

## The Fabrication and Characterization of the Photovoltaic Cells Composed of Polydiacetylene and Fullerene

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**Abstract:** Propargyl alcohol was coupled to 2,4-hexadiyne-1,6-diol (HDD) and crystallized in the process of ultraviolet irradiation-induced topochemical polymerization. The HDD polymer crystals were used as one component in the fabrication of organic photovoltaic cells, in combination with fullerene as the electron acceptor. The various structures of the produced photovoltaic cells included bilayer, trilayer, and bulk heterojunction structures. Their photovoltaic properties were analyzed in relation to crystal structure, electrochemical properties, and band structure of the HDD polydiacetylene polymers.

**Keywords:** Polydiacetylene, Topochemical polymerization, Photovoltaics, Bulk heterojunction

### Introduction

Photovoltaic cells based on polymeric materials have been widely studied, since they are expected to support cheap, flexible, and easily processable solar cells replacing conventional, silicon-based solar cells [1]. However, for the production of polymer solar cells, some difficulties such as photochemical degradation and low power conversion efficiency must be overcome. Therefore, scientists are searching for new materials, including conductive polymers, to make innovative polymeric solar cells. The structure, morphology, and device fabrication of conductive polymers that are suitable for application to new types of photovoltaic cells have been investigated, because their electrochemical behavior is similar to inorganic semiconductors.

The most widely used concepts for the fabrication of organic and polymeric solar cells are based on the combination of electron-donating and electron-accepting properties of organic materials, which use the same principles as the conventional, silicon heterojunction solar cells [2]. However, the semiconducting properties of polymers are fundamentally different from that of most inorganic semiconductor, which results in the more diverse microstructure of organic photovoltaic cells.

The intermolecular forces of organic materials are too weak to form a three-dimensional crystal lattice, which could not form a conduction band and valence band from the lowest unoccupied and highest occupied molecular orbitals. Thus charge transport in organic conductors usually proceeds by the hopping mechanism between localized states rather than by transport within a band [3]. Consequently, the charge carrier mobility and charge separation are much lower and more difficult in organic materials than in inorganic ones. Furthermore, the photon absorptions in organic materials produce excitons localized on molecular segments for which the separation into charges is difficult. The typical diffusion length of excitons in organic semiconductors lies in the range of

10 nm. The delocalization of excitons is much easier for conjugated conductive polymers than for low molecular weight organic semiconductors, which enables the greater number of analogous properties to the inorganic semiconductors.

All these barriers to the use of organic and polymeric materials for photovoltaic cells have resulted in a diverse range of research seeking new organic materials, nanopatterning, and fabrication methods of organic photovoltaic cells [4-7]. In the developments of early photovoltaic cells, most of the cells used principles of bilayer heterojunction that were similar to the conventional silicon solar cell. In the bulk (or dispersed) heterojunction photovoltaic device, the diffusion length of exciton, which is much shorter than the film thickness of the active layer, is overcome by simple blending of electron donors and acceptors, although it has very ineffective charge transport and electrode contacts. In order to increase the efficiency of bulk heterojunction, diverse ideas have been reported and tested, including molecular heterojunction, layer structure control with self-assembly technique, phase separation with block copolymer, liquid crystalline order. Sometimes, dye molecules have been utilized to enhance light absorption and energy transfer as in the case of so-called dye-sensitized solar cells.

We are seeking more effective interlocked or bicontinuous nanostructured systems composed of electron-donating and electron-accepting materials in order to raise the power conversion efficiency of organic photovoltaic cells [8,9]. Polydiacetylene is one of the polymers promising to satisfy this objective, as their backbone is fully conjugated with  $\pi$ -electrons. Additionally, their monomer crystals can be transformed to the polymer crystals without destroying the basic crystal structure by applying irradiation and heat. This transformation of monomers to polymers is called topochemical polymerization [10]. In this paper, we have chosen one compound of monomers that has a diacetylene moiety in its backbone. By the combination of polydiacetylene with the strong electron acceptor fullerene, diverse photovoltaic cells were fabricated and their photovoltaic performance was analysed.

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## Experimental

### Materials

Propargyl alcohol was purchased from Aldrich and used without further purification. The coupling oxidants copper (I) chloride was from Junsei Chem and ammonium chloride from Ducksan. Buckminsterfullerene C<sub>60</sub> was purchased from Aldrich. Poly(ethylene glycol) (PEG) of number average molecular weight 8000 g/mole was used as the binding material.

