

# Emerging Polymer Electrolyte Based On Methacrylate for Dye Sensitized Solar Cell

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**Abstract:** *This paper highlights on the application of polymer electrolytes membrane as an ionic conductor in DSSC. Polymer electrolyte is chosen for use in DSSCs to overcome the problem of leaking and sealing, flammability issues, shape flexibility and electrochemical stability faced by liquid electrolyte. In addition, the presence of liquid electrolytes posed challenges in integration of large area modules, difficulty in implementing tandem architectures, possible desorption and photodegradation of the attached dyes in DSSC, corrosion of counter electrode and photodegradation of some components which lead to lower lifetimes, performance and practical usage of the photovoltaic cells.*

**Keyword:** polymerization; methacrylate compounds; polymer electrolyte; photovoltaic cells

## 1. Background and development

### 1.1 Introduction

The development of new types of solar cells is promoted by increasing public awareness that the Earth's oil reserves could run out during this century. It is estimated that the world energy demand will proliferate by around 70% in between the years 2000 to 2030. Fossil fuels, providing 80% of all energy consumed worldwide, are now facing rapid resource depletion. Due to an increasing demand for energy, combined with the diminution of fossil resources, global warming and its linked climate change, there is an urgent need for environmentally sustainable energy technologies. Among all the renewable energy technologies, such as wind turbines, hydropower, wave and tidal power, solar cells, solar thermal, biomass-derived liquid fuels and biomass-fired electricity generation, photovoltaic technology using solar energy is considered as the most favorable one. The supply of energy from the sun to the earth is gigantic:  $3 \times 10^{24}$  J a year, or about 10,000 times more than that the global population currently consumes [1-3]. The development of solar cells is encouraged by increasing public awareness that the earth's oil reserves can run out during the coming decades. However, utilizing liquid electrolyte in dye sensitized solar cell have some problems such as leakage, evaporation of solvent, high-temperature instability and flammability, possible desorption and photodegradation of the attached dyes. Additionally, the solar cell devices utilizing liquid electrolytes are bulky and hard to move from one place to another. These devices also possess low energy and power density. In addition, the predicaments of solar cells are the reaction between the electrodes and the electrolyte steadily corrodes the electrodes. These will eventually reduce the lifetime of the device. Furthermore, the boiling point of the solvent used limits the temperature range of operation of the device [4].

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Much attention is given to create new material with able properties. Synthesis of new materials still suffers from some problems like miscibility of components in order to develop it for practical applications. The problems of miscibility or compatibility between two polymers in blending them can be overcome by using copolymerization techniques. Basically, copolymerization is an easy and inexpensive method to prepare new polymeric material. Compared to blending, copolymerization offers good properties in term of morphological properties and miscible properties. However, the main drawbacks of solid polymer electrolyte are low ionic conductivity at ambient temperature, poor electrode-electrolyte contact, and high internal resistance for its use in electrochemical device. Because of the these problems, the photopolymerization techniques were chosen to create new materials with desired properties. In regards to the copolymerization methods, free radical photopolymerization, which is one of the well-known processes for the preparation of polymeric materials could be a powerful technique, since it is a simple technique that does not require solvents, catalysts and heating steps. Moreover, the advantages of this preparation technique is faster curing process, less energy consumption and easy processing [6]. However, one of the significant approaches in increasing the ionic conductivity of solid polymer electrolytes is the introduction of a plasticizer into the polymer electrolyte. Introduction of plasticizers plays an important role in enhancing the conductivity of the material with sufficient mobility of ions [7]. This happens because these plasticizers increase the segmental motion of polymer backbone and generate free volume. For that reason, the ions can move easily, passing through the free space, resulting in ionic conductivity enhancement [8]. However, many efforts

have been made to replace liquid electrolytes with solid polymer electrolytes [9-10], gel polymer electrolytes (GPEs) [11], nanocomposite [12-13] polymer membranes [14] and ionic liquid-based gel electrolytes [15].

