Conduction in Polydiacetylene Bilayers

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Synopsis

Surface active diacetylene monolayers were polymerized at the gas–water interface and bilayers formed from these layers were deposited onto lock-and-key devices. Samples exhibited intial conductivities on the order of 10^{-7} Ω^{-1} cm^{-1}, which decayed at varying rates depending on sample composition to 10^{-11} Ω^{-1} cm^{-1}. This initial space charge current was found to be strongly dependent on the presence of small amounts of water. A current increase was observed of over three orders of magnitude in some samples upon doping with iodine. Current flow decreased, however, back to original values after removal of the iodine. Polydiacetylene bilayers were also found to exhibit photo conductive current increases of over an order of magnitude.

INTRODUCTION

It has long been suspected that polydiacetylene single crystals should exhibit good semiconduction properties in view of the nature of the fully extended conjugated backbone. Experiments have shown, however, polydiacetylenes to be insulators.[1] Doping of the polydiacetylene single crystals has resulted in a small increase in conductivity, in some cases, and in decomposition in others.[2]

It is possible that only slight increases in conductivity (in comparison to polyacetylene) are observed because of the low diffusion of the dopant to the inside of the polymer crystal. This has not been a problem with polyacetylene because of its spongelike morphology. Polymerized diacetylene monolayers are much better in this respect because of the high surface area and the very short path of diffusion for a dopant.

Conductivity of polymerized monolayers was measured by depositing them onto special lock-and-key* devices.[3] A lock-and-key device is equivalent to two long parallel electrodes but compacted into a small area (see schematic below).

Lock and Key Schematic

Electrode Pads

Lock and key measures 2.5 × 8.0 cm and has an effective parallel electrode length of 164 cm; electrode separation = 0.015 cm.

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* We are grateful to Professor S. D. Senturia for supplying these devices.

This geometry allows conductivity to be measured within the monolayer plane.

EXPERIMENTAL

Polydiacetylene monolayers were prepared by first forming a monomer monolayer on the surface of water and then polymerizing it with ultraviolet irradiation under a nitrogen atmosphere (Fig. 1).[4,5] Conductivity measurements were performed on bilayers (two monolayers) made by dipping the lock-and-key device twice through a polymerized monolayer on the water surface.[6] For these experiments, CH_3-$(CH_2)_{16}$-$C{\equiv}C$-$\equiv C$-$(CH_2)_8$-$COOH$ was used as the starting monomer. Lithium salts of this monomer were also formed by dissolving lithium hydroxide in the water substrate.[4,5]

Although molecular weights of the polymer in these polymerized diacetylene monolayers were not measured because of the minute amount of material, the existence of high polymer is implied by optical and electron microscope studies[6] and by the fact that collapsed monolayers form relatively high strength fibers with no backbone orientation.[7] It should be noted that because of the insolubility of most polydiacetylenes, few determinations of molecular weight have been made.

A constant voltage of 60-V dc was applied to the lock and key (with bilayer) and the resulting current was measured on a Keithley 616 electrometer. Current values given in the following pages are absolute. In order to relate these values to a standard conductivity value, one has to assume either a bulk or surface conduction mechanism. If a bulk conduction is assumed, the standard conductivity can be arrived at by multiplying the given current values by a factor of 2.2. This arises from the cross-sectional area of conduction and the conduction path length where:

$$Conductivity = I \cdot G$$

where I is the current measured; and G = path length/(voltage $\times$ cross-sectional area).
For lock and key:

$$path - 150\ \mu m = 0.015\ cm$$
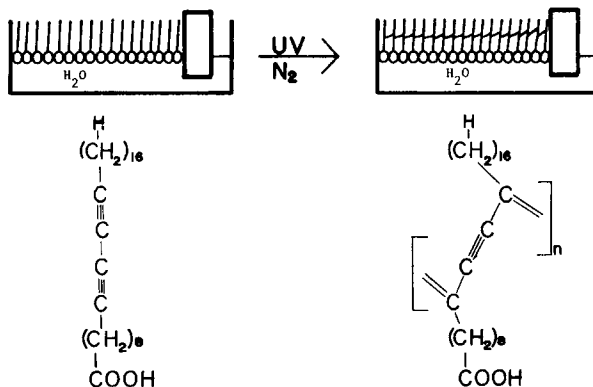
$$length = 164\ cm$$

Fig. 1. Polymerization reaction of diacetylene monolayers at gas–water interface.

