Photo-polymerization of methacrylate based polymer electrolyte for dye-sensitized solar cell

Abstract: The ionic conductivity of poly(glycidyl methacrylate-co-ethyl methacrylate) [P(GMA-co-EMA)]-lithium perchlorate (LiClO₄)-ethylene carbonate (EC) electrolyte and photovoltaic performances of dye-sensitized solar cells (DSSC) utilizing the electrolyte were investigated. P(GMA-co-EMA) as a host material of the electrolyte was synthesized by UV-curing and characterized by nuclear magnetic resonance (NMR). P(GMA-co-EMA) based solid polymer electrolyte containing 80 wt% EC exhibited the highest room temperature ionic conductivity. The crystallinity degree of the electrolyte decreases with the EC content, as confirmed by X-ray diffraction (XRD) studies. The electrochemical stability investigated by cyclic voltammetry (CV) reveals that the electrolyte is stable up to 4.8 V. A dye-sensitized solar cell of fluorine tin oxide (FTO)/TiO₂-dye/P(GMA-co-EMA)-LiClO₄-EC/Pt possessed the photovoltaic effect with a short-circuit current density ($J_{sc}$) of $4.85\times10^{-3}$ mA cm⁻² and open circuit voltage ($V_{oc}$) of 0.4 V, respectively, under light intensity of 100 mW cm⁻².

Keywords: dye-sensitized solar cells; methacrylate; polymer electrolyte; UV-curing.

1 Introduction

The development of renewable energy sources for future energy systems, especially solar energy, has been growing at an ever increasing pace due to increasing energy demands, environmental concerns about global warming and limited availability of fossil fuels. Dye-sensitized solar cells (DSSCs) have received considerable attention due to low manufacturing cost and simple preparation technique over conventional solar cells [1–5]. A power conversion efficiency of 13.0% has been obtained in DSSCs with organic solvent-based electrolyte [6]. However, the use of liquid electrolyte in DSSCs encounters some problems, such as leakage, evaporation of solvent, high-temperature instability and flammability, possible desorption and photodegradation of the attached dyes. Therefore, many efforts have been made to replace liquid electrolytes with quasi-solid/solid-state electrolytes such as solid polymer electrolytes [7, 8], gel polymer electrolytes (GPEs) [9, 10], polymer membranes [11] and ionic liquid-based gel electrolytes [12, 13].

However, the disadvantage of a solid polymer electrolyte is low room temperature conductivity. One of the significant approaches in increasing the conductivity of solid polymer electrolytes is the introduction of a plasticizer into the polymer electrolyte. The plasticizer, usually a low molar mass polyether, polyethylene glycol (PEG) or a polar organic solvent ethylene carbonate (EC) or propylene carbonate (PC) is introduced in small fractions into the polymeric matrix to ensure a high level of ion dissociation, resulting in high ionic conductivity and long life of the cell, offering a satisfactory overall conversion efficiency [14]. Glycidyl methacrylate (GMA), an ester of methacrylic and 2,3-epoxy propanol, is a well-known monomer being used to be coupled with an epoxy group to form stable covalent bone with biomolecules without any linker [15]. Poly(GMA) (PGMA) has promising applications in advance biotechnology, such as DNA separation, targeted drug delivery and enzyme immobilization.
because of the ease in conversion of epoxide groups into a variety of functional groups such as -OH, -NH$_2$, and -COOH [16]. Luo and co-workers [17] reported the chemical interaction and thermal properties of lithium ion salt on poly(acrylonitrile-GMA) (PAN-GMA) based GPEs [17]. In this study, we propose a copolymer of (PGMA-PEMA) added with EC plasticizer and LiClO$_4$ salt. Although PEMA is well known for its non-toxicity and low cost, to the best of our knowledge P(GMA-co-EMA) has never been used for the preparation of polymer electrolytes for photovoltaic devices. The problem statement of the work is to utilize a solid electrolyte of P(GMA-co-ethyl methacrylate) [P(GMA-co-EMA)]-EC-LiClO$_4$ for replacing liquid electrolyte in DSSC. The use of solid electrolytes will overcome the limitations encountered by liquid electrolytes.

