Synthesis and Characterization of Poly(1-vinyl-3-propylimidazolium) Iodide for Quasi-Solid Polymer Electrolyte in Dye-Sensitized Solar Cells

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ABSTRACT: The synthesis conditions of ionic liquid 1-vinyl-3-propylimidazolium iodide ($ViPrIm^+I^-$) and Poly(1-vinyl-3-propylimidazolium) iodide [$P(ViPrIm^+I^-)$] were studied in this work. $P(ViPrIm^+I^-)$ as a single-ion conductor providing iodine was designed to develop a quasi-solid polymer electrolyte based on PVDF/PEO film for dye-sensitized solar cells (DSSCs). The samples were characterized respectively by high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance imaging (NMRI), gel permeation chromatography (GPC), etc. The results showed that the single-ion conducting quasi-solid polymer electrolyte (SC-QPE) exhibited high ionic conductivity of 1.86×10^{-3} S cm^{-1} at room temperature measured by CHI660C Electrochemical Workstation. Moreover, solar cells assembled using the SC-QPE yielded an open-circuit voltage of 0.83V, short-circuit current of 8.01 mA cm^{-2} and the conversion efficiency of 2.42%. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1455–1461, 2010

Key words: Single-ion conductor; Polyelectrolyte; Heteroatom-containing polymer; electrochemistry; dye-sensitized solar cell

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted large attention in scientific research and for practical applications owing to the potential advantages of low cost, easy production, flexibility, and transparency relative to conventional crystalline silicon solar cells.[1,2] DSSCs have reached the efficiency of as high as 11.04% with liquid electrolyte.[3] However, one of the main problems is that the liquid electrolytes limit device stability due to easy evaporation and leakage. For improving the long-term stability, many attempts have been made to substitute the volatile liquid electrolytes with quasi-solid-state electrolytes (e.g., polymer gel,[4,5] low-molecular weight gel,[6] or ureasil/sulfolane gel[7]) or solid state electrolytes (e.g., p-type semiconductors,[8,9] organic hole-transport materials,[10,11] solid polymer electrolytes,[12–15] and plastic crystal electrolytes[16,17]). However, a disadvantage is that both anions and cations migrate toward the oppositely charged electrodes during discharge in these bi-ionic systems,[18] thereby polarizing the electrolyte and increasing its resistivity. It can be solved by using single-ion based conductors in which either the anions or the cations are immobilized. Therefore, it is necessary to reduce the mobility of cation connecting with iodine ion in dye-sensitized solar cell.

During last 10 years, the room temperature ionic liquids (RTILs) have been extensively studied as electrolytes in dye-sensitized solar cell, and the polymer forms of ionic liquids are increasingly used as electrolytes owing to exceptional properties, such as stability, electrochemical activity, and gas absorption ability.[19] But the ionic conductivity of gel-electrolyte component with polymerized ionic liquids and iodine only is too low (2.0×10^{-9} S cm^{-1} at 30°C)[20] to application. Therefore, polymerized ionic liquids electrolyte must be modified. Yu et al.[19] synthesized a poly ionic liquid 1-ethyl-3-(2-methacryloyloxy ethyl) imidazolium iodide (PEMEImI). They mixed it with I_2 and polyacrylonitrile(PAN) to form gel polymer electrolyte and the ionic conductivity of about 1.0×10^{-3} S cm^{-1} at room temperature was achieved. Azaceta et al.[21] reported a series of polymer electrolytes formulated as mixtures of the ionic liquid 1-methyl-3-propylimidazolium iodide and the poly(1-vinyl-3-alkylimidazolium) iodide polymers. Gel electrolytes was obtained by adding poly(1-vinyl-3-propylimidazolium) iodide into a typical acetonitrile electrolyte and tested in DSSCs. The results showed that DSSCs employing the gel polymer electrolyte yielded a maximum light-to-electricity conversion efficiency of 3.73%.

