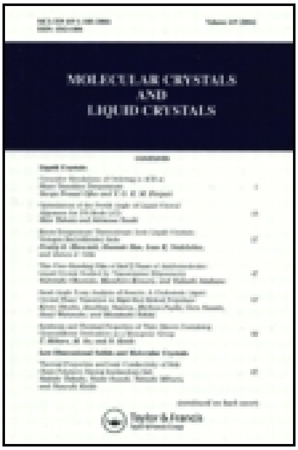

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Polymer-Sensitized Solar Cells Using Thiophene Copolymers

Mi-Ra Kim [a], Won Suk Shin [a], Woo-Seok Kim [b], Hyun-Jeong Lee [b], Sung-Hae Park [b], Jin-Kook Lee [b] & Sung-Ho Jin [c]

[a] Center for Plastic Information System, Pusan National University, Busan, Korea

[b] Department of Polymer Science & Engineering, Pusan National University, Busan, Korea

[c] Department of Chemistry Education & Center for Plastic Information System, Pusan National University, Busan, Korea

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Mi-Ra Kim
Won Suk Shin
Center for Plastic Information System, Pusan National University,
Busan, Korea

Woo-Seok Kim
Hyun-Jeong Lee
Sung-Hae Park
Jin-Kook Lee
Department of Polymer Science & Engineering, Pusan National
University, Busan, Korea

Sung-Ho Jin
Department of Chemistry Education & Center for Plastic Information
System, Pusan National University, Busan, Korea

Soluble thiophene-based copolymers, poly[(3-alkylthiophene)-co-(3-thiophene acetic acid)]s (P3AT-co-3TAA-n's), were synthesized to apply to the polymer sensitizer of the polymer-sensitized solar cell devices. In order to improve the solubility and the chemical adsorption onto nanoporous TiO_2 layers in the polymer-sensitized solar cell devices, thiophene-based copolymers having the chemical structures of the carboxyl group and the alkyl group were designed. We have fabricated solid-state polymer-sensitized solar cell devices using polymer sensitizers and polymer electrolytes, and investigated on the photovoltaic performances. In the polymer-sensitized solar cell devices using polymer sensitizers, V_{oc} is 0.37–0.46 V, J_{sc} is 0.82–7.71 mA/cm^2, and the power conversion efficiency is 0.14–0.38%, respectively.

Keywords: photovoltaic performance; polymer electrolyte; polymer-sensitized solar cells; thiophene copolymer

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Address correspondence to Mi-Ra Kim, Center for Plastic Information System, Pusan National University, Jangjeon-dong, Guemjeong-gu, Busan, 609-735, Korea. E-mail: mrkim2@pusan.ac.kr

INTRODUCTION

Dye-sensitized solar cells (DSSCs) consisting of dye molecules, nanocrystalline metal oxides and organic liquid electrolytes have attractive features of high power conversion efficiency. Recently, the solar power conversion efficiencies of DSSCs using Ruthenium complex dyes and liquid electrolytes have reached 10.4% (100 mW/cm^2, AM1.5) by Gratzel group [1]. However, it could not be applied to the commercialization because of its several problems such as the sealing to block the leakage of liquid electrolyte or expensive Ruthenium complex sensitizer materials. The replacement liquid electrolytes to solid type electrolytes, or the replacement expensive Ruthenium complex sensitizer to low cost thiophene-based copolymers sensitizers, have been able to solve the problems [2–4]. In particular, thiophene-based polymers have been practically interested in possible replacement for the liquid electrolyte or sensitizers on DSSC devices, because of their solubility [5], processability, environmental stability [6], and excellent conductivity [7]. The thiophene-based polymers generally are easy for structural modifications, such as the substitution of long alkyl group or carboxylic group, moreover, it can make the polymers soluble and the polymers adsorbed onto the surface of the nanoporous TiO_2 layers. The improvement of the adsorption onto the surface of the nanoporous TiO_2 layers by the chemical modifications of thiophene-based polymers allows us to the possibility of the replacement of expensive Ruthenium complex dyes. In spite of the replacement, the solar power conversion efficiencies of DSSCs using thiophene-based copolymer sensitizers can be decreased in compared to that using Ruthenium complex sensitizer, which has wide absorption range up to near-IR region.

