Synthesis and Characterization of Polymer Electrolytes Containing Phenothiazine-Based Click Polymers for Dye-Sensitized Solar Cell Applications

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Abstract: A new series of phenothiazine-based polymeric electrolytes were developed to obtain a high power conversion efficiency (PCE) of dye-sensitized solar cells (DSSCs). Phenothiazine-based click polymers were synthesized using Cu(I)-catalyzed click reaction methods. The resulting polymers were soluble in common organic solvents and had a reasonable molecular weight. The thermal properties, emission spectra, and energy band gap of synthesized click polymers were also investigated. The polymer electrolytes were composed of iodide and triiodide redox species embedded in phenothiazine-based click polymers or polyacrylonitrile (PAN) as a polymer matrix. DSSCs were fabricated with a configuration of SnO_2:F/TiO_2/N719 dye/polymer electrolyte/Pt devices using these click polymers or PAN as an electrolyte components and compared photovoltaic performance. The maximum PCE of the phenothiazine-based click polymers as polymer electrolytes for DSSCs was obtained 5.30% (at 1 sun). These enhanced click polymers are expected to find applications as an electrolyte component in DSSCs in the future.

Keywords: polymer electrolyte, click chemistry, phenothiazine, photovoltaic properties, dye-sensitized solar cells.

Introduction

In recent days, the conversion of solar to electrical energy has become important due to limitation of conventional energy sources. There are various natural resources available for sustainable energy. Converting solar energy into electrical energy is one such exploitation of among the various natural sources available for renewable energy. Since the report from the Grätzel group,[1] dye-sensitized solar cells (DSSCs) have obtained much attention among researchers. The Grätzel group reported power conversion efficiency (PCE) of 11% using a liquid electrolyte and was found to be very close to the PCE of amorphous silicon-based inorganic solar cells.[2] Although PCE of DSSCs based on liquid electrolytes has reached as high as 11% under AM 1.5G 1 sun light intensity (100 mW/cm^2), a major drawback that limits stability of DSSCs is the lost of liquid electrolyte solution due to leakage and/or volatility of the electrolyte solution. Several significant research works have been carried out to overcome this problem. These approaches include employing a polymeric electrolyte, solid-state or quasi-solid-state hole conductors and ionic liquid electrolytes for replacing the liquid electrolytes.[3,4] However, the efficiency of these solid-state or quasi-solid-state DSSCs was unsatisfactory compared to that using the liquid electrolytes due to the low charge transport capability of the *p*-type semiconductors and poor contact of the solid-state charge transport materials with the dye coated TiO_2 surface.[5] Among them, polymer electrolytes are considered as one kind of the most prospective substitute for liquid electrolytes to fabricate practical DSSCs due to their merits such as high ionic conductivity, good interfacial filling properties and relatively high long-term stability. In particular, the research on the chemical structure, morphology, optical and electrical properties of the electrolytes play a significant role in the design of high efficiency DSSCs.

Click chemistry was defined by Sharpless *et al*.,[6] as selection criteria for highly efficient coupling reactions. Ideally, the click reaction can be performed in water or organic solvents at room temperature, which makes this method suitable for most applications. Click chemistry mainly has been

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based on the use of 1,3-dipolar cycloadditions of azides and alkynes under Cu(I) catalysis[7] and Diels-Alder reactions. In polymer chemistry it has been used in numerous ways e.g. for end-group functionalization,[8] polymer to polymer couplings,[9] functionalization of linear polymers with selected groups,[10] dendrons,[11] and poly(ethylene glycol) (PEG).[12] Also, in reactions on surfaces the cycloaddition has been used with good results e.g. to bond metal surfaces together.[13] Carbon nanotubes[14] and gold surfaces for functionalization of self-assembled monolayers[15] have been reported with click chemistry. Recently click chemistry has also been used to synthesize organic dye[16] and polymers[17,18] for DSSCs applications. As an extension of our previous work,[17,18] in the present study, we have synthesized novel phenothiazine-based polymers by click chemistry and their electro-optical properties were investigated. These novel phenothiazine-based click polymers were used as a polymer matrix in preparing polymer electrolytes and measured the photovoltaic performance on DSSCs with device configuration SnO_2:F/ TiO_2/N719 dye/polymer electrolyte/Pt with respect to polyacrylonitrile (PAN) for a comparison.