Considering that solid-state polymer electrolytes (SPE) possess mechanical stability, safety, and

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necessary prerequisites for easy processing, many researchers have tried their best to unite both ILs and polymers and to gain the advantages from their combination. One vision of new composite materials was filled linear polymer films with different ILs.[22–26] In this research, a two-step route toward the synthesis of P(ViPrIm$^+$I$^-$) is presented. In the first step, the monomer is prepared by quaternization reaction under solvent-free conditions in Teflon-lined, stainless autoclaves. In the second step, the free-radical-initiated polymerization of ViPrIm$^+$I$^-$ is carried out in ethanol solution at 85°C using 2,2′-azobisisobutyronitrile as an initiator. A novel single-ion conducting quasi-solid polymer electrolyte film (SC-QPE) is fabricated by soaking a porous polymer membrane in electrolyte composed with P(ViPrIm$^+$I$^-$), I_2, 4-tert-Butylpyridine (4-TBP), propylene carbonate (PC), and ethylene carbonate (EC). Systematic studies are performed to understand the advantages of the SC-QPEs with P(ViPrIm$^+$I$^-$) providing iodine, such as single-ion transferring, producing simple, good mechanics, stably, suppressing dark current and saving easily etc. It can be potentially applied in the dye-sensitized solar cell.

EXPERIMENTAL

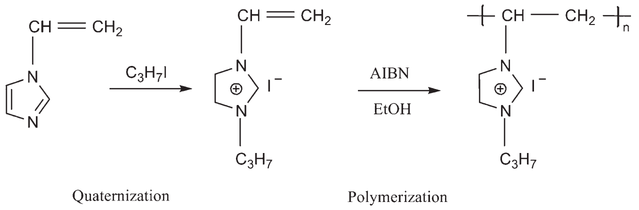
Materials

1-Vinylimidazole (Yancheng Baiyi Chem) and 2,2′-azobisisobutyronitrile (AIBN) (Sinopharm Chemical Reagent) were distilled under vacuum before use. 4-tert-butylpyrdine (TBP), Ethylene Carbonate (EC), Propylene Carbonate (PC) were purchased from Fluka and used as received. All other chemicals and solvents were obtained from Sinopharm Chemical Reagent.

Synthesis and characterization

The 1-vinyl-3-propylimidazolium iodide monomer (ViPrIm$^+$I$^-$) synthesis was similar to the previous report.[27] The mixture of 1-vinylimidazolium (50.0 mmol) and *n*-propyl iodide (52.5 mmol) was placed in a 50-mL Teflon-lined, stainless steel autoclave, and then was heated in an oven at 80°C (4 h), 100°C (4 h, 6 h, 10 h), 120°C (4 h), respectively. The product was washed twice by ethyl ether to remove residual 1-vinylimidazolium and little *n*-propyl iodide if necessary. The prepared ViPrIm$^+$I$^-$ were dried under vacuum for 24 h at 80°C.

Obtained ViPrIm$^+$I$^-$ were polymerized with 2,2′-azobis (isobutyronitrile) (AIBN) of different molar percents as a radical polymerization initiator in ethanol at 85°C under Ar ambience. The polymerized time was also investigated to achieve different degree of polymerization of polymers. The molten salt polymer P(ViPrIm$^+$I$^-$) was yield by removing ethanol from the solution and drying in a vacuum oven until constant weight. P(ViPrIm$^+$I$^-$) was got as a white-yellowish powder at room temperature (Scheme 1).



Scheme 1 Two-step route toward the synthesis of P(ViPrIm$^+$I$^-$).

Preparation of SC-QPE

The PVDF–PEO microporous membranes were prepared by a phase inversion method.[28] Different molar ration of P(ViPrIm$^+$I$^-$) were dissolved in the liquid electrolyte [0.05*M* iodine, 0.1*M* 4-TBP, PC and EC with 4 : 6 (w/w)]. For comparison, another conventional liquid electrolyte contained 0.5*M* NaI, 0.05*M* I_2, 0.1*M* 4-TBP in the binary organic solvents mixture PC and EC with 4 : 6 (w/w) was prepared. Afterwards, the dried polymer membranes were soaked in liquid electrolyte prepared above to form SC-QPE. The SC-QPE from 1 to 5 with the increase in contents of P(ViPrIm$^+$I$^-$) was marked.

