

Short Communication

Characterization of Random Methacrylate Copolymers Synthesized Using Free-Radical Bulk Polymerization Method

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Random copolymers with three different ratios of two types of methacrylate monomers, ethyl methacrylate and methyl methacrylate, were prepared via free-radical bulk polymerization method. The formation of the copolymer was confirmed by Fourier transform spectroscopy while the glass transition temperature was characterized using dynamic mechanical analyzer. The resistivity of the copolymers was determined using impedance spectroscopy and cross sectional morphology of the copolymers was studied using scanning electron microscopy. Among the three copolymer ratio, copolymer with methyl methacrylate: ethyl methacrylate percentage ratio of 90: 10 exhibited the most favorable characteristics as host of polymer electrolytes, namely lowest glass transition temperature, lowest resistivity and greatest amorphous region.

Keywords: random; copolymer; polymer electrolytes; characteristics

1. INTRODUCTION

Copolymerization is a technique of combining two or more types of different monomers to produce a copolymer. It is the most successful technique to obtain materials with tailor made properties [1, 2]. Many researches on copolymer systems have been done. According to Oh et al., modified copolymers with two or more functional monomers have been proposed as a solution to prevent the leakage problem of liquid electrolyte and improve the mechanical strength of gel polymer electrolytes [3]. Copolymers were also used to develop gel polymer electrolytes with enhanced ionic conductivity and charge-discharge cycle performance [4, 5].

There are many types of copolymers, namely alternating copolymers, block copolymers, random copolymers, graft copolymers, etc. Among all these types of copolymers, random copolymers are much easier to be synthesized. This type of copolymers can also self-assemble various nanostructures [6, 7, 8]. Furthermore, random copolymers of two different of monomers can be conveniently synthesized by free radical polymerization technique. There are a few methods of free-radical polymerization which are bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization, etc [9].

In recent years, many studies have been carried on acrylic monomers because they form the most versatile family of monomers that can be used to form acrylate polymers based on the structure of acrylic acid, which consists of a vinyl group and a carboxylic acid terminus. They can also be used to prepare polymers with rigid, flexible, ionic, nonionic, hydrophobic, or hydrophilic properties. There are a few types of acrylic monomers such as acrylate, methacrylate, acrylamide, acrylonitrile, etc [10]. Most researchers used methacrylate monomers to produce copolymers because of their very reactive double bonds at the vinyl group. Reddy et al. have investigated the copolymerization of phenyl monomer (n-phenyl methacrylamide) with ethyl methacrylate (EMA) [11]. Roy et al. have investigated the RAFT copolymerization of N,N-(dimethylamino)ethyl methacrylate and methyl methacrylate (MMA) [12]. To the author's knowledge there are no detail reports in the literature about the synthesis and properties of copolymer of MMA and EMA. Thus, this article describes the synthesis of novel random copolymers MMA and EMA using free radical bulk polymerization method. In this study, bulk polymerization method was chosen because this technique contains only initiator and monomer which are important to control the purity of the copolymers. It is a versatile method because it can be carried out on many monomers and at a wide range of temperatures [13]. In this method, the reaction involves a photosensitive species, for example a photoinitiator that generates either radicals or ions under illumination of UV light. The chain reaction starts from absorption of the monomers, which are usually in a liquid form followed by the formation of a polymer. This process is also known as UV-curing process. Compared to other processes, this process exhibits some advantages. Besides that, this process induces the polymer formation with a fast transformation (no more than minutes) of the liquid monomer into a solid film with tailored physical–chemical and mechanical properties. It can also be considered as an environmental friendly technique due to the solvent free process and it is usually carried out at room temperature ensuring save of energy [14]. The characteristics of the synthesized copolymers were investigated using Fourier transform infrared (FTIR), gel permeation chromatography (GPC), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM) and impedance spectroscopy in order to determine the most suitable ratio for use as host development of polymer electrolytes.

2. EXPERIMENTAL

2.1. Materials

EMA, MMA, 2, 2-dimethoxy-2-phenylacetophenone (DMPA) and methanol were purchased from Aldrich. Tetrahydrofuran (THF) was supplied by J.T. Baker. All materials were used as received without further purification.