Experimental

Materials and Characterization. All reagents used were purchased from Sigma-Aldrich Co., and used without further purification. The solvents were purified using normal procedures and were handled in a moisture free atmosphere. Column chromatography was carried out using silica gel (Merck, 250-430 mesh). Conventional Schlenk techniques were used and the reactions were carried out under a N_2 atmosphere unless otherwise noted. The ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer and the chemical shifts were recorded in ppm units with chloroform as an internal standard. The UV-visible absorption and PL spectra were measured by using a Shimadzu UV-3100 UV-visible spectrometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. The solid-state emission measurements were carried out by supporting each film on a quartz substrate that was mounted to receive front-face excitation at an angle < 45°. Each polymer film was excited with several portions of the visible spectrum from a xenon lamp. The molecular weight and polydispersity of the click polymers were determined by gel permeation chromatography (GPC) using Plgel 5 μm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851^e, DSC 822^e analyzer under an N_2 atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry (CV) was carried out using a Bioanalytical Systems CV-50W voltammetric analyzer at a potential scan rate of 50-100 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile. Each polymer film was coated on a

Pt disc electrode (0.2 cm^2) by dipping the electrode into a solution of the polymer (10 mg/mL). A platinum wire and an $Ag/AgNO_3$ electrode were used as the counter and reference electrodes, respectively. All the electrochemical experiments were carried out in a glove box under an Ar atmosphere at room temperature.

Procedures for the Synthesis of Monomers. 3,7-Diazido-10-n-hexyl-10H-phenothiazine (M1),[19] 3,7-diethynyl-10-n-hexyl-10H-phenothiazine (M2),[20] 2,7-diethynyl-9,9-dihexyl-fluorene (M3),[21] and diethyl dipropargylmalonate (M4)[22] were synthesized using a slight modification of the method reported in the literature.

M1: ^1H NMR (CDCl$_3$, 300 MHz, δ ppm) 7.23-7.20 (m-4H), 6.65 (d, 2H), 3.73 (t, 2H), 1.53 (m-2H), 1.37 (m, 2H), 11.27 (m, 4H), 0.86 (t, 3H). IR (KBr, cm^{-1}): 3146, 3087, 2929, 2850, 2300, 2102, 1480, 1350, 1049, 818. **M2**: 7.23-7.20 (m, 4H), 6.65 (d, 2H), 3.73 (t, 2H), 3.06 (s, 2H), 1.53 (m-2H), 1.37 (m, 2H), 11.27 (m, 4H), 0.86 (t, 3H).

IR (KBr, cm^{-1}): 3162, 3067, 2959, 2870, 2280, 1480, 1367, 1076, 858. **M3**: 7.77 (d, 2H), 7.72 (d, 2H), 7.68 (s, 2H), 3.10 (s, 2H), 1.99 (t, 4H), 1.17-1.05 (q, 24H), 0.98 (t, 6H). IR (KBr, cm^{-1}): 3202, 2940, 2819, 2300, 1480, 1380, 1110, 828. **M4**: 3.0 (s, 2H), 2.51 (d, 4H), 2.45 (m, 4H), 1.21 (t, 6H). IR (KBr, cm^{-1}): 3204, 2924, 2851, 2320, 1735, 1280, 1100, 860.

General Procedure for the Synthesis of Click Polymers (P1-P3). Diazide- and diethynyl-based monomers (1:1 equiv.) and sodium L-ascorbate (10 mol%) were dissolved in THF (2-3 mL) under N_2 flow in a flame dried Schlenk flask and added to a mixture of triethylamine (TEA) (0.2-0.3 mL) as a ligand. The flask was flushed with N_2 for 20-30 min. The mixture was frozen and evacuated three times, which was followed by the addition of CuSO$_4$·5H$_2$O (5 mol%) under a flow of N_2 gas. The mixture was stirred at 30-35 °C for 48 h. The THF was removed under reduced pressure and the mixture was dissolved in chloroform, washed with an aqueous NH$_4$OH solution followed by water. The organic layer was separated and the solvent was removed. The resulting click polymers were precipitated into methanol.

