Synthesis and Electrospun Fiber Mats of Low T_g Poly(propylene fumerate-*co*-propylene maleate)

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ABSTRACT: Many publications have examined the biodegradable polymer poly(propylene fumate) (PPF) for use in tissue engineering applications. We have examined a similar crosslinkable polymer system, poly(propylene fumerate)-*co*-(propylene maleate) (PPFcPM), derived from maleic anhydride (MA) and 1,2-propylene diol (PD). This copolymer system uses a less expensive monomer as well as leads to varied ratios of fumerate to maleate groups, allowing tuning of the crosslinked polymer properties such as degradation rate. Two different reaction conditions were used to synthesize the copolymer from MA and PD. In the first case (Method A), toluene was used as a solvent to azeotropically (85°C) remove water to drive the acid catalyzed esterification reaction. In the second case (Method B), the initial ring opening reaction was conducted, followed by addition of catalyst and removal of water to produce polymer of higher molecular weight. Both polymer systems had glass transition temperatures (T_g) below room temperature. The low T_g PPFcPM was dissolved in chloroform along with the photoinitiator phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) and electrospun. The polymer fibers were crosslinked soon after they formed to produce noncalendaring 3D porous scaffolds. Control experiments without the BAPO photoinitiator did not produce fiber mats. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1984–1991, 2010

Key words: biomaterials; copolymerization; crosslinking; fibers; polyesters

INTRODUCTION

Poly(propylene fumerate) (PPF) is an unsaturated polyester which may be crosslinked thermally or photochemically via the fumerate carbon–carbon double bond. PPF has been shown to be both biocompatible and biodegradable, having biocompatible degradation products and mechanical properties similar to bone.[1–5] Because of these properties PPF has been explored extensively as a scaffold for bone tissue engineering. In addition to tissue engineering scaffolds, PPF has shown to be a promising polymer for use in bone cements where the polymer is applied as a composite forming a putty-like mixture that can be hardened via crosslinking of the fumerate bond.[6] Because PPF is a liquid at room temperature, this polymer is particularly attractive as it can be injected, along with a leachable porogen, into an irregularly shaped defect site and crosslinked *in situ*.[7,8] Several methods have been developed to synthesize PPF including the fumaryl chloride route[9] as well as the ethyl fumerate route.[10]

In addition to the two PPF synthesis methods described earlier, which have been used to synthesize polymer specifically for tissue engineering applications, PPF has been previously synthesized as a synthetic resin using maleic anhydride (MA) as a starting material.[11] The previous investigation of the ring opening and polycondensation of MA and 1,2-propane diol (PD) provided much insight into factors that influence the final polymer material properties.[11–14] These factors include temperature, monomer ratio as well as the catalyst loading level and selection. A judicious choice of esterification catalyst as well as the reaction temperature can produce a poly(propylene fumerate-*co*-propylene maleate) (PPFcPM). The maleate to fumerate isomerization has been reported to be influenced by the diol. Sterically hindered diols tend to induce isomerization at elevated temperature to the energetically stable fumerate.[12]

In scaffold design biocompatibility and cell interaction are important variables, however; porosity is a significant parameter to evaluate when gauging the success of a particular scaffold because the cellular environment is crucial to cell viability and migration.[15] PPF porous structures have been previously

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produced using methods such as solvent casting/particulate leaching[16] and, more recently, high internal phase emulsions (HIPEs).[17]

Porous biomaterial structures have also been formed using techniques such as three-dimensional patterning through stereolithography,[18] phase seperation,[17] solvent casting/particulate leaching,[16] gas foaming,[16] as well as electrospinning.[15,19,20] Although electrospinning is a simple technique to produce fibers with nanometer to micrometer dimensions, there are many variables including solution concentration, applied voltage, needle gauge, and collector distance which influence the morphology of the produced fibers. Previously, low T_g polymers, such as polybutadiene and acrylic copolymers have been electrospun using an initiator and crosslinking agent.[21,22]

Herein, we describe an alternative synthesis of PPF that uses a less expensive monomer (MA) than fumeryl chloride or diethyl fumerate. Furthermore, we describe the synthesis of copolymer of fumarate and maleate monomers, poly(propylene fumerate)-*co*-(propylene maleate) (PPFcPM) from the step growth polymerization of MA and PD. In all cases, the polymers produced had a T_g below room temperature which normally inhibits the production of a porous mat comprised of continuous fibers. Electospun fiber mats were, however, produced from PPFcPM when we added a photoinitiator and performed the photocrosslinking *in situ*. These electrospinning experiments demonstrate the first example of electrospun mats fabricated from polymers with PPF or PPM repeat units. These electrospinning results are significant as they enable the fabrication of a porous scaffold structure with micro and nanoscale features as well as a high surface area to volume ratio that utilizes PPF materials which have been proven to be very good materials for tissue engineering applications.