### The Coupling of Propargyl Alcohol to 2,4-hexadiyne-1,6-diol (HDD)

Ammonium chloride (40 g, 0.75 mole) and copper (I) chloride (25 g, 0.25 mole) were added to 200 ml of distilled water. The reaction flask was bubbled with oxygen gas and 11.2 g (0.2 mole) of propargyl alcohol was added. After 5-hour coupling reaction at 50 °C the reaction mixture was cooled to room temperature and poured into 100 ml of distilled water. The HDD product was extracted with diethyl ether, dried with magnesium sulfate, filtered, and concentrated to yellow product by evaporation of diethyl ether in a rotary evaporator. For the purification of HDD, 1 g of HDD was dissolved in 50 ml of distilled water at 70 °C and the aqueous solution of HDD was recrystallized to needle-like crystals for 2 days at room temperature [11].

### Topochemical Polymerization of HDD to PHDD

HDD crystals were polymerized to PHDD by the irradiation of crystal needles for 1 day with UVP ultraviolet lamp (8900-21700 μJ/cm<sup>2</sup>).

### Fabrication of Photovoltaic Cells

In this study, the photovoltaic properties of four types of photovoltaic cells that had been fabricated were analyzed. They are summarized in Table 1 and abbreviations are explained at footnote. The first type, coded BL in Table 1, had a bilayer heterojunction cell structure, for which HDD was deposited on ITO under vacuum ( $2 \times 10^{-4}$  Torr) and irradiated for polymerization. Fullerene and aluminum were deposited sequentially on it ( $2 \times 10^{-5}$  Torr). The second type, coded HB, was fabricated through bulk heterojunction by blending fullerene with the HDD monomer. HDD and fullerene were dispersed in PEG solution in ethanol (2.5 wt%). The ratio of HDD to fullerene was varied according to samples. The prepared slurry was transferred onto ITO through dip or spin coating. The coated layer was irradiated for polymerization for 3 days and then aluminum was deposited on it. The third type, coded PB, was fabricated through bulk heterojunction by blending fullerene with the PHDD polymer. Fullerene was dispersed in PEG solution in benzene (2.5 wt%) for one day after which PHDD powdered crystals were added to give slurry. The prepared slurry was transferred onto ITO through dip or spin coating followed by drying and vacuum deposition of aluminum. The fourth type, coded TL had a

**Table 1.** Parameters for current-voltage characteristics of the photovoltaic cells using PHDD and fullerene as heterojunction materials as electron acceptor and donor, respectively

Samples <sup>1</sup>	$I_{sc}$ (μA/cm <sup>2</sup> )	$V_{oc}$ (mV)	$FF$	$P_{max}$ (10 <sup>-6</sup> mW/cm <sup>2</sup> )	$\eta$ (10 <sup>-4</sup> %)
BL	57.8	86	0.31	1562.4	64.6
HB-25	45.7	38	0.25	433.8	17.9
HB-50	6.6	62	0.26	105.6	4.4
HB-75	11.2	5	0.24	13.4	0.6
PB-25	5.4	106	0.27	151.7	6.3
PB-50	4.8	50	0.26	62.4	2.6
PB-75	5.0	23	0.26	30.2	1.2
TL-25	1.0	176	0.26	46.6	1.9
TL-50	0.2	120	0.32	8.1	0.3
TL-75	0.2	55	0.26	3.3	0.1

<sup>1</sup>Numbers in the sample codes indicate percentage ratio of PHDD to fullerene. Abbreviations in the sample codes are as follows: BL; bilayer, HB; HDD monomer blend for bulk heterojunction, PB; PHDD polymer blend for bulk heterojunction, and TL; trilayer.

trilayer structure, which was formed in the sequence of cell fabrication of ITO/PHDD/PHDD + Fullerene/Fullerene/Al. The PHDD layer was formed through the polymerization of precoated HDD. The other layers were formed using the same methods described above.

