

Poly(oxyethylene methacrylate)–poly(4-vinyl pyridine) comb-like polymer electrolytes for solid-state dye-sensitized solar cells

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Abstract Poly(oxyethylene methacrylate)–poly(4-vinyl pyridine) (POEM–P4VP) comb-like copolymers with 3:7, 5:5, and 6:4 wt ratio were synthesized via atom transfer radical polymerization and confirmed by ¹H-NMR and FT-IR spectroscopy. The copolymers were quaternized with 1-iodopropane to convert the pyridine groups into pyridinium ions, i.e., POEM–qP4VP. Transmission electron microscopy showed that strongly segregated microphase separation in POEM–P4VP was less prominent upon quaternization due to interactions between the ether oxygens of POEM and the quaternized pyridine groups of qP4VP, as confirmed by FT-IR spectroscopy. The energy conversion efficiencies of dye-sensitized solar cells (DSSCs) with quaternized polymer electrolytes were always greater than those with pristine electrolytes due to greater ionic conductivity and concentrations of free iodide ions. The maximum energy conversion efficiency of a DSSC employing POEM–qP4VP electrolyte reached 3.0% at 100 mW/cm² when a 6:4 wt.% of POEM–qP4VP was used.

Keywords Atom transfer radical polymerization · Comb-like polymer · Dye-sensitized solar cell · Polymer electrolyte · Ionic conductivity

Introduction

Dye-sensitized solar cells (DSSCs) have received great attention because of their high conversion efficiency and low cost [1]. The performance of DSSCs can be improved by developing or modifying a dye, nanocrystalline TiO₂ layer, thermal-resistance transparent conducting oxide, electrolyte or the interface of the electrode–electrolyte [2, 3]. Liquid electrolyte-based DSSCs have exhibited an energy conversion efficiency of approximately 11%. However, liquid electrolytes have some disadvantages such as solvent evaporation, electrolyte leakage and instability at high temperatures. Because of these shortcomings, many researchers have developed solid-state or quasi-solid-state DSSCs [3–8]. However, solid-state DSSCs have shown lower energy conversion efficiencies compared to liquid-state DSSCs due to poor interfacial properties between the electrode and electrolyte as well as a lower ionic conductivity electrolyte.

Polymer electrolytes are solid complexes consisting of salt with a low lattice energy dissolved in a polar polymer host, which can form as a result of coordinative interaction. The complex formation and solubility behavior in a polymer electrolyte is crucial in determining ionic conducting, mass transport and nanostructural properties. Poly(ethylene oxide) (PEO) is a representative polymer host that is commonly used in a polymer electrolyte due to its complex formation capability. However, one critical drawback of neat PEO is its strong tendency to crystallize due to the helical chain structure that consequently results in low ionic conductivity. Thus, studies on the modification of PEO based on controlling the

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polymer structure, such as blending, crosslinking, block copolymerization, and random copolymerization, have recently been conducted [9–13].

Poly(oxyethylene methacrylate) (POEM) is a well-known amorphous PEO that possesses a high-ionic conductivity but “liquid-like,” poor mechanical properties [12, 13] and thus cannot be readily applied to solid polymer electrolytes. Alternatively, poly(4-vinyl pyridine) (P4VP) has a high glass transition temperature (T_g), which imparts desirable mechanical properties but is not highly conductive ionically [14]. However, P4VP can form a stable complex with various metal salts based on a hard/soft and acid/base concept. If these properties of POEM and P4VP are combined, polymer electrolytes possessing both high ionic conducting properties and good mechanical properties are expected.

Thus, in this study, a POEM–P4VP comb-like copolymer was synthesized via atom transfer radical polymerization (ATRP) and quaternized with 1-iodopropane to enhance the ion conductivity of the electrolyte. Quaternized pyridine possesses weak Lewis basicity and large steric hindrance; thus, attraction between the quaternary nitrogen atoms and I^- ions will be weak, which produces a good transfer channel for iodide ions [15]. The synthesized materials were characterized using nuclear magnetic resonance (1H -NMR), Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Interfacial properties between electrodes and the electrolyte were characterized using electrochemical impedance spectroscopy (EIS). Ionic conducting properties and solid-state DSSC performances for POEM–P4VP comb-like polymer electrolytes were also reported.

Experiment

Materials

POEM (poly(ethylene glycol) methyl ether methacrylate, $M_n=475$ g/mol), 4-vinyl pyridine (4VP), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper (I) chloride (CuCl, 99%), methyl 2-bromo-propionate (MBP), 1-iodopropane, lithium iodide (LiI, 99%), 1-methyl, 3-propyl imidazolium iodide (MPII), and iodine were purchased from Aldrich. Dimethylformamide (DMF), ethanol, and acetonitrile were obtained from J.T. Baker. All solvents and chemicals were reagent grade and used as received.

