Synthesis and Characterization of Star-Shaped (PCL-B-PEG) as Potential Electrospun Microfibres
(Sintesis dan Pencirian Berbentuk (PCL-B-PEG) Berpotensi sebagai Elektrospun Mikrogentian)

WAFIUDDIN ISMAIL, RUSLI DAIK, SHAFIDA ABD HAMID & WAN KHARTINI WAN ABDUL KHUDIR*

ABSTRACT
Star-shaped polymers have vast potential in application due to their architecture. In this study, a 6-arm star-shaped of poly(ԑ-caprolactone)-b-poly(ethylene glycol), (6PCG) was synthesized via ring opening polymerization, (ROP) of ԑ-caprolactone and Steiglich esterification (coupling reaction) to attach the PEG arm to the star-shaped polymer with discrete core of dipentaerythritol. The polymer chemical structure was characterized by FT-IR. The molecular weight (Mn) determined from 1H NMR spectra showed that the star polymer has approximately the same molecular weight as the theoretical value. The polydispersity index indices (PDI) (>1.5) from GPC were narrow suggesting controlled polymerization reaction. Thermal stability of the star-shaped 6PCG were examined using thermogravimetric analysis, (TGA) and differential scanning calorimetry, (DSC) and showed slight increase compared to homopolymer star PCL due to the changes of end-group functionalities. Six-arm star-shaped PCL-b-PEG was dissolved in chloroform/methanol solvents and the resulting solution was used for electrospinning process. The morphology of nanofibres showed fine fibres without beads and thus a possible potential for several applications.

Keywords: Electrospinning; polycaprolactone; star polymer

INTRODUCTION
Fibres extensively used by human for centuries in many fields ranging from clothing, sensors, automotive and medical applications (Lee et al. 2015; Li et al. 2012; Rosic et al. 2013; Tao 2001; Zhu et al. 2003). The growth of fibre applications has led to the preparation of man-made fibre with better and increased properties such as nylon, polyesters and polypropylene (Fong et al. 2002; Zeiml et al. 2006; Zeronian et al. 1999). Nanofibres possess unique properties such has having extraordinary high surface area per unit mass with remarkably high porosity, good mechanical properties and low basis weight that enable them to be used for various applications (Bao et al. 2008; Bosworth & Downes 2011). Electrospinning is one of the several methods used to prepare small diameter fibre based on electrostatic field concept. It is increasingly used to develop nano scale ultra-thin fibres from a wide range of polymer materials (Frenot & Chronakis 2003). In this technique, droplets of the polymer solution are stretched immensely upon application of an electric field to overcome the surface tension of the droplet and a fine fibre is formed when solidified on ground collector. To date, electrospinning has been used for fabrication of scaffolds from numerous biodegradable polymers, such as poly(ԑ-caprolactone) (PCL) and poly(ethylene glycol). These polymers have been used to produce fibres via electrospinning either as a composite or block copolymer. Their great potential applications are mainly in the fields
of nanotechnology, tissue engineering, pharmaceuticals, and medicinal chemistry (Li et al. 2009; Meier et al. 2005). Block copolymer of PCL-PEG is used to overcome the limitation of individual polymer such as PEG by increasing the hydrophilicity of the compound while PCL can improve the drug loading capacity especially for non-water soluble drugs and increase the rheological properties (Gong et al. 2009; Zhou et al. 2003). PCL-PEG block copolymers have been synthesized in the form of linear and star-shaped polymers. Star-shaped polymer has more advance physical and chemical features compared to its analogous linear polymer which make it more useful especially in bioapplication.

