Preparation of poly(methyl methacrylate) fibers via electrospinning in different solvent and its morphology comparison

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GRAPHICAL ABSTRACT

White powder of
PMMA

ABSTRACT

In this study, poly(methyl methacrylate) PMMA was synthesized and electrospun into fibers in different solvents. Synthesis of PMMA was done by free radical polymerization (FRP). Benzoyl peroxide (BPO) acts as an initiator and methyl methacrylate (MMA) as a monomer. The reaction was done in tetrahydrofuran (THF) solvent at polymerization temperature 80 °C for 24 hours. Spectroscopic methods such as ^{1}H NMR and ATR was used to confirm the conversion and the structure of the synthesized polymer. Both synthesized and commercial PMMA is used to study the effect of solvent system and viscosity of polymer in electrospinning technique. Four different solvents, chloroform, dichloromethane (DCM), dimethyl sulfoxide (DMSO) and a binary solvent (1:1 ratio of chloroform and DCM) were studied. The parameters for the electrospinning such as concentration of polymer (0.2 g/ml), voltage (20 kV), volume of polymer (10 ml), flow rate (1.2 ml/h) and tip to collector distance (15 cm) are kept constant throughout the experiment. The PMMA was electrospun horizontally for approximately 8 hours. The morphology of PMMA fibers obtained were analyzed by using SEM. Beaded fibers are generated when PMMA in DCM and chloroform solution respectively. Commercial PMMA in binary solvent afforded more fibers with a few of beads while synthesized PMMA produced a lot of beads. However, electrospinning of PMMA in DMSO solvent cannot be done due to the highly dielectric constant of DMSO. Thus, this showed that the solvent system has an effect on the morphology of the fibers due to its boiling point and dielectric constant properties.

Keywords: Poly(methyl methacrylate), free radical polymerization, electrospinning, solvent systems.

1.   INTRODUCTION

Nowadays, the demand of polymer as the material with novel properties for specific advanced application especially in nanotechnology has been raised. The new invent materials should provide solution to the many application problems of the present day. Most of the current polymers produce should provide better chemical (compatibility, biodegradable) and physical (strength) properties. New polymeric materials may be derived from the synthesis of new monomer, and modification of the existing polymer. Recently, the development of polymers as nanoscale materials is emerging as a new technology with better commercial variability. Poly(methyl methacrylate) (PMMA) is one of the example of polymers that is famous in industry due to its unique properties such as high mechanical strength and thermoplastics [1]. Since 20th century, nanotechnology has become popular around the world due to the nanoscale size and structure of the materials. Electrospinning is one of the new technique that widely use to synthesis nanofiber of polymers. This technique has been popular among researcher due to high potential application in catalyst, filtration membrane and biomedical [2].

Electrospinning is one of the technique that use electrical force for the production of nanofibers. However, to achieve fibers that have a nanoscale size range is difficult to produce. In a previous study, there are many researchers reported that all the parameters such as applied voltage, collector distance, concentration, type of solvent must be optimized to produce good nanofibers [3].
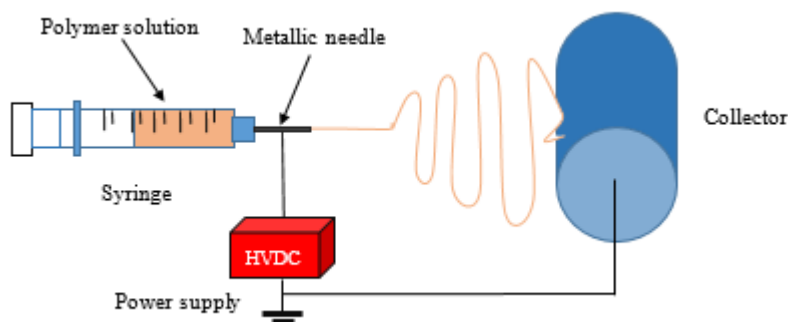

**Figure 1**: Schematic diagram of electrospinning set up.

The basic set up of electrospinning technique mainly involves four main parts which are a syringe that containing polymer solution, power supply, metallic needle and collector [4] as shown in Figure 1. The principal of electrospinning technique is to fabricate nanofiber by extracting polymer from the solvent and stretching it using electrical field and collected on the collector. The process begins once a high voltage of power supply is applied between the needle of the syringe and collector electrode. The flow of electrical charge moves into the polymer solution via metallic needle cause the instability within the polymer solution and induce the charge on polymer droplet.