EXPERIMENTAL SECTION

General procedure

All reactions were carried out under a dry atmosphere unless noted. ^{1}H-nuclear magnetic resonance (NMR) was carried out on a 400 MHz Bruker DRX-AVANCE. Proton chemical shifts (δ) are reported as shifts from the internal standard tetramethylsilane (TMS). Infrared spectroscopy (IR) was carried out on a Nicolet 6700 FTIR. Gel Permeation Chromatography (GPC) molecular weight determinations were performed using a Polymer Labs 220 PL-GPC equipped with a UV–vis detector. Two columns (PLgel 5 μm MiniMIC-C, 250 × 4.6 mm) and a guard column (PLgel 5 μm MiniMIX-C, 50 × 4.6 mm) were used in series with a flow rate of 0.4 mL/min and a run pressure of 6.0 MPa. Chloroform was used as the eluent and measurements were performed at 35°C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution (Fluka ReadyCal 400–2,000,000). Scanning electron microscopy (SEM) was carried out using a Zeiss Supera 55VP and a FEI DB235. Differential scanning calorimeter (DSC) measurements, used to determine T_g, were performed using a TA Instruments DSC100. Viscosity determination was done using a Brookfield DV-E Viscometer, reported in cP (60 rpm, spindle #14). *p*-Toluensulfonic acid (TsOH), monohydrate 99%, extra pure was purchased from Acros. Ethyl acetate, HPLC grade, anhydrous magnesium sulfate ($MgSO_4$), and sulfuric acid, certified ACS plus were purchased from Fisher. 1,2-Propanediol, 99% (PD), maleic anhydride (MA), briquettes 99%, Zinc chloride, anhydrous powder ≥99.995% trace metals, Iron (III) Chloride, reagent grade 97%, phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide, 97% and benzyl, 98% were all purchased from Aldrich. All chemicals were used as received from suppliers.

General method A poly(propylene fumerate-*co*-propylene maleate) synthesis

MA, PD, toluene, and catalyst were added to a round bottom flask equipped with stir bar and Dean-Stark (DS) trap for azeotropic distillation. The reaction was allowed to proceed at a maximum temperature of 110°C, until no more distillate (water) was collected. The reaction mixture was cooled to RT and the toluene was removed in vacuo. The crude polymer was then dissolved in ethyl acetate (EtOAc) and washed with distilled water (3×). The organic layer was then dried over anhydrous $MgSO_4$ and solvent again removed *in vacuo*.

General method B poly(propylene fumerate-*co*-propylene maleate) synthesis

MA, PD, and toluene were added to a round bottom flask. The reaction mixture was heated to 50°C and stirred overnight. The reaction mixture was allowed to cool to RT and the toluene was removed *in vacuo.* The reaction flask was then equipped with a DS trap and condenser to collect water through azeotropic distillation during the second reaction. Next, a protic acid catalyst was added to the product of the first reaction, and the mixture heated to a maximum temperature of 110°C, until the appropriate volume of water was collected. The reaction mixture was allowed to cool to RT, the solvent was removed *in vacuo*, and the crude polymer was dissolved in ethyl acetate and washed with distilled water (3×). Finally, the organic layer was dried over anhydrous $MgSO_4$ and solvent removed *in vacuo*.

PPF synthesis (1)

MA (10.0 g, 102 mmol), PD (7.8 g, 102 mmol), and tosic acid (0.02 g, 0.1 1 mmol) were added to a 100 mL round bottom flask equipped with a stir bar and distillation head. The reaction mixture was heated to 250°C with stirring. After 3 hr, the reaction was allowed to cool to RT. The resulting viscous crude polymer was dissolved in ethyl acetate (50 mL) and washed with distilled water (50 mL, 3×). The organic layer was dried over anhydrous $MgSO_4$, filtered and solvent removed *in vacuo* to yield a slightly yellow viscous polymer. IR (neat) 2984.1, 1714.7, 1645.4, 1454.7, 1379.0, 1290.2, 1255.5, 1153.4, 1116.2, 1075.9, 1022.5, 979.1, 837.3, 753.5, 666.4 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.88–6.78 (m, —CH=CH—), 5.25–5.2 (m, —CH(CH_3)), 4.68–2.8 (m, —OCO—CH_2—), 1.43–1.15 (m, (CH_3)CH_2). GPC (1 mg/mL, $CHCl_3$) M_w 949 M_n 473. T_g (°C) −15.24.

Method A PPFcPM synthesis (2)

MA (10.0 g, 102 mmol), PD (7.8 g, 102 mmol), toluene (30–50 mL), and the appropriate catalyst, TsOH (0.2 g, 1.0 mmol), H_2SO_4 (1 drop, 18*N*), $ZnCl_2$ (0.14 g, 1.0 mmol) or $FeCl_3$ (0.17 g, 1 mmol), were added to a 100 mL round bottom flask equipped with stir bar along with DS trap and condenser. The reaction mixture was allowed to progress overnight. The reaction was ended and brought to RT, upon cooling toluene was removed *in vacuo*. The crude polymer was then dissolved in ethyl acetate (50 mL) and washed with water (50 mL, 3x). The organic layer was dried over $MgSO_4$ with filtration and the solvent was removed in vacuo to yield a clear viscous polymer.