Polymer 1 (P1) [M1+M2]: yellow solid. ^1H NMR (CDCl$_3$, 300 MHz, δ ppm) 8.34 (s), 8.21 (s), 7.77 (m), 7.63 (m), 7.48 (m), 7.63 (m), 7.39-7.29 (m), 7.24-7.22 (m), 6.90 (m) 6.79 (m), 4.16 (t), 3.84 (t), 3.06 (s), 2.35 (s), 1.78-1.26 (m), 0.91-0.86 (m). IR (KBr, cm^{-1}): 3150, 2940, 2858, 2280, 2100, 1465, 1350, 1066, 870.

Anal Calcd for (C$_{40}$H$_{40}$N$_8$S$_2$)$_n$: C, 68.93; H, 5.79; N, 16.08; S, 9.20. Found: C, 68.21; H, 5.72; N, 15.91; S, 9.17.

Polymer 2 (P2) [M1+M3]: yellow solid. ^1H NMR (CDCl$_3$, 300 MHz, δ ppm) 8.42 (m), 8.01 (s), 7.97 (m), 7.91 (m), 7.82 (m), 7.70-7.61 (m), 7.56-7.40 (m), 4.20 (t), 3.65 (t), 3.17 (s), 2.35 (t), 2.11 (m), 1.67-1.06 (m), 0.95-0.75 (m). IR (KBr, cm^{-1}): 3146, 2979, 2840, 2300, 2101, 1465, 1350, 1100, 1048, 818.

Anal Calcd for (C$_{47}$H$_{53}$N$_7$S)$_n$: C, 75.46; H, 7.14; N, 13.11;

S, 4.29. Found: C, 74.93; H, 7.05; N, 13.07; S, 4.11.

Polymer 3 (P3) [M1+M4]: ash solid. ^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm) 8.32 (s), 8.06 (s), 7.97 (m), 7.48 (m), 4.28 (t), 3.62 (s), 3.48(s), 2.85 (s), 1.89-1.26 (m), 0.89 (m). IR (KBr, cm^{-1}): 3140, 2940, 2848, 2336, 2102, 1723, 1501, 1311, 1280, 1140, 1049, 860.

Anal Calcd for (C$_{31}$H$_{35}$N$_7$O$_4$S)$_n$: C, 61.88; H, 5.86; N, 16.29; O, 10.64; S, 5.33. Found: C, 61.54; H, 5.69; N, 16.07; O, 10.56, S, 5.23.

Fabrication of DSSCs. DSSCs were fabricated as follows. Screen-printable nanocrystalline-TiO$_2$ (nc-TiO$_2$) pastes were prepared using ethyl cellulose (Aldirich), lauric acid (Fluka) and terpineol (Fluka) as described elsewhere.[23] The prepared nc-TiO$_2$ paste was coated on a FTO conducting glass (TEC8, Pilkington, 8 Ωcm^{-1}, glass thickness of 2.3 mm), dried in air at an ambient temperature for 5 min and sintered at 500 °C for 30 min. The thickness of the annealed films was measured with Alpha-step IQ surface profiler (KLA Tencor). For dye adsorption, the annealed nc-TiO$_2$ electrodes were immersed in absolute ethanol containing 0.5 mM of N719 dye (Ru[LL'(NCS)$_2$], L=2,2'-bypyridyl-4,4'-dicarboxylic acid, L'=2,2'-bypyridyl-4,4'-ditetrabutyl-ammonium carboxylate) for 24 h at an ambient temperature. Pt counter electrodes were prepared by thermal reduction of thin film formed from 7 mM of H$_2$PtCl$_6$ in 2-propanol solution at 400 °C for 20 min. The dye-adsorbed nc-TiO$_2$ electrode and Pt counter electrode were assembled using 60 μm thick Surlyn (Dupont 1702). The polymer electrolyte was composed of I_2, tetrabutylammonium iodide (TBAI), 1-propyl-3-methylimidazolium iodide (PMII), ethylene carbonate/propylene carbonate (EC/PC, 3/1 as weight ratio), click polymers or PAN (M_w=86,200, Aldrich Co.) as a polymer matrix, and acetonitrile. The polymer electrolytes were filled between two electrodes using a vacuum pump in hotplate. A uniform polymer electrolyte layer was formed in the DSSCs after cooling down to room temperature. The active areas of dye-coated TiO$_2$ films were measured by an image analysis program equipped with a digital microscope camera (Moticam 1000). The performance of DSSCs were measured using a calibrated AM 1.5G solar simulator (Orel 300 W simulator, models 81150) with a light intensity of 100 mW/cm^2 adjusted using a standard PV reference cell (2 cm×2 cm monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer-controlled Keithley 236 source measure unit.