DSSCs assembly

The preparation of the dye-sensitized TiO_2 film was similar to the previous report.[29] A quasi-solid-state dye-sensitized solar cell was assembled by sandwiching a slice of gel polymer electrolyte between a dye-sensitized TiO_2 electrode and a platinum counter electrode (purchased from DYSEOL). The two electrodes were clipped together with clamps.

Measurement methods

HPLC of 1-vinyl-3-propylimidazolium iodine (ViPrIm$^+$I$^-$) was measured on Agilent 1100, using acetonitrile as solvent. The IR absorption spectra were taken using an attenuated total reflection Fourier transform infrared spectrometer (PerkinElmer1760). ^{1}H-NMR spectra of ViPrIm$^+$I$^-$ were studied on a Bruker DMX 500 spectrometer using $CDCl_3$ as solvent. The molecular weight of P(ViPrIm$^+$I$^-$) was recorded on GPC.

The poly ionic liquid electrolyte was analyzed by Raman spectroscopy (NEXUS670). An NDJ-9S rotational viscosimeter (Shanghai Ande Instrument Equipment) was used to examine the viscosities of the five poly ionic liquid electrolytes at room temperature in air. Conductivity measurements of the electrolyte were carried out by complex impedance method. To investigate the diffusion coefficients of I_3^- in the electrolyte, steady-state voltammograms of SC-GPE was also

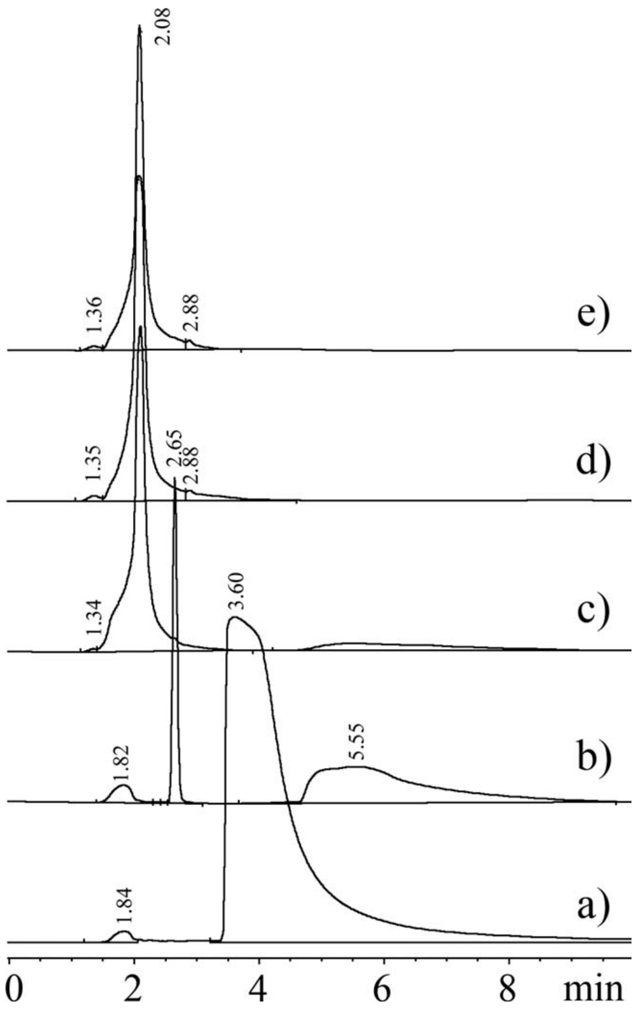


Figure 1 The HPLC of ViPrIm$^+$I$^-$ and starting materials: (a) 1-vinylimidazolium; (b) *n*-propyl iodide; (c) ViPrIm$^+$I$^-$(100°C, 4 h); (d) ViPrIm$^+$I$^-$ (100°C, 6 h); (e) ViPrIm$^+$I$^-$ (120°C, 4 h).

measured by CHI660C Electrochemical Workstation. Photocurrent-voltage measurements were performed upon 1 Sun illumination (AM1.5100 mW cm^{-2}).