PPFcPM synthesized with TsOH: IR (neat) 3490.0, 3058.6, 2983.4, 1711.9, 1643.6, 1455.3, 1384.2, 1252.6, 1077.7, 983.6, 828.7, 777.3 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17–7.14 (m, Ar), 7.09–7.03 (m, Ar), 6.83–6.76 (m, *trans* —CH=CH), 6.27–6.13 (m, *cis* —CH=CH—), 5.19–5.17 (bs, —CH(CH_3)), 4.34–3.61 (m, —OCO—CH_2—), 2.26 (s, CH_3-Ar), 1.25–1.03 (m, (CH_3)CH_2—). GPC (1 mg/mL, $CHCl_3$) M_w 995 M_n 728. T_g (°C) −40.38.

PPFcPM synthesized with $ZnCl_2$: IR (neat) 3516.3, 3079.6, 2984.3, 2943.7, 2883.4, 1711.1, 1644.0, 1452.5, 1381.1, 1356.2, 1289.2, 1251.9, 1224.0, 1149.6, 1116.0, 1075.9, 1019.6, 978.3, 835.7, 773.5, 668.1 cm^{-1}.^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.22–7.20 (m, Ar), 7.14–7.10 (m, Ar), 6.90–6.76 (m, *trans* —CH=CH), 6.23–6.20 (m, *cis* —CH=CH—), 5.27–5.07 (m, —CH(CH_3)), 4.40–4.02 (m, —OCO—CH_2—), 2.32 (s, CH_3-Ar), 1.51–1.23 (m, (CH_3)CH_2=). GPC (1 mg/mL, $CHCl_3$) M_w 1297 M_n 824. T_g (°C) −18.66.

PPFcPM synthesized with $FeCl_3$: IR (neat) 3445.0, 3235.5, 3081.1, 2985.9, 2661.0, 2362.5, 1716.2, 1751.0, 1700.4, 1646.7, 1455.9, 1386.3, 1355.4, 1324.4, 1279.4, 1190.8, 1121.8, 1080.2, 990.2, 838.6, 775.3 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.93–6.83 (m, *trans* —CH=CH), 6.33–6.23 (m, *cis* —CH=CH—), 5.27–5.10 (m, —CH(CH_3)), 4.40–4.10 (m, —OCO—CH_2—), 1.44–1.23 (m, (CH_3)CH_2—). GPC (1 mg/mL, $CHCl_3$) M_w 1871 M_n 1043. T_g (°C) −37.58.

PPFcPM synthesized with H_2SO_4: IR (neat) 3526.2, 3079.3, 2984.1, 1716.1, 1645.5, 1558.5, 1541.9, 1508.1, 1456.2, 1379.8, 1253.1, 1217.4, 1150.1, 1113.8, 1074.7, 977.1, 833.2, 773.2 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23–7.20 (m, Ar), 7.15–7.10 (m, Ar), 6.88–6.82 (m, *trans* —CH=CH), 6.34–6.24 (m, *cis* —CH=CH—), 5.24 (bs, —CH(CH_3)), 4.77–4.00 (m, —OCO—CH_2—), 2.32 (s, CH_3-Ar), 1.44–1.21 (m, (CH_3)CH_2—). GPC (1 mg/mL, $CHCl_3$) M_w 672 M_n 330. T_g (°C) −12.86.

Method B PPFcPM synthesis (2)

MA (10.0 g, 102 mmol), PD (7.8 g, 102 mmol), and toluene (15 mL) were added to a 100-mL-round bottom flask equipped with a stir bar. Under a nitrogen blanket, the reaction heated to 50°C with stirring was allowed to run overnight. The next day, the reaction mixture was allowed to cool to RT and the solvent removed *in vacuo*. The reaction flask was then equipped with a DS trap and condenser. To the product of the first reaction, toluene and either tosic acid (0.2 g, 1 mmol) or sulfuric acid (1 drop, 18*N*) was added. The reaction was allowed to run until 1.6 mL of water was collected via the DS trap. The reaction was allowed to come to RT and the solvent was removed *in vacuo*. The crude polymer was then dissolved in ethyl acetate (50 mL) and washed with water (50 mL, 3×). The organic layer was dried over $MgSO_4$ with filtration and the solvent was removed *in vacuo* to yield a slightly yellow viscous polymer.