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

with FF=P_{max} /($J_{sc} \times V_{oc}$)=($J_{max} \times V_{max}$)/($J_{sc} \times V_{oc}$), where P_{out} is the output electrical power of the device under illumination, and P_{in} is the intensity of incident light (e.g., in Wm^{-2} or mWcm^{-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}. All fabrication steps and characterization measurements were carried out in an ambient environment without a protective atmosphere. While measuring the current density-voltage (J-V) curves for DSSCs, a black mask was used and only the effective area of the cell was exposed to light irradiation. The data reported in this paper was confirmed by making each device more than 5 times.

Results and Discussion

Scheme I shows the click polymerization and structure of the click polymers. The molecular structure of the 2,7-diethynyl-9,9-dihexylfluorene (M3)[21] was already published elsewhere, but M1, M2 and M4 were used for the first time to synthesize click polymers using click chemistry by our group. We synthesized the click polymers (P1, P2 and P3) using click chemistry and compared their photovoltaic performance of DSSCs using P1, P2 and P3 as polymer electrolyte components. In order to improve the purity of the click polymers and the photovoltaic performance, the precipitated click polymers were further purified by multiple
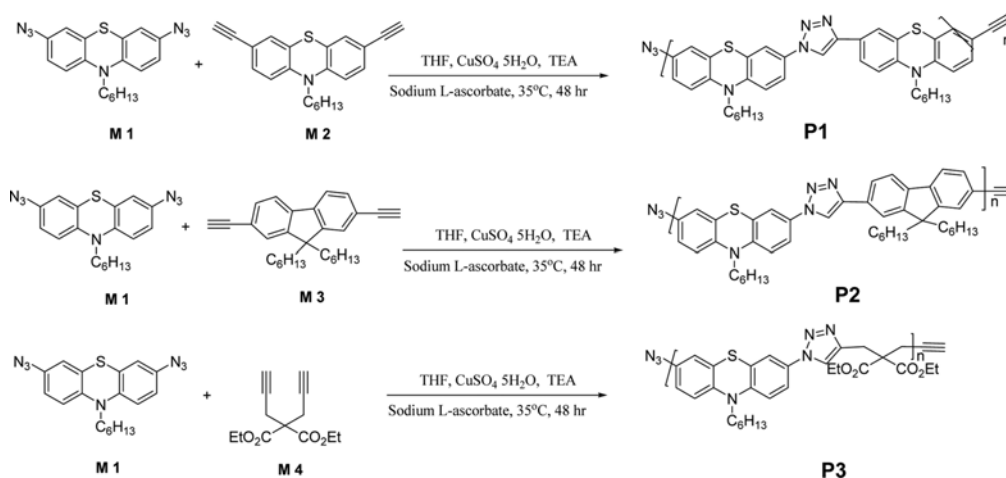
Scheme I. Synthetic scheme of polymers (P1-P3).

**Table I. Polymerization Results, Thermal, and Electro-Optical Properties of P1-P3**

Click Polymer	P1	P2	P3
Yield (%)	90	88	91
M_w[a]	8,080	15,970	10,620
PDI[a]	1.02	3.11	1.79
DSC (T_g)	124	72	43
TGA[b]	321	298	282
Abs$_{max}$ (nm)[c]	288,345	353	297,326
PL$_{max}$ (nm)[c]	476	416,438	395
E_g (eV)[d]	2.81	2.92	3.23
HOMO	5.13	5.68	5.86
LUMO	2.32	2.76	2.63

[a]M_w and PDI of the polymers were determined by GPC using polystyrene standards. [b]TGA was measured at temperature of 5% weight loss for the polymers. [c]Measured in the thin film onto the quartz substrate. [d]Determined from edge of absorption spectrum.