### Characterization of Components and Photovoltaic Cells

FT-IR spectra were observed with Nicolet MAGNA-560 FT-IR and ATR-IR was observed with travel IR of sensIR. Melting point was measured with DSC of Pyris + AS6. UV-VIS absorption spectra were taken with UV-2550 of Shimadzu. Scanning electron microscopy (SEM) images were taken with JSM-6300 of JEOL. Cyclic voltammograms and I-V curves were taken with an EG & G Parc model 273A potentiostat/galvanostat. Cyclic voltammograms were obtained with the ITO working electrode coated with polymer film and Ag/AgCl reference electrode. The solution of tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) in acetonitrile (0.1 M) was used as the electrolyte. Polymer film was made by spin coating at a scanning rate of 50 mV/sec in the range of -2 V~2 V. Xenon-Arc Lamp LH151 of Spectral Energy Corp was used as the light source for the measurement of I-V curves.

## Results and Discussion

For the topochemical polymerization of diacetylene compounds, the monomers should be taken in crystal form, in which the parallel diacetylene linkage can be transformed into the polymeric backbone by slight distortion, as shown in the chemical structure of Figure 1. The coupling of propargyl alcohol to HDD and the polymerization of HDD to PHDD

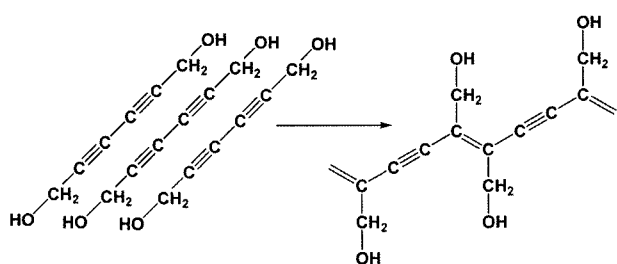


Figure 1. Chemical structure for the topochemical polymerization of HDD to PHDD.

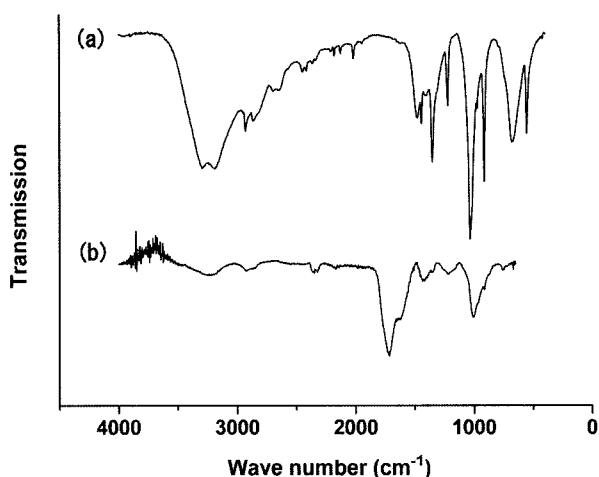


Figure 2. ATR-IR spectra of (a) HDD and (b) PHDD.

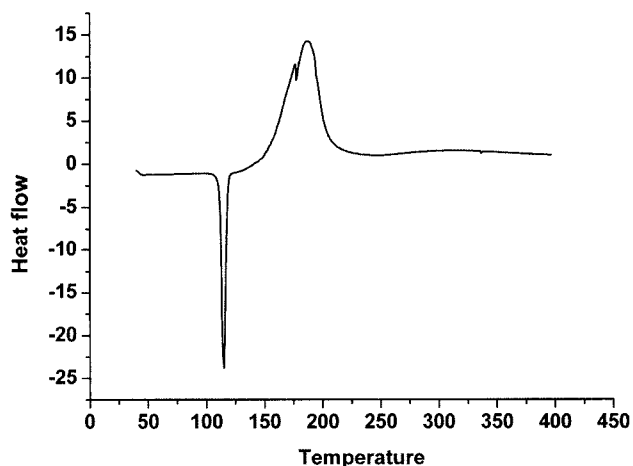


Figure 3. DSC thermogram of HDD.

were confirmed by the ATR-IR spectra of Figure 2. The common stretching vibration peaks of O-H, C≡C, and C-H were observed in (a) and (b) of Figure 2. The polymerization reaction was confirmed by the observation of the C=C characteristic absorption as a strong peak at 1680 cm<sup>-1</sup>. Crystals of HDD were confirmed with sharp melting point by strong and sharp endotherm at 114.5°C, as shown in