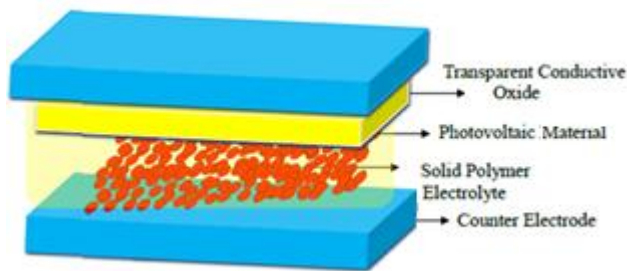
## 1.2 Photopolymerization Based on Methacrylate Polymers

Multifunctional methacrylates are the most commonly used monomers for many applications [16], due to their high reactivity leading to fast polymerization [17]. The activity of the methacrylates depends on their structural properties such as the type and flexibility of incorporated molecules, number of functional groups, the presence of heteroatoms, chain length, and hydrogen bonding. Methacrylate monomers consisting of an alkyl group, an acrylate ester group, and a functional carboxyl group can react with a wide range of monomers and functionalized molecules providing flexible polymer chains [18]. A polar functional group in its methacrylate compounds chain exhibits a high affinity for lithium ions. Theoretically, as a prosperous polymer host, the active part of a polymer should have a minimum of three essential characteristics. Special attentions are given to PMMA, PEMA and PGMA due to its compatible nature with other polymers, high chemical resistance, non-tracking characteristics, surface resistance, optical properties and electrical properties. The copolymerization of methyl methacrylate (MMA) with glycidyl methacrylate (GMA) with 2, 2'-azobisisobutyronitrile (AIBN) as radical initiator and in the presence of thiophenol (TP) as chain-transfer agent has been discovered by Zakir and Rzaev (1999) [19]. Someya and Shibata (2010), however, synthesized nanocomposites of P(GMA-co-MMA) cured with cyclohexanedicarboxylic anhydride (CDCA) and while, layered silicates of inorganic content 3 and 5 wt. % were prepared by casting the mixture solution and subsequent crosslinking at 200 °C [20]. The copolymer of (GMA) and (MMA) was made radiopaque by the epoxide ring opening of GMA using the catalyst *o*-phenylenediamine and the subsequent covalent attachment of elemental iodine [21]. The presence of bulky iodine group created a new copolymer with modified properties for potential use in biomedical applications. The authors concluded that the iodinated copolymer was thermally stable, blood compatible, non-cytotoxic, and highly radiopaque. Fei et al. (2010) have reported on the synthesis of photosensitive poly (MMA-co-GMA) and its application for optical waveguide devices. The results showed that the optical films of crosslinked poly (MMA-co-GMA) had low surface roughness and high thermal stability. Well-defined photolithography technique of the polymer was achieved in the presence of an appropriate photo acid generator and showed possibility for direct photolithography technique of waveguide structures [22]. Several kinds of copolymer which are poly (GMA-co-MMA), poly (GMA-co-EMA) and (GMA-co-BMA) were synthesized in 1,4-dioxane solution using 2, 2'-azobisisobutyronitrile (AIBN) as initiator at 60°C [23]. The glass transition temperatures of the poly (GMA-co-MMA), poly (GMA-co-EMA) and poly- (GMA-co-BMA) were found to be 100, 82 and 61 °C, respectively. That study also utilized inverse gas chromatography (IGC) technique to determine some thermodynamic properties of polymers such as the sorption enthalpy, sorption free energy, sorption