PPFcPM synthesized with TsOH: IR (neat) 2985.9, 1721.6, 1691.3, 1644.4, 1454.6, 1381.1, 1289.9, 1252.0, 1215.8, 1152.4, 1116.1, 1075.4, 979.0, 838.2, 774.3, 736.5, 669.0 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.86–6.83 (m, *trans* —CH=CH—), 6.29–6.23 (m, *cis* —CH=CH—), 5.24 (bs, —CH(CH_3)), 4.78–3.44 (m, —OCO—CH_2), 1.32–1.17 (m, (CH_3)CH_2—). GPC (1 mg/mL, $CHCl_3$) M_w 11,388 M_n 2347. T_g (°C) −13.78.

PPFcPM synthesized with H_2SO_4: IR (neat) 2985.7, 1717.7, 1643.6, 1454.7, 1382.5, 1253.8, 1151.8, 1116.5, 1075.3, 978.7, 889.8, 838.1, 7775.0, 734.6, 694.8 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24–7.21 (m, Ar), 7.16–7.11 (m, Ar), 6.83 (s, *trans* —CH=CH—), 6.25 (s, *cis* —CH=CH—) , 5.26 (bs, —CH(CH_3)), 4.78–2.75 (m, —OCO—CH_2—), 2.33 (s, CH_3-Ar), 1.33–1.17 (m, (CH_3)CH_2—). GPC (1 mg/mL, $CHCl_3$) M_w 5520 M_n 1739. T_g (°C) −13.78

General procedure for electrospinning

All polymer solutions were delivered at a constant rate via a syringe pump (KD scientific, model 100s)

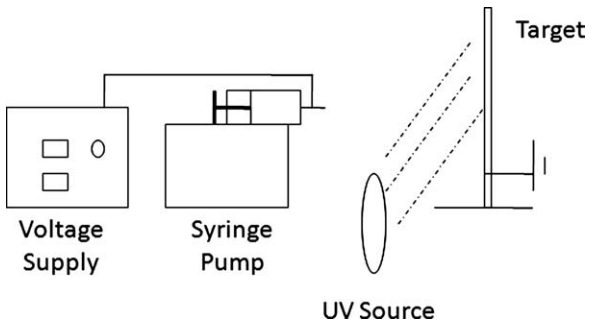


Figure 1 Schematic of electrospinning setup.

through a syringe fitted with a stainless steel blunt tip needle (Small Parts). The needle was charged through a high voltage supply (Glassman High Voltage, Series EL), and the resulting polymer fibers were collected on a grounded target (6 × 6 in^2 Cu plate fitted with Al foil). A UV source (UVP, Blak-Ray longwave ultraviolet lamp, model B100AP, λ = 365 nm) was used to crosslink the polymer *in situ* (Fig. 1).

Electrospinning PPF and PPFcPM

A 2-mL plastic syringe [inner diameter (ID) = 4.64 mm] equipped with a 20 gauge (g) × 1.5 in. stainless steel blunt tip needle was used to deliver solutions of polymer dissolved in chloroform (40, 50, and 60 wt %) at a volumetric flow rate of 0.2 mL/hr and a voltage difference of 1 kV/cm from needle tip to collection plate.

Crosslinking while electrospinning PPF and PPFcPM

A 2-mL plastic syringe (ID = 4.64 mm) equipped with a 20 g × 1.5 in stainless steel blunt tip needle was used to deliver a 50 wt % polymer solution with a 3 wt % initiator (benzil or phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO)) in chloroform. The polymer solution was spun at a constant rate of 0.1 mL/hr and a voltage of 1 kV/cm, from needle tip to collection plate. While the polymer was being collected on the target it was being crosslinked via the UV source.

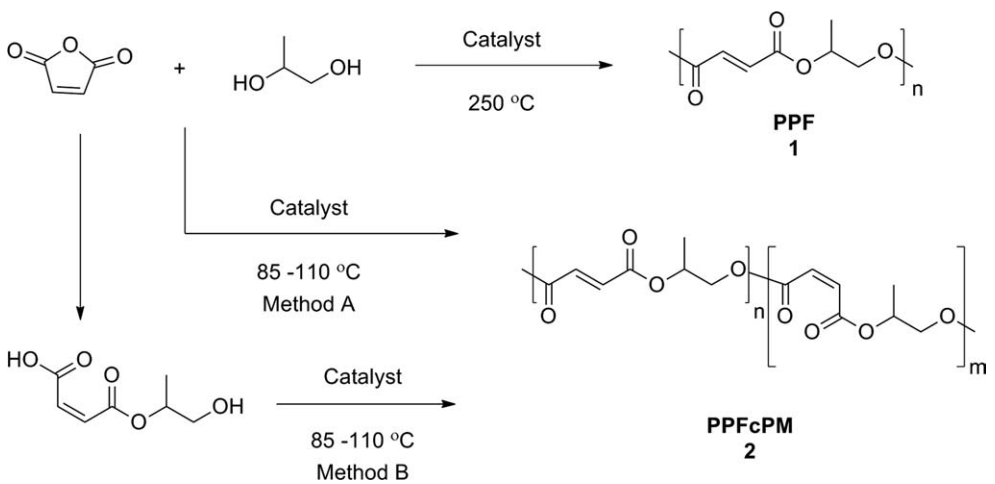
Crosslinked PPFcPM: IR (neat) 2957.6, 1719.1, 1643.6, 1453.2, 1382.9, 1254.2, 1209.4, 1150.8, 1114.3, 1073.3, 978.7, 813.9, 752.7, 667.5 cm^{-1}.