RESULTS AND DISCUSSION

Influence of reaction conditions on the synthesis of ViPrIm$^+$I$^-$ and P(ViPrIm$^+$I$^-$) HPLC measurement

Figure 1 shows the HPLC of ViPrIm$^+$I$^-$ and starting materials. The yield and purity of ViPrIm$^+$I$^-$ under different conditions are summarized in Table I.

TABLE I
Influence of Reaction Conditions on the Synthesis of ViPrIm$^+$I$^-$

ViPrIm$^+$I$^-$	Time (h)	Temperature (°C)	Yield (%)	Purity (%)
A	4	80	90.97	49.09
B	4	100	95.76	80.29
C	4	120	96.10	98.93
D	6	100	95.83	98.93
E	10	100	96.21	98.89

The starting materials, 1-vinylimidazole and *n*-propyl iodide, were nearly not detected in (d) and (e). This indicated that the resulting ViPrIm$^+$I$^-$ was high pure, the conversion rate of 1-vinylimidazole was close to 100% at suitable reaction temperature and time. Thus, the reaction condition of 120°C for 4 h is appropriate for synthesis of ViPrIm$^+$I$^-$ under solvent-free by Teflon-lined, stainless steel autoclaves. ^{1}H-NMR (500 MHz, $CDCl_3$)δ: 10.54(s, 1H), 7.84(s, 1H), 7.66(s, 1H), 7.43–7.46(m, 1H), 6.01–6.03(m, 1H), 5.45–5.46(m, 1H), 4.41–4.44(t, 2H), 2.00–2.06(m, 2H),1.02–1.04(t, 3H).

The molecular weights measurement and polymerization mechanism analysis

The molecular weights (M_n and M_w) and polydispersity index (PDI) of the P(ViPrIm$^+$I$^-$) were determined using GPC. The data are summed up in Table II.

These data indicated that the M_w/M_n increased mildly with polymeric time extension, but it varied strongly with initiator contents during reaction. The polymeric degree was so little that the sample was a viscous liquid but not a white-yellowish powder when AIBN was 2 mol%, though the reaction time was 30 h.

The P(ViPrIm$^+$I$^-$) with controlled molecular weight, narrow molecular weight distribution (i.e., M_w/M_n, or PDI < 1.1) was prepared. The possible reason why P(ViPrIm$^+$I$^-$) with small M_w/M_n, narrow PDI and long reaction time is that the monomer contained I$^-$, similarly to iodine and RI, which could form $(CH_3)_2C(CN)$-I with AIBN leading to a degenerative transfer polymerization(DTP). In other words, the polymerization process of ViPrIm$^+$I$^-$ is a

TABLE II
Influence of Reaction Conditions on the Synthesis of P(ViPrIm$^+$I$^-$)

P(ViPrIm$^+$I$^-$)	AIBN (mol %)	Time (h)	M_n (Daltons)	M_w (Daltons)	Polydispersity
a	5	12	7081	7147	1.009307
b	5	24	7209	7280	1.009794
c	5	30	7363	7426	1.008619
d	2	30	<1000	<1000	–
e	8	30	6788	6823	1.005190

DTP rather than a traditional ATRP. The mechanism is attributed to the I atom originated from the C—I bond cleavage and bonding, which can transfer reversibly between chain transfer agent and propagating radical, causing the control of free radical concentration and the stability of free radicals.

Obviously, the larger the molecular weights are, the greater the viscosity is. The P(ViPrIm$^+$I$^-$) acts as not only the single-ion conductor but also the sole source of iodide moving through porous polymer membrane. It means that the viscosity of single-ion conducting liquid electrolyte is neither great nor small. Consequently, the optimal polymerization condition is 5 mol % AIBN at 85°C for 24 h.

IR spectra study

The IR spectra ViPrIm$^+$I$^-$ and P(ViPrIm$^+$I$^-$) are shown in Figure 2.[30] The broad absorption band at 3456 cm^{-1} and 3453 cm^{-1} are assigned to a variety of hydroxyl vibration. The characteristic IR peaks at 2971, 2938, 2876 cm^{-1}, which are considered to arise from CH_3— and —CH_2— bands stretching vibration on side-chain of imidazole ring. No peaks observed at 967, 930, 1650 cm^{-1} in spectra of P(ViPrIm$^+$I$^-$) indicates that the C=C stretching vibration of vinylidene groups in unpolymerized ViPrIm$^+$I$^-$ monomer disappeared via polymerization.