For bilayer:

$$\text{height} = 70 \times 10^{-8} \text{ cm,} \qquad G = 2.18$$

Because conduction was measured in only one direction within the bilayer plane and the crystallites were oriented randomly, nothing could be deduced about conduction anisotropy. If, however, all measured conduction is parallel to the polydiacetylene backbone and is negligibly perpendicular to this direction, a higher conductivity would be implied along the polymer backbone than measured.

The ratio of the conductivity in a unidirectionally oriented bilayer to the actual randomly oriented bilayer can be calculated by integrating the vector components of the diacetylene backbones in a single chosen direction over the entire sample. This probably is not entirely correct but is sufficient to obtain a ball park estimate. From symmetry, the integration from 0 to $\pi/2$ suffices and the ratio is:

$$\text{Ratio} = \frac{n}{\sum\limits_{0}^{\pi/2} \left(\frac{\Delta\theta}{\pi/2} \times n\right) \cos\theta} = \frac{\pi}{2 \int_{0}^{\pi/2} \cos\theta \, d\theta} = \frac{\pi}{2 \int_{0}^{\pi/2} \sin\theta} = 1.57$$

where n is the total number of vectors in an all parallel sample; $\Delta\theta x n/(\pi/2)$ is the fraction of vectors in a small slice $\Delta\theta$ of a random sample, and $\Delta\theta x n/(\pi/2)$ $\cos\theta$ is the component of that fraction in a given direction.

From this, the conductivity along the chain direction can be said to be a factor of 3.4 higher (2.18×1.57) than the current values given in the subsequent data, if it is assumed that there is a bulk conduction mechanism and it occurs only in the chain direction. Even if these assumptions are not made, the changes in current that are measured are still directly proportional to the conductivity changes. Absolute current values varied by as much as an order of magnitude from experiment to experiment depending on film perfection and probably other unknown factors, but the changes in current (or relative conductivity) remained fairly constant. The effect of water on these measurements was determined. All doping experiments and conductivity measurements were made after evacuation and purging the sample with dry nitrogen until a constant conducitivity was obtained.

Both the free acid and Li salt bilayers were doped in the hopes of observing increases in conductivity. Of the many dopants commonly used with polyacetylene, iodine is the cheapest and safest, and was therefore used with the bilayers. The basic apparatus for doping is shown in Figure 2. The process consists of passing dry nitrogen over crystalline iodine and then over the bilayer on the lock and key.

Before iodine was passed over the bilayer samples, clean nitrogen was first passed through the chambers to purge it and obtain a steady current reading. Initially, large variations were obtained in the results until it was noticed that there was a large dependence on ambient lighting conditions.
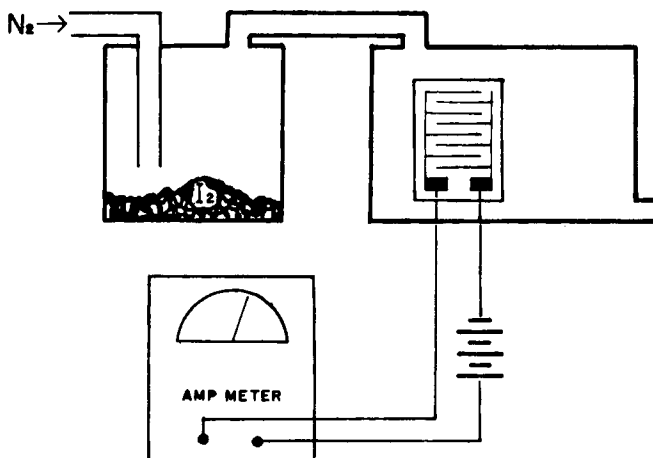
Fig. 2. Doping apparatus for diacetylene layers on lock-and-key device.