In this study, we have synthesized thiophene-based copolymers, poly[(3-alkylthiophene)-co-(3-thiophene acetic acid)]s (P3AT-co-TAA)s), as polymer sensitizers on solid-state polymer-sensitized solar cell devices. In order to apply to polymer sensitizers of polymer-sensitized solar cell devices, thiophene-based copolymers were designed as the chemical structures having both the carboxylic group and the alkyl group. These copolymers were covalently attached onto the surface of nanoporous TiO_2 layers *via* the carboxylic groups, which need to lead to satisfactorily high photo conversion efficiency after the absorption of the light. To examine the application of the thiophene-based copolymers as polymer sensitizers on solar cell devices, we have fabricated polymer-sensitized solar cell devices using thiophene-based copolymer sensitizers and investigated on the photovoltaic performance by Solar Simulator.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN, $M_w = 22{,}600$), tetrabutylammonim iodide (TBAI), iodine (I_2), 1-ethyl-3-methylimidazolium iodide, propylene carbonate (PC) and ethylene carbonate (EC) were purchased from Sigma Aldrich company and used as supplied without the purification. Fluorine-doped SnO_2-layered (FTO) glass (15 ohm/sq), Pt-Catalyst T/SP, and Ti-Nanoxide HT were purchased from Solaronix SA and used as supplied.

Synthesis of Thiophene-based Polymers

Anhydrous $FeCl_3$ (8.75 g, 54.15 mmol) was added into a reaction vessel which contained $CHCl_3$ (100 ml). The flask was equipped with a stirring bar and a N_2 inlet. After stirring for one hour at room temperature, 3-thiopheneacetic acid (**TAA**, 0.12 g, 0.82 mmol) and 3-hexylthiophene (**3HT**, 1.4 g, 8.2 mmol) in $CHCl_3$ (10 ml) was added via a syringe to the suspension. The reaction mixture was stirred at room temperature for 5 h under a flow of nitrogen. The reaction mixture was then poured into a large quantity of methanol and the black precipitate was collected by filtration. The resulting material was washed with methanol. It was collected and purified by soxhlet extraction with methanol, ether, and chloroform in turn and then dried in high vacuum. The yield of **P3HT-co-TAA-1** was 0.45 g (29%). **P3HT-co-TAA-2** was synthesized with different molar ratio (**TAA: 3HT** = 1: 20) of monomers in the same reaction condition of above procedure. Thiophene copolymers based on 3-thiopheneacetic acid and 3-dodecylthiophene (**P3DT-co-TAA-*n*'s**) were synthesized by the same process with **P3HT-co-TAA-*n*'s**. To compare with the photovoltaic effects of polymer-sensitized solar cell devices on the interface adsorption by the chemical structure of the polymer sensitizers, homopolymers (**P3HT** and **P3DT**) were synthesized using **3HT** and **3DT**, respectively, by the same reaction process with copolymers. The chemical structures of the thiophene-based copolymers and homopolymers were shown in Figure 1.