Raman spectra study

Raman spectra in the range of 100–300 cm^{-1} of the polymerized ionic liquid electrolyte is shown in Figure 3. The absorption band at 114 cm^{-1} is the symmetric stretching I_3^- ions, the weaker band at 143 cm^{-1} is assigned to characteristic the asymmetric stretching of I_3^- ions.[31,32] The result shown that I_3^- formed when I_2 was added to the liquid electrolyte.

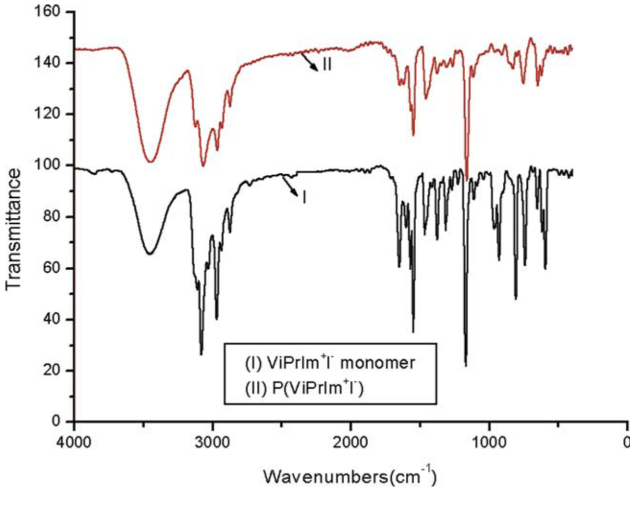


Figure 2 IR spectra of ViPrIm$^+$I$^-$ and P(ViPrIm$^+$I$^-$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

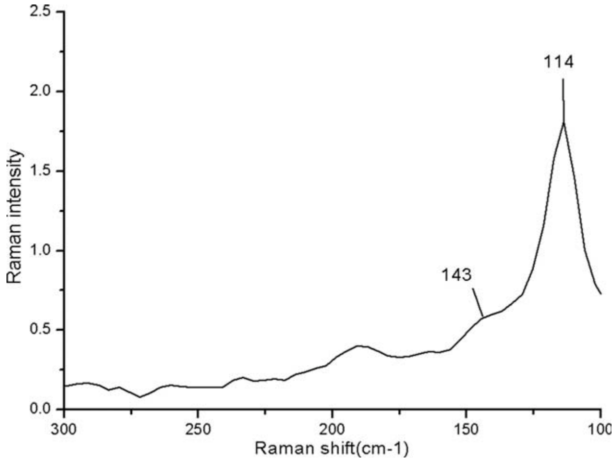


Figure 3 Raman spectra of the liquid electrolyte.

The viscosity and electrolyte uptake

Conductivity of the electrolyte is related to the molecular weight, density, size of ions, and especially viscosity. Viscosity studies provide a useful insight on the mobility of ions in liquid or gel electrolytes. The viscosity depends on hydrogen bonding and the van der Waals force, but mainly on hydrogen bonding.[33] The viscosity with different molar ratio of P(ViPrIm$^+$I$^-$) is displayed in Figure 4. It can be seen that the viscosity of electrolyte depresses with decreasing P(ViPrIm$^+$I$^-$) content.

The porosity, one of the important parameters of porous polymer membranes, can dominate the conduction properties of the carriers.[34] It also can be assessed by the tendency of the electrolyte uptake. The electrolyte uptake was calculated by:

$$\text{Uptake} = (W_\mathrm{i} - W_0)/W_0 \times 100\%$$

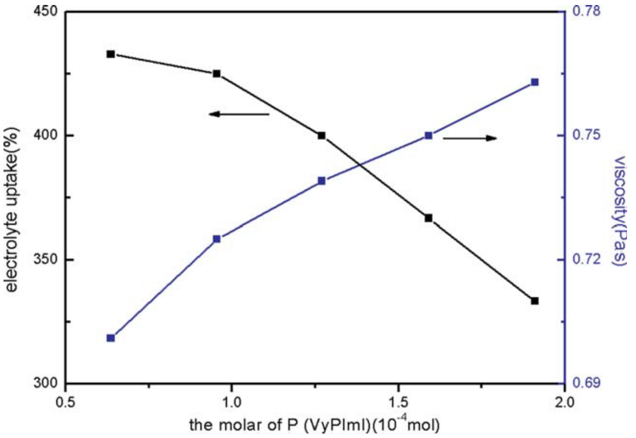


Figure 4 The viscosity and electrolyte uptake with different contents of P(ViPrIm$^+$I$^-$).