RESULTS AND DISCUSSION

Poly(propylene-fumerate) (PPF) and poly(propylene fumerate)-*co*-(propylene maleate) (PPFcPM) were synthesized via step growth polycondensation reactions (Scheme 1). The glass transition temperatures of all polymers synthesized were below room temperature and ranged from −13°C to −40°C (Table I). PPF was synthesized via the protic acid catalyzed neat reaction of maleic anhydride with 1,2-propanediol at high temperatures (~250°C), whereas the copolymer PPFcPM was obtained using a protic acid catalyst at lower temperatures (~85–110°C). Two different methods were explored to synthesize the copolymer.

The first method (Method A) used to synthesize the copolymer involved a protic acid or Lewis acid catalyzed polymerization reaction carried out at 85°C to 110°C to azeotropically remove water. The second method (Method B) involved an initial ring opening reaction carried out at 50°C without the use of a catalyst followed by an acid catalyzed condensation reaction in combination with azeotropic removal of water.

The ratio of fumerate to maleate in the polymer was influenced by both temperature and catalyst (Table I). Polymer synthesized at high temperatures (neat) produced only PPF however the molecular weight was low presumably due to side reaction



Scheme 1 Synthesis of PPF and PPFcPM.

TABLE I
Summary of PPF and PPFcPM Reaction Conditions and Polymer Characterization

	Catalyst	Reaction temperature (°C)	% Fumerate	T_g (°C)	M_n
	TsOH	250	100	−15.24	473
Method A	TsOH	85–110	33	−40.38	728
	H_2SO_4	85–110	79	−13.72	330
	$ZnCl_2$	85–110	89	−18.66	824
	$FeCl_3$	85–110	87	−37.58	1043
Method B	TsOH	50/85–110	55	−13.78	2347
	H_2SO_4	50/85–110	71	−13.65	1739

products which changed the monomer stoichiometry. As the catalytic activities of each catalyst are slightly different, only direct comparison between polymerization techniques using the same catalyst can be made. For example, polymer synthesized at low temperatures according to Method A using TsOH yielded a polymer with 33% fumerate, whereas Method B yielded polymer that contained 55% fumerate (Fig. 2). Polymer formed with mostly maleate had a very low T_g when compared to polymer having a much smaller amount of maleate. Furthermore, there appears to be no correlation between T_g and molecular weight as each polymer is a random copolymer.

PPFcPM synthesized using sulfuric acid as the catalyst resulted in toluene inclusion due to Friedel-Craft alkylation.[23] The influence of temperature and catalyst was also observed in all of the one step azeotropic distillation scenerios, thus providing a system which has the ability to be adjusted.

The molecular weights of all polymers produced were determined through gel permeation chromatography using narrow weight distribution polystyrene as the standards. PPF synthesized according to Method A had an average molecular weight (M_n) of 720, with poly dispersedity (PDI) of 2.0. The molecular weight did not increase with longer reaction times (data not shown). The low molecular weight is consistent with the initial production of PPFcPM oligomers which thermally isomerizes to the more stable fumerate form. Presumably the high temperature results in both isomerization and side reactions that limit the polymer molecular weight by changing the step growth stoichiometry. PPF synthesized in this fashion is about 70% lower in molecular weight than other reported synthesis,[10] however PPF is isolated via a two step synthesis in the previously reported synthesis. PPFcPM synthesized through one step synthesis (Method A) also resulted in polymers with low molecular weights (Table I). To increase the M_n of our polyester, a two step synthesis (Method B) was developed. Method B did not produce PPF; it did however, produce the copolymer PPFcPM. The copolymer molecular weight was significantly higher than the copolymer produced using Method A (Fig. 3). The PPFcPM molecular weight using TsOH displayed a M_n of 2,347 and a PDI of 4.85. Structural properties of crosslinked PPFcPM as well as biocompatibility studies will be evaluated in future work.