## 2 Materials and methods

### 2.1 Materials

GMA, EMA, 2,2-dimethoxy-2-phenylacetophenone (DMPP), lithium perchlorate (LiClO$_4$) and EC were purchased from Aldrich (St. Louis, MO, USA). Tetrahydrofuran (THF) was supplied by J.T. Baker (Phillipsburg, NJ, USA). Ti-nanoxide HT, platinum (Pt) paste under the commercial name Platisol HT and iodolyte AN-50 (iodide/tri-iodide based redox electrolyte) iodide/tri-iodide, lithium salt in ionic liquid and a pyridine derivative based with acetonitrile were obtained from Solaronix (SA, Aubonne, Switzerland). Tetrabutylammonium cis-bis (isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) dye (N-719) and fluorine tin oxide (FTO)-coated glass as a front transparent electrode with a sheet resistance of 8 $\Omega$ sq$^{-1}$ were supplied by Aldrich.

### 2.2 Synthesis of P(GMA-co-EMA) and preparation of solid polymer electrolyte

The copolymer of P(GMA-co-EMA) (80/20) was synthesized via the same experimental procedure that was reported in previous works [18, 19]. The copolymer (80/20) was synthesized by photopolymerization of 80 wt% GMA and 20 wt% EMA formulation. The DMPP was used as the photoinitiator with an amount of 1.6% w/w. The mixture was exposed to UV radiation under a continuous flow of nitrogen gas for 5 min. DMPP photoinitiator decomposes to free benzoyl and methyl radical under UV radiation and propagates into bimolecular on addition of monomers. The synthesis of P(GMA-co-EMA) is illustrated in Figure 1. Thin films of plasticized polymer electrolytes with a general formula P(GMA-co-EMA)-30 wt% LiClO$_4$-x wt% EC (x=20, 40, 60, 80) were prepared by the solution casting technique. An amount of 3 g of copolymer was added into 30 ml THF and stirred using a magnetic stirrer. LiClO$_4$ (0.9 g, 30 wt%) was added into different amounts of EC. The two separate solutions were mixed and further stirred for 24 h. The homogenous solution was then poured onto Teflon mold and left for slow drying at room temperature to form an electrolyte film. The electrolyte film was dried in a vacuum oven at 40$^\circ$C for 48 h to remove residual solvent.

### 2.3 Preparation of the DSSCs components

FTO-coated glass substrate was cut into a desired size (2.5 cm x 1.5 cm) and cleaned using acetone for 15 min and for another 15 min with ethyl alcohol in an ultrasonic bath. It was immediately rinsed with ethyl alcohol and cleaned using nitrogen gas to ensure the substrate was cleaned thoroughly. The titania paste was diluted by using ethanol. The solution containing the TiO$_2$ particles were spread over the glass substrate, and then dried in a vacuum oven at 70$^\circ$C for 30 min before the photoanode was prepared. Then the film was immersed into an ethanol solution of I$_2$/I$_3$ for 15 min, followed by rinsing with methanol and dried under nitrogen stream. The resulting I$_2$/I$_3$-doped titania film was then placed on the glass substrate and annealed at 400$^\circ$C for 2 h under nitrogen flow to form the photoanode. Finally, the photoanode was allowed to cool down to room temperature and then sandwiched between the electrolyte cell and FTO-coated glass substrate to form the DSSC.