RESULTS AND DISCUSSION

Lithium Salt Bilayer

Lithium salt bilayers (hydrophilic core) deposited on lock-and-key devices showed an initial current at 60-V dc of about 10^{-7} A. After minutes, this dropped to 10^{-8} A and after a period of days to approximately 10^{-11} A. This kind of behavior is common to most polymers where space charges migrate to the poles under an electric field.[8] After a period of time, this decays and only the so-called true current remains. If the voltage source is then shorted out, a current is observed in the opposite direction as the space charge flows back to the preferred "even" distribution, a behavior similar to that of a storage battery. It follows, then that the higher the ionic content of the polymer, the higher this initial conduction. In the case of the lithium salt bilayer, the initial conduction is probably largely due to lithium migration and has been found to be aided by trace amounts of water. If the initially formed Li salt bilayer is subject to a reduced pressure, the conductivity is observed to decrease (Fig. 3). The current at 10^{-2} μm (10^{-6} torr) is on the order of 10^{-11} A or equivalent to the true current. As air is brought back in contact with the bilayer the current was observed to increase nearly back to the original value. Dry nitrogen passed over the sample also caused the current to drop to the order of 10^{-11} A. Both these observations indicate that the presence of water aids somehow in the space charge migration process, possibly by the following scheme:
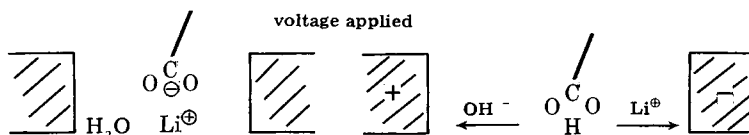
In order to eliminate the effects of space charge currents, measurements on Li salt bilayers were made after 60-V dc had been applied to the sample for three days. Any changes in current on a short time scale after this were assumed to be fluctuations in the true current.
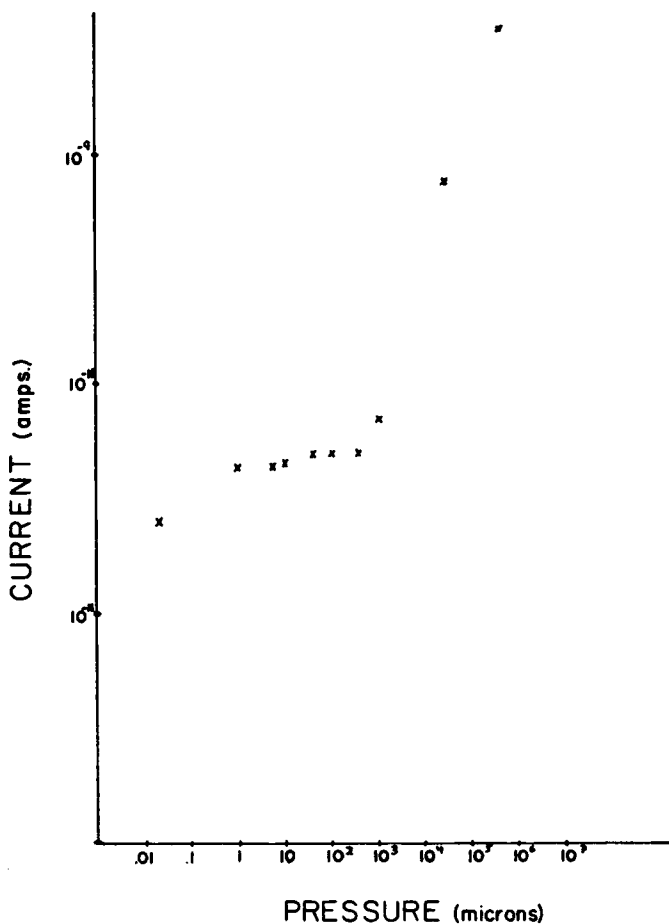
Fig. 3. Dependence of current on pressure.   Li-salt bilayer.