2.2. Preparation of MMA -EMA copolymer

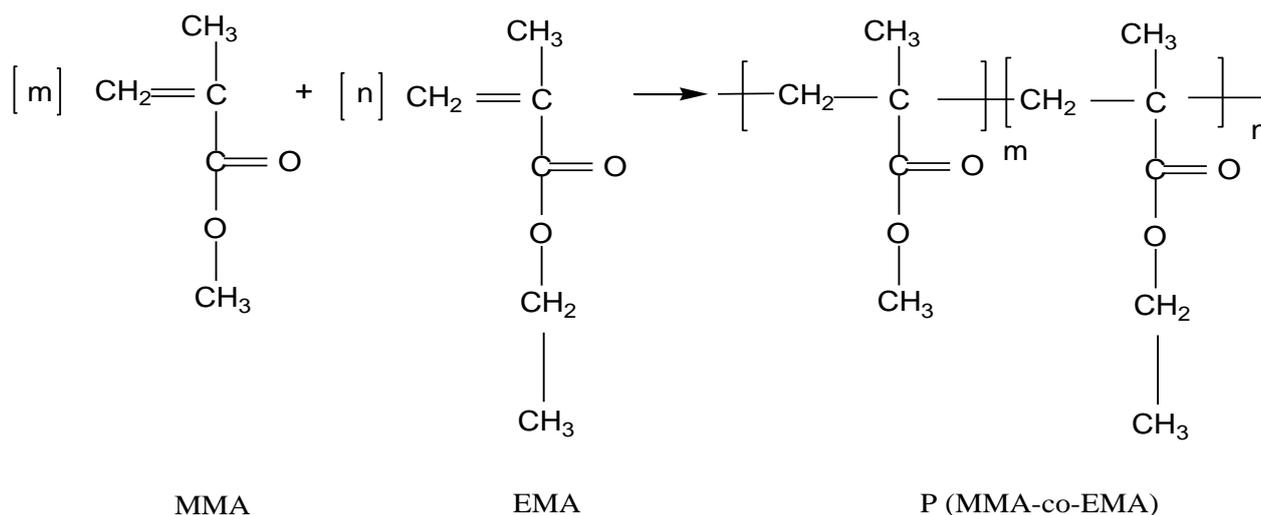


Figure 1. Structure of P (MMA-co-EMA)

Copolymers of three different MMA: EMA ratios were prepared in this study. $(100-x)$ wt% of MMA and (x) wt% of EMA solutions were mixed together in a beaker. Suitable amount of DMPA, used as photo-initiator, was added and the mixture was stirred until a clear solution was formed. The mixture was then exposed to UV radiation with continuous flow of nitrogen gas for a few minutes. The transparent copolymer formed was then washed using methanol to remove residual materials. The copolymerization of P(MMA-co-EMA) is illustrated in Figure 1.

2.3. Preparation of MMA-EMA copolymer film

The copolymers were dissolved in suitable amount of THF and stirred for 24 hours to obtain homogenous solutions. The solutions were then cast into glass petri dishes and left to dry to form films

2.4. Characterization of MMA-EMA copolymer film

2.4.1. Fourier Transform Infrared Spectroscopy.

FTIR spectra were recorded using Perkin Elmer Frontier FTIR spectrometer. Universal Attenuated Total Reflectance (ATR) accessory was used for FTIR study because it is more suitable to analyze solid sample. The prepared sample was placed on top plate of universal ATR and a pressure was applied to the sample pushing the sample onto the diamond surface. The FTIR analysis was carried out in the range of 4000 to 550 cm^{-1} with a scanning resolution of 2 cm^{-1} .

2.4.2. Gel Permeation Chromatography

The molecular weights of the copolymers were determined using gel permeation chromatography. Samples were dissolved at 40°C in THF for 24 hours to achieve equilibrium and

injected to the system. The injection volume is 100 μl and operation time was 55 minutes for each sample.

