

“TAILORED” CONDUCTIVITY OF SEGMENTED POLYDIPHENYLACETYLENE THIN FILMS FOR MICROELECTRONIC APPLICATION

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New types of segmented polymers based on polydiphenylacetylene (PDPA) were synthesized and characterized. Measurement of current-voltage (I-V) characteristics of a representative samples show that bulk charge carrier injection dominate the conductive process rather than contact limited transport. Comparing the I-V characteristics measured from different segmented polymers based on polydiphenylacetylene shows that increasing the length of the non-conjugated part of the molecule decreases the material conductivity. This result demonstrate the possibility of “tailoring” the conductivity by changing the length of the non-conjugated part of the segmented polymer molecule.

Keywords: organic semiconductors, molecular electronics, electrical conductivity

1. INTRODUCTION

Organic semiconductors are recently investigated due to their potential application in the microelectronics as solar cells, organic light emitting diodes, field effect transistors and gas sensors [1, 2]. The conjugated low molecular weight materials were the first candidates. Many of them have the disadvantage of being insoluble in commonly used solvents. The films deposited have the tendency to crystallize, especially when operating at elevated temperatures inside the microelectronic chips. This causes an instability and short life-time of the semiconductor devices. Advances including vacuum deposition of amorphous transport layers separating polycrystalline materials from the electrodes [3, 4] or dispersing the chromophores in a polymeric matrix [5, 6] in solid solution partially circumvented these problems.

Conjugated polymers pursues avoiding many of the aforementioned problems.

The use of conjugated polymers was then the most obvious way to improve morphological stability in organic semiconductor, in spite of the higher impurity levels of polymers, which still presented certain drawbacks. In fact, advancements in semiconducting polymers have progressed steadily, since their discovery in 1977 by Heeger et al. at the university of Pennsylvania [7].

Some of the conjugated polymers are still not soluble enough, as a result of the strong interaction between the alternated single and double bonds in the molecule chain. Many of the conjugated polymers could not be deposited in vacuum due to their heavy molecules. Thin films could be prepared by casting of their oligomeric precursors then causing polymerization on the substrate.

However, to optimize performance, the effect of polymer structure upon charge transport and emission properties must be understood and controlled. In this context,

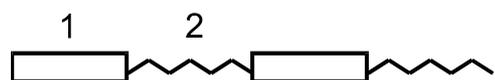


Fig. 1. Scheme of segmented polymer 1 – non-conjugated and 2 – conjugated parts.

synthesis of new type of polymers so called “segmented” polymers was introduced [8].

Segmented polymers consist of alternated conjugated and non-conjugated segments.

Among them the polymeric Schiff bases are interesting group having carbon-nitrogen

double bonded units in the main chain, capable of protonation and complexation. They have been studied intensively owing to their properties: good thermal stability, mechanical strength, non linear optical properties, ability to form metal compounds, semiconducting properties, environmental stability and fiber-forming properties, which are associated mainly with their conjugated backbone and the presence of imine sites. These polymers could become new materials suitable for use in polymer electronics, especially in view of a recent discovery that the photoluminescence and electroluminescence of conjugated polymers containing basic sites in the main chain can be strongly modified by protonic (acid-base) doping [9].

Measurement of current-voltage (I - V) characteristics gives valuable information about the intrinsic properties of semiconductor material from one side and the quality of electronic devices as well. It is known that the trap concentration and their distribution in the energy reflects the shape of the I - V characteristic [10]. By this method it is also possible to estimate the quality of single semiconductor devices.

This work aimed to investigate the electrical conductivity of segmented polymers, which consist of conjugated polydiphenylacetylene chains and non-conjugated parts of diaminohexane and diaminobutane. It is expected that changing the length of non-conjugated segments could be used to “tune” the polymer conductivity.

2. EXPERIMENTAL DETAILS

2.1. Polydiphenylacetylene synthesis

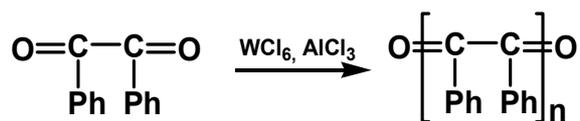


Fig. 2. Synthesis of polydiphenylacetylene.

Oligomeric polydiphenylacetylene (PDPA) possessing carbonyl end-groups was obtained via polymerization of benzil under the influence of the Friedel-Crafts olefin metathesis catalytic system $\text{WCl}_6 + \text{AlCl}_3$ as presented in Fig. 2. For this purpose

Benzil (Fluka) was sublimated and chlorobenzene was dried over P_2O_5 , distilled, then dried again over CaH_2 and distilled before use.