Study of the preparation of star-shaped block copolymer fibres via electrospinning is still limited but the trend is increasing. Chiellini’s group has extensively studied the preparation of star polymer fibres especially 3-arm star-shaped polycaprolactone for tissue engineering and wound healing applications (Gazzarri et al. 2013; Mota et al. 2013a, 2013b; Puppi et al. 2011). They developed fibre mat using the star polymer using wet-, melt- and electro-spinning techniques. They also successfully incorporated different kind of drugs based on the desired applications in the star polymer fibres. Mckee et al. (2004) managed to produce star-shaped block copolymer of poly(ethylene terephthalate-co-ethylene isophthalate) fibres via electrospinning process. The effects of concentration on molecular topology and the morphology of the star polymer fibre with analogous linear polymer fibre in response to different types of polymer solutions were studied. Previous study also showed that blending of different types of polymer enhanced the properties of the nanofibre produced. Star-shaped polymers were also blended with linear polymers to improve the fibres properties towards targeted applications. For example, two types of star-shaped polymer of polycaprolactone and polyethylene oxide were blended with polyactide, (PLLA) and linear block copolymer of poly(D,L-lactide-co-glycolide), respectively (Grafahrend et al. 2010; Li et al. 2015), to increase the mechanical properties of the fibre produced to be used in clinical applications.

Drug delivery system with star amphiphilic architecture has extensively been investigated especially for their drug loading capacities and has shown tremendous advantages in terms of drug loading, drug release pattern, critical micelle concentrations and cytotoxicity (Lim et al. 2013; Puppi et al. 2010). Some interesting studies showed improved transdermal drug delivery efficiency by using amphiphilic star block copolymers (Grayson et al. 2011; Uhrich et al. 2003). Star-shaped polymers have the ability to enhanced drug entrapment efficiency since they provide additional drug-conjugated sites and looser drug loading space. Despite all the advantages, star-shaped polymer fibres obtained via electrospinning have a few drawbacks. The polymers exhibit substantially lower solution viscosities compared to linear polymer because of fewer arm entanglement (Khanna et al. 2010; Soliman et al. 2010) and thus, will make it difficult to form fibres. Therefore, to produce fibres from star-shaped polymer, a relatively high molecular weight of star-shaped polymer is required, which is problematic due to difficulty in controlling the polymerization reaction. High molecular weight polymer will also give high polydispersity index (PDI) (more than 2). Hence, to produce star-shaped polymer fibres, several parameters must be taken into account during electrospinning process such as polymer solution, voltage, temperature, humidity, distance of the tips and the collector (Huang et al. 2003; Subbiah et al. 2005; Teo & Ramakrishna 2006). These parameters will help in producing polymer fibres without the need to synthesize high molecular weight star-shaped polymer.

The aim of the present study is to develop microfibres using 6-arms star-shaped block copolymer using electrospinning technique with the idea of increasing the capability of the fibres in drug entrapment. The drug encapsulation capability of polymer is very much dependent on its polymer architecture (Lim et al. 2013) since it contains more end-group functionality. Star-shaped polymer is a good candidate for biomedical applications because of their thermodynamics and kinetic stabilities and high drug loading encapsulation capacity especially for gene delivery and chemotherapeutic agents (Gaucher et al. 2005; Kakizawa & Kataoka 2002). Their architecture, constituting of hydrophobic and hydrophilic polymers provides useful properties such as protection of drug from premature degradation, elimination of additional surfactants in drug formulations and opportunities for controlled and targeted delivery (Nishiyama & Kataoka 2006). This star-shaped electrospun polymer is also expected to have good drug release pattern based on its amphiphilic structure that resembles micelle drug cargo system.

In this study, the star block copolymer was first synthesized using diverging methods from a well-defined dipentaerythritol core. Ring opening polymerization, (ROP) technique was used to attach the hydrophobic segment of PCL to the core and the hydrophilic PEG segment was introduced, producing six arms star-shaped block copolymer of PCL-PEG. The star-shaped polymer was then used to produce fibres using electrospinning technique. The parameters of the electrospinning process such as flow rate and applied voltage were determined and two types of polymer solutions were used to produce the fibres. The selection of solvent was based on the solubility of the star polymer. The effects of solvent properties associated with dielectric constant and surface tension were emphasized in preparing the star-shaped polymer fibres.