Soxhlet extraction with methanol and were finally extracted with chloroform. From these processes, highly purified click polymers with narrow polydispersity were obtained. The resulting click polymers were completely soluble in various organic solvents such as chloroform, chlorobenzene, THF, toluene, and xylene. Table I summarizes the polymerization results, thermal and electro-optical properties of the click polymers. The weight average molecular weights (M_w) of P1, P2 and P3 were 8,080, 15,970 and 10,620, respectively. The polydispersity of the click polymers were in the range of 1.02-3.11, respectively.

The structure and thermal properties of the click polymers were identified by ^{1}H NMR, infrared spectroscopy, elemental analysis, DSC, and TGA thermograms. The disappearance of the characteristics of the acetylenic proton peaks from the monomers at approximately 2.6-3.7 ppm in ^{1}H NMR and 2100 cm^{-1} in IR spectroscopy, and the appearance of 1,4-disubstituted 1,2,3-triazole peaks from the click polymers at approximately 8.42-8.06 ppm in ^{1}H NMR confirmed the polymerization reaction. The other proton signal positions and number from peak integration are consistent with the proposed chemical structure of the click polymers. As shown in Figure 1 and Table I, isothermal pyrolysis showed that the 1,4-disubstituted 1,2,3-triazole units were lost at approximately 282 °C followed by click polymer decomposition at higher temperatures.

P1 exhibited a higher glass transition temperature (T_g) of 124 °C than that of P2 with 72 °C. This is mainly due to the introduction of more rigid phenothiazine-based comonomer (M2) than fluorine-based comonomer (M3) into the polymer backbone. The higher thermal stability of the click polymers prevents the deformation and degradation of the active layer from the heat induced during the operation of
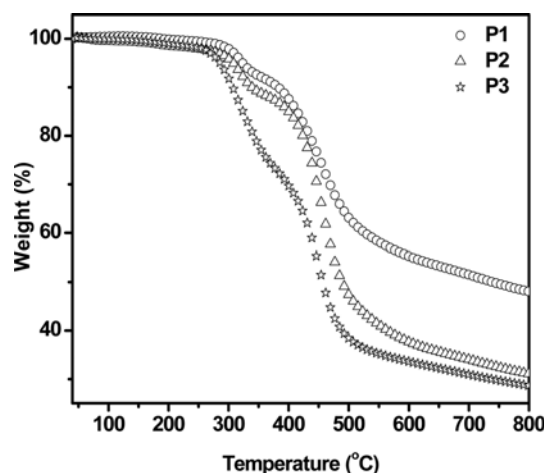
Figure 1. TGA thermograms of P1-P3 (at a heating rate of 10 °C/min).
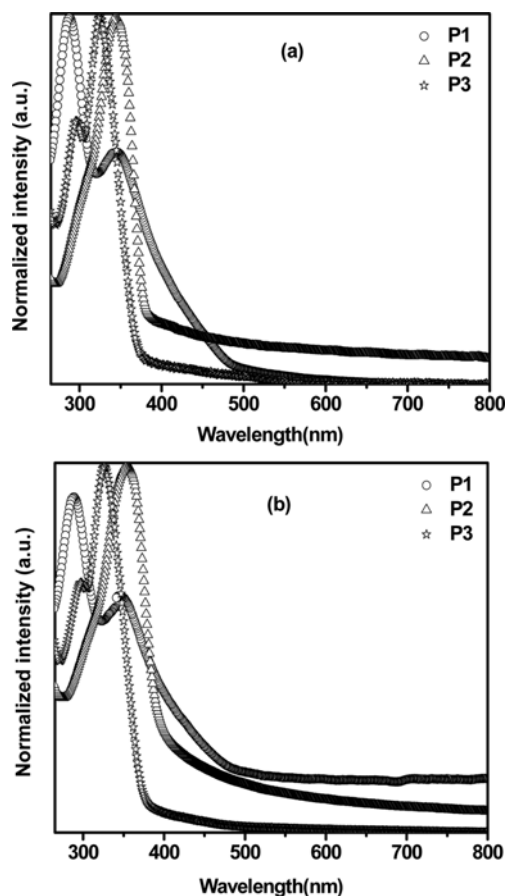
Figure 2. UV-visible absorption spectra in chloroform (a) and film (b) [concentration 1.5×10^{-4} M] of P1-P3.

the DSSCs.