Fabrications of Polymer-Sensitized Solar Cell Devices

We have prepared the polymer-sensitized solar cell devices, using thiophene-based polymers (**P3HT, P3DT, P3HT-co-TAA-*n*'s**, and **P3DT-co-TAA-*n*'s**) as a polymer sensitizer and a polymer electrolyte with polyacrylonitrile (PAN) matrix. The polymer-sensitized solar cell device was fabricated as following process; a volume of ca. $10\,\mu l/cm^2$ of the transparent pastes (Ti-Nanoxide HT) was spreaded on FTO

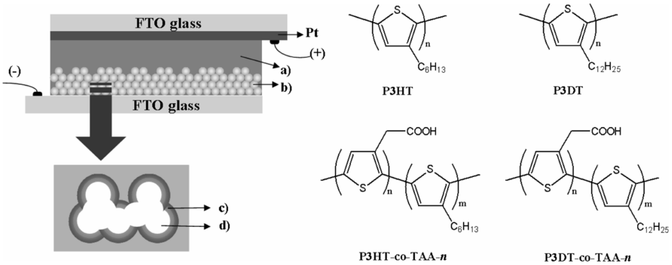

FIGURE 1 The cross section structures of the polymer-sensitized solar cell device (left) constructed by thiophene-based polymers (right) as a sensitizer, polymer electrolyte (a), and nanoporous TiO_2 film (b); inner structure is the sensitizer layers (c) adsorbed onto nanoporous TiO_2 film (d).

glass by the doctor blade method. After heating up the FTO glass spreaded TiO_2 nanoparticle to ca. 100°C for about 30 min and ca. 450°C for about 30 min, the sintering process was completed and the TiO_2 deposited electrode was cooled down from 100°C to ca. 60°C as the controlled cooling rate (3°C/min) to avoid cracking of the glass. Pt counter electrode was fabricated by spreading on FTO glass using the doctor blade method. After heating up the FTO glass spreaded Pt Catalyst T/SP to at 100°C for 10 min prior firing at 400°C for 30 min. The thiophene-based polymer sensitizer was dissolved in chloroform in a concentration of 20 mg per 100 ml of solution. Nanoporous TiO_2 film was dipped in this solution at room temperature for 24 hours. Afterwards, the polymer-sensitized TiO_2 electrode was rinsed with chloroform and dried in air. Without a sealant, the electrolyte solution was casted onto TiO_2 electrode impregnated thiophene-based polymers, and then was dried at 60°C for 2 hours. The electrolyte was composed of EC (ethylene carbonate)/PC (propylene carbonate) (EC:PC = 4:1(w/w)), and PAN as a polymer matrix. The cross-section structure of the polymer-sensitized solar cell device was shown in Figure 1. In Table 1, the compositions of the contents in polymer electrolyte solutions were listed. Tetrabutylammonium iodide (TBAI), I_2 and PAN were dissolved in acetonitrile solution, and then EC and PC as a plasticizer were added into this solution. Polymer electrolytes were usually consisted of 0.5 M of TBAI, 0.25 M of I_2, and 1.5 M of ionic liquid in acetonitrile solution. Typically, in dye-sensitized solar cells, an iodide/tri-iodide (I^-/I_3^-) redox couple dissolved in organic solvents has been used. However, use of the volatile organic solvents caused deterioration of the cell by evaporation of the solvent over the prolonged use. Ionic liquids were collected due to be the most appropriate solvents to solve such problems.

TABLE 1 Composition of Electrolyte for Solid-State Polymer-Sensitized Solar Cell Device

TBAI[a]/I_2 (mg)	EC[b]/PC[c] (ml)	I.L.[d] (mg)	PAN[e] (mg)	Acetonitrile (ml)
12/12	0.16/0.04	40	40	0.2

[a] Tetrabutylammonium iodide.
[b] Ethylene carbonate.
[c] Propylene carbonate.
[d] 1-Ethyl-3-methylimidazolium iodide (EMIM-I).
[e] Polyacrylonitile.