2.4.3. Dynamic Mechanical Analyzer

Perkin Elmer DMA 8000 instrument was used to get the glass transition temperatures of the copolymer samples. The analysis was done in tension mode. The samples used were of 20 mm length, 10mm width, and a thickness between 0.1 mm to 0.5 mm. The temperature range was from 30 $^{\circ}\text{C}$ to 100 $^{\circ}\text{C}$ at heating rate of 1 $^{\circ}\text{C}/\text{min}$ with frequency of 1 Hz.

2.4.4. Impedance Spectroscopy

The bulk resistivity measurements were carried out at room temperature using Solartron 1260 impedance analyzer over the frequency range from 10 Hz to 1 MHz with 100mV amplitude. The samples were sandwiched between stainless steel disc electrodes. The imaginary part of impedance was plotted against its real part with horizontal and vertical axes having the same scales. From the plot, bulk resistance, R_b of the samples was obtained.

2.4.5. Scanning Electron Microscopy

The cross sectional morphology of the copolymers film was observed by scanning electron microscopy using Zeiss EVO MA10 scanning electron microscope at 100 \times magnification.

3. RESULT AND DISCUSSION

3.1. FTIR Analysis

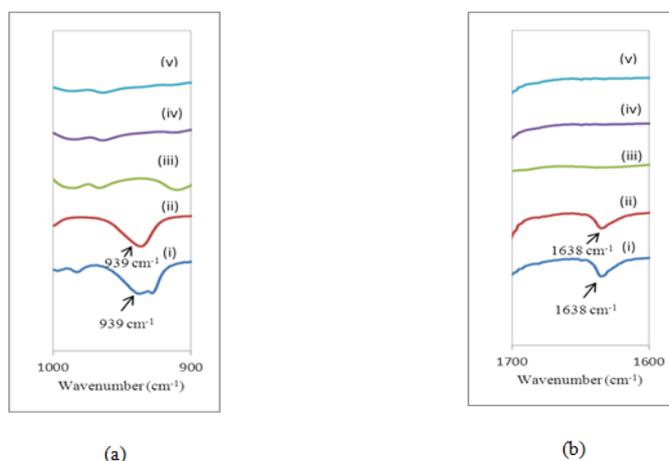


Figure 2. FTIR spectra of (i) MMA, (ii) EMA, (iii) 90MMA:10EMA, (iv) 70MMA:30EMA (v) 50MMA:50EMA copolymers in the wavenumber regions of (a) C-H bonding (b) C=C bonding

Figure 2 shows FTIR spectra for MMA and EMA monomers, and MMA-co-EMA copolymers of different MMA: EMA ratios. The chemical structure of EMA is quite similar to that of MMA where the only differences between them are the chain length and alkyl group bonded to methacrylate group. MMA contains the methoxy group (-OCH₃) bonded to the carbonyl (C=O) carbon while the ethoxy group (-OC₂H₅) is found in EMA. The main evidence to prove that the monomers have been successfully copolymerized is the disappearance of the absorption peaks at 939 cm⁻¹ which are assigned as C-H bonding due to C=CH₂ group and the stretching vibration band of C=C at 1638 cm⁻¹ [15] as can be seen in Fig. 2. According to Han et al (2013), the disappearance of the absorption peaks indicates that the monomers had participated in the reaction [16].