MATERIALS AND METHODS

MATERIALS

e-Caprolactone, succinic anhydride and dipentaerythritol, 4-(dimethylamino)pyridine, DMAP and 1,3-dicyclohexylcarbodiimide, DCC were purchased from Acros Organics (Geel, Belgium) and were used without
purification. Stannous octoate, Sn(Oct)2, was purchased from Sigma-Aldrich (Darmstadt, Germany). Succinylated methoxy-polyethylene glycol (mPEG-COOH) (Mn = 5000) was prepared according to literature (Aryal et al. 2009). All other chemicals and solvents were purchased from Merck (Darmstadt, Germany), and of analytical (AR) grade.

SYNTHESIS OF 6-ARM STAR-SHAPED PCL (6PC) AND PCL-B-PEG (6PCG)

Figure 1 shows structures of 6PC and 6PCG. Approximately, 10 g (0.87 mol) of ε-caprolactone was added with 64 mg (0.25 mmol) of dipentaerythritol. The mixture was heated to 110°C and upon homogeneity, 0.005 g (0.1 mmol) of stannous octoate catalyst was added. The reactions was maintained using silicone oil bath, at the specified reaction temperature for approximately 24 h to insure total conversion of ε-caprolactone. The resulting star-shaped polymer was isolated by precipitation into cold diethyl ether followed by several washing with copious amounts of precipitating solvent and dried under vacuum for 48 h. The 6-arm PCL, (6PC) (0.9 g, 0.02 mmol), was then dissolved in 10 mL of methylene chloride and mixed with mPEG-COOH (0.8 g, 0.14 mmol), DMAP (20 mg, 0.33 mmol) and DCC (70 mg, 0.17 mmol). The reaction was carried out at room temperature for 48 h under dry nitrogen. Dicyclohexylcarbodiurea by-product was removed by filtration and the star block copolymer PCL-b-PEG, (6PCG) was precipitated with cold diethyl ether. The final product was dried at ambient temperature for 48 h. Scheme 1 represents the schematic route for the reaction.

FIGURE 1. Structure of a) 6PC and b) 6PCG

SCHEME 1. Schematic route of preparation of 6-arm star-shaped PCL-b-PEG (6PCG)
PREPARATION OF STAR-SHAPED POLYMER FIBRE VIA ELECTROSPINNING

The synthesized star polymer 6-arm PCL-b-PEG was dissolved in chloroform and the mixture of chloroform and methanol (3:1 v/v) with 15% (w/v) for each solution and was stirred using magnetic stirrer for 24 h to obtain homogenous solution. The electrospinning process was conducted using electrospinning apparatus (Figure 2) and was based on previous study (Wan Abdul Khodir et al. 2018). The samples were electrospun under ambient condition (28°C) with 50% ± relative humidity. All samples were dried at room temperature to remove any residual solvents.

![Electrospinning apparatus](image)

FIGURE 2. Electrospinning apparatus

Different condition of electrospinning process flow rate and tip needle distance were studied; 0.5 mL/h, 0.8 mL/h and 1.0 mL/h and 10 cm, 12 cm, 14 cm, respectively. However, only polymer solution at parameters flow rate of 0.5 mL/h and a distance of 12 cm between the collector and the tip of the needle produced fibres and others did not produce fibres. All solutions were employed with fixed electrical 14 kV to charge the tips. The sample was collected on a conductive collector plate and dried overnight in a fume hood for at least 48 h to allow the evaporation of the residual organic solvent and used for the fibres characterization. The morphology of the fibres was studied by field emission scanning electron microscope (FESEM) and quantitative evaluation of characteristic particle sizes was completed visually using freeware software (Image J, ver. 3.7) on five random images at the same magnification with scale bar 1 m (ca. 20 fibres for each image).

FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR)

Fourier transform infrared (FTIR) spectra were recorded with Perkin-Elmer Spectrum 400/FTIR/FT-NIR spectrometer. Solid samples were ground with anhydrous potassium bromide (KBr) and compressed into thin pallet. Infrared spectra were recorded in the region 4000-400 cm⁻¹.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

¹H-NMR spectra of the polymeric materials dissolved in deuterated chloroform (CDCl₃) were recorded on a Varian 400 spectrometer at 400 MHz. Tetramethylsilane (TMS) was used as the internal reference. All chemical shifts were reported in parts per million (ppm).