RESULTS AND DISCUSSION

The thiophene-based polymers were synthesized as the compositions of two type thiophene monomers with alkyl or carboxylic group, and their structures were confirmed by FT-IR and ^{1}H-NMR spectroscopy. The FT-IR spectra of polymers exhibited characteristic absorption peaks at 2952–2853 cm^{-1} due to hexyl or dodecyl group of **3HT** or **3DT**, and 1713-1700 cm^{-1} due to the carboxylic group of **TAA**. Table 2 was listed the feed composition of thiophene monomers (**TAA**, **3HT**, or **3DT**) and the mole fraction in copolymer composition. The mole fraction in copolymer composition was estimated from the integral ratio of the methylene protons in the acetic acid group and the methylene protons in the alkyl group by ^{1}H-NMR spectroscopy.

In order to compare with the adsorption effects of polymer sensitizers onto TiO_2 layers on the chemical structure of the polymers, UV-vis absorption spectra of thiophene-based polymers in chloroform solution and thiophene-based polymer adsorbed onto nanoporous TiO_2 film were recorded on UVIKON 860 spectrophotometer. Figure 2(a) shows that the absorption spectra of thiophene-based polymers (**P3HT**, **P3HT-co-TAA-1**, and **P3HT-co-TAA-2**) in chloroform solution were appeared broadly the maximum at 444, 432, and 465 nm, respectively. This solution was prepared by adding 1 mg of thiophene-based polymers into 5 ml of pure chloroform solution. After the adsorption of the thiophene-based polymers onto nanoporous TiO_2 film deposited on FTO glass, their absorption spectra were showed in Figure 2(b). The absorbance of the TiO_2 film adsorbed **P3HT** sensitizers on FTO glass considerably decreased in the region of visible spectrum. However, the absorbance peaks and intensity of the TiO_2 film adsorbed **P3HT-co-TAA-1** sensitizers had not been mostly changed except the absorbance peak of 350 nm according to titanium. Moreover, we confirmed it absorbed up to 600 nm in the region of the visible spectrum. The

TABLE 2 Feed Composition of Thiophene Monomers and Copolymers Composition

	Mole fraction in feed composition		Mole fraction in copolymer composition	
	M_1[a]	M_2[b]	m_1[c]	m_2[d]
(a) P3HT-co-TAA-*n*'s system				
P3HT	0	1	0	1
P3HT-co-TAA-1	0.09	0.91	0.19	0.81
P3HT-co-TAA-2	0.05	0.95	0.10	0.90
(b) P3DT-co-TAA-*n*'s system				
P3DT	0	1	0	1
P3DT-co-TAA-1	0.09	0.91	0.14	0.86
P3DT-co-TAA-2	0.05	0.95	0.08	0.92

[a] Mole fraction of 3-thiopheneacetic acid in feed composition.

[b] Mole fraction of 3-hexylthiophene or 3-dodecylthiophene in feed composition.

[c] Mole fraction of 3-thiopheneacetic acid in copolymer composition confirmed by ^{1}H-NMR spectroscopy.

[d] Mole fraction of 3-hexylthiophene or 3-dodecylthiophene in copolymer composition confirmed by ^{1}H-NMR spectroscopy.

UV-vis absorption results were obtained similarly in **P3DT-co-TAA-*n*'s** in Figures 3(a) and (b). the Homopolymers (**P3HT** and **P3DT**) in Figures 2(b) and 3(b) having no carboxylic group could not absorb almost the light in the visible region, due to the difficulty of the covalent adsorption onto nanoporous TiO_2 layers. Consequentially, the