Synthesis of the POEM–P4VP comb-like copolymer

Different amounts of POEM and 4VP, i.e., POEM:P4VP=3:7, 5:5, and 6:4, were mixed in 50 ml of DMF. The

corresponding mole ratios of POEM/P4VP were approximately 10:90, 20:80, and 25:75, respectively. Next, 0.247 g of CuCl and 0.575 ml of HMTETA were added to the solution, and the reaction flask was sealed with a rubber septum. After N_2 purging for 30 min, 0.248 ml of MBP (target molecular weight=40,000 g/mol) was added to the solution using a syringe, and the reaction vessel was immersed in an oil bath at 90 °C. The reaction was allowed to proceed for 24 h. The solution was passed through a column with activated Al_2O_3 to remove the catalyst and precipitated into ether. The polymer was purified by re-dissolving in methanol and re-precipitating in ether several times. Finally, the polymer was dried in a vacuum oven overnight at room temperature.

Quaternization of POEM–P4VP

Quaternized POEM–P4VP, i.e., POEM–qP4VP, was synthesized by N-alkylating the pyridine nitrogens with 1-iodopropane. Three grams of POEM–P4VP was dissolved in 60 ml of methanol with 5 ml of 1-iodopropane and then allowed to react at 60 °C for 24 h. The polymer was then isolated by precipitation in diethyl ether and dried under vacuum for 24 h.

Preparation of the polymer electrolyte

Appropriate amounts of POEM–P4VP or POEM–qP4VP were dissolved in methanol whereas LiI and I_2 were separately dissolved in acetonitrile. A homogeneous solution was obtained by combining these two solutions at 1:1 v/v under continuous stirring. After casting the polymer solution onto an appropriate dish and drying completely under vacuum for 24 h, polymer electrolyte films were obtained. The mole ratio of [EO]/[LiI] was fixed at 10:1, and the amount of I_2 was fixed at 10 wt.% with respect to LiI.

Construction of the DSSCs

DSSCs with an active area of 0.4 cm² were constructed according to a previously reported procedure [16–18]. Titanium bis(ethyl acetoacetato) diisopropoxide solution (in butanol) was coated onto F-doped SnO_2 (FTO) conducting glass and sintered at 450 °C for 30 min. A nanocrystalline TiO_2 photoelectrode was fabricated by coating TiO_2 colloidal paste (Ti nanoxide, D, Solaronix, Aubonne, Switzerland) onto FTO using a simple doctor-blade technique. The layer was heated to 450 °C for 2 h, held at 450 °C for 30 min, and cooled to 30 °C for 8 h. The TiO_2 electrode was immersed in a solution of 0.22 mM Ru (dcbpy)₂(NCS)₂ dye (dcbpy=2,2-bipyridyl-4,4-dicarboxylato) (535-bisTBA, Solaronix, 13 mg) dissolved in distilled ethanol

(50 g) for 2 h at 50 °C. The dye-sensitized TiO₂ electrode was rinsed with absolute ethanol and dried under N₂. The counter electrode was prepared by spin-coating of the H₂PtCl₆ solution (in isopropyl alcohol) onto the conductive FTO glass and then heated at 450 °C for 2 h. A dilute polymer electrolyte solution was first cast onto a dye-adsorbed TiO₂ electrode and evaporated slowly to facilitate the easy penetration of electrolytes through the nanopores of the TiO₂ layer. A concentrated polymer electrolyte solution was cast onto the photoelectrode to minimize the time required for solvent evaporation and to prevent the formation of cavities between the two electrodes during solvent evaporation. Both electrodes were superimposed and pressed between two glass plates to achieve slow solvent evaporation and obtain a thin electrolyte layer. The cells were placed in a vacuum oven for 24 h to completely evaporate the solvent and then sealed with an epoxy resin.

Photoelectrochemical performance characteristics including the short-circuit current (J_{sc} , mA/cm²), open-circuit voltage (V_{oc} , V), fill factor (FF), and overall energy conversion efficiency (η) were measured using a Keithley Model 2,400 and 1,000 W xenon lamp (Oriel, 91193). The light was homogeneous up to an 8×8 in² area, and its intensity was calibrated with a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si+KG filter, Certificate No. C-ISE269) for a sunlight intensity of one (100 mW/cm²). This calibration was confirmed with a NREL-calibrated Si solar cell (PV Measurements Inc.). The photoelectrochemical performances were calculated using

the following equations:

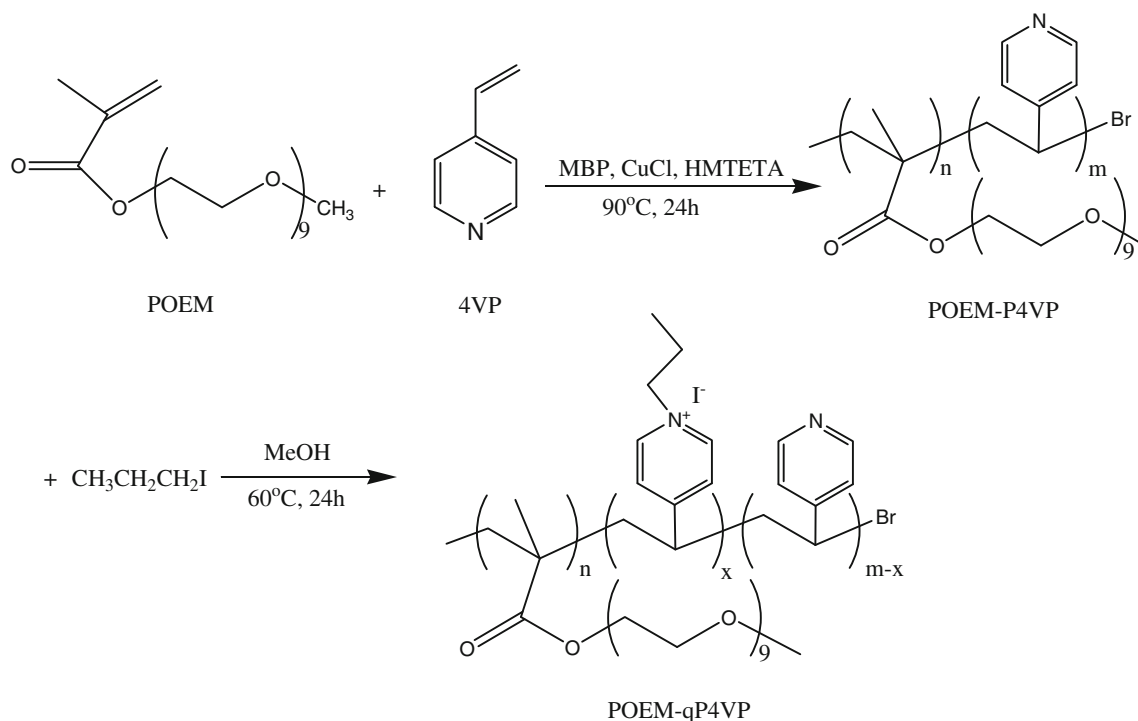
$$FF = \frac{V_{max} \cdot J_{max}}{V_{oc} \cdot J_{sc}} \quad (1)$$

$$\eta(\%) = \frac{V_{max} \cdot J_{max}}{P_{in}} \times 100 = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}} \times 100 \quad (2)$$

where J_{sc} is the short-circuit current density (mA/cm²), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} (mA/cm²) and V_{max} (V) are the current density and voltage in the J - V curve, respectively, at a maximum power output.

Characterization

¹H-NMR measurements were performed with a 600 MHz, high-resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Germany, Bruker). FT-IR spectra were collected using an Excalibur Series FT-IR (DIGLAB Co.) instrument between a frequency range of 4,000 to 400 cm⁻¹ using ATR. TEM images were obtained using a Philips CM30 microscope operating at 300 kV. For TEM measurements, the polymer was dissolved in methanol and then a drop was placed onto a standard copper grid. XPS measurements were performed using a VG Scientific ESCALAB 220 spectrometer equipped with a hemispherical energy analyzer. A non-monochromatized Al_{K α} X-ray source ($h\nu=1486.6$ eV) was operated at 12.5 kV and 16 mA. Before data acquisition, the



Scheme 1 ATRP synthesis of the POEM–P4VP comb-like polymer and quaternization of POEM–P4VP with 1-iodopropane

