



# Poly(methyl methacrylate-co-butyl acrylate-co-acrylic acid): Physico-chemical characterization and targeted dye sensitized solar cell application



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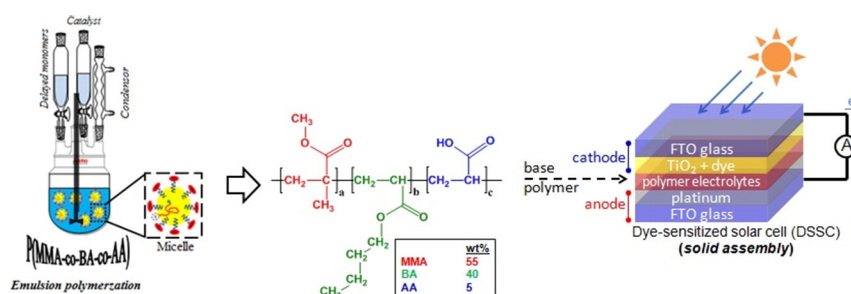
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## HIGHLIGHTS

- We have synthesised ultra-high molecular weight copolymer based on acrylates.
- Highest conversion efficiency of 3.22% at 1 Sun, and prolonged durability is attained.
- It is not always true that copolymer with large molecular weight will obstruct electrochemical function.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A random poly(methyl methacrylate-co-butyl acrylate-co-acrylic acid) [P(MMA-co-BA-co-AA)] was synthesized via emulsion polymerization utilizing thermally-activated persulfate radicals. The successful synthesis of high molecular weight copolymer at high monomer conversion rate was confirmed by NMR study. Various techniques were employed to characterize the structure, electrical and thermal properties of copolymer. The removal of unreacted monomers from the end product by casting technique was rationalized from the disappearance of C=C FTIR characteristic peak in the cast film. The drying of the emulsion above the glass transition temperature ( $T_g = 24^\circ\text{C}$ ) yields an amorphous film with smooth surface morphology. The suitability of the formed continuous film as a base polymer for iodide-based electrolytes in dye sensitized solar cell (DSSC) fabrication was investigated. The polymeric solid state electrolytes (PSSE) were formulated by varying the doping concentrations of sodium iodide (NaI) in fixed ratio of iodine ( $\text{I}_2$ ) and mixtures of ethylene carbonate: propylene carbonate (EC:PC, 1:1). The DSSC fabricated using PSSE with 15 wt.% NaI showed the highest solar-to-electrical energy conversion efficiency ( $\eta$ ) of 3.22% under  $100 \text{ mW cm}^{-2}$  sunlight intensity. This implies that the physico-chemical properties of the synthesized copolymer are suitable for the development of photoelectrochemical device.

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## 1. Introduction

Polymeric solid-state electrolyte (PSSE) is a class of electrolytes that has been intensively studied in recent years for its advantages over liquid electrolytes in electrochemical application such as battery, supercapacitor, solar cell, etc. The working efficiency of the energy application developed utilizing PSSE material is always not satisfactory. This is often caused by the poor electrode-electrolyte interfacial contact and constrained chain mobility (or low ionic conductivity) [1,2]. Addressing to these limitations, an attempt was taken in this work to synthesize a new type of acrylate-based copolymer, poly(methyl methacrylate-co-butyl acrylate-co-acrylic acid) [P(MMA-co-BA-co-AA)] using emulsion polymerization technique. The core of this paper focuses on the synthesis and characterization of P(MMA-co-BA-co-AA). The feasibility of this material as a base polymer for photoelectrochemical device was also studied with the fabrication of dye sensitized solar cell (DSSC).

Emulsion technique has high commercial value over other reported synthesis routes, such as reversible addition-fragmentation chain transfer, suspension, solution, etc. This owes to the relative simplicity of this technology in producing high molecular weight polymers in short reaction time [3]. Several emulsion copolymers, given by the combination of butadiene, styrene, acrylic esters and acrylonitrile were previously studied, targeting wide product developments in cosmetics, biomaterials, electrochemical devices and high-tech applications. There have been many reports in recent years on copolymers synthesized with two different monomers. They are poly(methyl methacrylate-co-ethyl methacrylate) [4], poly(methyl methacrylate-co-butyl acrylate) [5,6], poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) [7], poly(methyl methacrylate-co-methyl acrylic acid) [8,9] and poly(MMA-co-palm oil). The excellence of the product performance of two-monomer combinations drove interest to the synthesis of multi-monomer combinations. Examples of the tertiary co-monomers reported in previous works are propylene glycol diacrylate [6], 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy) benzophenone [10], etc. Through the literature studies, it is noted that these copolymers were generally synthesized in combinations of MMA and BA segments with different tertiary and quaternary co-monomers compositions [11,12].

