Flexible, Dye-Sensitized Nanocrystalline Solar Cells Employing Biocatalytically Synthesized Polymeric Electrolytes

Rajesh Kumar,[†,‡] Ajendra K. Sharma,[‡,§] Virinder S. Parmar,[§]
Arthur C. Watterson,[‡] Kethinni G. Chittibabu,[∥] Jayant Kumar,[*,†] and
Lynne A. Samuelson[*,⊥]

Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts, Lowell, Massachusetts 01854, Institute for Nano-Science Engineering and Technology, Department of Chemistry, University of Massachusetts, Lowell, Massachusetts 01854, Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi 110007, India, Konarka Technologies, 100 Foot of John's Street, Lowell, Massachusetts 01852, and U.S. Army RDECOM, Natick Soldier Center, Kansas Street, Natick, Massachusetts 01760

Received March 1, 2004. Revised Manuscript Received September 28, 2004

A variety of tethered PEGylated polymers were synthesized using a mild, environmentally benign, and highly selective biocatalytic approach for preparing a quasi-solid electrolyte system for dye-sensitized nanocrystalline solar cells (DSSC). The biocatalytic approach developed is based on immobilized *Candida antarctica* lipase B (Novozyme-435)-catalyzed copolymerization reactions; the polymeric materials thus-obtained were further functionalized with hydrophobic and hydrophilic side chains using mild chemical reactions. All these polymeric materials were used in formulating quasi-solid electrolyte compositions and incorporated into flexible DSSCs, and solar conversion efficiency of as high as 4.6% was obtained.

Introduction

Dye-sensitized solar cell (DSSC)-devices based on molecular dyes capable, in their photoexcited state, of injecting electrons into the conduction band of oxide semiconductors are currently attracting wide interest due to their potential for converting solar light into electricity at low cost. The efficiency of dye-sensitized, nanocrystalline solar cells has already reached over 11%.[1] DSSCs offer the advantage of a significant reduction in the cost of solar electricity due to the inexpensive raw materials used and simple fabrication process involved in the production of DSSC-based solar modules. The practical exploitation of this technology ultimately requires cheap fabrication of devices that exhibit both efficient power conversion and long operating lifetime. The use of liquid electrolytes in flexible DSSCs, however, poses several practical problems including leakage of the electrolyte, desorption of the sensitizing dye by the organic solvent used in the electrolyte, and toxicity of some of the organic solvents. Efforts have been made by many academic and industrial laboratories to develop practical, high-performance DSSC modules that combine high efficiency and good stability with easy processability. The dye desorption problem, for example, can be overcome by using an amphiphilic dye such as Z907 [ruthenium sensitizer, *cis*-RuLL′$(SCN)_2$ (L = 4,4′-dicarboxylic acid-2,2′-bipyridine, L′ = 4,4′-dinonyl-2,2′-bipyridine)] that was developed at EPFL, Lausanne, Switzerland.[2] Exceptional thermal stability at elevated temperatures has been demonstrated using DSSC sensitized with Z907 dye.[2]

A solid or quasi-solid charge-transporting material will avoid the leakage problems, in addition to allowing easy application of these materials using a cost-effective manufacturing process. Studies have been focused on the development of all solid-state dye-sensitized photovoltaic devices using organic hole-conducting materials, but these have achieved only modest device efficiencies.[3]

An alternative approach is focused on the development of polymeric or quasi-solid matrixes for efficient functioning of already well-known redox electrolytes for DSSCs.[4−7] Attempts were made to solidify the liquid electrolytes by using polymeric matrixes[2,5] or organic gelators,[7] or through chemical cross-linking of poly(vinyl pyridine) using multifunctional alkyl halide com-

---

[*] Authors to whom correspondence should be addressed. E-mail: jayant_kumar@uml.edu.

[†] Center for Advanced Materials, University of Massachusetts.

[‡] Institute for Nano-Science Engineering and Technology, University of Massachusetts.

[§] University of Delhi.

[∥] Konarka Technologies.

[⊥] U.S. Army RDECOM.

(1) Gratzel, M. *Nature* **2001**, *414*, 338.

(2) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Nazeeruddin, M. K.; Sekiguchi, T.; Grätzel, M. *Nat. Mater.* **2003**, *2*, 402.

(3) Nogueira, A. F.; De Paoli, M.-A. *Sol. Energy Mater. Sol. Cells* **2000**, *61*, 135.

(4) Cao, F.; Oskam, G.; Searson, P. C. *J. Phys. Chem.* **1995**, *99*, 17071.

(5) Wang, P.; Zakeerudin, S. M.; Cornte, P.; Exnar, I.; Gratzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 1166.