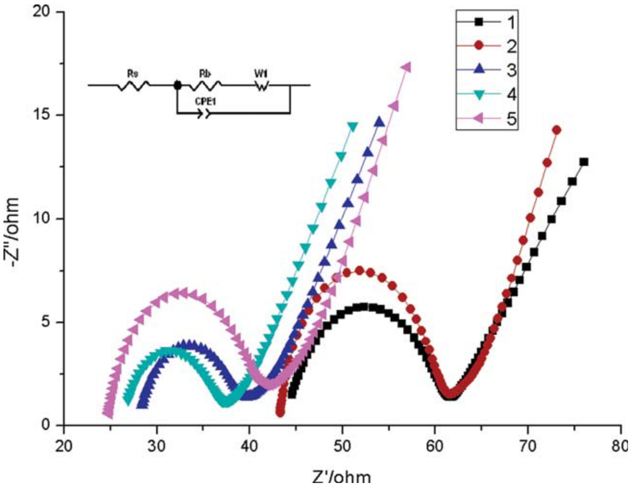


Figure 5 Impedance plot for the quasi-solid polymer electrolyte: (1) The QPE contains P(ViPrIm$^+$I$^-$) of 6.35 × 10^{-5} mol; (2) The QPE contains P(ViPrIm$^+$I$^-$) of 9.52 × 10^{-5} mol; (3) The QPE contains P(ViPrIm$^+$I$^-$) of 1.27 × 10^{-4} mol; (4) The QPE contains P(ViPrIm$^+$I$^-$) of 1.59 × 10^{-4} mol; (5) The QPE contains P(ViPrIm$^+$I$^-$) of 1.91 × 10^{-4} mol. Symbols Z' and Z'' refer to the real and imaginary component; R_s is the interfacial resistance, R_b is bulk electrolyte resistance, CPE1 is constant phase element and W is Warburg impedance. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where W_i and W_0 are the weight of the wet and dry membranes, respectively.

According to Saito and coworkers,[35] there are two distinct steps for liquid electrolyte uptake in PVDF-PEO-based porous gel polymer membranes. First, the liquid electrolyte occupied some pore spaces of the membrane. Then, those electrolytes in pores penetrated and swelled the polymer chains to form the gel. It is obviously shown in Figure 4, the tendency of the electrolyte uptake is similar to that of viscosity.

Ionic conductivity and triiodide diffusion coefficients characterization

Electrochemical impedance spectroscopy (EIS) was used to characterize the electrochemical behavior of the gel polymer electrolyte. The impedances of different QPE are displayed in Figure 5. Simulated curve is figured as solid line. Its corresponding equivalent circuit is shown in inset. R_s (Fig. 5) is reduced from 1 to 5 owning to the amount of P(ViPrIm$^+$I$^-$) increased, which make the film softer and better contact with the Pt electrodes.

The ionic conductivities are obtained by ZView2 software simulated and formula ($\sigma = d/R_bS$, Where d is the thickness of electrolyte and S is the area of electrolyte) calculated. As shown in Figure 6, the ionic conductivity increases up to a maximum value with the initial increase of the P(ViPrIm$^+$I$^-$) concentration and then decreases with a further increase. According to the previous study of Chen et al.,[36] the more ions exist in the solution the higher ion conductivity is. However, after the highest conductivity reached, the conductivity is determined by the mobility of ionic carriers. From 1 to 5, EIS results revealed that I_3^- transportation in the electrolyte and charge transfer at the counter electrode both became slower with the viscosity of the electrolyte increased.