Free Acid Bilayers

For polymerized free acid bilayers formed on the lock-and-key device, the initial current flow as measured is 10^{-7} A, similar to the Li salt bilayer.   The decay was much faster, however, and a "true" current value of 10^{-11} A was reached on the order of minutes after voltage application instead of days, as is the case with the Li salt bilayer.   The much quicker leveling off in the free acid is in accordance with the fact that there are almost no ions present.[8]   The initial space charge current that is observed is probably due to impurities in the water and possibly even aluminum from evaporated electrodes.   The free acid bilayers also exhibited similar behavior to that of the lithium salt bilayer membranes under the influence of vacuum and dry nitrogen.

Doping and Photoconduction

The free acid bilayer exhibits an initial dark current of about 10^{-11} A, as previously mentioned; but, as the iodine is introduced, a large increase in current is observed (Fig. 4).   A maximum is reached after about 12 min at about 3×10^{-8} A, which is an increase of over three orders of magnitude.   Although this is a very
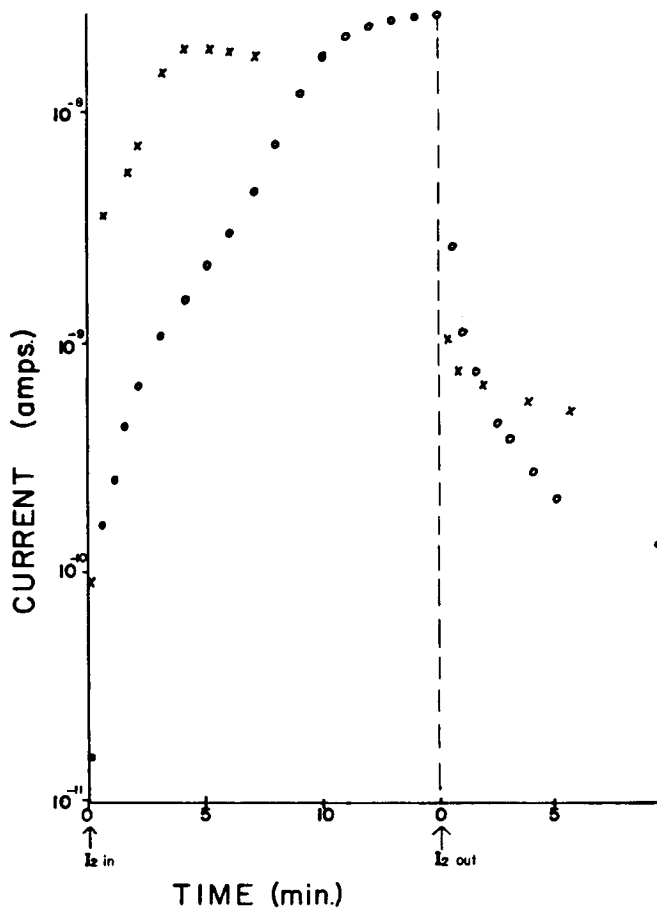
Fig. 4. Photoconductive and doping behavior of free acid bilayer. O, dark current; x, illuminated sample.

large increase, the bilayer has in reality only changed from a good insulator to a poor one.   When pure nitrogen is switched back into the bilayer chamber, the current decays back, almost to its original value.   When the same experiment is run under illuminated conditions (75-W light bulb 1 in. from bilayer) the result is very similar (heating from the light bulb was prevented by an intermediate glass barrier).   A difference in the initial current is observed of about one order of magnitude owing to a photoconductive effect.   Upon doping, about the same maximum is reached and this also decays to the original value after the iodine is removed.   Iodine content of the nitrogen and the flow rate were not monitored so the difference in rate of increase of the dark and illuminated samples in Figure 4 cannot be compared and may be artifact.

In the case of the Li salt bilayer, the dark current was initially about 5×10^{-11} A and increased only slightly upon exposure to iodine to a value of 1.3×10^{-10}. Illuminated samples were observed to have a photoconductive increase of over an order of magnitude (Figure 5).   Upon doping the illuminated sample an increase in current was observed comparable to the free acid bilayer.