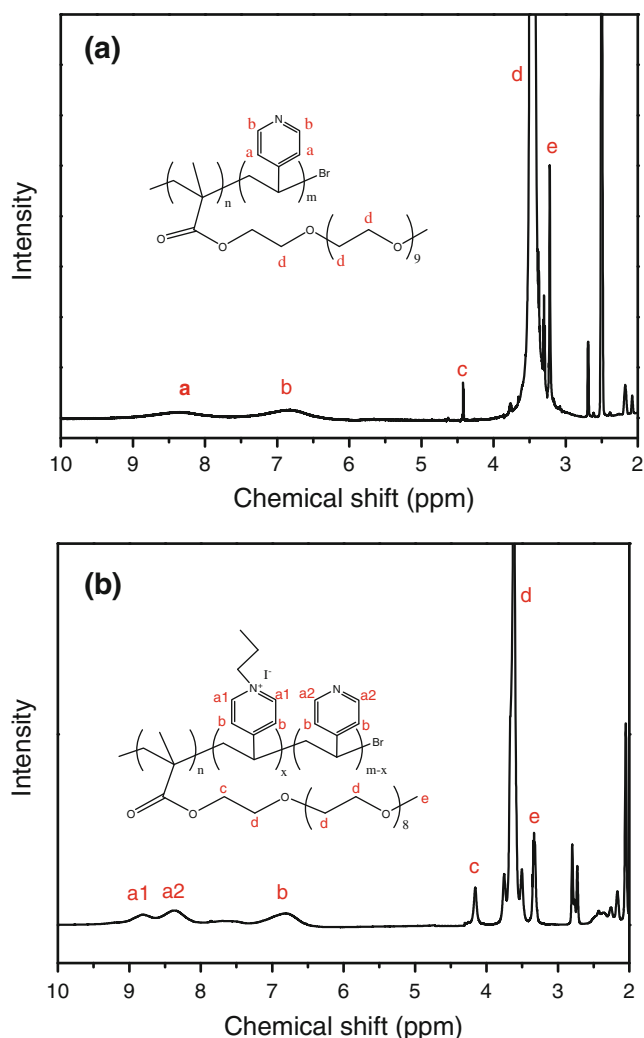


Fig. 1 ¹H NMR spectra of **a** POEM-P4VP and **b** POEM-qP4VP comb-like polymers synthesized with a POEM/P4VP=5:5 wt.%

samples were degassed for 3 h at 298 K under a pressure of 1.0×10^{-9} Torr to minimize the surface contamination. Ionic conductivity was measured under a dry atmosphere using an impedance analyzer (IM6, ZAHNER, Germany) and a lab-made, 2-probe conductivity cell. The impedance spectra of the electrolytes were used to generate Nyquist plots and the ionic conductivity was calculated from the plots.

Results and discussion

The reaction scheme for the synthesis of the POEM-P4VP comb-like copolymer before and after quaternization is presented in Scheme 1. Polymerization of POEM-P4VP was performed at 90 °C for 24 h using CuCl and HMTETA as a catalyst and ligand, respectively. Quaternized POEM-P4VP, i.e., POEM-qP4VP, was synthesized by N-alkylating the pyridine nitrogens with 1-iodopropane at 60 °C for

24 h. Figure 1 shows the ¹H NMR spectra of the POEM-P4VP comb-like copolymer synthesized with POEM/P4VP = 5:5 before and after quaternization. NMR peaks located at 8.8 and 8.4 ppm are assigned to the protons of the pyridine rings after and before quaternization, respectively [19]. The peaks in the chemical shift region of 4.2, 3.6, and 3.2 ppm are attributed to the signals of proton atoms from POEM groups of the side chain [20]. The composition of the copolymer was determined from the integral ratio of the signals originating from POEM chains and the pyridine ring. The actual mass ratios of the comb-like copolymer were POEM/P4VP=21:79, 52:48, and 63:37 when prepared with the added mass ratios of POEM/P4VP=3:7, 5:5, and 6:4, respectively. The actual mass ratios of the copolymer did not differ greatly from the added ratios, implying a similar reactivity of POEM and P4VP for ATRP. Thus, the comb-like copolymers synthesized with the added mass ratios of POEM/P4VP=3:7, 5:5, and 6:4 will be referred to as POEM3-P4VP7, POEM5-P4VP5 and POEM6-P4VP4, respectively. After the quaternization reaction, half of the pyridine rings were converted to quaternized pyridines. For example, the calculated mass ratio of the POEM-qP4VP polymer synthesized with POEM/P4VP=5:5 was POEM/P4VP/qP4VP=52:22:25 wt.%.

Figure 2 shows the FT-IR spectra of the POEM macromonomer, POEM5-P4VP5, and its quaternized counterpart, POEM-P4VP (POEM5-qP4VP5). The POEM macromonomer exhibited absorption bands at 1,716, 1,622, and 1,097 cm^{-1} , which were assigned to the stretching vibration of C=O, C=C and C-O-C groups, respectively [21]. Upon copolymerization of POEM with P4VP, the absorption bands of C=O and C-O-C were shifted to a higher wavenumber at 1,724 and 1,099 cm^{-1} , respectively, due to the change in electron polarization. In addition, the

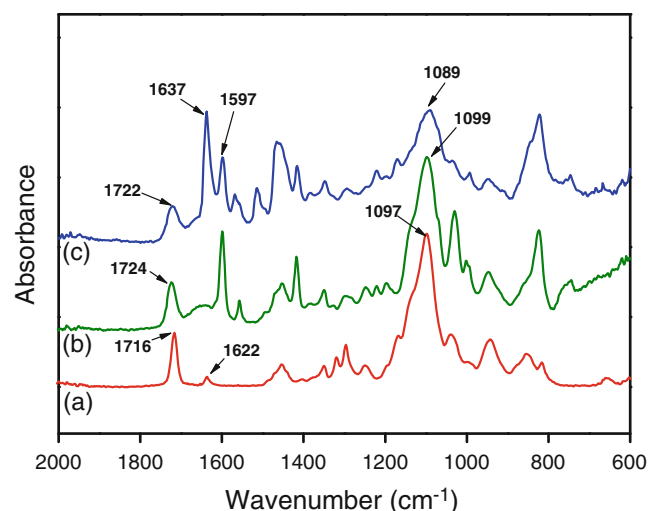


Fig. 2 FT-IR spectra of **a** pristine POEM, **b** POEM5-P4VP5 and **c** POEM5-qP4VP5