(6) Kubo, W.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S. *Chem. Commun.* **2002**, 374.

(7) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133.

10.1021/cm0496568 CCC: $27.50

pounds.[8] In many cases, organic solvents are used as additives during the preparation of the electrolyte to increase chain mobility and the ionic conductivity of the polymer electrolyte[9,10] and the addition of polymeric gelling agents to the liquid electrolyte to promote its solidification.[11] These approaches have yielded "quasi-solid-state" dye-sensitized cells with energy conversion efficiencies similar to those achievable with liquid electrolytes. However, this approach still retains a significant volume of volatile liquid encapsulated in the gel pores, resulting in a large increase in vapor pressure as the temperature is raised, and therefore the sealing of such cells remains a problem.

Recently, growing attention has been paid to room-temperature ionic liquids (RTILs) especially those with 1,3-dialkylimidazolium cations due to their favorable properties such as thermal stability, high ionic conductivity, negligible vapor pressure, and wide electrochemical window.[12] Combination of RTILs with polymers[13,14] and low-molecular-weight gelators[15] can produce quasi-solid-state materials that have been employed as stable electrolytes for electrochemical devices. These striking and significant observations have triggered our interest for the use of ionic liquid in combination with polymeric materials to develop gelled redox electrolytes for dye-sensitized nanocrystalline solar cells. The charge-transport properties of electrolyte gels could be improved by improving the polarity of the polymer matrix, reducing the local viscosity, lowering the glass transition temperature (T_g) of the polymers, and suppressing crystallization of the ion−polymer complexes. High ionic conductivity in polymer−ion complexes could be achieved by designing a polymer system with oligomeric complexable units such as poly(ethylene oxide) (PEO) chains tethering from very irregularly arranged polymer chains. Such a system should provide very high free volume resulting in good segmental mobility while maintaining good mechanical properties. The polarity of such a system should also be tunable to improve the ion-dissociation and, consequently, provide excellent redox charge-transport properties. Moreover, such a polymer system should be very inexpensive and environmentally stable. Such complexable macromolecules can be synthesized using enzymes in a cost-effective manner. Recently our laboratory has demonstrated the successful applications of enzymes for the synthesis of polyanilines,[16] polyphenols,[17,18] polyesters,[19,20] and polyamides.[21] The main motivation for using enzymes in place of traditional chemical approaches for polymer modification is to add value for specific applications. Enzymes might add value if they provide elements of selectivity to these reactions. Furthermore, enzymes might lower the temperature at which polymer modification reactions are conducted, and they do not generate toxic waste during the reaction. Herein we report: (1) biocatalytic synthesis and modification of copolymers of poly(ethylene glycol) (PEG), and (2) photovoltaic performance of enzyme-derived polymers **3**−**6** and **10**−**12**-based quasi-solid polymeric electrolyte systems incorporated in photovoltaic cells.

Experimental Section

Materials and Methods. Novozyme-435, an immobilized enzyme, was a gift from Novozymes Inc., Denmark. All other chemicals and solvents were of analytical grade and were used as received unless otherwise noted.

Dialkylimidazolium iodide derivatives were prepared by mixing 1-methylimidazole with the corresponding alkyl iodide either in bulk or in solution of methyl ethyl ketone, and subsequently heat-treating the reaction mixture between 80 and 100 °C under nitrogen for 1−2 days. After completion of the reaction, the solvent was removed using a rotary evaporator. Trace amounts of reactants in the product were removed by washing with copious amounts of ethyl acetate. The resultant product was heated at 60 °C under vacuum overnight to remove trace amounts of solvent used in the washings. The dialkylimidazolium iodide derivatives were characterized using ^{1}H NMR spectroscopy, on a 250 MHz Bruker instrument, with DMSO-d_6 as solvent.

1-Butyl-3-methylimidazolium Iodide. ^{1}H NMR (DMSO-d_6, 250 MHz): δ 0.85 (t, 3H), 1.25 (m, 2H), 1.87 (m, 2H), 3.87 (s, 3H), 4.20 (2H, t), 7.70 (s, 1H), 7.80 (s, 1H), 9.20 (s, 1H).

1-Propyl-3-methylimidazolium Iodide. ^{1}H NMR (DMSO-d_6, 250 MHz): δ 0.88 (t, 3H), 1.85 (m, 2H), 3.90 (s, 3H), 4.20 (t, 2H), 7.75 (s, 1H), 7.85 (s, 1H), 9.17 (s,1H).

Characterization. Gel-permeation chromatography (GPC) using conventional calibration was used to determine the molecular weights and molecular weight distributions, M_w/M_n of polymer samples. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 250 MHz ARX spectrometer equipped with a Silicon Graphics station.