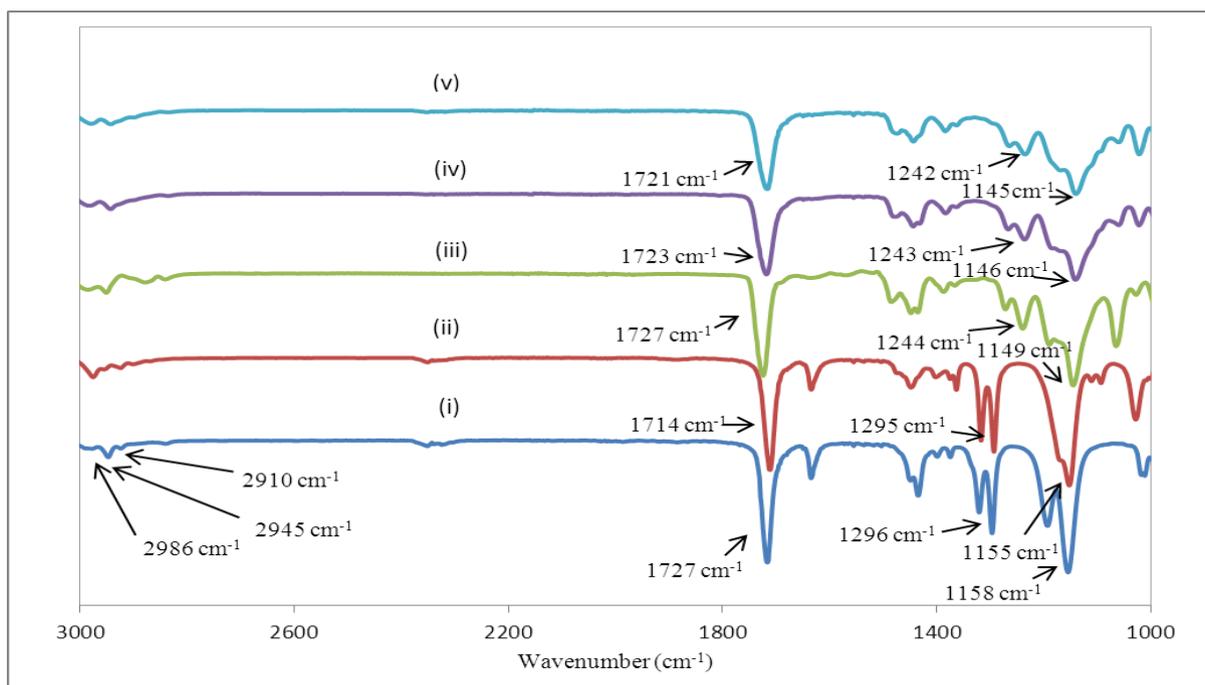


Figure 3. FTIR spectra of (i) MMA, (ii) EMA, (iii) 90MMA:10EMA, (iv) 70MMA:30EMA (v) 50MMA:50EMA copolymers

Illustrated in Fig. 3 is the strong absorption peaks observed at 1720 cm⁻¹, 1158 cm⁻¹ and 1253 cm⁻¹ which are assigned to carbonyl group (C=O), ether group (C-O-C), and epoxy group (C-O-C) respectively. The peaks are all shifted to the lower wavenumbers with addition of EMA indicating that the occurrence of interactions between the two monomers. In the region 2900 to 3000 cm⁻¹, the peaks at 2986, 2945, 2910 cm⁻¹ are due to the C-H stretching vibration of the methylene (C-CH₃) and ethylene (O-C₂H₅) groups. Similar observation has been reported by Venkatesh and co-workers [17].

3.2. GPC study

Table 1 shows the molecular weight for MMA-EMA copolymers which have been analyzed using GPC. From the table, it can be seen that 90MMA:10EMA copolymer gives the lowest molecular

weight value followed by 50MMA:50EMA and 70MMA:30EMA. Shi and Vincent (1993) reported that the ionic conductivity is increases with decrease of molecular weight [18]. It is because, when the molecular weight is lower the chain flexibility is greater. This helps in enhancing ion transport and hence conductivity [19]. Therefore, 90MMA:10EMA is the best copolymer composition to be host for application in polymer electrolytes as it is expected to give highest conductivity.