In this work, a terpolymer was synthesized in combination of MMA and BA with the selection of AA as the tertiary co-monomer. The selection of MMA as a major segment of the copolymer is conceived to attain a matrix with high mechanical strength, UV retention and high transparency upon film processing. In order to alleviate the brittleness (or improvising the chain flexibility) of PMMA, rubbery PBA (at room temperature) was copolymerized in random arrangement. This can improve the thermal stability of the copolymer. With short AA segments present within the P(MMA-co-BA) chain, the cast film may show a good wetting properties (adhesiveness), which may be beneficial in attaining good interfacial contact between the electrode and electrolyte in energy applications. The combination properties of these monomers were hypothesized to yield a competitive advantage copolymer that is suitable for electrolytes development for DSSC over homopolymer or physically blended polymers.

In previous studies, majority of the PSSE development for DSSC fabrication were focused utilizing poly(ethylene oxide) PEO and little work was denoted with acrylate-based polymers. The PEO was actively used in the forms of homopolymer [13], copolymer [e.g. poly(epichlorohydrin-co-ethylene oxide)] [14] and homopolymer doped with nanoparticles TiO<sub>2</sub> or SiO<sub>2</sub> [15,16]. Whilst for the DSSC fabrication utilizing acrylate-based copolymer, only the work reported by Dzulkurnain and coworkers was found and the highest solar-to-light conversion efficiency ( $\eta$ ) was reported at 0.62% [17]. The poor device efficiency is due to the confined chain flexibility in acrylate polymers as compared to that of PEO that having low  $T_g$ . This is quite common in PSSEs made from acrylic polymers. It is thus crucial to choose a base polymer with low glass transition temperature, in order to make sure

the  $T_g$  of the PSSEs falls close to the assembling temperature of DSSC or other energy applications. This may give good device performance and durability. Our hypothesis led us to develop a solid state-DSSC utilizing electrolytes from the synthesized P(MMA-co-BA-co-AA). The detail of synthesis, characteristic of the copolymer and its suitability to be used in DSSC assembly were enclosed.

## 2. Experimental

### 2.1. Synthesis of P(MMA-co-BA-co-AA)

#### 2.1.1. Materials and reactor assembly

**2.1.1.1. Materials.** The chemicals used to carry out the polymerization reaction were as listed; methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA), potassium persulfate (KPS, 99% purity) and anionic surfactant of sodium dodecyl sulfate (SDS). All the chemicals were purchased from Sigma Aldrich and used as received except for MMA and BA, which were purified in 10 wt.% of NaOH prior to synthesis. Fresh distilled water was used to prepare the reaction medium.

**2.1.1.2. Reactor assembly.** The synthesis was carried out in a five neck reactor flask with each neck connected to thermometer, motor-mechanical stirrer, distillation condenser and two dropping funnels, respectively. The reactor was immersed in water bath throughout the synthesis, with water level kept well above the level of reaction mixture in the vessel.

#### 2.1.2. Emulsion polymerization method

The polymerization was performed by semi-batch process comprising three types of solution mixtures; (1) initial charge solution which was the first solution mixture added into the reactor flask, (2) delayed monomer solution and (3) catalyst solution. Mixture (2) and (3) were respectively stored in two different dropping funnels. The composition of each solution mixture was summarized in Table 1.

As the initial step, the polymerization medium was prepared from mixture (1). The mixture of water and SDS was charged into the reactor flask and the solution was heated to 80 °C at a constant stirring speed of 600 rpm. After the solution temperature reached 80 °C, the pre-weight monomer mixtures and initial KPS solution were added into the reactor flask initiating the in-situ seeding stage. The solution mixture was stirred at 80 °C until the reaction mixture turned to slight bluish in color, evidencing the formation of growing oligomeric radical chains. The reaction forming long polymer chain was then preceded in the feeding stage via the addition of mixture (2) and (3), which were respectively stored in two dropping funnels, into the reactor for a time interval of an hour. Then the reaction was allowed to prolong for another hour to complete the polymerization. The completion of the reaction yielded a milky-white emulsion with pH close to neutral. The filtered emulsion was safely stored in a capped poly(ethylene) bottle and

**Table 1**

Chemical composition of three solution mixtures; 1) initial charge solution, 2) delayed monomer solution and 3) catalyst solution.

Solution mixture type	Materials	Quantity (g)
Initial charge solution	Distilled water	200.0
	SDS (30%)	1.0
	Monomer mixtures <sup>a</sup>	12.5
Delayed monomer solution	KPS <sup>b</sup>	0.35
	Distilled water	140.0
	SDS (30%)	9.0
Catalyst solution	Monomer mixtures <sup>a</sup>	87.5
	Distilled water	30.0
	KPS	0.35

<sup>a</sup> Monomer mixtures: The composition of MMA (55 wt.%), BA (40 wt.%) and AA (5 wt.%).

<sup>b</sup> 0.35 g KPS in 20.0 g of distilled water.

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