the two (log ρ vs. 1/T) enabled the activation energy to be determined. The calculated value of $\sim$0.18eV[11] is to be compared with the infrared spectra and theoretical value of the band gap which is approximately

0.40 eV[19].

ACKNOWLEDGEMENT

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