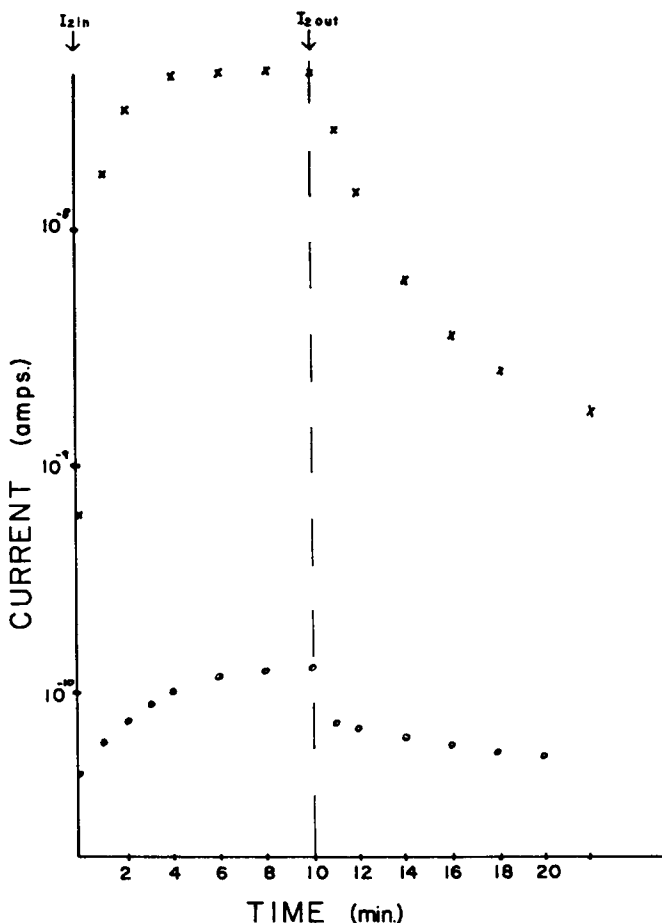The conductivity increases of an order of magnitude for illuminated samples

Fig. 5. Photoconductive and doping behavior of Li-salt bilayer. O, dark current; x, illuminated sample.

and three orders of magnitude for doped samples is in good agreement with published results for single crystals[1] and multilayers.[2]   This also indicates, however, that the high surface area and short diffusion path does not faciliate higher conductivities in polydiacetylene bilayers at room temperature.

Monomer Bilayers

Monomer bilayers were made and measured in the same way as the polymerized layers as a check for backbone participation in the conduction mechanism. Very similar space charge currents were observed for the monomer bilayers of both the free acid and Li salt bilayers.   Both types of bilayers, however, showed absolutly no response to illumination and almost none to doping.   This indicates that the polymer backbone has little effect in the conduction mechanism of a dark undoped sample, but only comes into play upon illumination or doping.

Conduction Mechanism

Although the effect of a dopant in a conjugated system is not well understood, one possible mechanism that has been generally accepted is the association of the dopant directly with a double or triple bond. Depending on the dopant, it either acts to donate or withdraw electrons, creating an extra electron or a hole in the chain which can then migrate. For iodine in polyacetylene it has been suggested[9] that the following may occur:
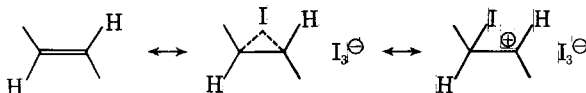
Once the hole is formed then migration can occur:
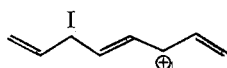
If this were all that was occuring in the bilayer systems, no difference should be observed between the free acid and Li salt bilayers. Quite a significant difference is exhibited, however, in the unilluminated doped free acid bilayer (high current flow) and the unilluminated doped Li salt bilayer (low current flow). The conduction which is known to be occuring along the polymeric backbone (from lack of monomer response) is somehow affected by the hydrophilic portions of the bilayer. At the present time, however, the cause of these phenomena are not well understood.

CONCLUSION

Diacetylene monolayers polymerized at the gas–water interface have a very poor conductivity. They do, however, exhibit a photoconductive and doping effect which can raise the conductivity over three orders of magnitude. Because of the initially low conductivity, the polydiacetylene monolayers could at best only be considered a poor semiconductor after doping. Increases in conductivity from doping and photoconduction are comparable to those measured in diacetylene single crystals and multilayers.

References

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