absorption band at $1,597\text{ cm}^{-1}$ was observed, which was assigned to the C–N stretching band in the pyridine ring [22]. After the POEM–P4VP copolymer was reacted with 1-iodopropane, a new absorption band appeared at $1,637\text{ cm}^{-1}$, indicating quaternized pyridine rings. Meanwhile, the intensity of the absorption band at $1,597\text{ cm}^{-1}$ was reduced but not completely eliminated. This FT-IR spectroscopic result indicates that the pyridine groups were partially quaternized to pyridinium ions, consistent with the NMR result in Fig. 1. In addition, the absorption band at $1,099\text{ cm}^{-1}$ shifted to a lower wavenumber, $1,089\text{ cm}^{-1}$, implying that the oxygen atoms in the ether group of POEM interacted with the quaternized pyridine groups.

The FT-IR spectra of POEM5–P4VP5 and POEM5–qP4VP5 and their complexes with LiI/I_2 were measured separately to investigate coordinative interactions in the polymer electrolyte, as shown in Fig. 3. In Fig. 3a, the absorption band at $1,099\text{ cm}^{-1}$ attributed to the C–O–C

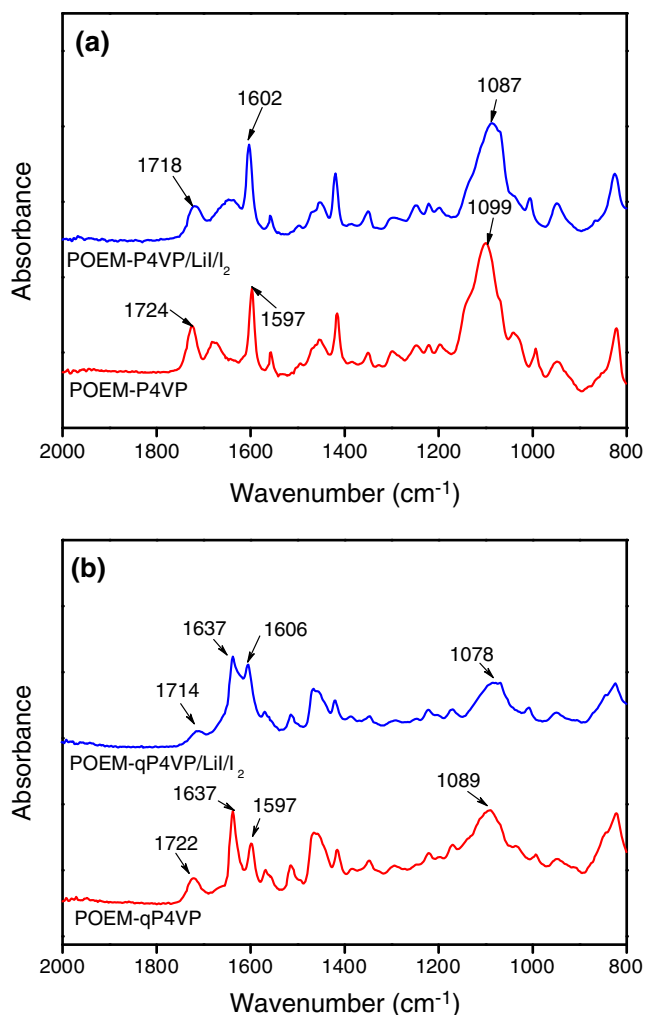


Fig. 3 FT-IR spectra of **a** POEM5–P4VP5 and **b** POEM5–qP4VP5 electrolytes containing LiI/I_2

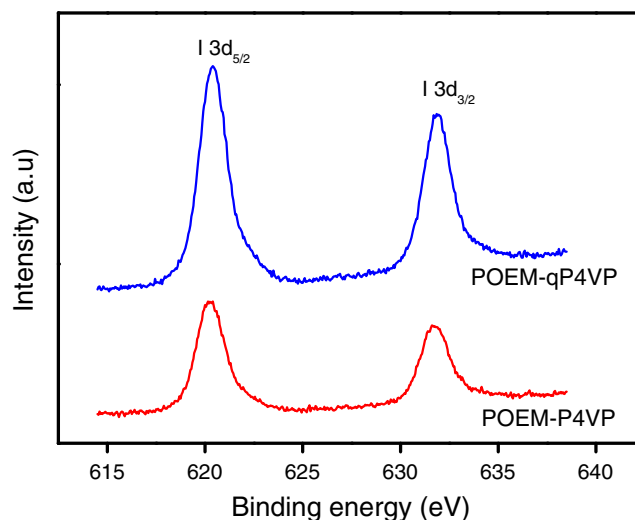


Fig. 4 XPS spectra of POEM5–P4VP5 and POEM5–qP4VP5 electrolytes containing LiI/I_2