entropy, Flory–Huggins interaction parameters the partial molar free energy of mixing, the weight fraction activity coefficients and the partial molar heats of mixing at infinite dilution. Random copolymer of GMA with (MMA), ethyl methacrylate (EMA) and (EA) were prepared by radical polymerization using (AIBN) at 70±1°C [24]. The copolymer products of glycidyl methacrylate have been modified by incorporation of indole groups through the ring opening reaction of the epoxy groups. GMA oligomers were grafted onto polypropylene (PP) via UV photopolymerization using benzophenone (BP) as initiator, which was initiated by the free radicals generated through the reactivation of semipinacol dormant groups in the oligomers. The obtained results established that the melting temperature, crystallinity and the initial decomposition temperature of the grafted (PP) were all increased, compared with those of the origin (PP); the functionalization of (PP) led to the change of the crystal form [25]. [P(MMA-co-MMA)/PEG] polyblend with viscoelasticity was synthesized by a copolymerizing reaction between (MMA) and (MA) using (AIBN) as initiator in (PEG) methanol solution [26]. The copolymerization of methyl methacrylate with glycidyl methacrylate and the kinetics of the reaction of copolymer with secondary amines were investigated by Iwakura et al. (1966) [27]. However, copolymerization GMA-co-MMA to low molecular weights and modification by ring-opening reaction of epoxy side groups and in the absence of thiophenol were reported by Paul and Ranby (2003) [28]. The ternary copolymerizations of (GMA), (MMA), styrene (St), and maleic anhydride (MA), considered as acceptor (A1)-donor-acceptor systems, were reported by Zakir and Rzaev (1995) [29]. The polymer was modified by opening the oxirane ring of GMA by reaction with diethanolamine (DEA). This system was carried out in methyl ethyl ketone in the presence of benzoyl peroxide as initiator at 50-80°C.

## 1.3 A Dye Sensitized Solar Cell Components

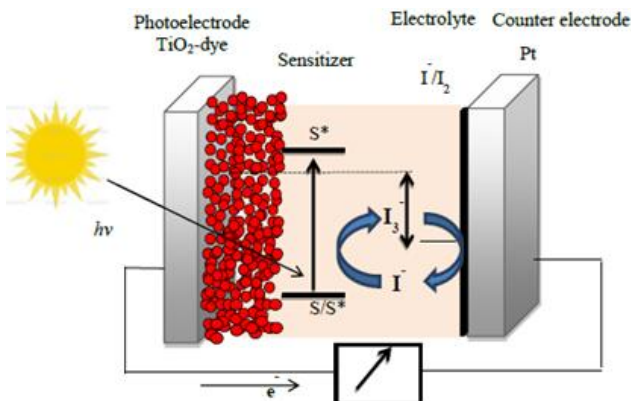
The cell consists of two main electrodes, namely; photoelectrode and counter electrode deposited onto the thin layer of transparent conducting oxide (TCO). A DSSCs is made by sandwiching the electrolyte (replace electrolyte) between a dye-sensitized nanocrystalline semiconductor (TiO<sub>2</sub>) (anode) and platinum counter electrode (cathode) [30]. Figure 1. Showed general structure of a dye-sensitized solar cell (DSSCs). O'Regan and Grätzel (1991) established a basic DSSCs structure which most DSSCs investigators adapted or modified. They are separated by an electrolyte containing redox mediators [31]. In DSSCs, the photovoltaic semiconductor material is then covered with organic dye – typically ruthenium based complex, as a photo absorber material [2, 31]. The photovoltaic semiconductor material commonly metal chalcogenides or metal oxides semiconductor is used material for the photoelectrode [32-33] which is deposited onto the TCO including indium-doped SnO<sub>2</sub> (ITO), fluorine-doped SnO<sub>2</sub> (FTO), or aluminum-doped ZnO (AZO) substrate [33-36], a various types of electrolyte containing redox mediator such as iodide based, thiocyanate based, and cobalt based electrolytes [37-39] and a counter electrode film at the back contact of the photovoltaic cell as the catalyst surface [40].