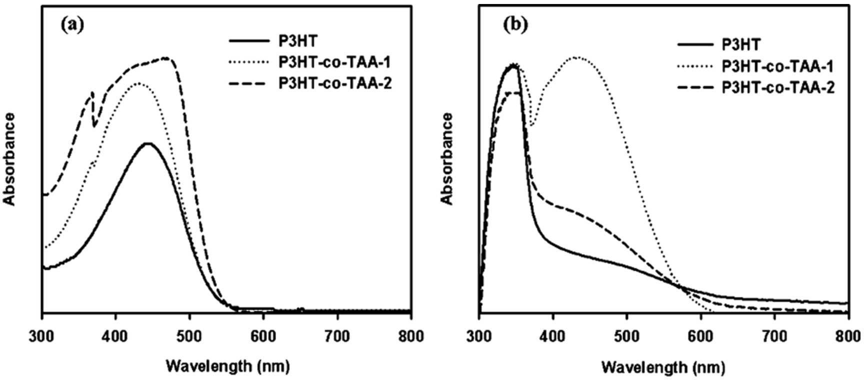

FIGURE 2 UV-vis absorption spectra of P3HT and P3HT-co-TAA-*n*'s (a); P3HT and P3HT-co-TAA-*n*'s adsorbed TiO_2 films on the FTO glass (b).

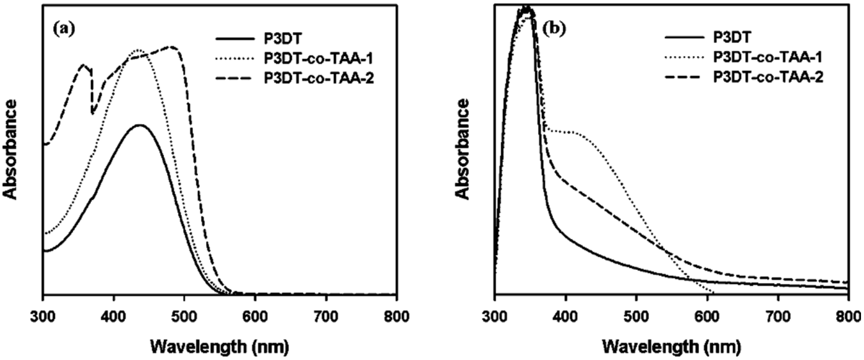

FIGURE 3 UV-vis absorption spectra of P3DT and P3DT-co-TAA-*n*'s (a); P3DT and P3DT-co-TAA-*n*'s adsorbed TiO_2 films on the FTO glass (b).

covalent adsorption of polymer sensitizers onto TiO_2 layers plays an important role on the light absorption in the polymer-sensitized solar cell devices.

In order to the photovoltaic performances of the polymer-sensitized solar cell devices using the thiophene-based polymers as a sensitizer, the measurement of the I-V characteristics of PSSC devices was carried out using a Solar Simulator (300 W simulator, models 81150) under simulated solar light with ARC Lamp power supply (AM 1.5, $100\,mW/cm^2$). The measurements were made on open cell, and the active area was $0.25\,cm^2$. The power conversion efficiency (η) of a PSSC device is given by

$$\eta = P_{out}/P_{in} = (J_{sc^*}V_{oc}) * FF/P_{in}$$

with

$$FF = P_{max}/(J_{sc^*}V_{oc}) = (J_{max^*}V_{max})/(J_{sc^*}V_{oc})$$

where P_{out} is the output electrical power of the device under illumination, P_{in} represented the intensity of the incident light (e.g., in W/m^2 or mW/cm^2). V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, and fill factor (FF) is calculated from the values of V_{oc}, J_{sc}, and the maximum power point, P_{max}. The results are shown in Figure 4.

In Table 3, in case of using the thiophene-based copolymers as the polymer sensitizer (**P3HT-co-TAA-1**, **P3HT-co-TAA-2**, **P3DT-co-TAA-1**, or- **P3DT-co-TAA-2**), V_{oc} is 0.37–0.46 V, J_{sc} is 0.82–7.71 mA/cm^2 and FF is about 0.45–0.49, respectively. In using the thiophene-based homopolymers as the polymer sensitizer (**P3HT**,