![Figure 1](https://example.com/image1.png) Synthesis of poly(glycidyl methacrylate-co-ethyl methacrylate) [P(GMA-co-EMA)].
was coated on an FTO-coated glass by spin coating at 2000 rpm for 30 s. The solution was coated five times onto the substrate to get sufficient thickness. A platinized FTO counter electrode was prepared by spin coating at 2000 rpm for 30 s. The electrode was sintered at 450°C for 30 min. For dye adsorption, the annealed-TiO₂ electrodes were immersed in absolute ethanol containing 0.5 mM of N719 dye for 24 h. The thickness of the TiO₂ film on the surface of the FTO electrode is around 748.1 nm. The polymer electrolyte film with thickness of 0.3 mm – 0.36 mm was cut into rectangular shapes to suit the area of TiO₂ film. It was then sandwiched between the TiO₂ film and the Pt layer. The TiO₂ photoanode electrode was then assembled with a Pt counter electrode and filled with iodide based electrolyte with 50 mM of triiodide in acetonitrile. The liquid electrolyte was then replaced with the P(GMA-EMA)-LiClO₄-EC based electrolyte. Figure 2 displays the fabrication procedure of FTO/TiO₂-dye/P(GMA-co-EMA)-EC-LiClO₄/Pt solar cell.

2.4 Characterization techniques

Nuclear magnetic resonance (¹H-NMR and ¹³C NMR) was used to confirm chemical composition of the copolymer P(GMA-co-EMA). ¹H-NMR and ¹³C NMR spectra of polymer samples were recorded on a Fourier transform (FT)-NMR spectrometer (Bruker 600 MHz and Bruker 150 MHz, respectively, Bremen, Germany). Analysis on ionic conductivity of P(GMA-co-EMA) films was carried out using electrochemical impedance spectroscopy under a scanning frequency range of 10 Hz to 1 MHz. The bulk resistance, $R_b$ (Ω) of the samples was determined with Z-View software. The conductivity was calculated using Eq. (1):

$$\sigma = \frac{l}{R_b A}$$  (1)

where $l$ is the film thickness (0.3–0.35 mm) and $A$ (2.01 cm²) is the effective contact area of the electrolyte and electrode.

The ionic conductivity was measured in the range from 25°C to 100°C. The electrochemical stability window was examined by cyclic voltammetry (CV) using ZIVE MP2 (Seoul, Korea) multichannel electrochemical workstation. The structural properties of the polymer electrolyte, namely crystallinity and amorphyocity, were studied using X-ray diffraction (XRD) (model D-5000 Siemen, Karlsruhe, Germany) in the range ($10^\circ \leq 2\theta \leq 50^\circ$). The photocurrent-voltage ($I$-$V$) curves of the device in dark and under illumination were recorded using a Keithley high voltage source model 237 with a tungsten light source at the light intensity of 100 mW cm⁻² controlled by a radiometer. The illuminated cell area was set to 0.9 cm².

3 Results and discussion

3.1 NMR spectroscopy

3.1.1 NMR spectrum

The ¹H NMR spectrum of P(GMA-co-EMA) is shown in Figure 3. The chemical shifts at 3.232 (d), 2.635 and 2.842 ppm (e) are attributed to the epoxide group, while the signals at 3.818 and 4.294 ppm (c) correspond to the methyl proton of GMA. The neighboring signal at 4.046 ppm (f) corresponds to the methylene proton in the EMA segment. The methyl peak of the O-CH₂-CH₃ group shows a signal at 1.262 ppm (g). The broad signal at 1.092 and 0.934 ppm corresponds to the $\alpha$-methyl group of the copolymer of GMA and the presence of EMA is due to the methylene groups of the backbones. The methylene group of the backbone in GMA and EMA copolymer shows broad signals at 1.898 and 1.965 ppm (b) [20, 21]. The peak at 1.699 ppm is attributed to H₂O CDCl₃. The structural formation of the copolymer can be simply determined by reducing the intensity of the vinyl peaks at 5.45 and 6.0 ppm in the copolymer spectrum and the methylene peak that appears at 1.898 and 1.965 ppm in the spectrum of EMA.
3.1.2 $^{13}$C NMR spectrum of copolymer