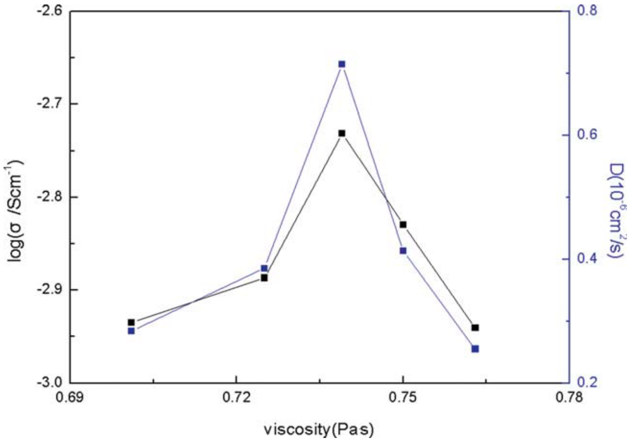


Figure 6 Ionic conductivity and diffusion coefficient with different viscosities.

According to Stokes–Einstein relation,[37] the electron diffusion coefficient decreases with the increase of the molecule radius and electrolytic viscosity. For our single-ion transfer system, ionic conductivity and diffusion coefficient have the same trend (Fig. 6). The addition of P(ViPrIm$^+$I$^-$) brings an improvement of the viscosity of the electrolyte, which blocks the transfer of charge carrier. The ionic conductivity and diffusion coefficient are as high as 1.86 × 10^{-3} S cm^{-1} and 7.15 × 10^{-7} cm^2 s^{-1} at room temperature, respectively.

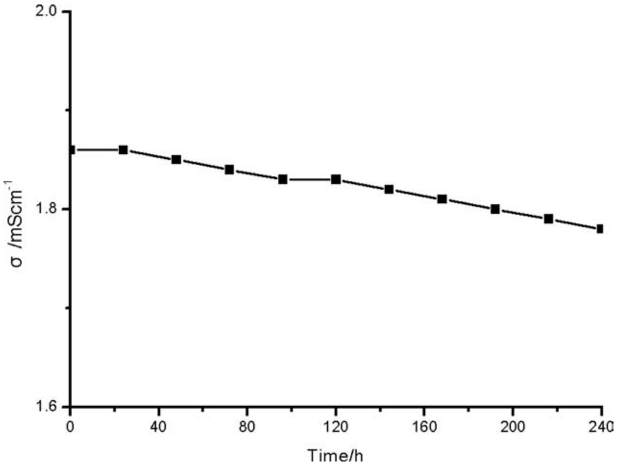


Figure 7 The stability of the QPE contains P(ViPrIm$^+$I$^-$) of 1.27 × 10^{-4} mol.

As expected and been desired, the SC-QPE in this study showed an excellent stability. Figure 7 shows the conductivity of SC-QPE with 1.27×10^{-4} mol $P(ViPrIm^{+}I^{-})$. The conductivity was measured once per day, while the SC-QPE was stored under dark at room temperature. The conductivity of SC-QPE remained almost unchanged after being stored for more than 240 h. Thus, these results proved beyond doubt that the stability of the SC-QPE was satisfactory.

Photovoltaic performance

The photocurrent performances for dye-sensitized solar cell with different SC-QPE were tested. The I–V curves are shown in Figure 8, cell parameters corresponding to these DSSCs are summarized in Table III.

