

ELECTROSPRAYING/ELECTROSPINNING OF POLY(γ -STEARYL-L-GLUTAMATE): FORMATION OF SURFACES WITH SUPERHYDROPHOBICITY*

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Abstract Electrospaying/electrospinning of poly(γ -stearyl-L-glutamate) (PSLG) was investigated on a series of solutions with different concentrations in chloroform. Field emission scanning electron microscopy (FESEM) and attenuated total reflectance Fourier transform infrared spectroscopy (FT-IR/ATR) were used to characterize the morphology and structure of the electrospayed/electrospun polypeptide mats. It was found that electrospaying of PSLG with concentrations lower than 16 wt% afforded beads, while microfibers could be electrospun at the concentration of 22 wt%. The hydrophobicity of the electrospayed/electrospun PSLG mats was investigated with static water contact angle (WCA) and tilt angle measurements. It was demonstrated that the superhydrophobic surfaces of PSLG with WCAs and tilt angles in the ranges of 150°–170° and 16.5°–4.2°, respectively, were obtained through electrospaying/electrospinning process.

Keywords: Electrospinning/electrospaying; Poly(γ -stearyl-L-glutamate); Polypeptide; Water contact angle; Superhydrophobic surface.

INTRODUCTION

In recent years, electrospaying and electrospinning have been widely used to fabricate polymer surfaces with controlled morphology, such as beads and fibers with diameter in the range of micro- to nanometer^[1–3]. Both of the electroprocesses involve the use of a high voltage to induce the formation of a liquid jet from polymer solutions or melts. As a combination result of surface tension, viscoelastic force and electrostatic repulsion between charges on the jet surface, small droplets or particles are generally formed in electrospaying with a polymer solution of low viscosity, whereas fibers are formed in electrospinning with a highly viscous polymer solution or melt. Since the electrospayed/electrospun mats exhibit remarkable features of high surface area and large porosity, considerable efforts have been made to explore the method to produce functional surfaces with special wettability. For example, polymeric surfaces with water contact angles higher than 150° were recently fabricated from polystyrene^[4], polyaniline/polystyrene blend^[5], poly[bis(2,2,2-trifluoroethoxy)phosphazene]^[6], poly(2,3,4,5,6-pentafluorostyrene) and its copolymers^[7], poly(styrene-*block*-dimethyl siloxane)^[8], and poly(caprolactone)^[9] (coated with fluorinated polymers by CVD at last) through electrospinning process. These superhydrophobic surfaces have drawn great scientific and industrial interest due to their potential applications involving water repellency, self-cleaning and antifouling properties^[10].

Poly(γ -stearyl-L-glutamate) (PSLG) has been studied as an appealing model for the fundamental study of “hairy-rod” polymer, which exhibits not only the stiffness arising from its helical backbone (rod) but also the solubility in common organic solvents due to its long flexible side chains (hair)^[11]. In addition to the interesting

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physicochemical properties, PSLG is attractive as a synthetic polypeptide for surface modification. In our previous work, PSLG was tethered on the surface of polypropylene microporous membrane to improve the surface hydrophobicity and biocompatibility simultaneously for lipase immobilization^[12–14]. In this communication, electrospraying/electrospinning was first applied to PSLG, and a stable superhydrophobic surface with a water contact angle of 169.3° and a tilt angle of 4.2° was obtained.

EXPERIMENTAL

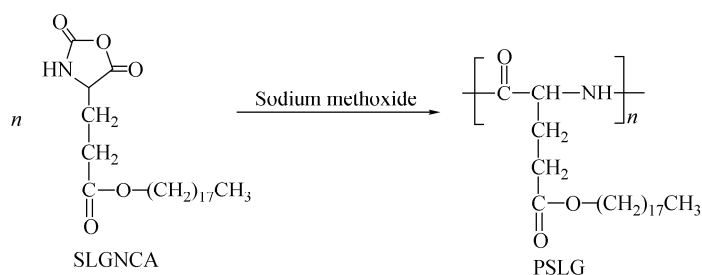
A preparative method of the monomer, γ -stearyl-L-glutamate *N*-carboxyanhydride (SLGNCA), has already been described previously^[15]. After recrystallized three times from dry THF and hexane, SLGNCA was polymerized in THF using sodium methoxide as initiator to give PSLG^[11]. The molecular weight and molecular weight distribution (M_w/M_n) of obtained PSLG were determined with GPC measurements on a Waters Associates-208 gel permeation chromatograph using THF as eluent.

For electrospraying/electrospinning process, PSLG solution in chloroform was placed in a syringe (5 mL) bearing a capillary (0.8 mm inner diameter) as spinneret, which was connected with a high voltage power supply (GDW-a, Tianjin Dongwen High-voltage Power Supply Plant, China). A sheet of aluminum foil, connected to the ground, was placed under the syringe as collector. A voltage of 15 kV was applied to PSLG solution with the distance between the syringe tip and the collector being 12 cm. The feed rate of the polymer solution was kept at 20 μ L/min by a micro-infusion pump (WZ-502C, Zhejiang University Medical Instrument Co., LTD, China). The resultant mats were dried under vacuum at room temperature to remove residual solvent. Cast films of PSLG were prepared by casting the solution onto slide glass and then dried under vacuum.