For use as a scaffold for tissue engineering, the polymer needs to be easily processed into a highly porous scaffold with a high surface area to volume ratio and an interconnected pore network. Previously, members of the Mikos and Yazasemski research groups have fabricated PPF scaffolds using solvent casting/salt leaching techniques and,[2,7,8] more recently, high internal phase emulsions

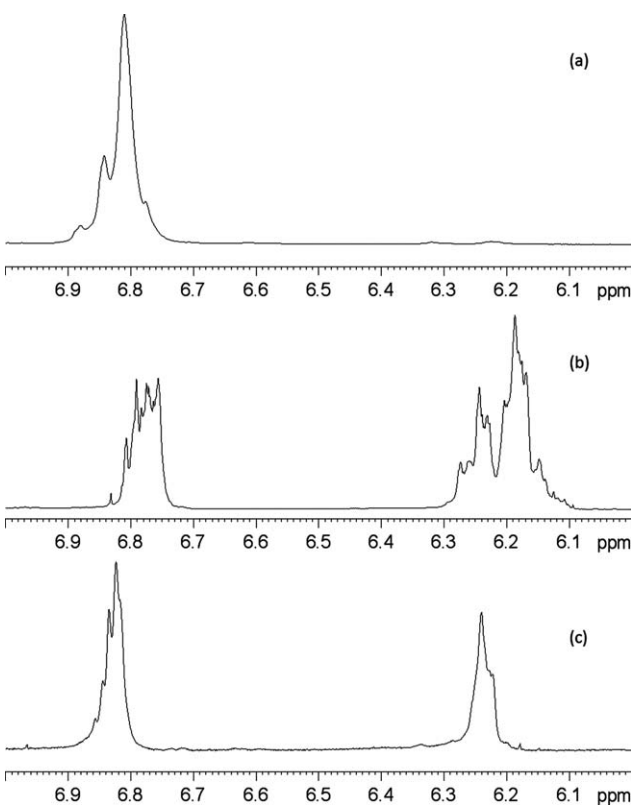


Figure 2 1H-NMR of polymer, peak at 6.8–6.9 ppm corresponding to fumerate where the peak at 6.2–6.3 ppm represents the maleate (a) PPF, (b) Method A, and (c) Method B.

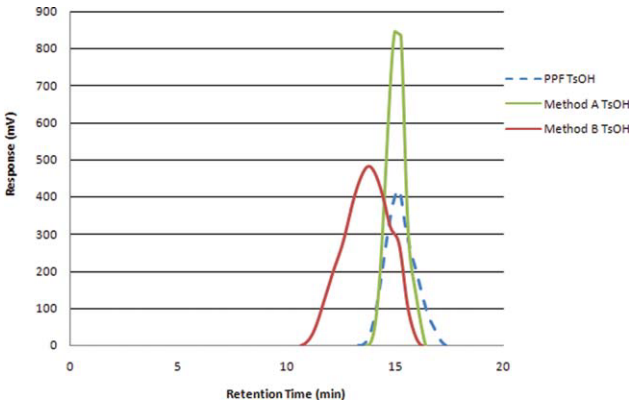


Figure 3 GPC results, showing elution times of the PPFcPM polymer using the protic acid catalyst TsOH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(HIPEs).[17] Here, we present the fabrication of PPFcPM scaffolds using the established technique of electrospinning. Electrospinning is an attractive technique for forming polymer scaffolds for tissue engineering as it produces a network of fibers of the same order of magnitude as the biological molecules found in the extracellular matrix. To form a network of PPFcPM copolymer fibers, the copolymer was spun using standard electrospinning techniques. Three different solution concentrations ranging from 40–60% (w/w) dissolved in chloroform were used to determine the solution concentration that would allow for the production of continuous fibers at 1kV/cm (Fig. 4). Fibrous mats were not produced when low T_g polymers were electrospun. Instead the polymer self-calendared to form one layer of a porous material (Fig. 4). The flow rate was reduced to 0.1 mL/hr from 0.5 mL/hr in hopes of reducing the self-calendaring effect and allow for three-dimensional fibrous scaffold formation. Unfortunately, even with the reduced flow rate self-calendaring, due to the flow of polymer at RT, was still observed via scanning electron microscopy (SEM) imaging.

In order to produce a fibrous 3D network that did not self-calendar the copolymer was crosslinked using *in situ* photopolymerization during the electrospinning process. Crosslinking the polymer before electrospinning was not possible as the polymer would no longer be soluble. PPF has previously been crosslinked using acyl phosphine oxides as photoinitiators, as they are known to undergo a rapid alpha cleavage. An example of these reactive acyl phosphines is phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) which generates two radical phosphinoyl pairs upon UV irradiation.[24]

Either benzyl or BAPO was incorporated at 3% (w/w) into a PPFcPM solution [40–60% (w/w)] in chloroform, yielding a solution viscosity of 1863 cP (Brookfield DV-E) at RT. Both solutions were electrospun using the aforementioned parameters and set up. The nano- and microfibers fabricated from a polymer solution containing benzil were exposed to UV light ($\lambda = 365$ nm) as they were spun and deposited onto the aluminum foil coated copper plate held at ground potential. After deposition the polymer was exposed to UV radiation for an additional 15 min. Fibers produced in this way did not exist as individual fibers but rather as a self calendared layer (Fig. 5). Presumably too few radicals were produced to initiate photocrosslinking during fiber formation. PPFcPM/BAPO solutions were loaded in a plastic syringe and electrospun using the same conditions as the polymer/benzyl solution. A fibrous mat was