stretching vibration of POEM was shifted to a lower wavenumber, $1,087\text{ cm}^{-1}$, upon the introduction of salt, demonstrating that the lithium ions of LiI interacted with the ether oxygen in POEM. In addition, the stretching bands at $1,724$ and $1,597\text{ cm}^{-1}$, assigned to C=O of POEM and C–N of P4VP, respectively, shifted to $1,718$ and $1,602\text{ cm}^{-1}$, respectively. As a result, the lithium ions of LiI interacted with the C=O of POEM and the C–N of P4VP via a coordination bond. Similar results were observed for POEM–qP4VP electrolytes containing LiI/I_2 . For example, the C=O and C–O–C stretching band of POEM shifted to a lower wavenumber (from $1,722$ to $1,714$ and from $1,089$ to $1,078\text{ cm}^{-1}$), whereas C–N of P4VP shifted to a higher wavenumber (from $1,597$ to $1,606\text{ cm}^{-1}$). However, the stretching band at $1,637\text{ cm}^{-1}$ remained unchanged, indicating that the quaternized pyridine rings were not involved in coordination bonding interactions.

XPS is a useful quantitative spectroscopic technique to determine the quantity of elements, the binding energy of one or more electronic states and the density of the electronic states [23]. In the survey scan of the XPS spectra, C, N, O, Li and I atoms were present in both POEM–P4VP and POEM–qP4VP electrolytes. With the exception of iodine, all the elements existed at nearly the same ratio in the two electrolytes. Figure 4 presents I in the 3d XPS data of POEM5–P4VP5 and POEM5–qP4VP5 electrolytes containing LiI/I_2 . Two well-defined peaks at 620.4 and 631.6 eV corresponding to $\text{I } 3d_{5/2}$ and $\text{I } 3d_{3/2}$, respectively, were observed in the spectra [24]. The peak intensity of the POEM–qP4VP electrolyte was greater than that of the POEM–P4VP electrolyte, indicating a greater iodine concentration. This increased concentration of iodine ions is expected to increase the current density of DSSCs due to the enhanced diffusion rate.

Microphase separation of copolymers can be used to create well-defined periodic microdomains with controlled nanoscale morphology. Figure 5 shows the TEM images of POEM5–P4VP5 and POEM5–qP4VP5 comb-like copolymers. Because the samples were stained with iodine (I_2), the dark regions represent P4VP domains and the bright regions represent the POEM domains. Both POEM–P4VP and POEM–qP4VP exhibited a microphase-separated morphology into P4VP domains interweaved with POEM chains in a nanometer scale range, which is a common