FT-IR/ATR spectra were recorded with a FT-IR spectrometer (Nicolet, Nexus-470, USA) with the accessories of attenuated total reflection. The morphologies of electroprocessed PSLG surfaces were recorded with a field emission scanning electron microscope (FEI, Sirion-100, USA). Samples for FESEM were coated with a 2–3 nm layer of Au to make them conductive. The diameter of beads or fibers was determined from FESEM micrographs. Water contact angle and tilt angle measurements were carried out using a CST-200 contact angle goniometer (Ningbo Xungao Intelligent Technology Co., China) equipped with a digital video camera. A water drop of 8 μ L was used. For each sample, five measurements on different locations of the surface were done for an average.

RESULTS AND DISCUSSION

The ring-opening polymerization of amino acid *N*-carboxyanhydride is the most economical and expedient process to synthesize high molecular weight poly(amino acid)s. In this work, γ -stearyl-L-glutamate *N*-carboxyanhydride (SLGNCA) was accordingly polymerized to give PSLG with a weight-average molecular weight of 3.1×10^4 and molecular weight distribution of 2.1, as shown in Scheme 1.



Scheme 1 Schematic representation for the synthesis of PSLG

The obtained PSLG was electrosprayed/electrospun from a series of solutions with concentrations from 2 wt% to 22 wt% in chloroform. At 2 wt% PSLG concentration, dish-shaped particles with diameter of about

1 μm were produced, which stuck together to form irregular cluster, as shown in Figs. 1(a), 1(b). Varied morphology was observed with increasing the concentration. Solutions of 5–16 wt% PSLG resulted in beads with a collapsed surface and size ranging from 0.5 μm to 12 μm (Figs. 1c–1j). Nanopores were observed on the surface of the beads produced from solution of 16 wt% PSLG, as shown in Fig. 1(j). Although the size range of the obtained beads was rather wide, the mean diameters of the beads was found to increase with the solution concentration in some extent, as listed in Table 1. At 17 wt% PSLG concentration, ladle type structures (Fig. 2a) were observed, while fibers with beads (Fig. 2b) occurred when the concentration of PSLG increased to 19 wt%. By increasing the concentration of PSLG to 22 wt%, microfibers with relatively regular shape and mean diameter of 4.7 μm were electrospun as indicated in Fig. 2(c). The electrospinning of PSLG solution with concentrations over 22 wt% was not successfully performed in our case because the homogenous solution was not obtained due to the limited solubility of PSLG in chloroform.

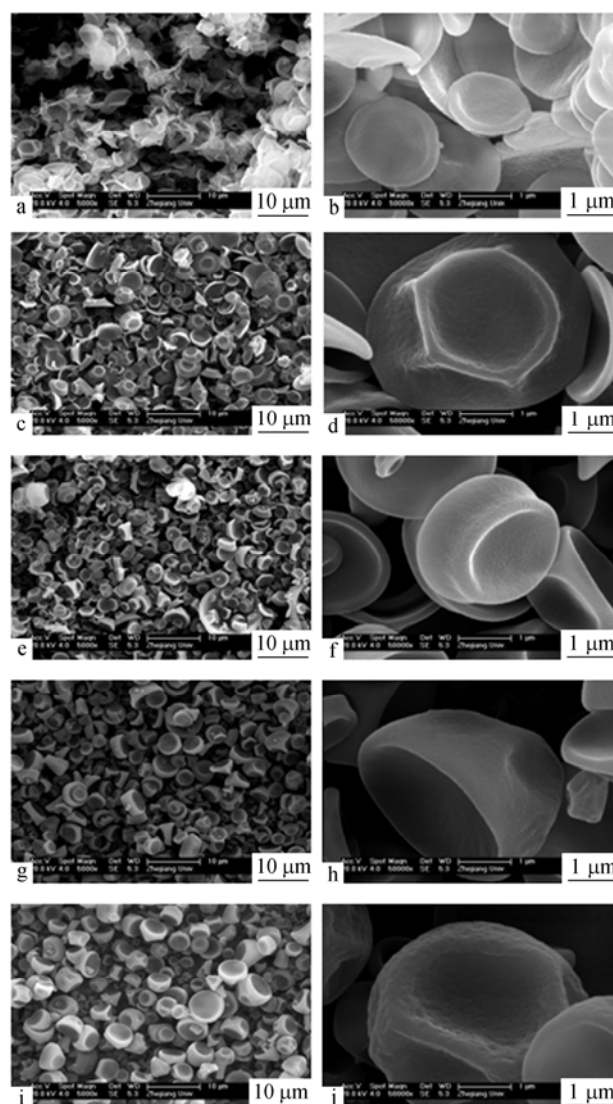
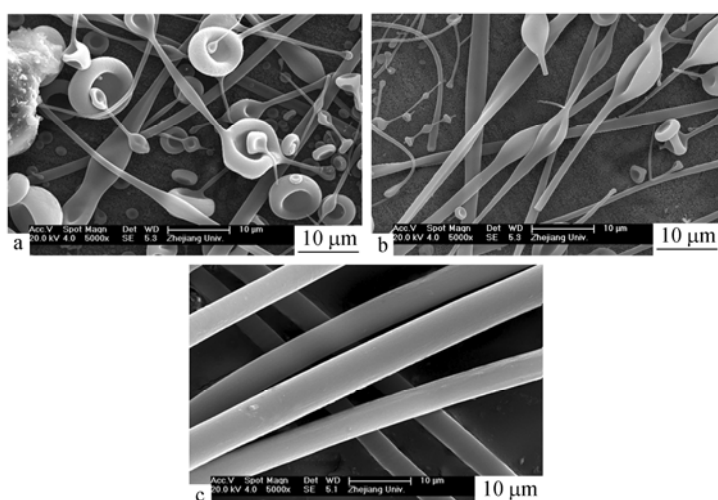