The UV-visible absorption and photoluminescence (PL) data of the click polymers were measured in both solution and film states. Figure 2 shows the UV-visible absorption spectra of the click polymers in chloroform and in thin film
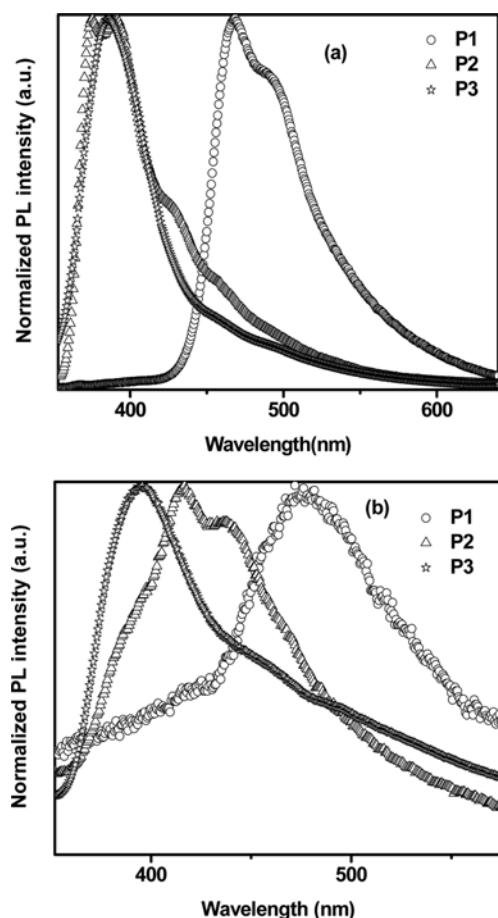
Figure 3. PL emission spectra in chloroform (a) and film (b) [concentration 1.5×10^{-4} M] of P1-P3 (excited at 345 nm).

Figure 4. The energy diagram of polymers, N719 dye, and TiO_2.

Figure 5. Photocurrent-voltage characteristics of the DSSCs fabricated with P1-P3 and PAN as a polymer matrix of solid-state electrolyte under AM 1.5 sunlight illumination (100 mW/cm²).

coated onto the quartz substrates. The UV-visible absorption spectra of click polymers were similar in solution and film state with similar maximum absorption peak. This indicates a similar conformation of the click polymers in both states with tailing structures in the low energy regions in front of steep main absorption band edges.

Figure 3 shows the PL spectra of the click polymers in chloroform and in thin film state. The PL spectra of the click polymers in chloroform were emitted a blue color between 375 and 468 nm as shown in Figure 3(a). The PL spectra of click polymers in film states as shown in Figure 3(b) are slightly different compared to the solution states, which results from the formation of an interchain excimer. The polymer, P2 had a maximum emission peak at 416 nm with a residual blue band at 438 nm, which is due to the introduction of fluorene and phenothiazine moiety *via* 1,2,3-triazole linkage into the polymer main chain. Due to the more electron donating character of phenothiazine moiety than fluorene unit, the emission peak of P1 is more red-shifted than P2. The UV-visible absorption and PL spectra of click polymers as thin films are summarized in Table I.

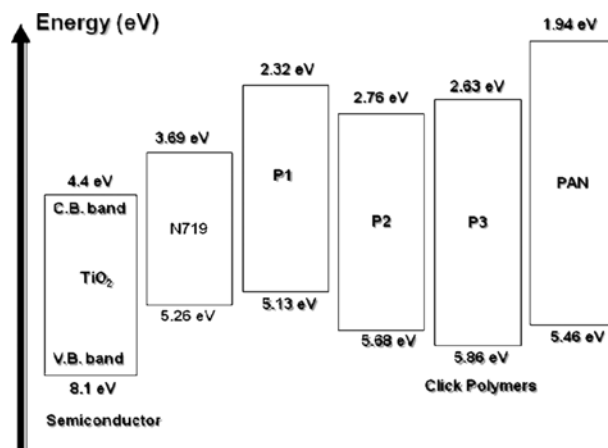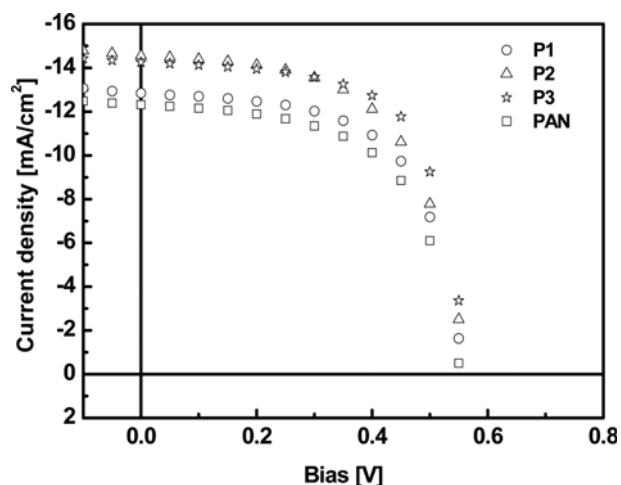Redox measurements were carried out using CV to deter-