To the solution of 2g benzil in 10 ml chlorobenzene were added 2g WCl_2 . The mixture was kept at $100^\circ C$ for 2 hr. then $AlCl_3$ (0.7g) was added. The solution was kept at $100^\circ C$ for another 14 hr. and cooled down. After addition of 2 ml ethanol the solution was washed with aqueous sodium hydroxide and water until neutral. Finally the polymer was precipitated in ethanol, filtered off, redissolved in chloroform and again precipitated in ethanol (yield 1.6g, $M_w=4500$).

The chemical reaction of synthesis of polydiphenylacetylene with Schiff base-end groups is presented in Fig. 3. 0.400g of PDPA and 0.400g of 1,6-diaminobutane (Fluka) were heated and stirred at $100^\circ C$ for 24 hr. The mixture was cooled down, dissolved in chloroform and precipitated in methanol. The modified with

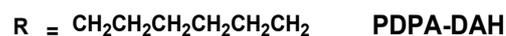
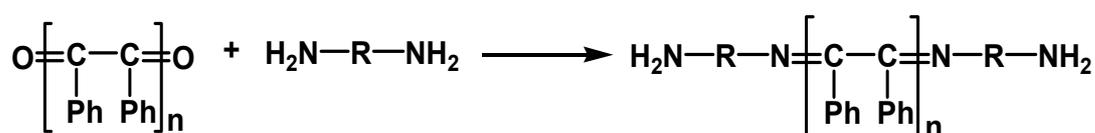


Fig. 3. Synthesis of polydiphenylacetylene with Schiff base-end groups.

diaminobutane polydiphenylacetylene (PDPA-DAB) powder ($M_w=2513$) was dried for 24 hr. at $100^\circ C$ [8].

The modified with 1,4-diaminobutane polydiphenylacetylene (PDPA-DAB) was synthesized under the same conditions.

2.2 Sample preparation and measurements

The sample consists of polymer active layer “sandwiched” between two electrodes (ITO and Al) as shown in Fig 4. The bottom ITO electrode was deposited by magnetron sputtering following a procedure explained elsewhere [11]. Solutions of the three types of polymers – PDPA, PDPA-DAB, PDPA-DAH in chloroform

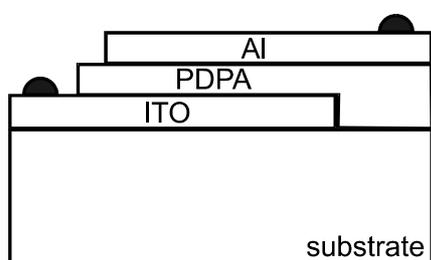


Fig. 4. Schematic draw of the sample used for electrical measurements.

were prepared in a concentration of 50 mg/ml. Thin films were deposited by spin-coating at 3300 rpm keeping the speed for 5 s. After deposition the films were dried for 24 h at room temperature to remove the residual solvent. The film thickness was measured with Talystep thickness profilometer on films deposited at the same conditions on glass substrates. Top electrodes for the electrical measurements were deposited in vacuum of 1×10^{-5} Torr by thermal evaporation of Al through a mask. The structures prepared were wired by silver paste

outside of the measurement area avoiding short connection between the electrodes. I - V characteristics were measured in vacuum of 1×10^{-5} Torr by computer controlled Keithley 617 electrometer.

3. RESULTS AND DISCUSSION

3.1. Material characterization

The chemical structure of the reaction products was proved by IR analysis. IR spectra were measured on KBr pressed pellets by Fourier infrared spectrometer Bruker Vector 22. The spectrum taken from PDPA sample is plotted in Fig. 5., Curve 1. Characteristic peaks for C=O groups can be observed at 1737 cm^{-1} and 1687 cm^{-1} respectively. In Fig. 5., Curve 2 IR PDPA-DAH spectrum is presented. It is clearly seen that the the peaks corresponding to C=O groups diminish and new peak connected with C=N group (1653 cm^{-1}) appear. This is a clear indication of successful PDPA-DAH synthesis.

The same change was observed in spectra obtained from PDPA-DAB.

Formation of Schiff bases is also proved by a peak in the ^1H NMR spectrum at 3.4 ppm assigned to $-\text{CH}_2\text{-N}=\text{}$ protons [8].

