



## Effect of self-assembly on triiodide diffusion in water based polymer gel electrolytes: An application in dye solar cell



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### ABSTRACT

The preparation of ordered polymer gels from the amphiphilic block copolymers, Pluronic® F77, P123 and polyethylene glycol in the presence of ionic liquid, iodine and organic additives is presented. At 35%(w/w) concentration these copolymers (F77 and P123) self-assembled into cubic liquid crystalline phase in aqueous solution and characterized by using SAXS and AFM measurements. The effects of micellar aggregation formed by polymers on the ionic transport and triiodide diffusion have been studied by electrochemistry and SANS experiments. The ionic migration or triiodide diffusion through these polymer gels is found to be affected by the PEO/PPO content in the polymer backbone. These gels were successfully employed as an electrolyte in a dye sensitized solar cell. A remarkable solar to electricity conversion efficiency and good stability was obtained using Pluronic® F77 based gel, which is attributed to its thermoreversible sol to gel transition.

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### 1. Introduction

Polymers have been recently extensively investigated for applications in advanced energy harvesting and storage devices such as dye solar cell, organic solar cell or lithium ion batteries where they play a vital role ranging from active material to neutral backbone [1,2]. In particular, amphiphilic block copolymers are now used as a backbone material in polymer gel electrolytes (PGE) for dye solar cell and lithium ion batteries [3,4] owing to many advantages in terms of safety and easy handling. PGE have unique hybrid structure having cohesive properties of solid and diffusive properties of liquids. PGE also have comparable conductivity as that of liquid electrolytes and have good penetration property. Due to these reasons, PGE are potential substitute for conventional liquid electrolytes. In addition, the use of ionic liquid (IL) and/or water in gel electrolyte will confer a greener and safer approach toward sustainable technology. It has been reported that a thermoreversible gel electrolyte based on the composite mixture of IL and a triblock copolymer (containing 10% polymer in IL) shows better ionic conduction [5].

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Photoelectrochemistry for solar to electricity conversion has been extensively investigated for a long time and was accelerated by Gratzel's pioneering work on Dye Sensitized Solar Cell (DSSC) which paved way for the efficient, low cost and cleaner energy from sunlight [6]. Highest 11% efficiency has been reported for DSSC using N719 dye and liquid electrolyte [7]. Traditional organic liquid electrolytes create significant technical problems associated with sealing, corrosion and a lack of stability of the cells, hence awaiting the commercialization of DSSC [8]. Thus, solid and gel based electrolytes such as *p*-type semiconductors (CuI, CuSCN, etc.) [9,10], organic hole conducting materials [11,12], plastic crystal electrolyte [13,14], solid polymer electrolytes and PGE [15,16], etc. have been used as an alternative for liquid electrolytes. The first report on quasi-solid state DSSC appeared in 1995 using poly(acrylonitrile), ethylene carbonate, acetonitrile and NaI with 4.4% power conversion efficiency [15]. After that a series of polymer and polymer composites such as polyethylene glycol, (PEG), poly(ethylene oxide-co-propylene oxide), poly(acrylamide)/PEG, poly(methyl acrylate), poly(vinylidene fluoride-co-hexafluoropropylene) were employed for fabricating solid and quasi-solid DSSC [17–20]. Like solid polymer electrolytes, PGE reduces the efficiency of the DSSC compared to those with liquid electrolytes. This is due to the imperfect contact with the photoelectrode and increase in viscosity upon gelation [21,22]. Because of these drawbacks, most of the

recent studies have used combination of polymer/copolymer with IL in order to improve the ionic conductivity and the mechanical properties of the PGE [3,4,23–25].