The fabricated cells were characterized for photovoltaic (PV) performance using a commercial solar simulator (Thermo-Oriel) at AM1.5 conditions.

Synthesis of Hydrophobically Modified Polymeric System 6. The copolymer **5** (1.679 g, 1.0 mmol) was dissolved in anhydrous dichloromethane (DCM, 15 mL) under nitrogen atmosphere. To that was added diisopropyl ethylamine (DIEA, 0.209 mL, 1.2 mmol), and the resulting solution was cooled to 0 °C. To this ice-cooled reaction mixture was added nonanoyl chloride (1.1 mmol), and the reaction mixture was stirred overnight under nitrogen. After completion, water (15 mL) was added and the organic layer was washed two times with water and dried over sodium sulfate, and solvent was evaporated under reduced pressure. The structures of the polymers were confirmed from their ^{1}H NMR spectra, and the molecular weights of the polymers were determined by GPC.

PEG 1500-*co*-Dimethyl 5-Nonanoyloxyisophthalate, 6. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 0.85−0.95(t, C-21H & C-30H), 1.15−1.40 (bm, C-16H to C-20H & C-25H to C-29H), 1.60(m,

---

(8) Murai, S.; Mikoshiba, S.; Sumino, H.; Hayase, S. J. *Photochem. Photobiol., A* **2002**, *148*, 33.

(9) Matsumoto, M.; Miyasaki, H.; Matsuhiro, K.; Kumashiro, Y.; Takaoka, Y. *Solid State Ionics* **1996**, *89*, 263.

(10) Tennakone, K.; Senadeera, G. K. R.; Perera, V. P. S.; Kottegoda, I. R. M.; De Silva, L. A. A. *Chem. Mater.* **1999**, *11*, 2474.

(11) Kubo, W.; Murakoshi, K.; Kitamura, T.; Wada, Y.; Habusa, K.; Shirai, H.; Yanagida, S. *Chem. Lett.* **1998**, 1241.

(12) Dupont, J.; De Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.

(13) Kubo, W.; Makimoto, Y.; Kitamura, T.; Wada, Y.; Yanagida, S. *Chem. Lett.* **2002**, 948.

(14) (a) Fuller, J.; Breda, A. C.; Carlin, R. T. *J. Electrochem. Soc.* **1997**, *144*, L67. (b) Doyle, M.; Choi, S. K.; Proulx, G. *J. Electrochem. Soc.* **2000**, *147*, 34. (c) Branco, L. C.; Crespo, J. G.; Afonso, C. A. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2771.

(15) Kimizuku, N.; Nakashima, T. *Langmuir* **2001**, *17*, 6759.

(16) Liu, W.; Cholli, A.; Nagarajan, R.; Kumar, J.; Tripathy, S.; Bruno, F. F.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 11345.

(17) Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 71.

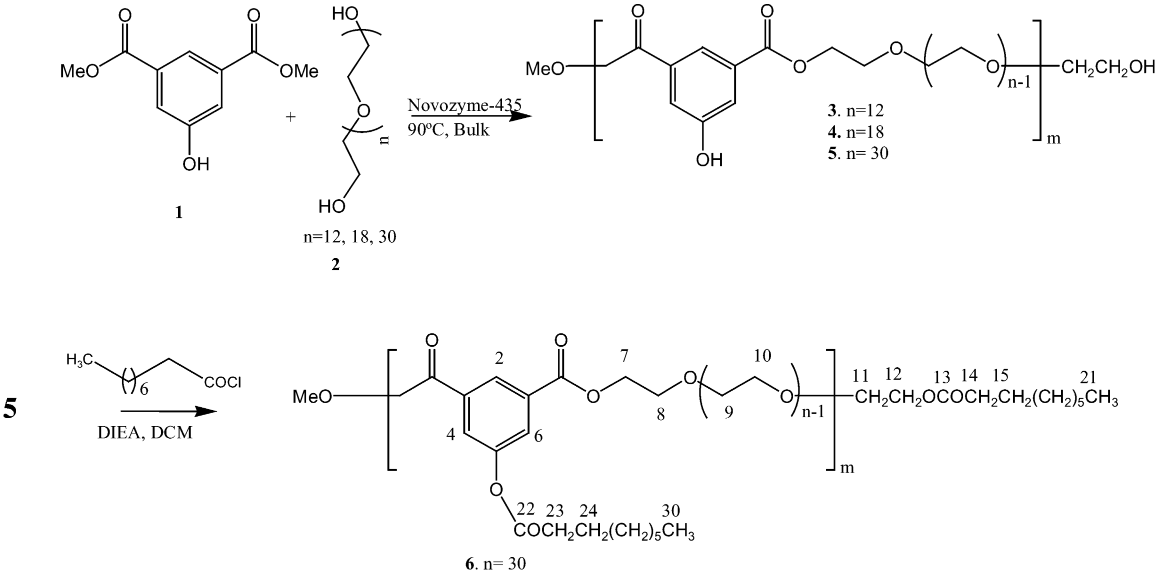
(18) Kim, Y. G.; Walker, J.; Samuelson, L. A.; Kumar, J. *Nano Lett.* **2003**, *3*, 523.