The open circuit voltage (V_{oc}) of SC-QPE was significantly higher than that of conventional QPE without $P(ViPrIm^{+}I^{-})$. It should be contributed to the unique advantages of polymeric ionic liquid $[P(ViPrIm^{+}I^{-})]$. It is known that I_m^{+} is adsorbed on the TiO_2 surface and that adsorption of cations changes its conduction band edge positively. A positive shift causes a decrease in the V_{oc}. Thus, a lower degree of adsorption of solvated I_m^{+} is desirable for larger V_{oc}.[38] $P(ViPrIm^{+}I^{-})$ with larger charge densities are expected to adsorb to a lesser degree on to the positive sites of the TiO_2 surface, which causes larger V_{oc} for the DSSCs. Furthermore, polyvinyl chains can interact laterally to impair the back electron transfer from the conduction band of TiO_2 to I_3^{-}. The expected reduced performance of the cells from 3 to 5 was attributed to the one order of magnitude decreased ionic conductivity of the SC-QPE. The formation of I_3^{-} plays an important role in the redox reactions between I^{-} and I_3^{-} contributed to the charge transfer process in DSSCs.[39,40] From cell (3), cell (4) to cell (5) the photovoltaic performances were poorer with the increasing of I_3^{-} Among the reasons, the fast composite rate from electronics to I_3^{-} through the conduction band of titanium dioxide and fuel-excited state may be an essential one, leading to the increasing of the dark current. Another underlying reason is the absorption of incident light by I_3^{-} which makes weak both the intensity of incident light and efficiency of incident light-current conversion. Most of all, they could be influence on photovoltaic performances eventually.

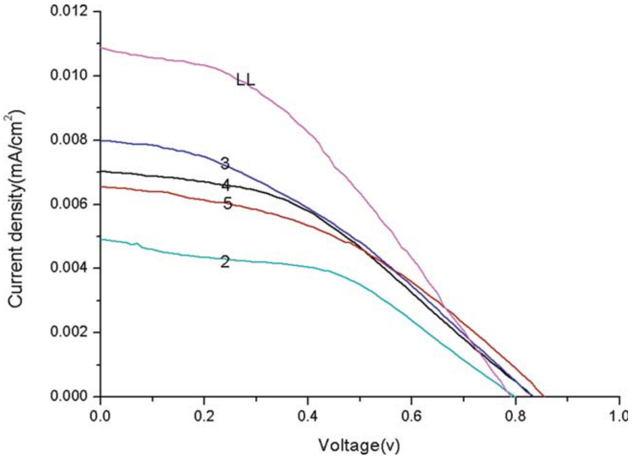


Figure 8 I–V curves of DSSCs fabricated of various SC-QPEs at 1 sun illumination. The SC-QPE in Cell (2) contains $P(ViPrIm^{+}I^{-})$ of 9.52×10^{-5} mol; in Cell (3) contains $P(ViPrIm^{+}I^{-})$ of 1.27×10^{-4} mol; in Cell (4) contains $P(ViPrIm^{+}I^{-})$ of 1.59×10^{-4} mol; in Cell (5) contains $P(ViPrIm^{+}I^{-})$ of 1.91×10^{-4} mol; The QPE in Cell (LL) is conventional QPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Photovoltaic Performance of SC-QPE Dye-Sensitized Solar Cells

	V_{oc} (V)	J_{sc} (mA/cm^2)	ff	η (%)
Cell (2)	0.79	5.20	0.429	1.76
Cell (3)	0.83	8.01	0.364	2.42
Cell (4)	0.83	7.03	0.404	2.37
Cell (5)	0.85	6.55	0.414	2.32
Cell (LL)	0.79	10.91	0.387	3.33

CONCLUSIONS

The experimental conditions of $ViPrIm^{+}I^{-}$ and $P(ViPrIm^{+}I^{-})$ were investigated in this article. The prepared condition of 120°C for 4 h was optimal appropriate for synthesis of $ViPrIm^{+}I^{-}$ under solvent-free by Teflon-lined, stainless steel autoclaves. The polymerization condition of 5 mol % AIBN at 85°C for 24 h was adopted in the end. A new SC-QPE based on $P(ViPrIm^{+}I^{-})$ for dye-sensitized solar cells was prepared. SC-QPE composited with 0.127 $MP(ViPrIm^{+}I^{-})$, 0.05 MI_2, 0.1 M4-TBP, and PC/EC showed higher conductivity owning to moderate viscosity of single-ion conducting liquid electrolyte. A dye-sensitized solar cell employing SC-QPE yielded open-circuit voltage of 0.83 V, short-circuit current of 8.01 mA cm^{-2} and the conversion efficiency of 2.42 at 1 sun illumination, which was 73% efficiency of DSSCs employing conventional QPE. The prepared SC-QPE indeed shows good properties for application in dye-sensitized solar cell, and further investigations in application are in progress.

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