Table 1. Molecular weight values for (100-x) MMA:(x) EMA copolymer

Sample	Molecular weight (g/mol)
90MMA:10EMA	46941
70MMA:30EMA	64605
50MMA:50EMA	57566

3.3. DMA

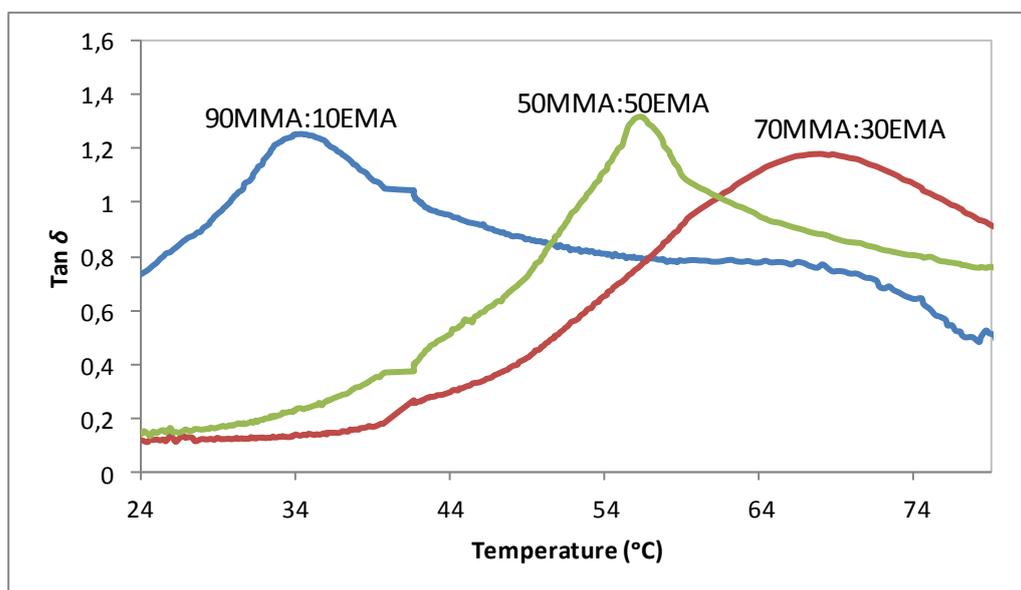


Figure 4. DMA spectra for MMA-EMA copolymer

Presented in Figure 4 are $\tan \delta$ – temperature curves for the MMA-EMA copolymers. Temperature corresponding to the maximum peak of $\tan \delta$ is attributed to T_g while height of $\tan \delta$ curves is related to the mechanical nature of the copolymers [20]. The values of T_g determined from the plots are 33.8 °C, 67.8 °C and 55.9 °C for the samples of 90MMA:10EMA, 70MMA:30EMA and 50MMA:50EMA respectively. It can be seen that the T_g shows no specific trend with the increase in EMA concentration. Logically, EMA has longer side chain compared to MMA which allows greater

chain mobility and spaces between the chains leading to reduction in entanglement interactions and T_g . In this study there is no correlation between T_g and EMA content. However, the T_g values are constant with the molecular weight results reported earlier. According to Sichina [21], the relationship between T_g and composition is not always linear for random copolymer but the presence of a single T_g indicates that the copolymers are homogeneous [22, 23].