(19) Kumar, R.; Chen, M.-H.; Parmar, V. S.; Samuelson, L. A.; Kumar, J.; Nicolosi, R.; Yoganathan, S.; Watterson, A. C. *J. Am. Chem. Soc.* **2004**, *126*, 10640.

(20) Kumar, R.; Bruno, F. F.; Parmar, V. S.; Kumar, J.; Chittibabu, K. G.; Watterson, A. C.; Samuelson, L. A. *Chem. Commun.* **2004**, 862.

(21) Kumar, R.; Tyagi, R.; Parmar, V. S.; Samuelson, L. A.; Kumar, J.; Schoemann, A.; Westmoreland, P. R.; Watterson, A. C. *Adv. Mater.* **2004**, *16*, 1515.

Scheme 1. Biocatalytic Synthesis and Chemical Functionalization with Hydrophobic Chains



C-15H), 1.80(m, C-24H), 2.35 (t, C-14H), 2.60(t, C-23H), 3.40−3.70(bm, C-9H to C-11H), 3.85(t, C-8H), 3.90 (s, OCH_3 end gp), 4.20 (t, C-12H), 4.50 (t, C-7H), 7.90 (bs, C-4H & C-6H), and 8.50 (s, C-2H).

Synthesis of Mono Hexanamide of PEG Acid, 9. PEG-diacid600 (**7**, 1 mmol) and hexylamine (**8**, 1 mmol) were mixed together in a round-bottom flask, and to that was added Novozyme 435 (10% w/w wrt monomers). The reaction mixture was kept at 50 °C and progress of the reaction was monitored by thin-layer chromatography using a gradient solvent system of methanol in chloroform. After completion, the reaction was quenched by adding chloroform and filtering off the enzyme. The filtrate obtained was concentrated on a vacuum rotary evaporator to get a gummy mass, which was purified by column chromatography using a gradient solvent system of methanol in chloroform to obtain **9** as a highly viscous oil.

^1H NMR ($CDCl_3$, 250 MHz): δ 0.90 (3H, CH_3), 1.20−1.30 (6H, 3×CH_2), 1.40 (2H, $C\mathit{H}_2CH_2NH$), 3.10 (2H, CH_2NH), 3.30−3.60 (PEG main chain protons), 3.89 ($OC\mathit{H}_2CONH$), 3.95 ($OC\mathit{H}_2COOH$).

^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.4 (CH_3), 22.8 ($CH_3\mathit{C}H_2$), 26.6 ($CH_3CH_2\mathit{C}H_2$), 29.8 ($\mathit{C}H_2CH_2CH_2NH$), 31.8 ($\mathit{C}H_2CH_2NH$), 39.3($\mathit{C}H_2NH$), 69.2 ($O\mathit{C}H_2COOH$), 70.5−70.8 (PEG main chain carbons), 71.29 ($O\mathit{C}H_2CONH$), 170.4 (CONH), 172.93 (COOH).

PEGylation of Poly[PEG-*co*-5-hydroxydimethylisophthalate]s, 3−5. Monohexanamide of PEG acid (**9**, 1.0 mmol) was dissolved in anhydrous DCM (15 mL) under an atmosphere of nitrogen, and the solution was cooled to 0 °C. Oxalyl chloride (0.017 mL, 2.0 mmol) was added and the reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was taken up in anhydrous DCM (5 mL) and evaporated under reduced pressure (2×) to remove the traces of unreacted oxalyl chloride. The residue was redissolved in DCM (20 mL) and to this was added the polymer (**3**, **4**, or **5**, 1.0 mmol), followed by addition of DIEA (0.209 mL, 1.2 mmol). The reaction mixture was stirred overnight under nitrogen, water (15 mL) was added, and the organic layer was washed 2× with water, dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The structure of the polymer was characterized from its ^1H NMR spectra, and the molecular weight of the polymer was determined by gel permeation chromatography (GPC).