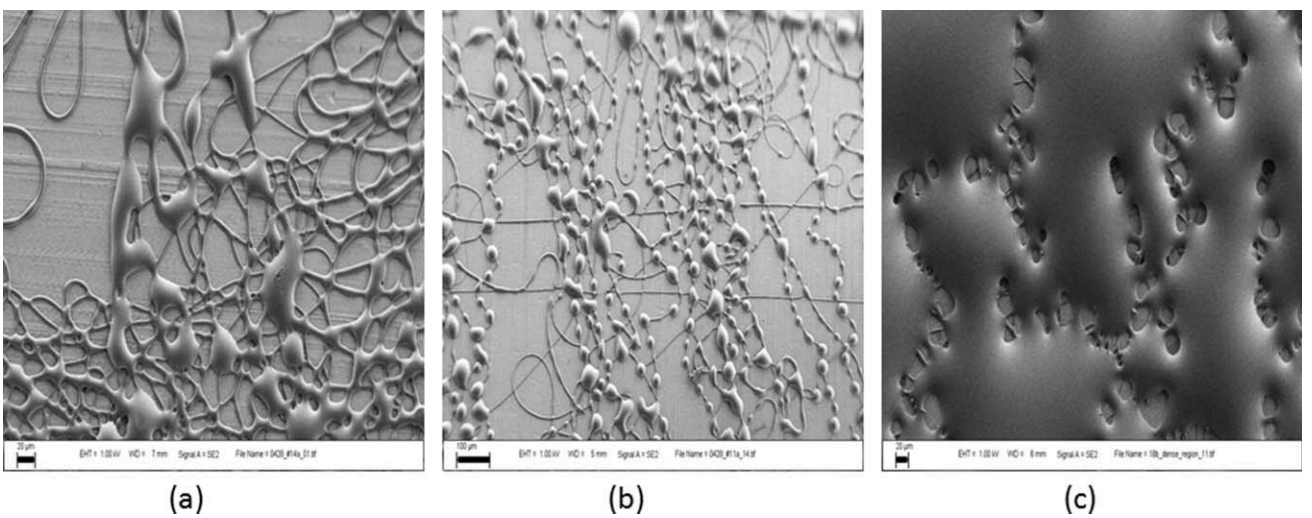


Figure 4 Effect of concentration on PPFcPM produced through two-step synthesis. The voltage applied was 15kV/15 cm, (a) 40 wt % (b) 50 wt %, and (c) 60 wt % polymer in chloroform. (scale bar is 20, 100, and 20 μm, left to right).