The $^{13}$C NMR spectrum of P(GMA-co-EMA) is shown in Figure 4. The 18.7 ppm is attributed to the methyl carbon of O-CH$_2$-CH$_3$ and the methyleneoxy carbon of PGMA and EMA gave a signal at 65.8 and 60.9 ppm, respectively [22, 23]. The peaks at 48.8 and $\delta$ 44.7 ppm correspond to the methyl and methylene carbon of the epoxy group, respectively [20, 21]. The carbonyl carbon and $\alpha$-methyl carbon of the copolymer appear at 177.0 (13.8 and 16.8) ppm, respectively. The tertiary carbon of the copolymer is observed at 45.5 ppm. By contrast, the double bond carbon peaks at $\delta$ 126.3 and $\delta$ 129 ppm disappear. As a result of the vinyl opening reaction of the polymerization, the methylene peak of the polymer backbone, -CH$_2$-, appears at $\delta$ 54.12 ppm. Some traces of double bond are observed at 126 and 129 ppm because of the disproportionation reaction of termination [23].

3.2 XRD measurements

The XRD patterns obtained for P(GMA-co-EMA)-EC-LiClO$_4$ films are depicted in Figure 5. The XRD patterns display a broad peak in the region between 10° and 25° for all samples. We did not calculate the crystallinity degree of the electrolyte samples since the change in the peak intensity was insignificant. The intensity of the peaks slightly decreased as the plasticizer concentration was increased, except for the 80 wt% EC sample which showed the lowest peak intensity. This implies that the amorphous nature of the film increases as a function of concentration of the plasticizer. The diffraction patterns in Figure 5 show that the peaks pertaining to the LiClO$_4$ salt are absent in the complexes, which has been reported in previous works [18, 24]. This indicates complete dissolution of the salt in the polymer matrix. Ahmad et al. [25] reported that the ionic conductivity enhancement is
associated with the amorphous phase of the samples. It is suggested that there are interactions between the polar groups in the polymer matrix and the organic plasticizer, which would contribute to both the compatibility of the electrolyte components and the ionic dissociation of the salt in the electrolyte system. The plasticizer plays the role of increasing the disorder of the material, which is related to enhancement in segmental motion of the polymer host [26].

### 3.3 Electrical properties

#### 3.3.1 Room temperature–ionic conductivity

The conductivity as a function of the EC plasticizer concentration in the P(GMA-co-EMA)-30 wt% LiClO 4 system is presented in Figure 6. The conductivity increased slowly from 2.8×10^{-5} S cm^{-1} for the EC free film to a maximum of 4.9×10^{-4} S cm^{-1} for the film with 80 wt% EC. The electrolytes with the composition higher than 80 wt% EC were mechanically unstable and hence the conductivity was difficult to measure. The mechanical properties of the electrolyte films with 80% EC were not free standing, not flexible, sticky and gelly. Hence, we stopped at 80 wt% EC while preparing the electrolyte. Figure 7A and B show the impedance spectra of P(GMA-co-EMA), P(GMA-co-EMA)-30 wt% LiClO 4, and P(GMA-co-EMA)-30 wt% LiClO 4 -80 wt% EC. The complex impedance spectra show two well-defined regions; a semicircle in the high frequency range that is related to the conduction process in the bulk of complex, and the linear region in the low frequency range that is attributed to the bulk effect of blocking electrodes. In an ideal case at low frequency, the complex impedance plot shows a straight line parallel to the imaginary axis; however, the curvature is caused by the double layer at the blocking electrode. No charge crosses the electrodes from the dielectric material to the metal electrode for the blocking contacts, and vice versa. The film without LiClO 4 and EC as a host polymer is expected to have very low conductivity, which is 9.2×10^{-12} S cm^{-1}. Generally, the enhancement of ionic conductivity in the plasticized solid polymer electrolyte can be explained by the interactions between P(GMA-co-EMA), LiClO 4, and EC. There are three main interactions: (i) interaction between Li^+ cations and ClO_4^- anions; (ii) ion-dipole interactions between Li^+ cations and chlorine in P(GMA-co-EMA); and (iii) ion-molecule interactions between Li^+ and EC. These interactions are important to form P(GMA-co-EMA)-LiClO 4-EC polymer electrolyte, in which three different compounds of P(GMA-co-EMA)-Li^+, P(GMA-co-EMA)-Li^+-EC and Li^+-EC exist. The oxygen of C=O in EC is an electron donor, which participates in competition with ClO_4^- and P(GMA-co-EMA).
The Li⁺-EC interactions exist not only between Li⁺ and oxygen atoms of the C=O group, but also between Li⁺ and another two oxygen atoms in the ring structure of EC. In addition, the Li⁺-EC interaction plays an important role in the conductivity of the P(GMA-co-EMA)-LiClO₄-EC system. The addition of EC leads to the formation of an Li⁺-EC complex and enhances the flexibility of P(GMA-co-EMA) chains by decreasing the crystalline fraction of the P(GMA-co-EMA)-Li⁺ complex. The decrease in crystallinity degree of the electrolyte is related to the XRD results, which were discussed in Section 3.2. The high dielectric constant of EC (εᵣ = 85.1) effectively reduces the inter-ion coulomb interactions; hence, more Li⁺ contributed to the conductivity of the electrolyte [27, 28]. Furthermore, EC molecules are relatively small in size compared to the size of polymer host molecules, and therefore can easily transfuse into the polymer matrix, causing an interaction between plasticizer molecules and polymer chain molecules. This reduces the cohesive forces operating between the polymer chains, resulting in an increase in the chain segmental mobility [29]. The increase in chain segmental mobility facilitates ion transportation, leading to enhancement of conductivity.