GEL PERMEATION CHROMATOGRAPHY (GPC)

Gel Permeation Chromatography, (GPC) analysis was performed by Waters 2414 Gel Permeation Chromatography to determine molecular weight of the polymeric material and its distribution. Waters Breeze was used as data processing software. Tetrahydrofuran (THF) was used as eluting solvent at a flow rate of 1 mL/min. The columns were calibrated with polystyrene standards with a narrow molecular weight distribution.

THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric TGA/DTG analysis of the synthesized polymers were carried out using Mettler Toledo Thermogravimetric Analyzer. The temperature used is in the range of 30°C to 600°C, under nitrogen (N₂) with a flow rate of 50 mL/min. A heating rate of 10°C and a crucible of aluminum containing 5 mg of sample were used for the TGA analysis.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The differential scanning calorimetry, (DSC) analysis was carried out using a Mettler Toledo Differential Scanning Calorimeter under nitrogen flow (10 mL/min) at a heating rate of 10°C/min over the range of 30-400°C. The crystalline melting temperature (Tm) were recorded.

SCANNING ELECTRON SPECTROSCOPY (SEM)

The fibre samples were covered with a gold-palladium mixture for 3 min under vacuum prior to the morphological analysis. Morphology of the fibre produced were examined by scanning electron microscopy EVO 50, Carl Zeiss AG, Germany.

RESULTS AND DISCUSSION

STAR-SHAPED BLOCK COPOLYMER

The star poly(ε-caprolactone) was prepared by ring opening polymerization of lactone. The precipitation of the reaction mixture into cold diethyl ether gave white precipitate with 87% yield. The FTIR spectrum (Figure 3(a)) shows that the ROP of ε-caprolactone was successful as can be seen by the appearance of ester group, C=O stretching at around 1720 cm⁻¹. The C-O stretch bands appeared at around 1172 cm⁻¹.

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while the C-H band of methylene group of the PCL polymer chain is around 2944 cm\(^{-1}\) and 2865 cm\(^{-1}\). The presence of polymer backbone band in the spectrum indicates the occurrence of ROP of cyclic ε-caprolactone. There is only one hydroxyl group per PCL chain therefore the intensity of the hydroxyl band was obscured indicating the low content of –OH in the compounds (Nabid et al. 2011). Figure 3(b) depicts the FTIR spectrum of the star-shaped block copolymer 6PCG with 75% yield. The band approximately at 1119 cm\(^{-1}\) was due to C-O-C stretching vibrations of the repeated –OCH\(_2\)CH\(_2\) units consistent with the addition of PEG ether unit. The band at 1293 cm\(^{-1}\) was attributed to the –COO- stretching vibrations. The C=O stretching band of 6-arm star-shaped PCL-b-PEG appeared slightly shifted at around 1723 cm\(^{-1}\) and C-H stretching was shown at around 2887 cm\(^{-1}\). The C-O-C and –COO- functional groups appeared at 1279 cm\(^{-1}\) and 1101 cm\(^{-1}\), respectively. No –OH band was observed in the spectrum confirming the conjugation of PCL end group towards mPEG-COOH (Wang et al. 2005).

The \(^1\)H NMR analysis was done to determine the molecular structure of the star-shaped polymer. Figure 4 shows the \(^1\)H NMR spectra for both star polymer PCL and star polymer block PCL-b-PEG. The peaks at 4.05 ppm (t, -CH\(_2\)-O-) and 3.6 ppm (t, -CH\(_2\)-OH) in Figure 4(a) denote the ether group from the backbone and the terminal end group for the polymer arm, respectively, indicating the presence of hydroxyl group at the end of the PCL polymer chain. The multiplets at chemical shifts between 1.3 and 2.4 ppm (δ1.6, δ1.3 (m, 2H, -CH\(_2\)-),(t, 2H, -CH\(_2\)-)) represent the polymer backbone of the PCL indicating the occurrence ROP of ε-caprolactone monomer. The polymerization reaction towards each arm of the initiator/core are assumed to be the same. This is due to all core arms possess the same terminal active group (hydroxyl) that can initiate the ROP of ε-caprolactone (Letchford et al. 2005). Based on this assumption and in correlation with \(^1\)H NMR data obtained, it is concluded that each arm of the macroinitiator (di-pentaerythritol) undergo ROP of ε-caprolactone to 6-arm star-shaped homopolymer PCL.