Poly[PEG600-*co*-dimethyl 5-(monohexanamide PEG600 acid) isophthalate], 10. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.90 (t, C-23H), 1.20−1.30 (bm, C-19H to C-22H), 1.50(m, C-18H), 3.30 (C-17H), 3.50−3.75 (bm, C-9H to C-11H, C-14H & C-15H), 3.85 (t, C-8H), 3.90 (s, C-16H), 3.95 (s, OCH_3 end gp), 4.20 (t, C-12H), 4.50 (bs, C-7H and C-13H), 6.90 (bs, NH), 7.75 (bs, C-4H & C-6H), 8.20 (bs, C-2H).

Poly[PEG900-*co*-dimethyl 5-(monohexanamide PEG600 acid) isophthalate], 11. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.88 (t, C-23H), 1.20−1.35 (bm, C-19H to C-22H), 1.48(m, C-18H), 3.30 (C-17H), 3.55−3.80 (bm, C-9H to C-11H, C-14H & C-15H), 3.85 (t, C-8H), 3.90(s, C-16H), 4.00(s, OCH_3 end gp), 4.15(t, C-12H), 4.35 (s, C-13H), 4.50(t, C-7H), 7.05(bs, NH), 7.70 (bs, C-4H & C-6H), 8.15 (bs, C-2H).

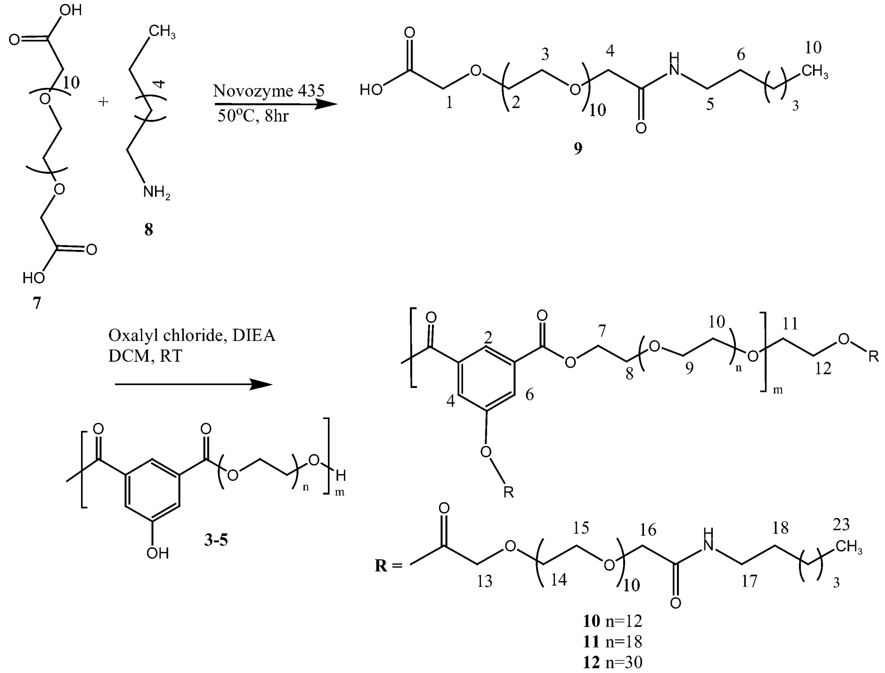
Poly[PEG1500-*co*-dimethyl 5-(monohexanamide PEG600 acid) isophthalate], 12. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.85 (t, C-23H), 1.10−1.30 (bm, C-19H to C-22H), 1.60(m, C-18H), 3.15 (C-17H), 3.45−3.65 (bm, C-9H to C-11H, C-14H & C-15H), 3.70 (t, C-8H), 3.80(s, C-16H), 3.85(s, OCH_3 end gp), 4.20(t, C-12H), 4.45(bs, C-7H and C-13H), 7.68 (bs, C-4H & C-6H), 8.15 (bs, C-2H).

Fabrication of Photoelectrochemical Cells and Photovoltaic Characterization. An aqueous suspension containing colloidal titanium dioxide nanoparticles was coated on either a SnO_2:F conducting oxide coated glass slide (sheet resistance of 15 Ω/cm^2) or a flexible polyester substrate. The titanium dioxide coated glass slides were sintered at 120−450 °C for 30 min depending on the substrate. Titanium dioxide coating on ITO/polyester film was prepared using a low-temperature interconnection process. The treated titanium dioxide coatings on glass or flexible substrates were sensitized with Z907 [ruthenium sensitizer, *cis*-RuLL′$(SCN)_2$ (L = 4,4′-dicarboxylic acid-2,2′-bipyridine, L′ = 4,4′-dinonyl-2,2′-bipyridine)] in an appropriate solvent. Quasi-solid electrolytes were prepared from the biocatalytically derived polymers **3**−**6** and **10**−**12** by adding 25−75 wt % of 2 M solution of 1,3-propylmethyl imidazolium iodide (ionic liquid) in butyrolactone. Prepared electrolytes or electrolyte gels were applied onto dye-sensitized titanium dioxide film and sandwiched with platinum-coated transparent conducting oxide glass or plastic substrate and sealed. The fabricated glass or flexible DSSCs were characterized using solar simulator under AM1.5 irradiation using a Xenon lamp with appropriate filters.