### 3.3.2 Temperature dependence of conductivity

Figure 8 illustrates the Arrhenius plot for the P(GMA-co-EMA)(80/20)-30% LiClO₄-80% EC. The ionic conductivity increases with temperature. A higher temperature not only promotes the migration of carrier ions, but also results in expansion of the polymer [27, 30]. This expansion produces a local empty space and increases the free volume, which promotes the motion of polymer segments and carrier ions [31, 32]. This linear relation also suggests that no phase transition occurred in the polymer matrix or domain formed by the addition of EC. The plot shows that this electrolyte system obeys the Arrhenius rule, since the correlation factor (R²) of the plot is above 0.950. The Arrhenius equation is expressed as follows:

\[
\sigma = \sigma_0 e^{(-E_a/RT)}
\]

where \(\sigma\) is the conductivity of the electrolyte, \(\sigma_0\) is a pre-exponential factor, \(E_a\) is the activation energy, \(k\) is Boltzmann’s constant, and \(T\) is absolute temperature [27]. Since the electrolyte sample shows Arrhenius behavior, we can find the pre-exponential factor and activation energy of the electrolyte. The purpose of calculating the activation energy is to determine the energy required to dissociate Li⁺ and ClO₄⁻ of the electrolyte. The \(E_a\) for the P(GMA-co-EMA)-30% LiClO₄-80% EC film calculated using Eq. (2) is 0.20 eV.

### 3.4 Electrochemical stability

Figure 9A and B present the cyclic voltammograms of P(GMA-co-EMA)(80/20)-30% LiClO₄-wt% EC and 80 wt% EC complex. The electrochemical stability of PGMA-co-EMA(80/20)-30 wt% LiClO₄-wt% EC at interface with stainless steel (SS) as electrode is limited by the potential of +3.8 V at anodic side and of -3.8 V at the cathodic side. An improvement in electrochemical stability is observed after the addition of 80 wt% of EC, where the potentials are +4.8 V at the anodic side and -3.8 V at the cathode side. From the CV data, the cathodic and anodic peaks of the cell are not observable in this range. This is related to non-interaction of lithium in the polymer electrolyte with the SS electrode [33, 34].