\(^1\)H NMR spectrum of the block copolymer (Figure 2(b)) shows chemical shifts between 1.3 and 2.4 ppm (δ1.3, δ1.6 (m, 2H, -CH\(_2\)-)) which denote the poly(ε-caprolactone) backbone that is attached to the central core. A triplet at 2.65 ppm (t, -COCH\(_2\)CH\(_2\)CO-) is associated to the methylene group linker. This peak is slightly shifted downfield due to the de-shielding effect after attachment with PCL backbone. A singlet at 3.4 ppm (s, -OCH\(_3\)) is associated with the methylene group at the end terminal in mPEG while chemical shifts between 3.5 and 3.7 ppm (m, -OCH\(_2\)CH\(_2\)OCH\(_3\)) denote poly(ethylene glycol) backbone. Meanwhile a triplet at 4.0 ppm (t, -CH\(_2\)O-) is associated with methylene ester on the polycaprolactone backbone (Wang et al. 2005). The functional end group of homopolymer PCL peak is absent in the \(^1\)H spectrum of 6PCG, signifying the successful conjugation of PCL and PEG blocks, which indicates the formation of block star co-polymers. The data obtained is in agreement with the previous study (Maglio et al. 2004).

The molecular weight calculation of the star polymer was determined using GPC and \(^1\)H spectra (Izunobi & Higginbotham 2011). Calculation of PCL star molecular weight by \(^1\)H NMR spectrum was determined by the ratio of the peak between methylene groups (2.30 ppm) and the hydroxyl end group (3.65 ppm). Determination of molecular weights for star block copolymer was evaluated between the peak ratio of the area for PCL block (2.30 pp
The molecular weight of each star polymer synthesized was summarized in Table 1.

The ROP reactions that were carried out is based on the ratio of molecular weight, $M_n$ with 40k of PCL. The $M_n$ of the star polymer should be within this range to make sure the star polymer suitable for electrospinning process to ensure the polymer solution can form fibres via electrospinning.

Figure 5 shows the GPC analysis of the synthesized star-shaped polymers. Based on the $^1$H NMR and GPC analysis for the $M_n$ of the star-shaped polymers, the molecular weight is near to theoretical value which shows that the polymerization is controlled based on their molar feed ratio. The $^1$H NMR and GPC have different values due to the fact that both have different types of measurement. The $^1$H NMR gives an absolute value, while GPC gives the relative value. GPC also has limited resolution of the separation of star-shaped polymer compared to linear polymer. The shape of the polymer also affects the molecular weight measured by GPC. The resolution of the separation of star-shaped polymers by GPC is quite limited because the hydrodynamic volume of star-shaped polymers is considered as independent to the number of arms, assuming that all of the arms bear the same molecular weight (Lee et al. 1998). However, GPC is used to determine the $M_w$ of the star-shaped polymers.