There are several factors that affect the electrospinning process such as solvent system, polymer concentration and viscosity, applied voltage, flow rate, and distance between collector and needle tip. All the parameters will affect the production of smooth and beads-free nanofiber during the electrospinning process. For the solvent selection, the polymer must dissolve completely in the chosen solvent. Second, the solvent should have a moderate boiling point. Simultaneously, dielectric constant of solvent must be high to ensure the production of fibers. However, highly dielectric constant cause the difficulty solubility of polymer in the solvent chosen. The viscosity of polymer solution affect the morphology of the fibers. According to Shamim et al. (2012) the morphology of beads droplet change from round beads to smooth the fibers as increasing the viscosity of polymer solutions [5].

This research will emphasize on synthesizing and characterizing PMMA by free radical polymerization (FRP). This polymerization technique is relatively insensitive towards impurities, solvent, and atmosphere conditions. Both commercial and synthesized PMMA were used to reveal the effect of viscosity towards electrospinning process while four different solvent chloroform, dichloromethane (DCM), dimethyl sulfoxide (DMSO) and a binary solvent (1:1 ratio between chloroform and DCM) were used to study the effect of solvent system in electrospinning.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage was focused on the synthesized of PMMA by using FRP technique. Methyl methacrylate (MMA) (10 g) act as a monomer and benzoyl peroxide (BPO) (0.1 g) as an initiator. The reaction was done in THF solvent., temperature 80˚C oil bath under the nitrogen protection for 24 hours. The polymer solution from the flask was purified by precipitation into methanol for three times and the resulting white solid gel polymer was dried vacuum at 40˚C for 24 hours. Scheme 1 shows the free radical polymerization of MMA monomer.
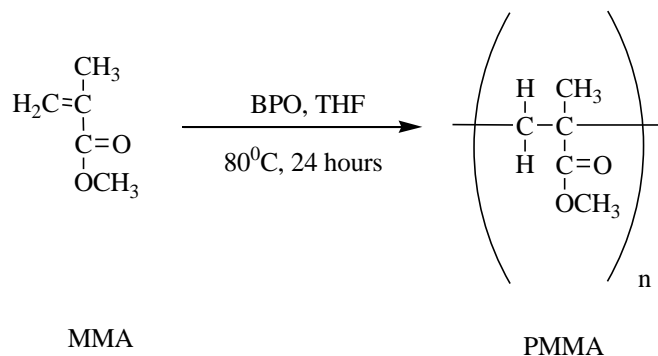
Scheme 1: FRP of MMA

The second stage is characterization of synthesized PMMA by using Bruker 400 MHz nuclear magnetic resonance (NMR) Spectrometer using chloroform ($CDCl_3$) as solvent and with TMS (^1H NMR) as an internal standard. Attenuated total reflectance (ATR) spectrum was obtained using FT-IR Perkin Elmer Frontier. The spectrum was recorded in the region of 4,000 to 600 cm^{-1}.

The last stage is electrospinning of both commercial and synthesized PMMA. Synthesized poly(methyl methacrylate) was dissolved in chloroform. The concentration of PMMA in electrospinning solution was 0.2 g/ml. A high voltage power supply (N Fiber High Voltage Power Supply- HV 35P OC) was employed to generate the high voltage, and the voltage was 20 kV. The syringe pump (FANAVARAN Nano-meghyas) was used during the electrospinning process. The tip-to-collector distance was fixed at 15 cm. The PMMA solutions were loaded into a 5 ml syringe, volume was 10 ml flow rate 1.2 ml/ h and the inner diameter of metal needle was 0.6 mm. After electrospinning, the PMMA fibers were dried in vacuum oven at temperature 40 ˚C overnight to dry off remaining solvent. The procedure was repeated with different types of solvent which are dichloromethane (DCM), dimethyl sulfoxide (DMSO) and 1:1 ratio of binary solvent between chloroform and DCM. Then, the electrospinning of commercial PMMA was performed with the same parameters. The morphology of the fibers was examined by using COXEM EM-30AZ PLUS scanning electron microscope (SEM) at accelerated voltage of 5 kV.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of PMMA