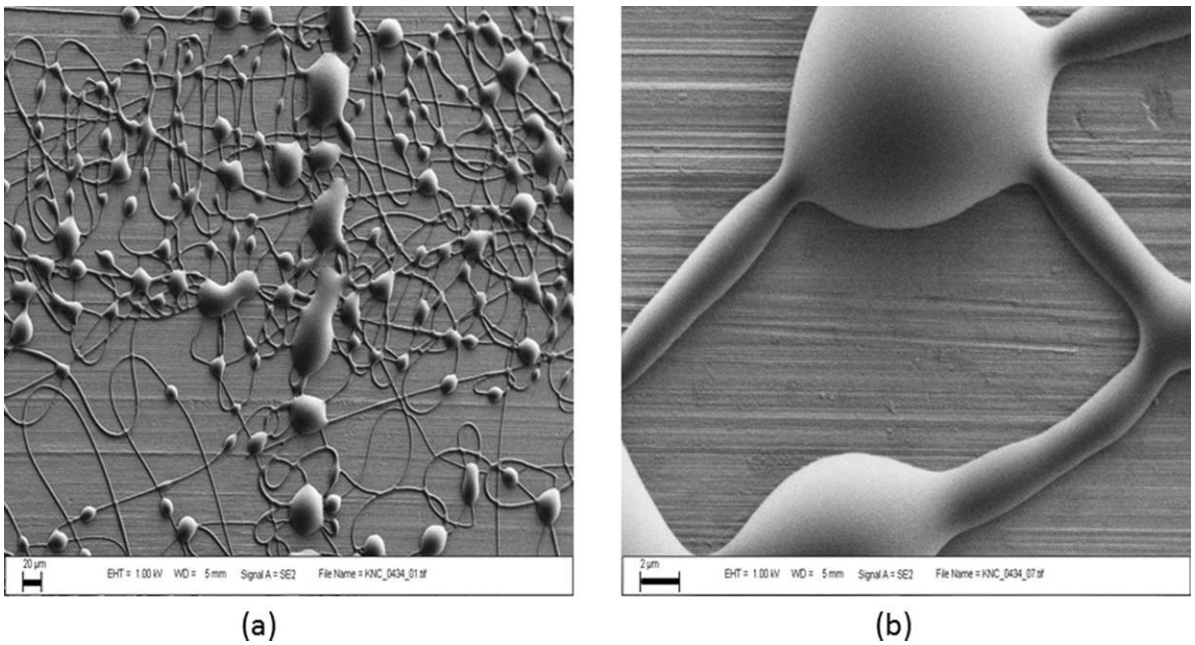


Figure 5 Effect on polymer (50 wt %) after cross linking with Benzil (3 wt %), spun at 15 kV/15 cm and flow rate of 0.1 mL/hr (a) zoomed out on larger area, beads and fibers (b) node-like intersection where "wetting" occurred.

formed using BAPO as the photoinitiator. However, the crosslinked polymer began to form pillars after 0.1 mL of solution was delivered (Fig. 6).

To determine the cause of the pillar formation, a temperature mapping of the aluminum foil coated plate was performed by splitting the aluminum foil into a 3 × 3 array of 2″ squares to form a total of nine regions. Using an IR thermometer, the temperature was recorded in each of the regions to determine if the UV lamp was locally heating the aluminum surface, potentially leading to pillar formation. No local heating of the surface was observed over a typical period of electrospun fiber deposition. Further examination of the electrospinning apparatus revealed that the UV radiation was being reflected off of the aluminum foil exposing the PPFcPM/BAPO filled syringe, promoting photocrosslinking of the polymer solution altering the solution viscosity. However, when the syringe was shielded from the reflected UV radiation the PPFcPM/BAPO was spun successfully and produced a noncalendared mat, free of pillar formation (Fig. 7). Using ImageJ, 30 random fibers in the SEM image were measured to determine the average fiber diameter per sample. With the PPFcPM/BAPO conditions described earlier, fibers with diameters of 6.94 ± 3.64 μm were

Figure 6 Effect on mat from PPFcPM-BAPO collecting in same area on target (scale bar is 20 and 2 lm, left to right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

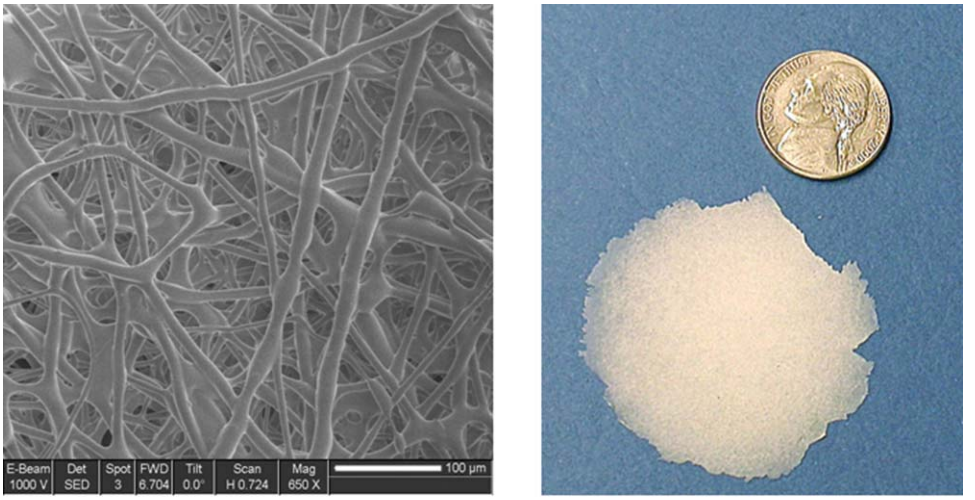


Figure 7 (a) 50 wt % PPFcPM, 3 wt % BAPO in $CHCl_3$ (scale bar is 100 µm), (b) mat of SEM image seen in (a). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

formed. The T_g of the polymers prior to crosslinking did not significantly affect the structure of the electrospun fibers formed as they were crosslinked *in situ*.

CONCLUSIONS

Poly(propylene fumerate) and poly(propylene-fumerate)-*co*-poly(propylene-maleate) were successfully synthesized using maleic anhydride and 1,2-propanediol, via a step growth polycondensation using the protic acid catalysts *p*-toluensulfonic acid (TsOH) and sulfuric acid (H_2SO_4) and Lewis acid catalysts $ZnCl_2$ and $FeCl_3$. Electrospinning of PPFcPM solutions containing a highly active photoinitiator under UV exposure produced nano- and microfibrous mats. The technique should be applicable to all polymers with a T_g lower than room temperature, which also contain a photocrosslinkable functional group. Future work will examine cellular response to the nano- and microfibrous copolymer mats as well as its application as a scaffold for bone tissue engineering applications.

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