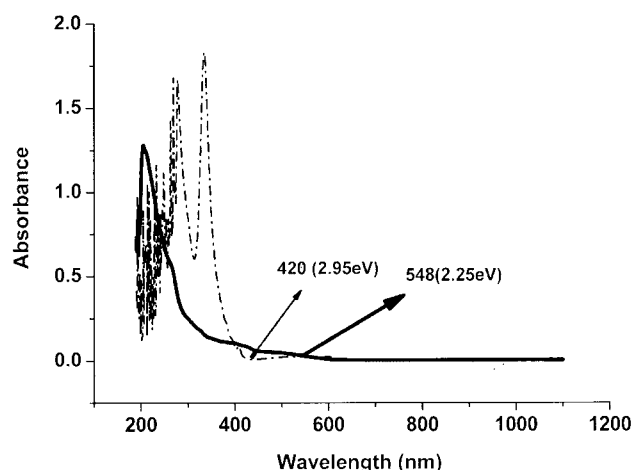


Figure 4. UV/VIS spectra of PHDD in ethanol (solid) and fullerene in benzene (dash).

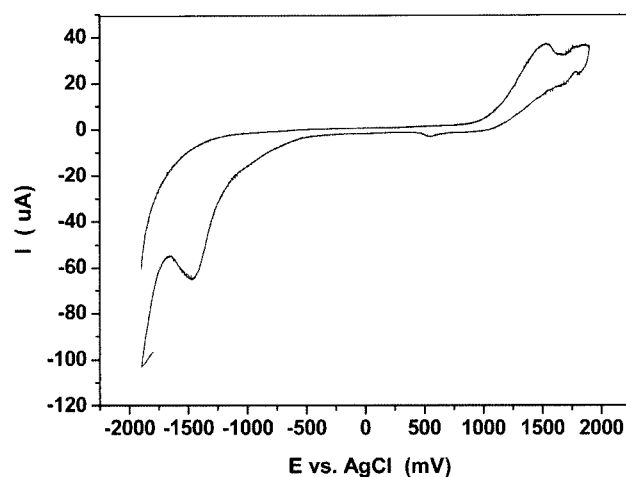
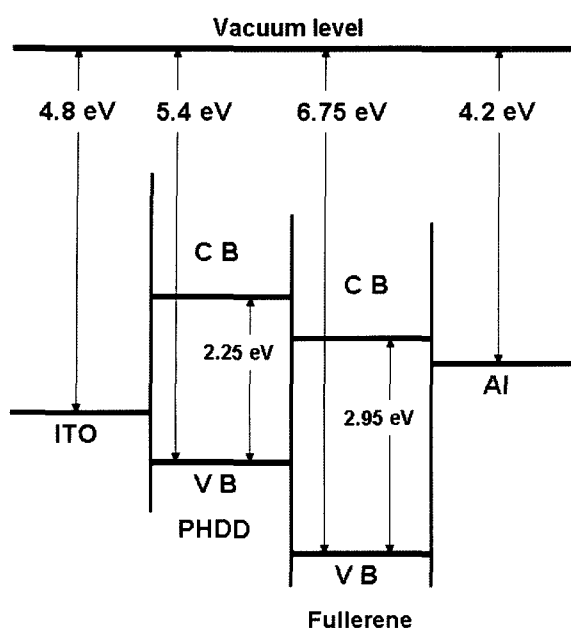


Figure 5. Cyclic voltammogram of PHDD with 0.1 M TBABF<sub>4</sub> solution in acetonitrile (scanning rate 50 mV/s).

Figure 3. The broad and strong exothermic peak around 200°C indicates the thermal topochemical polymerization of HDD to PHDD.

The energy level of PHDD and fullerene was analyzed using cyclic voltammetry and spectroscopic absorption data [12]. The absorption spectra of PHDD and fullerene, those offer the band gap of electron donor and acceptor, are shown in Figure 4. The onset points of 2.25 eV and 2.95 eV were chosen as the approximated band gaps of donor PHDD and acceptor fullerene, respectively. Figure 5 shows the cyclovoltammograms of pure PHDD, which were obtained from the polymer film coated on ITO glass in 0.1 M TBABF<sub>4</sub> solution in acetonitrile. From the PHDD redox scans, the electrochemical potentials at vacuum level can be derived by comparing with a known reference value of -4.8 eV for ferrocene with a measured half wave potential of 395 mV. As shown in Figure 5, PHDD showed an oxidation onset potential of 1.0 V giving an