**Figure 1:** Schematic representation the general structure of a dye-sensitized solar cell (DSSCs)

#### 1.4 A Dye Sensitized Solar Cell Operation

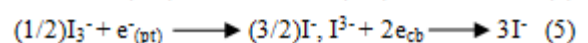
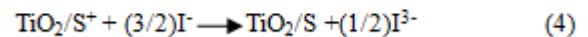
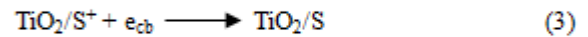
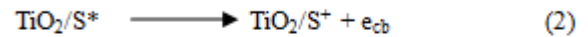
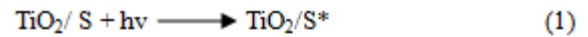
The principle of power generation in DSSC uses the same electrochemical principles by generating electricity upon illumination. It is very similar to that of photosynthesis of plants, so it is often referred to as artificial photosynthesis. General mechanism of the dye-sensitized solar cell is shown in Figure 2. The photoanode materials usually used in photoelectrochemical cell are CdSe, CdS, ZnO, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, SiC and TiO<sub>2</sub>. The energy gap of TiO<sub>2</sub> is 3.2 eV. The TiO<sub>2</sub> as a semiconductor material has many advantages for sensitized photochemistry and photo-electrochemistry [41] It is low cost, widely available, non-toxic and biocompatible material. The material used as counter electrode in DSSCs should have a low charge transfer resistance and high exchange current density for the reduction of the oxidized form of the charge mediator. The counter electrode serves as a medium of accepting electrons from external circuit [42] So far, platinum electrode is desired material for the counter electrode since it is an excellent catalyst for I<sup>3-</sup> reduction.



**Figure 2:** Schematic representation of the principle of operation of a dye-sensitized solar cell (DSSCs)

The performance of solar cell considerably depends on the electrolyte. The electrolyte used in DSSCs mostly contains I<sup>-</sup>/I<sup>3-</sup> redox ions, which mediate electrons between the TiO<sub>2</sub> photoanode and the counter electrode. Light absorption is made by a monolayer of dye (S) adsorbed at the semiconductor surface and excited by a photon of light (Equation 1). After having been excited (S\*), the excited electron is injected to conduction band of TiO<sub>2</sub> particle, leaving the dye molecule to an oxidized state S<sup>+</sup> (Equation 2). The injected electrons pass through the porous nanocrystalline structure to the transparent conducting oxide layer of the glass substrate (positive electrode) and finally through an external load to the counter electrode (negative electrode) (Equation 3). At the cathode, the electron is

transferred to triiodide in the electrolyte to yield iodide (Equation 4), and the cycle is closed by reduction of the oxidized dye by the iodide in the electrolyte (Equation 5). For high efficient operation of the cell, the rate of electron injection must be faster than the rate of regeneration ion of the dye excited state. In addition, the rate of the oxidized dye (Equation 4) must be higher than the rate of back reaction of the injected electrons with the dye cation (Equation 3), as well as the rate of reaction of injected electrons with the electrons acceptor in the electrolyte (Equation 4) [2, 43-45].



Salt with iodide anion have been used in of DSSCs and these include LiI [46], ammonium iodide (NH<sub>4</sub>I) [47], 1, 2 dimethyl-3- propylimidazolium iodide (MPIII) [48] and tetrapropyl ammonium iodide (PrN<sup>+</sup>I) [49]. The electrolyte composition also affects the photovoltage (VOC) of the DSSC, which is the difference between the Fermi level of the semiconductor and the electrochemical potential of the redox pair. Furthermore, the photovoltage can also be affected by non-electroactive species in the electrolyte, particularly by small cations such as protons, Li<sup>+</sup>, etc. These species can adsorb or intercalate onto the surface of the TiO<sub>2</sub> oxide, shifting its conduction band edge to a lower energy level. This can lower the photovoltage, but enhance the efficiency of interfacial charge injection, increasing the photocurrent and the overall efficiency of the DSSC [50-52]. The role of polymer electrolyte as a polymer passivating layer in minimizing the charge recombination at TiO<sub>2</sub>/electrolyte interphase is reported by Mor et al. (2007) [53]. Polymer electrolytes are also used as adhesive between the working electrode and photoactive electrode.

#### 1.5 A Dye Sensitized Solar Cell Based on Metahacrylate Polymer Electrolyte

The dye-sensitized solar cells (DSSCs) have received considerable attention due to low manufacturing cost and simple preparation technique over conventional solar cells. Dye-sensitized solar cells (DSSCs) are considered as third generation photovoltaics that combine high-energy conversion efficiency together with low production cost. The efficiency of a DSSC is lower than the classical crystalline silicon cells and the next generation of solid-state thin films technology such as copper indium gallium selenide solar cells (CIGS). Dye sensitized solar cell (DSSCs) based on nanocrystalline TiO<sub>2</sub> sensitized by dye molecules have been intensively investigated because of its lower cost and potential alternatives to traditional photovoltaic solar cells operated by converting sunlight directly into electricity through a process known as the photovoltaic effect [1]. The most important issue of the dye-sensitized cells is the stability over the time and the temperature range which occurs under outdoor conditions. A photoelectric conversion efficiency of 12.5 % has been obtained in DSSCs with organic solvent-based electrolyte [39]. Even though, high conversion efficiencies obtained for the dye-sensitized solar