In this study, poly(methyl methacrylate) (PMMA) was prepared by free radical polymerization (FRP) in an organic solvent as white solid (**Figure 2**). In this polymerization process, the first step that takes place is the reaction between methyl methacrylate (MMA) monomer (10 g, 100 mmol) and benzoyl peroxide (BPO) (0.10 g, 0.41 mmol) which acts as an initiator. The activated BPO can combined with MMA monomer. In the process of transferring the unpaired electrons to the monomeric units, the initiator will be activated. Thus, the monomer can be attached and then activated in the same way as before. The polymer MMA can continue growing with the active part shifted towards the end chain. In this study, the polymerization time was 24 hours. The polymerization was performed in tetrahydrofuran (THF) using the monomer concentration of 1.0 M, which yielded a polymer with a mass of 9.37 g.

Figure 2: White powder of synthesized PMMA

Figure 3 and **Figure 4** shows the ^{1}H NMR spectra of crude polymer solution and pure PMMA, respectively. The mixture of polymer, monomers and initiator were presence in crude solution. From both ^{1}H NMR of crude solution and pure PMMA, peak (a) is indicated for the CH_3 of PMMA polymer where peak (b) is attributed to the CH_3 of monomer due to incomplete polymerization. The chemical shift for polymer is lower than monomer due to the shielded position of CH_3 in polymer compared to monomer. **Figure 4** shows the resonance of the CH_3 proton which gives peak (a) at 0.6-0.9 ppm. While 1.5-2.0 ppm indicates the resonance of CH_2 proton side substituent (f) and the most intense peaks at 3.6 ppm shows OCH_3 (g) structure. Besides, **Figure 4** shows that there is no presence of an initiator and MMA monomer in the pure PMMA. Both structure for MMA and PMMA can be seen in **Figure 5**.

Based on **Figure 3** and **Table 1**, the presence of monomer, polymer and an initiator was being observed. The peak (a) is indicated for the CH_3 of PMMA polymer where peak (b) gives the peak for CH_3 of monomer. The chemical shift for polymer is lower than monomer due to the shielded position of CH_3 in polymer compared to monomer. Besides, it reveals that the percentage conversion of MMA to PMMA is 18%, which gives the value of repeating unit (n) is 44.
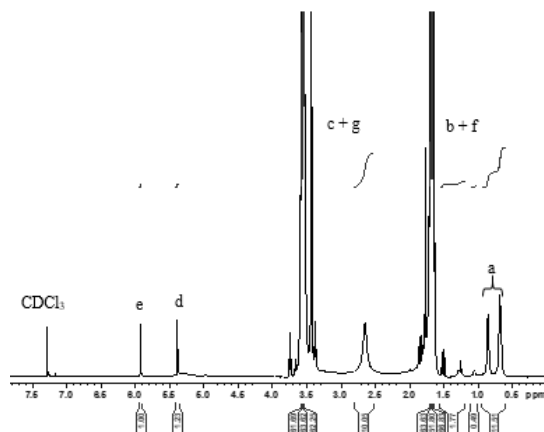

Figure 3: ^{1}H NMR spectrum of crude polymer solution using CDCl$_3$ as a solvent

Table 1: ^{1}H NMR of crude polymer solution

Entry	Type of proton	Chemical shift (ppm)
a	CH$_3$-C (polymer)	0.6-0.9
b + f	CH$_3$-C (monomer) CH$_2$-C (polymer)	1.8
c + g	CH$_3$-O (monomer + polymer)	3.4-3.7
d	CH$_2$=C (monomer)	5.4
e	CH$_2$=C (monomer)	5.9
-	CDCl$_3$ (solvent)	7.3