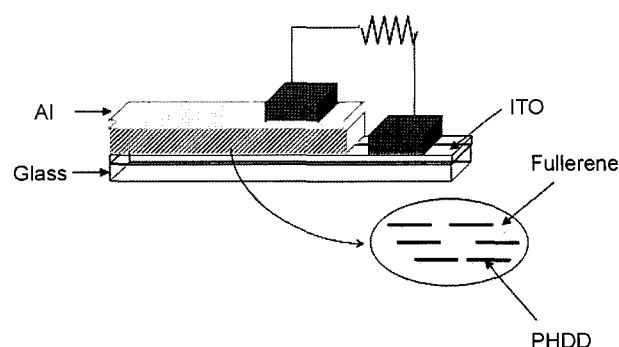


**Figure 6.** Schematic energy-level diagram of components consisting of photovoltaic cells.

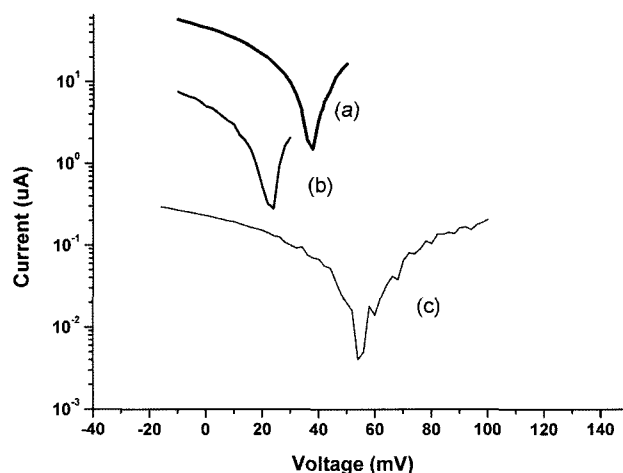
ionization potential of 5.4 eV, and thereby indicating the valence band level. The energy levels of fullerene for conduction band, band gap, and valence band were measured and used as described in the literature [8]. The work functions of aluminum and ITO were also used as previously described. By combining the absorption data with the obtained band levels and the known work function of ITO and aluminum, all necessary energy levels could be analyzed, as shown in Figure 6.

Figure 6 shows that energy level of PHDD is similar with the energy level of p-type semiconductor of pn-heterojunction silicon solar cell. The photovoltaic current is based on the mobility of electrons from p-semiconductor to n-semiconductor, which are generated from the photons absorbed in p-semiconductor region. This comparison results in the assumption that PHDD acts as a p-semiconductor and effective light absorber and electron-donating material and that fullerene is an electron accepting material, as proposed in the literature. But in the case of organic material like PHDD, additional charge separation process from exciton is necessary for the photovoltaic current. The heterojunction of PHDD and fullerene, shown as an active layer in Figure 7, can be divided into four types: a bilayer type, two bulk heterojunction types and a trilayer heterojunction type. In the two bulk heterojunction types, fullerene is blended with HDD or PHDD following the coating to active layer. The blended HDD is polymerized by UV irradiation. The photovoltaic devices are varied according to the ratio of PHDD to fullerene. The photovoltaic characteristics are summarized in Table 1.

The typical shapes of the I-V curves for the fabricated cells are shown in Figure 8. All the cells exhibited a clear



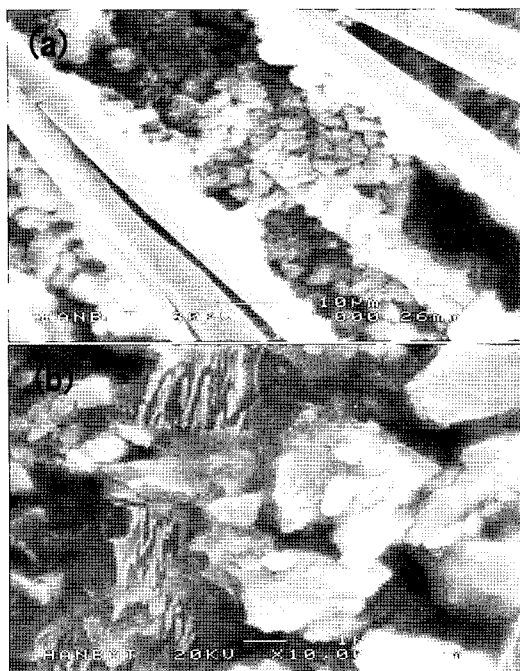
**Figure 7.** Scheme of the photovoltaic cell showing the fabrication of electron donor, acceptor and electrode materials.