Results and Discussion

Synthesis of PEG-Based Polyesters. The development of efficient and stable quasi-solid electrolyte involves: (1) preparation of efficient redox electrolyte composition, and (2) gelling the efficient electrolytes using noncrystallizable, ion-transporting polymeric materials. On the basis of these considerations we have been working on the development of readily processable conducting polymers and polyelectrolytes having high ionic conductivity and stability through biocompatible

Scheme 2. Chemo-enzymatic PEGylation of the Biocatalytically Derived Polymers 3−5



processes.[16−18] We have already initiated the work on the synthesis of a series of noncrystallizable, ion-transporting polymeric host materials using biocatalytic processes.[19,20] The highly irregular tethering groups on the biocatalytically derived polymers will avoid crystallization of the polymers and consequent failure of the gel-electrolyte-incorporated solar cells that are exposed to extreme temperature variations.

Schemes 1 and 2 show the synthesis and functionalization of the systems with comblike structures, having long alkyl chains (**6**) and oligomeric PEG chains (**10**−**12**) tethering to very irregularly arranged polymer chains, to reduce the crystallization of PEG using chemo-enzymatic methodologies. The copolymers **3**−**5** were synthesized by the Novozyme-435 (*Candida antarctica* lipase B)-catalyzed condensation polymerization of PEG of varying molecular weights with dimethyl 5-hydroxyisophthalate according to our earlier reported procedure.[19] All the synthesized copolymers were functionalized by acylation of the phenolic hydroxyl group with nonanoyl chloride and mono-functionalized PEG diacid. The acylation of phenolic hydroxyl of **5** with nonanoyl chloride was performed at room temperature using diisopropyl ethylamine and dichloromethane as solvent to give hydrophobically modified polymeric system **6**. The ^{1}H NMR spectrum of **6** showed a new signal at δ 2.60 which was assigned to methylene protons (C-23H), indicating the attachment of the nonanoyl chain to the phenolic hydroxyl of **5**. The degree of functionalization was determined from its ^{1}H NMR spectrum by comparing the integration of the signal at δ 2.60 (CH_2COO, C-23H) with the signal at δ 4.5 ($COOCH_2$, C-7H) of the main chain and found to be 95%. During the reaction of polymer **5** with nonanoyl chloride, the alcoholic hydroxyl end group of PEG was also acylated, as indicated by the presence of a new signal at δ 2.35 in the ^{1}H NMR spectrum of **6** assigned to methylene protons (C-14H).

The side chain PEGylation of copolymers **3**−**5** was carried out by acylation of their phenolic hydroxyl by mono hexanamide PEGdiacid600 (**9**) to give the polymers **10**−**12**. The monoprotected PEGdiacid 600, **9**, was prepared by a highly selective amidation of PEGdiacid600 (**7**) with hexylamine catalyzed by Novozyme 435.[20] The ^{1}H NMR spectrum of **9** showed two sets of signals at δ 3.89 and δ 3.95, each integrating for two protons and assigned as OCH_2CONH and OCH_2COOH, respectively, suggesting the highly selective amidation of only one carboxylic acid group of PEGdiacid600. The selective amidation was further confirmed by the ^{13}C NMR spectrum of **9**, as it shows two signals in the carbonyl region corresponding to CONH (δ 170.4) and COOH (δ 172.93). The acylation of phenolic hydroxyl group of **3**−**5** with the free carboxylic group of **9** was carried out using oxalyl chloride (to convert acid to acid chloride) and DIEA in anhydrous DCM. The resulting polymers **10**−**12** were characterized by their ^{1}HNMR spectra, which showed the attachment of **9** to the phenolic hydroxyl as well as to alcoholic hydroxyl end group of the polymers **3**−**5**. The number-average molecular weights of the synthesized polymers were measured by GPC (Table 1).