Table 2:^{1}H NMR of PMMA

Entry	Type of proton	Chemical shift (ppm)
a	CH_3-C	0.6-0.9
f	CH_2-C	1.5-2.0
g	CH_3-O	3.6-3.7
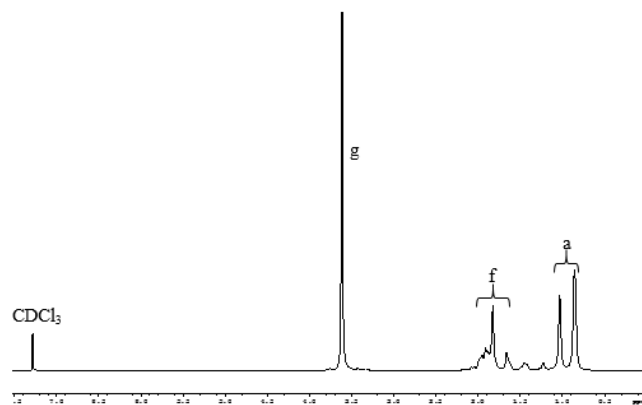
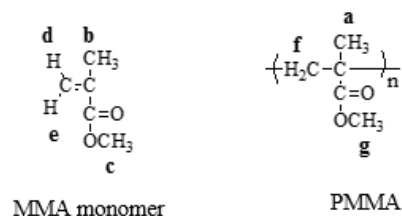**Figure 4**: ^{1}H NMR spectrum of PMMA using $CDCl_3$ as a solvent

Figure 5: The structure of MMA and PMMA

While **Figure 4** and **Table 2**, shows the resonance of the CH_3 proton gives peak at 0.6-0.9 ppm. While 1.5-2.0 ppm indicates the resonance of CH_2 proton side substituent and the most intense peaks at 3.6 ppm shows OCH_3 structure. Besides, Figure 4.3 shows that there is no presence of an initiator and monomer in the PMMA.

Infrared spectroscopy was used to confirm the functional group presence in poly (methyl methacrylate) compound. **Figure 6** represents ATR spectra of PMMA scanned in the range of 650 – 4000 cm^{-1}. The characteristic band due to C=O stretching occurs at 1722 cm^{-1} while, the characteristic peak at 1143-1444 cm^{-1} indicates the presence of the C-O bond. The peak at around 3000 and 2947 cm^{-1} is due to the C-H sp^2 and C-H sp^3 stretching of the polymer backbone respectively.
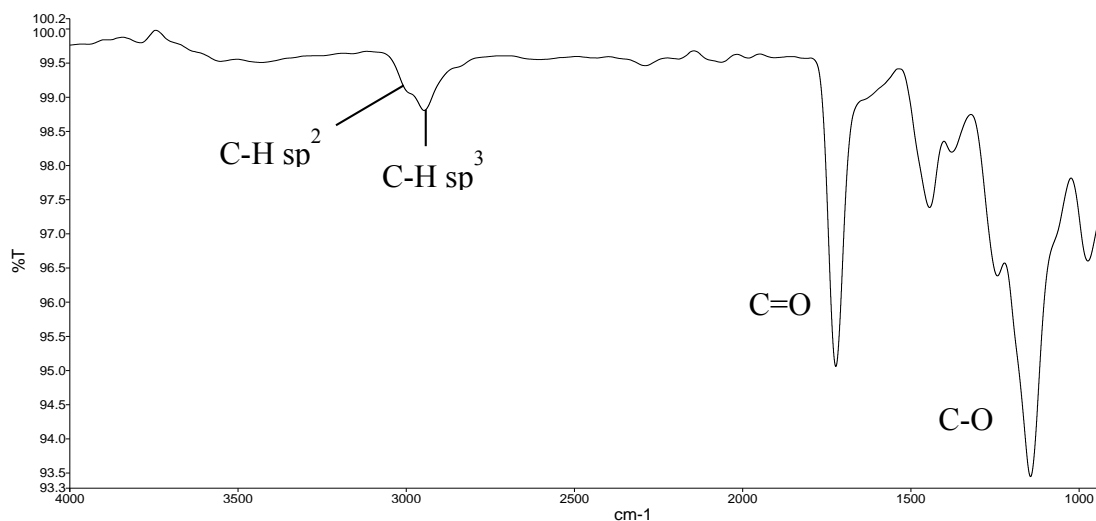

Figure 6: ATR spectra of PMMA

3.2.   Electrospinning of PMMA

Dielectric constant of PMMA is in the range 2.8 to 4 depending on its molecular weight [6]. All the solvent above are able to dissolve PMMA and have higher dielectric constant than PMMA. According to Sun. Z and et al, a having high dielectric constant of the solvent is better for electrospinning process due to the electrostatic energy that require to ionize a solute of polymer solution. However, most of the polymer dissolved in solvent with low dielectric constant [7]. Even though DMSO has

a high dielectric constant, it considers as a poor solvent in electrospinning [8]. Thus, PMMA cannot be electrospinning in this solvent due to highly repulsion charge. Table 3 shows the properties of solvents.