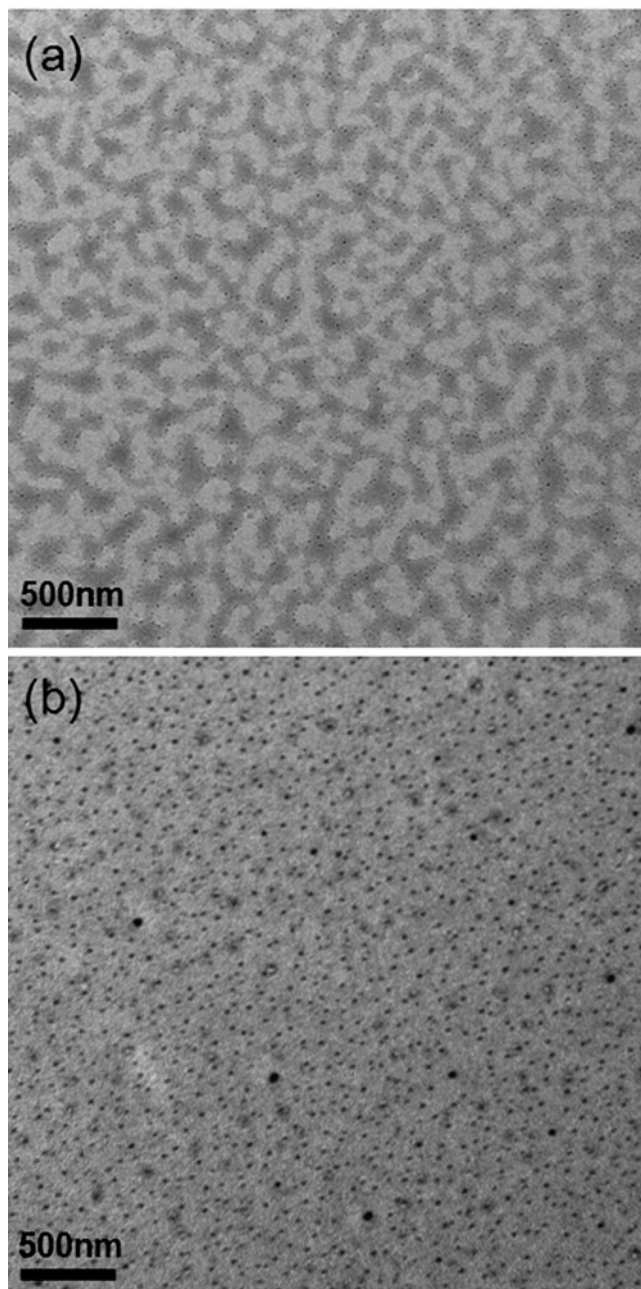


Fig. 5 TEM images of **a** POEM5–P4VP5 and **b** POEM5–qP4VP5 comb-like polymers

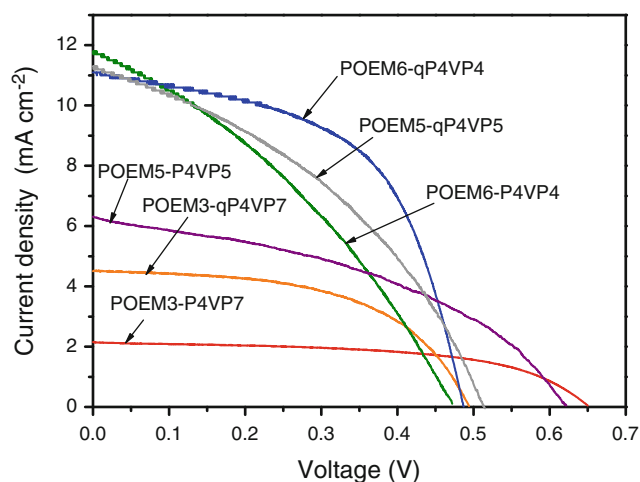


Fig. 6 J – V curves of DSSCs fabricated using POEM–P4VP and POEM–qP4VP polymer electrolytes with LiI/I_2 at 100 mW/cm^2

morphology of graft or comb-like copolymers [25–28]. However, the strong segregation observed in POEM–P4VP was less prominent in POEM–qP4VP due to interactions between the ether oxygens of POEM and the quaternized pyridine groups of qP4VP, as confirmed by FT-IR spectroscopy. These microphase-separated structures provide a mechanism for facile ion transport and high mechanical stability of the comb-like polymer.

DSSCs with POEM–P4VP and POEM–qP4VP electrolytes containing LiI/I_2 were constructed and their J – V characteristics were measured at 100 mW/cm^2 , as shown in Fig. 6. DSSC performance measures including V_{oc} , J_{sc} , FF, and energy conversion efficiency (η) are summarized in Table 1. The J_{sc} of the DSSC with POEM–P4VP electrolytes increased with increasing POEM content because the ethylene oxide units of POEM interacted with a metal salt more favorably to produce more Γ^- ions, resulting in a higher concentration of the Γ/I_3^- redox couple. DSSCs with the POEM–qP4VP electrolyte exhibited a greater J_{sc} than DSSCs with the POEM–P4VP electrolyte, resulting in a greater concentration of Γ/I_3^- ions in the electrolytes. In general, a higher ionic concentration enhances the ionic conductivity and the diffusion rate of Γ/I_3^- [29, 30]. However, the high concentration of I_3^- may result in an increase in collision frequencies between the electrons in the TiO_2 electrode and I_3^- in the electrolyte, leading to an increased recombination rate and decreased V_{oc} [29, 30]. The ionic conductivities of polymer electrolytes at 25°C are also shown in Table 1. The ionic conductivities of quaternized POEM–qP4VP electrolytes were always greater than those of POEM–P4VP electrolytes. For example, the ionic conductivity of the POEM5–P4VP5/ LiI/I_2 electrolyte was $1.9 \times 10^{-6} \text{ S/cm}$, which increased to $2.0 \times 10^{-5} \text{ S/cm}$ upon quaternization of the pyridine groups. Ionic conductivity is directly affected by the concentration of Γ/I_3^- in a polymer

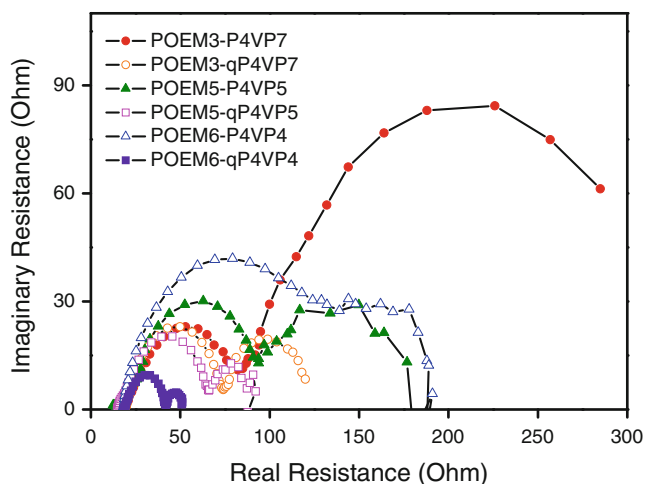


Fig. 7 EIS curves of DSSCs fabricated using POEM–P4VP and POEM–qP4VP polymer electrolytes with LiI/I₂ at 100 mW/cm²