cells with liquid electrolytes, potential problems caused by liquid electrolytes, such as leakage and volatilization of the liquid and possible corrosion of the counter electrode, have brought about difficulties in cell fabrication and limited limiting the long-term performance and practical use of these dye-sensitized solar cells [44]. Several methods have been introduced to prevent electrolyte leakage. One of the strategies is to replace the volatile solvents with ionic liquids [54]. Secondly, P-type semiconductors [55-56] inorganic hole transport materials [57], organic hole transport materials [58] and finally polymer/ redox couples blends [59] have been introduced as substitutes for traditional liquid electrolyte in all solid – state photoelectrochemical cell configurations. Nanocomposite [12,13] polymer gel [11] and solid state or quasi- solid state polymer materials [60-61] have been used to replace the organic liquid electrolyte.

Li et al. (2007) studied the role of (methyl methacrylate-co-methacrylate acid) blend with poly (ethylene glycol) and doped with KI/I<sub>2</sub> in quasi-solid state dye-sensitized solar cell. [P(MMA-co-MAA)/PEG] was copolymerization by using solution polymerization in presence of azobisisobutyronitrile (AIBN) as initiator. Based on the polyblend gel electrolyte P(MMA-co-MAA)/PEG- KI- I<sub>2</sub>, a light-to-electricity conversion efficiency of 4.85 % for QS-DSSC was achieved under AM 1.5 simulated solar light illumination at 60 °C [26]. Polymer electrolytes based on 90 wt% of methyl methacrylate and 10 wt% of ethyl methacrylate (90MMA-co-10EMA) incorporating different weight ratios of sodium iodide were reported by Dzulkurnain et al. 2015. A DSSC based on (90 MMA-co-10 EMA) has been fabricated using the most conductive electrolyte film and showed an efficiency of 0.62%. Many researcher have demonstrated that the efficiency of solar cell can be improve by using micro-porous film[ 62]. Micro-porous polystyrene (PS) – poly methyl-methacrylate (PMMA) film utilized as gel polymer electrolyte for dye-sensitized solar cell after soaking with liquid electrolyte. polymer film of micro-porous can be prepared by spin-coating of the polystyrene( PS)- polymethyl-methacrylate (PMMA) blend of different concentrations on sputtered platinum electrode (counter electrode) [63]. This film was used to improve the long-term durability of DSSC which is polymer film of micro-porous. The film can effectively absorb the liquid electrolyte and reduce its evaporation rate significantly. Another advantage is that the film is spin-coated on the overall surface of the counter electrode; it functions like a spacer which can effectively separate the photo-anode and counter electrode. An energy conversion efficiency of 4.58 % was obtained with 2 wt. % PS- 2 wt. % PMMA blend proportion under AM 1.5, 1 sun illumination.

Chiromawa & Ibrahim 2015 evaluated the attenuations in light transmissions through PMMA films of different layer thicknesses on SiO<sub>2</sub> substrates for solar cell applications. The results show that, film thickness decreases as rotational speed increased and light transmission decreases as film thickness increases [64]. According to Yang and coworkers (2008), the quasi-solid-state DSSCs of PMMA–EC/PC/DMC–NaI/I<sub>2</sub> based gel polymer electrolyte with ionic conductivity of  $6.89 \times 10^{-3} \text{ S cm}^{-1}$  possessed a good long-term stability and a light-to-electrical energy conversion efficiency of 4.78 % under irradiation of 100