On the other hand all these quasi-solid electrolytes are based on organic solvent and the substitution of these organic solvents in polymer gel with water is one of the important research topics in the context of environment as well as economy. Before 1990, all the DSSC studies were carried out in water based electrolytes with maximum efficiencies 2% and 1.2% at 0.07 sun and 0.5 sun respectively (max.  $J_{sc}$  = 0.8 mA/cm<sup>2</sup>) [23]. Dai et al. reported 1 mA/cm<sup>2</sup> and 0.45 V using natural dye and water based electrolyte [24]. In 2003, Kaneko et al. reported first quasi-solid DSSC using natural polysaccharides in water containing LiI and I<sub>2</sub> having ~0.6% efficiency [25]. Afterward no efforts have been made to optimize the performance of DSSC using water based PGE. Very recently, Law et al. ruled out the opinion that water is poisonous to DSSC by achieving 2.4% photovoltaic performance of water based DSSC ( $J_{sc}$  = 4.7 mA/cm<sup>2</sup> and  $V_{oc}$  = 0.74 V) [26]. To the best of our knowledge, no report has been made on microstructured amphiphilic block copolymer based hydrogel as a redox mediator in dye solar cell as well as the effect of PEO/PPO ratio on triiodide diffusion. Recently we have developed aqueous polymer gels doped with LiI/I<sub>2</sub>, which exhibit microcrystalline phase dependent conductivity [27]. The amphiphilic block copolymer, Pluronic® F77 (PEO<sub>52</sub>-PPO<sub>35</sub>-PEO<sub>52</sub>) which self-assembles into liquid crystalline phases such as cubic, hexagonal, lamellar, was used to prepare polymer gel. The result shows that due to interconnected micellar channels in the bi-continuous cubic phase, polymer gel exhibits higher ionic conductivity compare to other crystalline phases [27].

Here we report, the effects of the PEO/PPO ratio and self-assembly in block copolymers on the diffusion of triiodide using cyclic voltammetry at thin layer cell. The variation in triiodide diffusion as a function of PEO/PPO ratio is justified by tracing the location of triiodide species using Small Angle Neutron Scattering (SANS). The diffusion of triiodide and its effect on the performance of DSSC is discussed as a function of mobility of triiodide species.

## 2. Experimental

### 2.1. Materials

Pluronic® F77 and P123 were obtained as gift samples from BASF, USA and purchased from Sigma–Aldrich, India respectively and their details are given in Table 1. Polyethylene glycol was purchased from Sigma–Aldrich. D907 dye was received as gift sample from Eversolar Inc., Taiwan (see Supporting Information Fig. S1). Unless and otherwise stated all the chemicals were purchased from Sigma–Aldrich and used as received. All solvents and IL (1-butyl-3-methyl imidazolium iodide, [BMIM][I]) were purchased from Merck, India and used as received. Water used in this study was Milli – Q grade (18 MΩ).

### 2.2. Methods

#### 2.2.1. Preparation of polymer gels

All the polymer gels were prepared in situ by mixing 500 mM [BMIM][I], 50 mM I<sub>2</sub>, 0.5 M 4-tert-butyl pyridine (TBP), appropriate

amount of water and polymer in a glass bottle. These bottles were sealed and stored at lower temperature until homogeneous gels were formed. It is worth to mention that all the gels were composed of 35%(w/w) block copolymer.