The thermal properties of the synthesized 6-arm star-shaped polymer were examined using thermogravimetric analysis, (TGA/DTG) and differential scanning calorimetry, (DSC). TGA was carried out to measure the change of mass with increased temperature to determine the thermal stability of synthesized polymer. Table 2 shows the thermogravimetric analysis of all polymers. Both star-shaped polymers showed high thermal stability based on initial major thermal decomposition temperature occurring at range between 275-354°C. However, the

**TABLE 1. Molecular weight characteristics of multi-armed star polymers**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^aM_n$ theoreical (g/mol)</th>
<th>$^bDP$ star</th>
<th>$^aM_n$ NMR (g/mol)</th>
<th>$^cM_w$/GPC (g/mol)</th>
<th>$^dM_n$/M_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>6PC</td>
<td>40100</td>
<td>52</td>
<td>36300</td>
<td>52000</td>
<td>1.53</td>
</tr>
<tr>
<td>6PCG</td>
<td>71200</td>
<td>55</td>
<td>70500</td>
<td>60800</td>
<td>1.09</td>
</tr>
</tbody>
</table>

$^a$Theoretical $M_n$ was determined from monomers feed ratio. $^b$Calculated from $^1$H-NMR spectra. $^c$Obtained from GPC

![FIGURE 4. $^1$H NMR spectra of star-shaped (a) 6PC and (b) 6PCG](image)

![FIGURE 5. GPC analysis of (a) 6PCG and (b) 6PC](image)
initial degradation temperature of 6PCG before the major decomposition was due to water loss (Ghalia & Dahman 2015). All thermograms showed a single step degradation (Figure 6). However, the thermal stability increased for 6PCG after the attachment of mPEG into each arm of the star polymer. These thermal changes are as expected since PEG has high thermal stability, therefore its addition to PCL increases the decomposition temperature of the copolymer (An et al. 2001). 6PCG have stable chain terminal groups (-OCH3), leading to a higher thermal stability compared to star 6PC homopolymer which has lower thermal stability due to hydroxyl terminal end group (-OH), that are prone to rapid thermal degradation (Wang et al. 2005).

Thermal analysis using DSC was used to gain insight into the self-organization and the crystallization behavior of the star-shaped polymers in bulk. The melt crystallization of copolymers is rather complex since both PCL and PEG have close melting temperatures that lead to the occurrence of coincident crystallization of both components or the crystallization of one block may affect the crystallization of the second block (Castillo & Muller 2009; Hua & Dong 2007). Slight decrease of crystalline melting point (Table 3) of star-shaped 6PCG was observed compared to 6PC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_d-initial (°C)</th>
<th>T_d-max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6PC</td>
<td>275.3</td>
<td>329.3</td>
</tr>
<tr>
<td>6PCG</td>
<td>354.1</td>
<td>409.1</td>
</tr>
</tbody>
</table>

$T_{d-initial}$ = temperature at which 2% of weight loss was measured, $T_{d-max}$ = temperatures of maximum decomposition obtained from DTG thermograms

As observed in 6PC, the polymer has crystalline melting point within the melting range of PCL. Monomodal peaks of melting (Figure 7) for the block copolymer can be attributed to the crystalline domain of PEG. The melting temperature of the PCL block was not observed separately possibly because of the insufficient phase separation and increased phase compatibility of the PCL.
blocks within dominant PEG blocks (Lu et al. 2006). The single exothermic peak is also attributed to the cooperated crystallization of PEG and PCL blocks (Sun et al. 2011). Such finding may be related to the presence of PEG blocks which crystallized first and consequently disturbed the organization of PCL segment that altered the Tm value of PCL. The structure also reflected the Tm behavior of the star-shaped polymers. PCL is in the inner segment of the star-shaped polymer system that is held together by the rigid core making it difficult for PCL to rearrange to form lamellae region. Meanwhile the PEG in the outer segment of the star shaped polymer is freer to move for rearrangement of the polymer chain making it more dominant for its crystallinity. Since there was no significant observable PCL melting peaks in the copolymer samples, it can be concluded that both star block copolymers consisted of a semi-crystalline PEG phase, while PCL dispersed within the part of semi-crystalline PEG phase (Colwell 2008).

MORPHOLOGICAL ANALYSIS

The morphology and fibre diameter were characterized by SEM analysis (Figures 8 and 9). 6PCG solution with chloroform formed fibres with bead-on-string morphology (Figure 8(a)). On the other hand, neat block 6-arm star-shaped polymer without beads was obtained using a mixture of chloroform and methanol solvents (Figure 9(a)).