mine the electrochemical properties of the click polymers and to evaluate their HOMO and LUMO energy levels. The HOMO energies of the click polymers with respect to the ferrocene/ferrocenium (4.8 eV) standard were approximately 5.13, 5.68 and 5.86 eV for P1, P2 and P3, respectively. From the onsets of the absorption spectra, the band gaps of P1, P2 and P3 were calculated to be 2.81, 2.92 and 3.23 eV, respectively. The LUMO energy levels of the click polymers were calculated from the band gaps and HOMO energies and the results are summarized in Figure 4 and Table I.

Figure 5 shows the current density-voltage (J-V) curves of SnO_2:F/TiO_2/N719 dye/polymer electrolyte/Pt device using P1, P2, P3, and PAN as the polymer matrix for the polymer electrolyte at 1 sun condition and the photovoltaic performances of the DSSCs are summarized in Table II. The DSSCs exhibited photovoltaic performance with power conversion efficiency (PCE) of 4.38, 4.84, 5.30, and 4.05% for P1, P2, P3, and PAN, respectively. PAN-based polymer

Table II. The Photovoltaic Performances of DSSCs under 1 sun (100 mWcm^{-2})

Click Polymers	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
P1	12.84	0.60	56.85	4.38
P2	14.56	0.60	55.40	4.84
P3	14.25	0.60	62.0	5.30
PAN	12.32	0.60	54.89	4.05

electrolyte exhibited a lower short-circuit current density (J_{sc}) and PCE than the P1-, P2- and P3-based polymer electrolytes. The decrease in J_{sc} of the DSSC with PAN-based polymer electrolyte was due to the high molecular weight of PAN. The gelation of PAN-based polymer electrolyte raises its viscosity, dramatic decrease of triiodide diffusion, which reduced the supply of I$_3$ ion to the counter electrode and retarded the regeneration of N719 dye. Among click polymers, P3 shows the highest photovoltaic performance, which reached at 5.30% (V_{oc}: 0.60 V, J_{sc}: 14.25 mA/cm^2, FF: 62.0%) at 1 sun condition. The higher photovoltaic performance of P3-based polymer electrolyte with lower T_g is attributed to the reasonable molecular weight and flexibility of polymer backbone due to the incorporation with diethyl dipropargylmalonate comonomer instead of more rigid phenothiazine and fluorene comonomers. From these results, P3-based polymer electrolyte can easily penetrate into the dye adsorbed nc-TiO$_2$ electrode and as a result increased both fill factor and PCE. Thus, the redox couple can diffuse freely in the polymer matrix of the electrolyte despite its gel nature. Further developments of new electrolytes for better DSSC performance are currently underway.

Conclusions

We synthesized a new series of phenothiazine-based click polymers using click chemistry and compared photovoltaic performance on DSSCs. The photovoltaic performance was compared with respect to PAN. The P3-based polymer electrolyte showed the highest PCE of 5.30% (V_{oc}: 0.60 V, J_{sc}: 14.25 mA/cm^2, FF: 62.0%) at 1 sun with device configuration of SnO$_2$:F/TiO$_2$/N719 dye/polymer electrolyte/Pt. This highest PCE of click polymer-based electrolyte in DSSCs as ever reported. Thus, we hope that these results will support the application of the Cu^I-catalyzed click reaction and click polymer as an electrolyte components in DSSCs in future.

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