electrolyte. As revealed by XPS analysis, the iodine concentration of POEM–qP4VP was greater than that of the POEM–P4VP electrolyte. Therefore, the POEM–qP4VP electrolyte exhibited more enhanced ionic conducting properties than the pristine electrolyte, which would, in turn, affect the solar cell performances. The maximum energy conversion efficiency of the DSSC employing the POEM–qP4VP/LiI/I₂ electrolyte reached 3.0% at 100 mW/cm².

EIS analysis was used to investigate the internal resistance and charge-transfer kinetics in DSSCs. An applied bias of *V*_{oc} at a frequency range of 0.01 Hz to 0.1 MHz was used with an AC amplitude of 0.02 V and a light intensity of 100 mW/cm². The Nyquist plots of the DSSCs fabricated with POEM–P4VP and POEM–qP4VP are shown in Fig. 7, and their electrochemical parameters are summarized in Table 2. There are two semi-circles in all the EIS spectra; *R*_s, *R*_{ct1}, and *R*_{ct2} are the ohmic resistance, charge transfer resistance of the Pt/electrolyte interface, and charge transfer resistance of the dye adsorbed TiO₂/electrolyte interface, respectively [31]. All DSSCs exhibited nearly identical values of *R*_s, indicating that the modification of the polymer electrolyte has little effect on the FTO glass resistance. However, the charge transfer resistances, *R*_{ct1} and *R*_{ct2}, exhibited substantial differences. The *R*_{ct1} and

Table 2 Electrochemical parameters of DSSC with of POEM–P4VP and POEM–qP4VP electrolytes with various compositions determined from EIS analysis

	<i>R</i> _s	<i>R</i> _{ct1}	<i>R</i> _{ct2}
POEM3–P4VP7	19	77	228
POEM3–qP4VP7	19	55	46
POEM5–P4VP5	18	75	95
POEM5–qP4VP5	19	47	21
POEM6–P4VP4	17	71	85
POEM6–qP4VP4	15	23	10

*R*_{ct2} of the DSSCs fabricated with POEM–P4VP electrolytes were greater than those of DSSCs with POEM–qP4VP electrolytes. The greater iodide concentration and iodide transport channel in the POEM–qP4VP electrolyte enhanced the diffusion of iodide, resulting in an easier charge transfer in the quaternized systems.

Conclusions

Solid-state DSSC was constructed based on quaternized POEM–P4VP comb-like polymers. POEM–P4VP comb-like polymers were synthesized via the ATRP process using MBP as an initiator. These comb-like polymers were quaternized with 1-iodopropane to enhance the iodide diffusion and ionic conductivity. The polymer electrolytes were prepared by complexation between the comb-like polymers and metal salt. LiI was complexed with the oxygen atoms of POEM chains and the nitrogen atoms of P4VP, as revealed by FT-IR spectroscopy. XPS analysis showed that the concentration of iodine ions in the POEM–qP4VP electrolyte was greater than that of the pristine POEM–P4VP electrolyte. As a result, both the ionic conductivity and energy conversion efficiency of the DSSC were improved by using the quaternized polymer electrolyte. For example, the ionic conductivity increased from 4.2×10^{−6} to 3.3×10^{−5} S/cm at 25 °C, and the energy conversion efficiency increased from 1.9% to 3.0% at 100 mW/cm² when the POEM6–P4VP4 electrolytes were used.

Table 1 Ionic conductivities and DSSC performances of POEM–P4VP and POEM–qP4VP electrolytes with LiI/I₂ at room temperature and 100 mW/cm²

Polymer electrolyte	Conductivity (S/cm)	<i>V</i> _{oc} (V)	<i>J</i> _{sc} (mW/cm ²)	FF	η (%)
POEM3-P4VP7	9.6×10 ^{−7}	0.65	2.2	0.56	0.8
POEM3-qP4VP7	7.8×10 ^{−6}	0.49	4.5	0.55	1.2
POEM5-P4VP5	1.9×10 ^{−6}	0.62	6.3	0.42	1.6
POEM5-qP4VP5	2.0×10 ^{−5}	0.51	11.3	0.39	2.3
POEM6-P4VP4	4.2×10 ^{−6}	0.47	11.8	0.35	1.9
POEM6-qP4VP4	3.3×10 ^{−5}	0.49	11.1	0.55	3.0

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