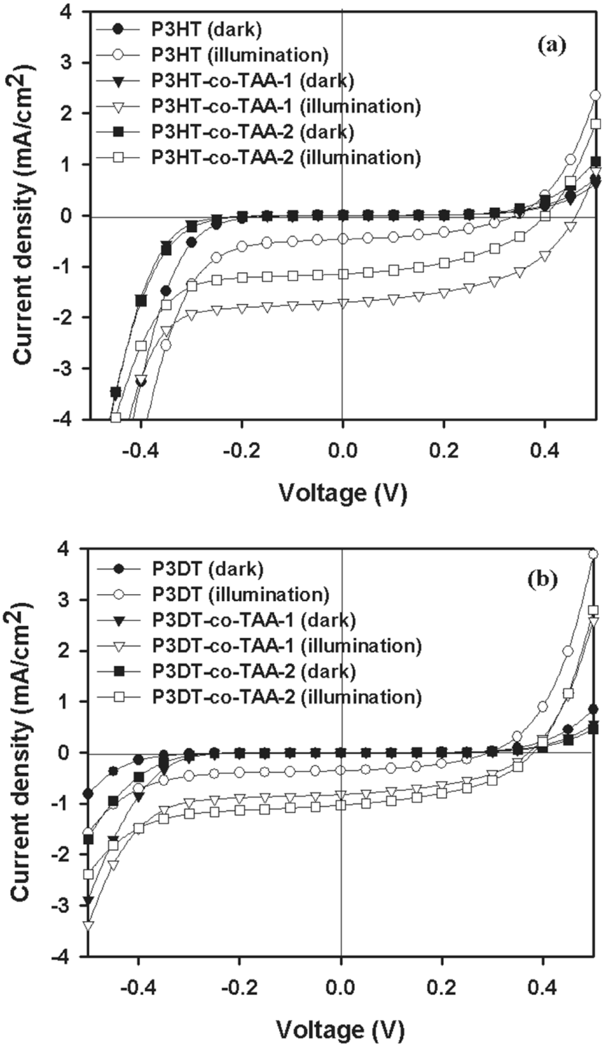

FIGURE 4 I-V curves of the polymer-sensitized solar cell devices using P3HT and P3HT-co-TAA-*n*'s as a polymer sensitizer in the dark and in illumination (a); using P3DT and P3DT-co-TAA-*n*'s as a polymer sensitizer in the dark and in illumination (b).

or **P3DT**), V_{oc} is 0.29 and 0.34 V. J_{sc} is 0.47 and 0.35 mA/cm^2 and FF is about 0.42 and 0.43, respectively. This result was due to availability of electron transfer the increase of the surface contact by covalent adsorption between polymer sensitizers and nanoporous TiO_2 layers. The

TABLE 3 Photovoltaic Performances of Polymer-Sensitized Solar Cell Devices Using Thiophene-Based Polymers as a Polymer Sensitizer

	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	Eff. (%)
P3HT	0.34	0.47	0.42	0.07
P3HT-co-TAA-1	0.46	7.71	0.49	0.38
P3HT-co-TAA-2	0.40	1.15	0.45	0.20
P3DT	0.29	0.35	0.43	0.04
P3DT-co-TAA-1	0.37	0.82	0.49	0.14
P3DT-co-TAA-2	0.38	1.03	0.45	0.18

power conversion efficiency of devices using copolymers as the polymer sensitizer were shown over two times of value at its of cells using homopolymers having the difficulty of the surface adsorption due to the absence of carboxylic groups. Therefore, the chemical structure of the sensitizer in polymer-sensitized solar cells is very important role in order to increase power conversion efficiency of devices.

CONCLUSION

In this work we showed that thiophene-based copolymers (**P3HT-co-TAA-*n***'s and **P3DT-co-TAA-*n***'s) can act as a polymer sensitizer of DSSC device due to the adsorption onto TiO_2 layer by carboxylic groups in copolymers. Homopolymers (**P3HT** and **P3DT**) having no carboxylic group have lower value of power conversion efficiency because of the difficulty of the interface adsorption onto nanoporous TiO_2 layers. These devices showed the possibility of the polymer sensitizer for the replacement of the Ruthenium complex dye in the solar cells.

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