Table 3: Characteristics of solvents

Type of solvent	Formula	Boiling Point	Dielectric Constant
Chloroform	$CHCl_3$	61.2 °C	4.81
Dichloromethane (DCM)	CH_2Cl_2	39.6 °C	8.93
Binary solvent	-	-	6.87
DMSO	C_2H_6OS	189 °C	46.7

3.3 Morphology of PMMA

Table 4 shows the morphology and diameter of the fibers for both synthesized and commercial. Based on the table, PMMA in DCM solvent produced smallest fibers compared to other solvent due to high dielectric constant of the DCM solvent.

Table 4: Morphology and diameter average of PMMA

Type of PMMA	Type of solvent		
	Chloroform	**DCM**	**Binary solvent**
Synthesized	Fibers with a lot of beads Beads: 18 ± 0.8 μm Fibers: 2 ± 0.2 μm	Beaded fibers Beads:18 ± 0.7 μm Fibers: 0.8 ±0.2 μm	Beads (21 ± 0.2 μm)
Commercial	Beaded fibers Beads: 11 ± 0.2 μm Fibers:1 ± 0.2 μm	Beaded fibers Beads: 12 ± 0.5 μm Fibers: 0.6 ±0.2 μm	Fibers with a few of beads. Beads: 5 ± 0.2 μm Fibers: 1 ± 0.2 μm

The commercial PMMA produced more fibers compared to synthesized PMMA as shown in **Figure 7**, due to the high viscosity of commercial polymer solution than synthesized polymer. It can be concluded that, the higher viscosity of polymer solution will generate more fibers.

Based on **Figure 8**, both synthesized and commercial PMMA produced highly porous morphology. In binary solvent, porous beaded fibers can be obtained by using a combination of two different boiling point solvent. During the fiber formation, more volatile solvent (DCM) will be evaporated earlier than less volatile solvent (chloroform). With the evaporation of DCM during injecting of fibers towards the collector, caused the formation of high dense jet. The increasing viscosity of polymer jet facilitated the formation of porous fibers due to hardly migration of the polymer to the collector.
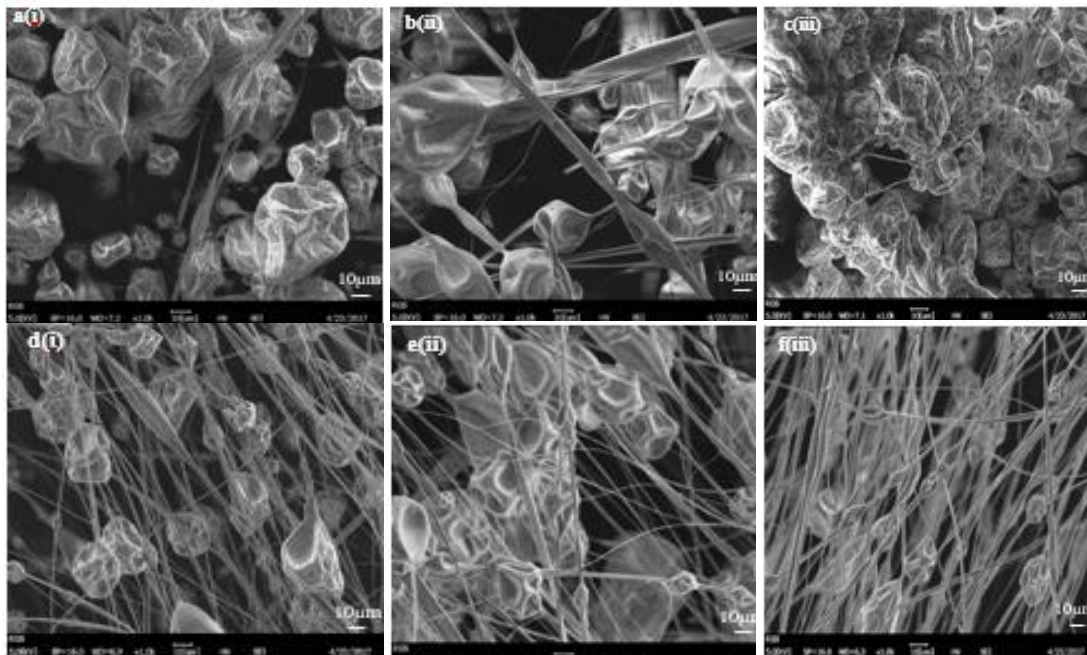
Figure 7: SEM image of synthesized PMMA (a-c) fibers, commercial PMMA (d-f) fibers in solvent (i) chloroform (ii) DCM and (iii) Binary solvent respectively at magnification 1000x