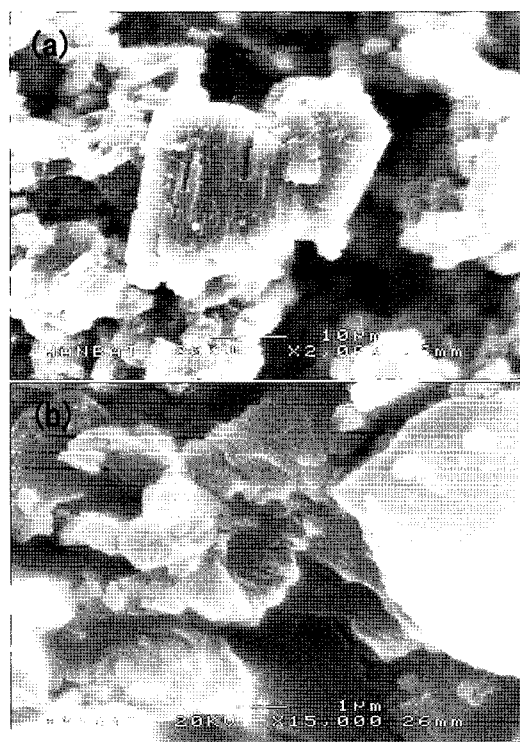
**Figure 8.** Examples of typical I-V curves of photovoltaic cells; (a) HB-25, (b) PB-75, and (c) TL-75.

photovoltaic effect as confirmed by the offset of minimum current from zero point, although the photocurrent was very low compared with that of a conventional solar cell. The open-circuit voltages  $V_{oc}$  were also much lower than the value expected from Figure 6. It is assumed that these differences between the expected and measured values were resulted from the unclear onset point of the absorption spectrum and cyclovoltammogram.

The crystal PHDD structures, being the most important feature of interest in this study, were observed with SEM. The shape of the crystals was observable, even though their size was reduced. We assumed that the photovoltaic effect resulted from the well-arrayed semiconductive polydiacetylene skeleton of the polymer structures. The crystals of the HB type cells could be divided in well-grown needle shape and small crystals of uncertain angles, whereas the crystal powder in the PB type cells presented broken shapes with well-arrayed microstructure. Usually, bulk heterojunction type cells show lower photovoltaic performance than the bilayer type. Additionally, the increase of PHDD to fullerene ratios usually decreases the photovoltaic performance. As shown



**Figure 9.** SEM micrographs of photoactive layers of HB-type bulk heterojunction.



**Figure 10.** SEM micrographs of photoactive layers of PB-type bulk heterojunction.

in Figures 9 and 10, the size of the crystals is much larger than the exciton diffusion length. We assume that the larger size

of crystals to exciton diffusion length causes low photovoltaic current by depressing charge separation in PHDD layer with increasing PHDD content. Additionally, it is meaningless to analyze in detail the interfacial morphology of donors and acceptors, because most of excitons are assumed not to reach the step of charge separation due to large bulk size of donor.

The photovoltaic cell using bilayer heterojunction showed the best maximum power  $P_{\max}$  of  $1.56 \times 10^{-3}$  mW/cm<sup>2</sup>. In this study, no detailed spectral analysis was performed. The best  $P_{\max}$  value corresponded to a photoelectric power conversion efficiency of  $6.5 \times 10^{-3}$  %, although this was only roughly estimated from the power of the 240 W/m<sup>2</sup> Xe lamp without any analysis of the spectral response. All the cells showed a relatively low fill factor in comparison to other studied solar cells, indicating the presence of diverse interfacial energy levels in the PHDD/fullerene heterojunction. The power conversion efficiencies of all the cells tested in this study still remained much lower than those of conventional silicon solar cells. However, new photovoltaic devices using organic materials in active layer have usually shown power conversion efficiency values lower than 1 %, which explains the research attention on finding new, cheap and easy producible photovoltaic materials and devices.

## Conclusions

Among the various methods presently being investigated in the search for and testing of new materials for more flexible and larger area organic solar cells, this study examined polydiacetylene as a photoactive material. The backbone structure of polydiacetylene was successfully fabricated into the photovoltaic cells. Polydiacetylene showed a photovoltaic effect in combination with fullerene, although the magnitudes of current and open circuit voltage of the tested cells were far too low for practical application. For improved performance of these organic solar cells, the use of nano-sized and defect-free crystals is proposed.

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