### 3.5 Device performance in dark and under illumination

Figure 10A and B illustrate the I-V curves of the DSSC utilizing a conventional liquid electrolyte containing an iodide/triiodide redox couple and the solid polymer electrolyte of P(GMA-EMA)-LiClO₄ in the dark and under illumination of 100 mW cm⁻² tungsten light, respectively. The short-circuit current density (\(J_{sc}\)), open circuit voltage (\(V_{oc}\)), fill factor (FF) and power conversation efficiency (\(\eta\)) were obtained from the intersection axis of current and voltage axis from the curves under illumination, respectively [8]. The DSSC with the liquid electrolyte gave a photovoltaic...
response, with the $J_\text{sc} = 4.41$ mA cm$^{-2}$, $V_\text{oc} = 0.68$ V, $FF = 0.39$ and $\eta = 1.14\%$. The solar cell of the FTO/TiO$_2$-dye/P(GMA-EMA)-EC-LiClO$_4$/Pt shows a photovoltaic response with the $J_\text{sc} = 4.85 \times 10^{-3}$ mA cm$^{-2}$, $V_\text{oc} = 0.4$ V, $FF = 0.32$ and $\eta = 0.00625\%$. The efficiency of 0.00625\% is significant for the DSSC utilizing solid polymeric electrolyte of P(GMA-co-EMA)-EC-LiClO$_4$. The efficiency of the DSSC utilizing the liquid electrolyte was 224 times higher than that utilizing the solid electrolyte. This is due to the fact that the conductivity of the liquid electrolyte is higher than that of the solid electrolyte. Higher conductivity results in faster reduction and oxidation reaction at the interface of the electrolyte/Pt and electrolyte/dye, respectively. This leads to the enhancement of the photocurrent and consequently improves power conversion efficiency. The low generated photocurrent is caused by poor interfacial contact in the device [35]. The poor interfacial contact results in a high internal resistance in the devices, leading to a low current in the devices. The use of polymer limits the charge transport between the electrodes. This can affect the rate of dye reduction. Basically, for high efficiency cells, the rate of oxidized dye regeneration must be faster than its recombination reaction with electrons injection into TiO$_2$. The low $V_\text{oc}$ might be due to Lewis type basic nature of the polymer, or to the interaction of polymer with the Lewis type acid site of TiO$_2$ surface. A higher resistance of ion migration retards the kinetic of dye regeneration, and therefore, decreases the $J_\text{sc}$. The charge transfer processes at Pt/electrolyte interface and ions diffusion process in the electrolyte are important for power conversion efficiency of DSSCs [36].

Ahmad and his co-workers [37] reported the use of iodine as an electrolyte in a DSSC. Yum and his co-researchers [38] utilized a cobalt complex redox shuttle in a DSSC. Burschka and his group [39] utilized the disulfide/thiolate redox electrolyte in a DSSC. Ahmad and his group [40] utilized an ionic liquid electrolyte in a DSSC. They achieved relatively high power conversion efficiencies ranging from 7.9% to 10%.

4 Conclusions

A new solid polymer electrolyte of P(GMA-co-EMA) with LiClO$_4$ and EC was successfully prepared by the solution
casting technique and utilized in a DSSC. XRD analysis showed that the electrolyte turns to a more amorphous phase, due to the increase in EC content. The electrolyte exhibited ionic conductivity at room temperature in the range of 10^{-5} to 10^{-4} S cm^{-1}. The ionic conductivity was 4.9×10^{-4} S cm^{-1} at room temperature and 12×10^{-3} S cm^{-1} at 373 K at 80 wt% EC. It was found that the P(GMA-co-EMA)-30 wt% LiClO_4-80 wt% EC showed good electrochemical stability, which was up 4.8 V. A DSSC of ITO/TiO_2-dye/P(GMA-co-EMA)-LiClO_4/Pt exhibited a photovoltaic effect, with J_sc=4.85 mA cm^{-2} and V_oc=0.4 V, under light intensity of 100 mW cm^{-2}.

Acknowledgments: The authors are very thankful to the Faculty of Science and Technology, Universiti Kebangsaan Malaysia for allowing the work to be carried out. This work was funded by the UKM-DLP-2012-021 grant.

References