Figure 8: SEM image of synthesized PMMA (a-c) fibers, commercial PMMA (d-f) fibers in solvent (i) chloroform (ii) DCM and (iii) Binary solvent respectively at magnification 1000x.
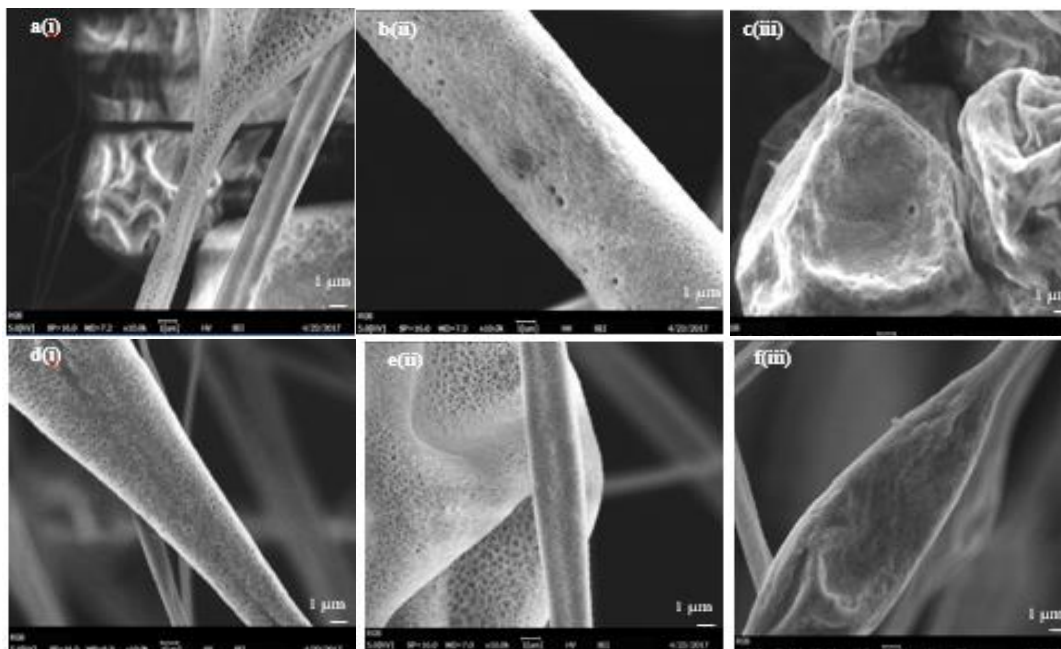
4.   CONCLUSION

PMMA was completely prepared by the FRP technique with MMA is a monomer and BPO act as an initiator. The polymer formed was characterized by using ^{1}H NMR and ATR spectra. Both spectra showed positive results in the formation of PMMA. Both commercial and synthesized PMMA were undergoing an electrospinning process at different solvent system which are chloroform, DCM, DMSO and a binary solvent (ratio 1:1 chloroform to DCM). The SEM was used to investigate the morphology of polymer fibers. Beaded fibers are generated by PMMA in DCM and chloroform solution. Commercial PMMA in binary solvent afforded fibers with a few of beads while synthesized PMMA produced a lot of beads. However, electrospinning of PMMA in DMSO solvent cannot be done due to the highly dielectric constant of DMSO. Thus, it can be concluded that the solvent system and the viscosity of the polymer solution can affect the morphological surface of the polymer fibers.

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