3.2. Current-Voltage measurements

I - V characteristic of a representative PDPA sample measured in both direction of the voltage axis is presented in Fig. 6. The symmetrical curve shows that the carrier injection in the bulk of the material dominates the conductivity process than contact limited transport. Plotting the same curve in log scale (Fig 7, Curve 1.), supports this

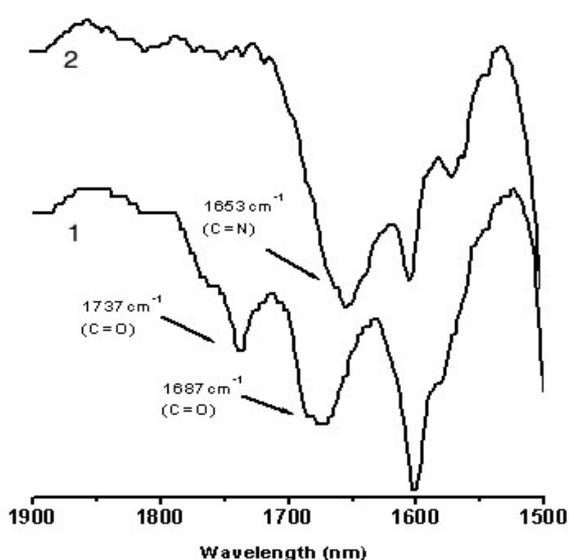


Fig. 5. FTIR spectra of 1 – PDPA, 2 - PDPA-DAH.

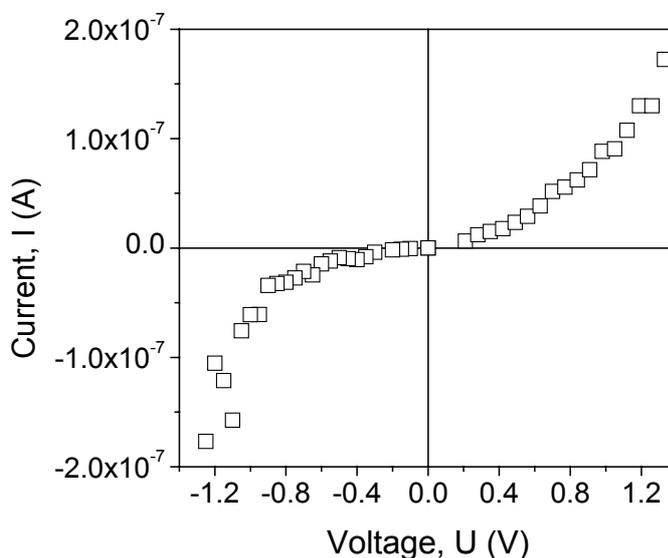


Fig. 6. Typical I - V characteristic of PDPA 450 nm thick film in ITO|PDPA|Al structure.

injection in the bulk of the material dominates the conductivity process than contact limited transport. Plotting the same curve in log scale (Fig 7, Curve 1.), supports this

assumption as the slope of two could be related to charge carrier bulk injection in trap-free case. Increasing the voltage causes the Fermi level to cross trap levels, which results in an increase of the slope of the characteristic.

Comparing this result with those obtained from I - V measurements of segmented polymers with different length of the non-conjugated part (PDPA-DAH and PDPA-DAB) (Fig. 7., Curves 2 and 3) shows that the total resistivity of the sample increases, as should be expected. The slope of the curve slightly decreases. It could be supposed that the spacer of non-conjugated amine groups could act as contact barriers between the PDPA conjugated segments. This result demonstrates the possibility of “tailoring” the conductivity by changing the length of the non-conjugated part of segmented polymer molecule.

5. CONCLUSION

New types of segmented polymers based on polydiphenylacetylene were synthesized and characterized by FTIR spectroscopy. Measurement of current-voltage characteristics (I - V) of a representative sample show that bulk charge carrier injection dominates the conductive process rather than contact limited transport. Comparing the I - V characteristics measured from different segmented polymers based on polydiphenylacetylene shows that increasing the length of non-conjugated part of the molecule decreases the material conductivity. This result demonstrates the possibility of “tailoring” the conductivity by changing the length of the non-conjugated part of the segmented polymer molecule.

6. ACKNOWLEDGEMENTS

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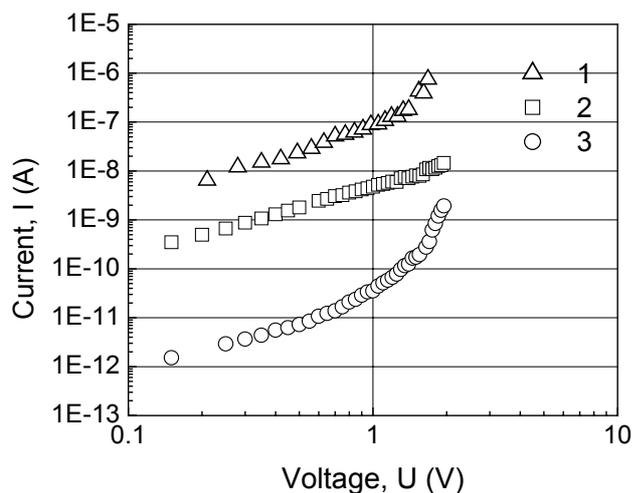


Fig. 7. I - V characteristics in of 1 - PDPA, 2 – PDPA-DAB, and 3 – PDPA-DAH plotted in log-log scale.

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