As observed from the SEM results, the type of solvent in the polymer solution influenced the electrospinning process and the fibre produced. The diameters of the fibres in the SEM images were measured and analyzed using ImageJ® Software. Sixty measurements were made and the data was converted into a histogram (Figures 8(b) and 9(b)).

The mean diameter of the star-shaped polymer fibres produced was 0.278 μm for fibres with chloroform solution and ±0.136 μm for fibres with mixture of chloroform and methanol solvents.

Dielectric constant and conductivity of the solvent used play an important role in producing fine fibres particularly in electrospinning solutions (Pierozynski 2011). Dielectric constant measures the capability of the certain solvent in holding electric charge in electric field and therefore it is highly dependent on the type of solvent used. The use of solvent with lower dielectric constant in the production of fibres via electrospinning will lower the...
capability of the solutions for split whereas the growth of electric charge brings instability to the jet flow that lead to the jet flow to split and become thinner (DerScheueren et al. 2011). Table 4 shows huge different of dielectric constants between chloroform and methanol that affect the 6PCG fibres morphology even though both solvents have the same boiling point and viscosity.

Chloroform has low dielectric constant that leads to lower productivity and difficulty in the electrospinning process of the 6PCG/chloroform solutions. From Figure 8, the electrospinning process of this solutions produced collectible fibres, but, the diameter of the fibre was thicker and the quantity of the fibres per unit area was fewer compared to fibres produced from a mixture of solvents. Eventhough methanol has high dielectric constant, 6PCG is insoluble in methanol at room temperature and thus cannot be electrospun while, although 6PCG can be dissolved in chloroform, it does not produce good fibres. These two solvents need to be mixed together to overcome the solubility issue along with having dielectric constant property. The increased dielectric constant/conductivity in the polymer solution was found to be the main parameter to produce beads-free fibres of 6PCG with uniform structure due to their greater charge density and to yield fibres with smaller diameters (Lee et al. 2010). The solvent mixture also has different viscosity that could also affects the fibre produced (Qian et al. 2010; Tsou et al. 2015). The slightly higher viscosity of the solvent mixture compared to viscosity of individual solvent (Fong et al. 1999; Kaur & Juglan 2015) could also reduce the number of beads formed in the fibre. The selection of solvent used for the star-shaped polymer to produced fine fibres must be homogenous with the polymeric system used and the final solution has to be in high viscosity with lower surface tension. Both chloroform and methanol also have high evaporation rate that give less time for the uniform fibre to form beads.

**CONCLUSION**

To conclude, 6-arm star-shaped block copolymer PCL-b-PEG has been synthesized and characterized. Electrospin of the polymer solution via chloroform and solvent mixture of methanol/chloroform produced fibres with different properties. Fine fibres with small diameter were produced by the mixture of solvents suggesting that the production of 6PCG fibres are dependent on high dielectric constant solvent, while using chloroform alone will lead to bead-on-strings fibres.

### Table 4. Properties of solvent

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole moment (D)</th>
<th>Density(a) (g/cm³)</th>
<th>Viscosity(a) (mPa.s)</th>
<th>Boiling point (°C)</th>
<th>Dielectric constant (F/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>1.1</td>
<td>1.48</td>
<td>0.57</td>
<td>61.1</td>
<td>4.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.7</td>
<td>0.79</td>
<td>0.6</td>
<td>64.7</td>
<td>32.6</td>
</tr>
</tbody>
</table>

*(a) value at 25°C (Smallwood 1996)*

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Wafiuddin Ismail, Shafida Abd Hamid & Wan Khartini Wan Abdul Kho. *Department of Chemistry* Kulliyyah of Science International Islamic University Malaysia Kuantan Campus, Bandar Indera Mahkota 25200 Kuantan, Pahang Darul Makmur Malaysia

Rusli Daik School of Chemical Science and Food Technology Faculty of Science and Technology Universiti Kebangsaan Malaysia 43600 UKM Bangi, Selangor Darul Ehsan Malaysia

*Corresponding author; email: wkhartini@iium.edu.my

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