3.4. Morphology study

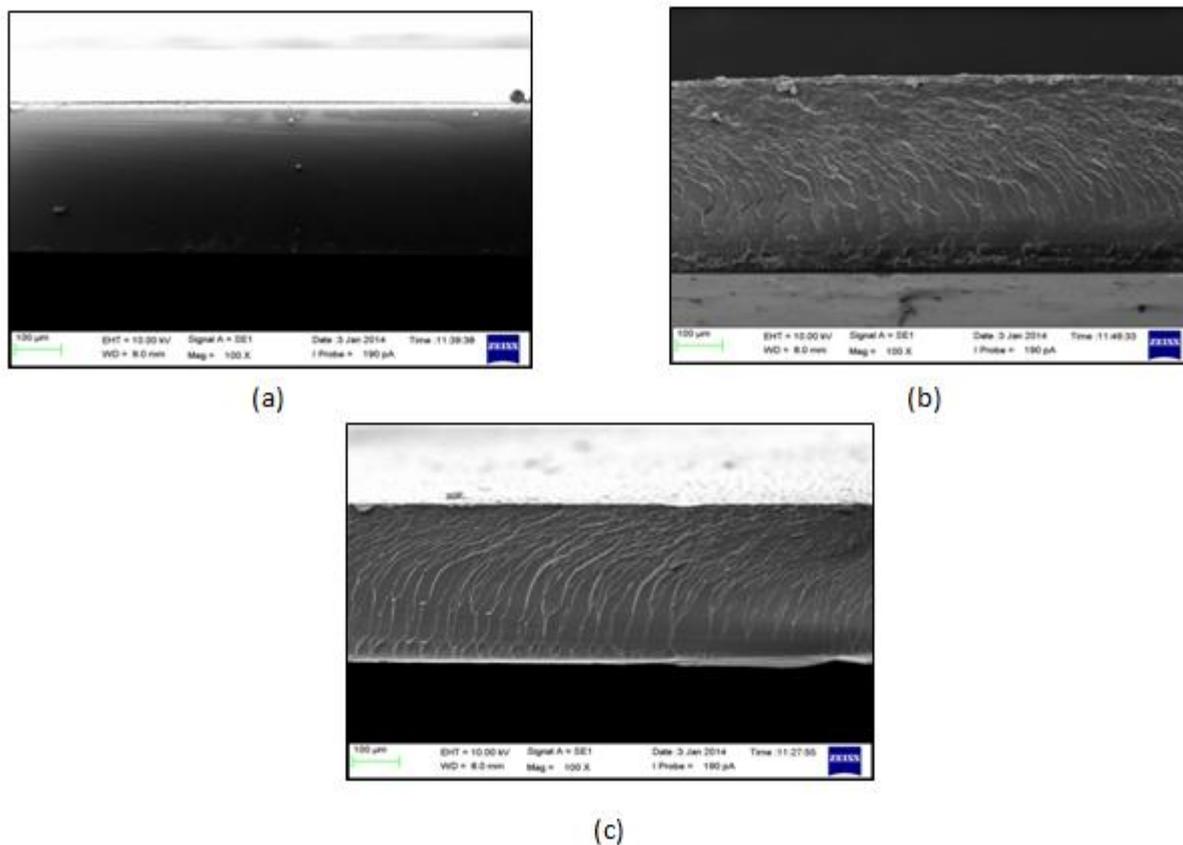


Figure 5. Cross section morphology of (a) 90MMA:10EMA, (b) 70MMA:30EMA, and 50MMA:50EMA samples

Cross sectional morphologies of the three MMA-EMA copolymers are depicted in Figure 5. The images of the 70MMA:30EMA and 50MMA:50EMA samples show unsmooth and compact layers structures. In contrast, the 90MMA:10EMA sample shows smooth surface. This suggests the sample is highly amorphous.

3.5. Electrical study

The room temperature resistivities of MMA-EMA copolymers with different EMA concentrations are listed in Table 2. Resistivity is the material property which shows how strongly the

material opposes the flow of electric current. The lower the resistivity value, the more suitable of the copolymer to become host in polymer electrolytes. This is because from the Equation 1, resistivity is inversely proportional to the conductivity.

$$\sigma = \frac{1}{\rho} \quad (1)$$

From the table, 90MMA:10EMA shows the lowest resistivity value followed by 70MMA:30EMA and 50MMA:50EMA. This shows that the ratio of 90MMA:10EMA is the most suitable for application in polymer electrolytes by adding doping salt to this copolymer.

Table 2. Conductivity values for (100-x) MMA:(x) EMA copolymer

Copolymer	Resistivity (Ω)
90MMA:10EMA	6.16×10^8
70MMA:30EMA	3.11×10^9
50MMA:50EMA	1.51×10^9

4. CONCLUSION

Different ratios of MMA and EMA monomers were randomly copolymerized via free-radical bulk polymerization method. The disappearance of the main peak in infrared analysis confirmed that the monomers were successfully copolymerized. 90MMA:10EMA showed the lowest resistivity value, low molecular weight and glass transition temperature. The observation from the cross sectional morphology studies by SEM indicated that 90MMA:10EMA was the most amorphous copolymer synthesized in this study. From the results, it can be inferred that this copolymer is the most suitable to be used as host in polymer electrolytes.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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