mWcm<sup>-2</sup> simulated sunlight. Li et al. (2011) modified nanocrystalline porous titanium oxide (TiO<sub>2</sub>) electrodes for dye-sensitized solar cells (DSSCs) by adding polymethyl methacrylate (PMMA). PMMA was used in order to form large holes on the surface of the TiO<sub>2</sub> electrode film, which supply the light scattering centers that enhance the light capture of the solar cells. It noted that solar cells with large holes showed an enhancement of short circuit photocurrent (J<sub>sc</sub>) and conversion efficiency ( $\eta$ ) compared with the blank. The highest conversion efficiency was obtained with TiO<sub>2</sub> electrode films by adding 7.5 wt. % of PMMA, increasing the overall conversion efficiency by 27.5% [65]. Seo et al. in 2010 used 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 as polymer electrolyte for DSSCs. The efficiency of a DSSC employing POEM–qP4VP electrolyte reached 3.0% at 100 mW/cm<sup>2</sup> when a 6:4 wt.% of POEM–qP4VP was used. Polymer gel electrolytes (PGEs) with high ionic conductivity based on polyvinyl (acetate-co-methyl methacrylate) [P(VA-co-MMA)] were prepared by soaking porous copolymers in an organic electrolyte solution [acetonitrile (ACN) or 3-ethoxypropionitrile (MPN)] that contained an I<sub>3</sub><sup>-</sup>/I<sup>-</sup> as redox couple [66]. Quasi-solid-state dye-sensitized solar cells (QS-DSSCs) were fabricated with the PGEs, and the best PGE was selected and optimized. Using the best PGE and under 100 mW cm<sup>-2</sup> light illumination (AM 1.5), the QS-DSSC achieved a high photovoltaic conversion efficiency of 9.10%. They find that, introduction of TiO<sub>2</sub> nanoparticles into the PGEs further enhanced PGEs ionic conductivity and the conversion efficiency to 9.40%. [67].

The nanostructural amphiphilic graft copolymer electrolyte based on poly(ethylene glycol) behenyl ether methacrylate (PEGBEM) and poly(oxyethylenemethacrylate) (POEM) synthesized via a facile free radical polymerization [68]. They found that the addition of 1-methyl- 3-propylimidazolium iodide (MPII) reduced the degree of crystallinity of the graft copolymer, resulting in improved ionic conductivity up to  $1.4 \times 10^{-6} \text{ S/cm}$  at 25 °C. The efficiency of dye-sensitized solar cells (DSSCs) with this graft copolymer electrolyte (3.6%) was higher than those of DSSCs with homopolymer electrolytes (2.3 to 2.5%), indicating the effectiveness of the nanostructural graft copolymer. The higher efficiency resulted from an improved current density (J<sub>sc</sub>) due to enhanced polymer flexibility and reduced crystallinity.

The homopolymers poly(glycidyl methacrylate), PGMA and poly(vinyl phosphonic acid), PVPA were synthesized by free-radical polymerizations of the monomers glycidyl methacrylate, GMA, and vinyl phosphonic acid, VPA, respectively. The graft copolymers were produced by grafting of PVPA onto PGMA via ring opening of ethylene oxide groups. To examine the influence of the concentration of VPA on the proton conductivity, several graft copolymers were produced at various stoichiometric ratios with respect to monomer repeat units. The proton conductivities of humidified and dry samples were studied via impedance spectroscopy. In the anhydrous state, the proton conductivity of P(GMA)-graft-P(VPA)10 was  $5 \times 10^{-5} \text{ S/cm}$  at 150 °C. The proton conductivity of the same material increased with

the humidity content and reached to 0.03 S/cm at 80 °C under 50 % of RH, which approached to that of Nafion at the same humidification level [69].

Free standing polymer electrolytes films, containing poly(glycidyl methacrylate) (PGMA) as the polymer host, lithium perchlorate (LiClO<sub>4</sub>), and ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide [Bmim] [TFSI] as a plasticizer was successfully prepared via the solution casting method. The maximum ionic conductivity of the solid polymer electrolyte was found at  $2.56 \times 10^{-5}$  S cm<sup>-1</sup> by the addition of 60 wt % [Bmim] [TFSI] at room temperature and increased up to  $3.19 \times 10^{-4}$  S cm<sup>-1</sup> at 373 K, as well as exhibited a transition of temperature dependence of conductivity: Arrhenius-like behavior at low and high temperatures [70].

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