Photovoltaic Characterization of Biocatalytically Derived Polymer-Gel-Electrolyte Incorporated in Flexible Solar Cells. Quasi-solid electrolytes were prepared from the bioderived polymers **3**−**6** and **10**−**12** by adding 25 wt % of the bioderived polymer to 75 wt % of 2 M solution of 1,3-propylmethyl imidazolium iodide (ionic liquid) in butyrolactone. The photo electrochemical cells were fabricated by sensitizing the nanocrystalline TiO_2-coated flexible plastic substrate with hydrophobic dye Z 907. After applying the polymer gel electrolyte, the dye-sensitized titanium-oxide-coated flexible substrate was sandwiched with a platinum coated ITO/PET substrate and heat-sealed to obtain flexible plastic cells. The fabricated cells were characterized for photovoltaic (PV) performance using a solar simulator at AM1.5 conditions.

As shown in Figure 1, the current density (mA/cm^2) and photovoltage observed by the quasi-solid electrolyte

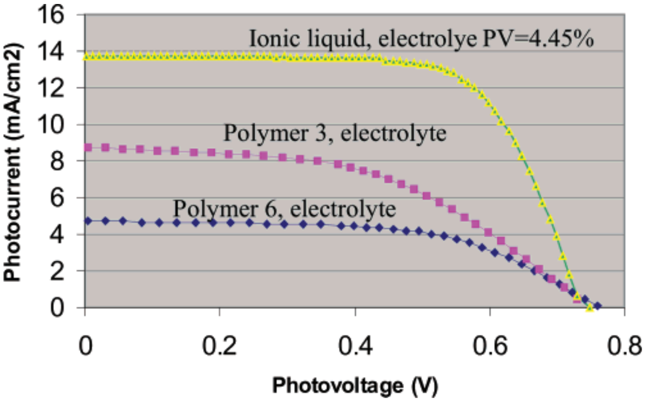


Figure 1. Comparison of I−V characteristics of polymeric electrolytes with ionic liquid.

Table 1. M_n, PD, and % Isolated Yields of Polymers 3−6 and 10−12

polymer	M_n (Da)	PD	% isolated yield
Poly[PEG600-*co*-dimethyl 5-hydroxy isophthalate], **3**	9666	2.5	80
Poly[PEG900-*co*-dimethyl 5-hydroxy isophthalate], **4**	10300	2.3	82
Poly[PEG1500-*co*-dimethyl 5-hydroxy isophthalate], **5**	11200	2.1	88
Poly[PEG 1500-*co*-dimethyl 5-(nonanoyloxy)isophthalate], **6**	17580	2.0	78
Poly[PEG600-*co*-dimethyl 5-(monohexanamide PEG600 acid) isophthalate], **10**	22150	2.0	76
Poly[PEG900-*co*-dimethyl 5-(monohexanamide PEG600 acid) isophthalate], **11**	22140	1.9	82
Poly[PEG1500-*co*-dimethyl 5-(monohexanamide PEG600 acid) isophthalate], **12**	27260	1.7	80

Table 2. PV Characteristics of Polymer-Based Electrolyte-Incorporated Cells

polymer	open circuit voltage (volts)	short circuit current density (mA/cm^2)	efficiency	fill factor
3	0.71	8.07	2.58	0.450
4	0.72	8.84	2.71	0.423
5	0.74	8.58	3.15	0.496
6	0.71	8.20	2.0	0.435
10	0.648	9.664	4.04	0.645
11	0.681	9.485	4.32	0.668
12	0.671	9.712	4.27	0.656

of polymers **3**−**5**-incorporated DSSC on plastic substrate were around 2.5−3.1% (Table 2). It was also observed that the PV efficiency decreased when alkyl chains were grafted as side chains (in case of **6**) and gave an average PV efficiency of 2.0% (Table 2).

Quasi-solid electrolytes prepared from biocatalytically synthesized polymers **10**−**12** by adding at least 25% of the polymer in ionic-liquid-based electrolyte composition showed PV efficiency around 4.30% (Table 2). Almost identical results (PV 4.45%) were observed from the cells containing ionic-liquid-based electrolyte that did not contain the polymers **10**−**12** (Figure 1), thus indicating that the presence of polymers **10**−**12** has no adverse effect on the conversion efficiency. On the contrary, it increases the stability of the devices as it forms a gel and does not contain any volatile solvents. The measured ionic conductivity[22] of the formulation used in these devices is ~2 × 10^{-5} siemens(S)/cm. The ionic conductivity is not an intrinsic property of PEG polymer but depends on the details of the formulation used. The redox properties of the matrix (PEGylated) polymer are not relevant as it just behaves as a gelling matrix which allows efficient functioning of the iodide/triodide redox couple which is well understood. Gratzel et al.[23] also observed a similar effect, and found that the calculated diffusion coefficients of triiodide and iodide in polymer gel electrolyte are the same as those in blank liquid electrolytes. The results from photovoltaic characterization studies on polymer **10**−**12**-based gel electrolytes incorporated in flexible solar cells show that the PV performance is similar irrespective of the viscosity of the polymer electrolyte, at similar polymer concentration. This is a very promising result, as the viscosity of the gel can be altered without affecting the PV perfor-