#### 2.2.2. DSSC fabrication

Dye coated TiO<sub>2</sub> electrodes were fabricated as per our earlier report [28]. A thin layer of nanoporous TiO<sub>2</sub> was deposited from ethanolic titanium tetra-isopropoxide solution on a cleaned FTO (15 Ω/cm<sup>2</sup>, Solaronix, SA, Swiss) conducting glass with >80% transmittance in visible region, by spin coating at 2000 rpm. This thin layered titania was annealed at 450 °C for 20 min. Titania paste consists of TiO<sub>2</sub> (P-25, Degussa), and ethyl cellulose and α-Terpineol were deposited on above pretreated FTO glass by screen printing technique [29]. The electrodes were fired into a tubular furnace at 500 °C for 30 min and the net thickness of titania film was about 12 μm. Working electrodes were soaked into the TiCl<sub>4</sub> solution for 20 min at 60 °C and sintered in air at 450 °C for 10 min. The electrodes were allowed to cool at 70 °C and immersed into the 30 mM solution of D907 dye (Eversolar, Taiwan) [30], in anhydrous acetonitrile: tert-butyl alcohol (1:1) for 12 h. Electrodes were washed thoroughly with acetonitrile and dried under the stream of nitrogen gas. Counter electrodes were prepared from Platisol solution (Solaronix, SA, Swiss) by spin coating method and rapidly fired into the furnace at 450 °C for 20 min. Gel was dropped onto the dye sensitized electrode and applied two heating and cooling cycles between 10 and 40 °C (in order to get good penetration of gel). By keeping 25 μm spacer, cells were sealed using epoxy adhesive and stored in dark for 12 h prior to measurements. The active cell area was 0.5 cm<sup>2</sup>. For comparison purpose, DSSC was also fabricated with same procedure just by replacing PGE with liquid electrolyte containing 0.5 M IL ([BMIM][I]), 0.05 M I<sub>2</sub>, 0.5 M 4-tert-butyl pyridine in acetonitrile.

#### 2.2.3. Characterization of polymer gels and DSSC

Small Angle X-ray Scattering (SAXS) measurements were carried out using the Rigaku SAXS diffractometer equipped with a Gabriel 2D wire detector (sample to detector distance 830 mm and wave length 0.154 nm at IMMM, Le Mans, France). Measurements were collected over a typical time of 10000 s. SANS experiments were carried out on micellar solutions of triblock copolymers, P123 and F77. All the final solutions used for SANS measurements were prepared in D<sub>2</sub>O (99.9 atom D%, Sigma–Aldrich, India). This provides very good contrast between micelles and solvent in a SANS experiment. SANS measurements were performed using a fixed geometry SANS instrument with sample-to-detector distance 1.8 m at the DHRUVA reactor, Trombay, INDIA [31]. This spectrometer makes use of a BeO filtered beam which provides a mean wavelength of 5.2 Å and a wavelength resolution of about 15%. The angular distribution of scattered neutrons was recorded using an indigenously built one-dimensional position sensitive detector. The accessible wave transfer ( $q = 4\pi \sin 0.5\theta/\lambda$ , where  $\lambda$  is the mean wavelength of the incident neutrons and  $\theta$  is the scattering angle) range of this instrument is 0.015–0.35 Å<sup>-1</sup>. The solutions were held in 0.5 cm path length UV-grade quartz sample holder with tight fitting Teflon stoppers sealed with parafilm. The liquid fluid mixtures were inserted in 1 mm quartz capillaries, whereas gels were mounted in an aluminum cell having transparent windows. I–V characterizations were carried out using Keithley 2400 source meter and 100 W xenon lamp as light source equipped with band pass filter and light intensity was set to 100 mW/cm<sup>2</sup> (the light intensity was calibrated using standard Si-photodiode). Electrochemical Impedance Spectra (EIS) of DSSC were obtained by using frequency range from 120 kHz to 50 mHz with 10 mV AC amplitude. Conductivity of the polymer gels were measured using Solartron 1260 (Impedance

**Table 1**  
Description of polymer sample and lattice dimension in polymer gels.

Polymer	Mol.wt. (g mol <sup>-1</sup> )	% EO	$\phi_{\text{PPO}}$	$a$ (nm)
P123 (EO <sub>20</sub> -PO <sub>70</sub> -EO <sub>20</sub> )	5750	30	0.73	16.6
F77 (EO <sub>52</sub> -PO <sub>35</sub> -EO <sub>52</sub> )	6600	70	0.30	25.7
Polyethylene glycol (PEG)	6000	100	–	–

$\phi_{\text{PPO}}$  = Volume fraction of apolar domain.

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