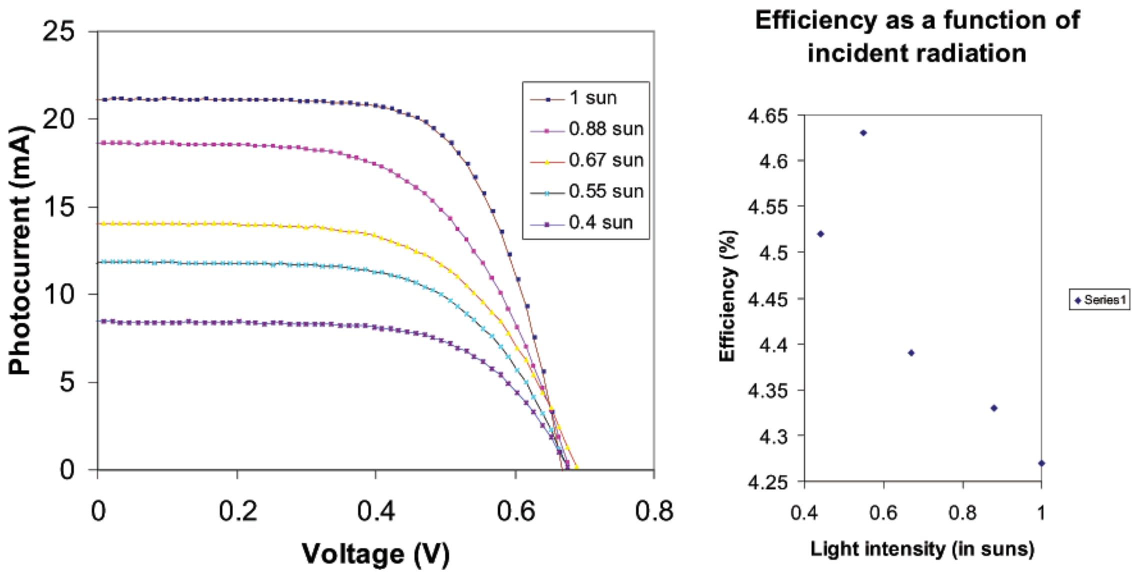


Figure 2. (Left) Current−voltage curves of flexible solar cell fabricated using polymer gelled electrolyte-**12** (cell size = 2.21 cm^2) at various light intensities (1 sun = 100 mW/cm^2). (Right) Efficiency of **12**-based gel-electrolyte-incorporated flexible solar cells at various light intensity levels.

mance of the solar cells. In fact, the macroscopic viscosities of the polymer gel electrolytes are much higher than that of the blank liquid electrolyte, but their similar performance could be attributed to the open structure of the present polymer gels, which results in the liquid channels and provides free diffusion of iodide and triiodide in these channels.

Intensity-dependent PV characteristics were studied from polymer-**12**-based gel-electrolyte-incorporated flexible cells and the current voltage characteristics of this cell at various intensity levels are shown in Figure 2.

The intensity-dependent PV characterization study suggests that maximum PV performance is achieved at around 0.5 Sun (50 mW/cm^2) intensity level. An efficiency of over 4.6% was achieved for polymer-**12**-based-gel-incorporated flexible cell at 55 mW/cm^2, which is about 10% higher than 1 Sun conditions.

Conclusions

In summary, biocatalytic routes based on *Candida antarctica* lipase B for the synthesis of PEGylated polymers to make gel electrolyte systems have been developed. These copolymers were further functionalized to generate a variety of tethered PEGylated polymers for preparing quasi-solid electrolytes. The enzymatically synthesized noncrystallizable polymeric materials were used in formulating quasi-solid electrolyte compositions and incorporated into flexible dye-sensitized titanium oxide solar cells (DSSC). Solar conversion efficiencies of 4.3 and 4.6% were achieved from biocatalytically synthesized gel-electrolyte-incorporated flexible solar cells at corresponding 1 and 0.55 Sun equivalent of solar irradiation conditions.

Acknowledgment. We acknowledge the Office of Naval Research (ONR), STTR program, and U.S. Army RDECOM Natick Soldier Center for financial support.

CM0496568

---

(22) Bruno, F. F.; Nagarajan, R.; Kumar, J.; Samuelson, L. A. *J. Macromol. Sci. Pure Appl. Chem.* **2002**, *A39*, 1061.

(23) Wang, P.; Zakeeruddin, S. M.; Exnar, I.; Gratzel, M. *Chem. Commun.* **2002**, 2972.