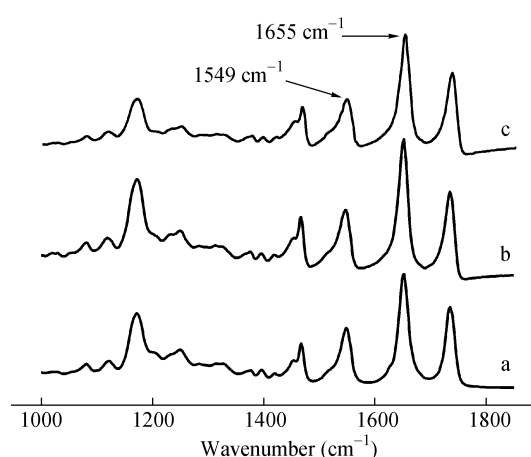
Fig. 1 FESEM images of electroprocessed structures obtained from solution of PSLG in chloroform with concentrations of 2 wt% (a, b), 5 wt% (c, d), 8 wt% (e, f), 12 wt% (g, h) and 16 wt% (i, j)

Table 1. Dimensions of the beads obtained from different PSLG concentrations

Con. (wt%)	Range of diameter (μm)	Mean diameter (μm)
2	0.86–6.65	3.02
5	0.56–5.56	3.55
8	0.90–12.33	3.65
12	1.42–6.90	3.83
16	1.85–6.22	4.45

**Fig. 2** FESEM images of electroprocessed structures obtained from solutions of PSLG in chloroform with concentrations of 17 wt% (a), 19 wt% (b) and 22 wt% (c)

Spectroscopy with attenuated total reflection (FT-IR/ATR) was used to characterize the electrosprayed/electrospun PSLG mats (Fig. 3). The spectrum of the cast PSLG film was recorded also for comparison. It was found that the electroprocessed mats displayed the same adsorption bands as those of the cast film at 1655 cm^{-1} and 1549 cm^{-1} , which had been assigned to the backbone amide of PSLG in α -helix conformation^[16]. This result indicates that PSLG main chain keeps its helical structure before and after the electroprocessing, which is consistent with that reported by Minato *et al.*^[17].

**Fig. 3** FT-IR/ATR spectra of (a) cast film, (b) beads electrosprayed from 2 wt% PSLG, and (c) microfibers electrospun from 22 wt% PSLG

The hydrophobicity of the electrosprayed/electrospun PSLG mats was investigated with static water contact angle (WCA) measurements. WCA on the cast film of PSLG was also measured for comparison. Typical images for water droplets on the cast film and electroprocessed mats are shown in Fig. 4. In comparison with the WCA of 119° for the cast film, the electrosprayed/electrospun mats displayed much higher values (150° – 170°), indicating that the hydrophobicity of PSLG surface could be changed distinctly with its morphology. It is known that the amount of air trapped between the solid surface and water droplet is the key factor for the WCA. The enhanced WCA of electroprocessed PSLG surfaces was attributed to their high surface area and roughness which lead to much air trapping. In our previous work, PSLG was tethered on the ammonia plasma treated surface of polypropylene microporous membrane to improve the hydrophobicity and biocompatibility simultaneously^[12]. WCA of the membrane surface was increased to about 112° as the graft degree of PSLG increased. This value is even lower than that of PSLG cast film. However, it seems reasonable because those amino groups generated on the membrane surface by ammonia plasma have negative effect on the WCA (about 70°). Furthermore, it was found that the roughness of polypropylene microporous membrane was decreased by the tethering of PSLG.

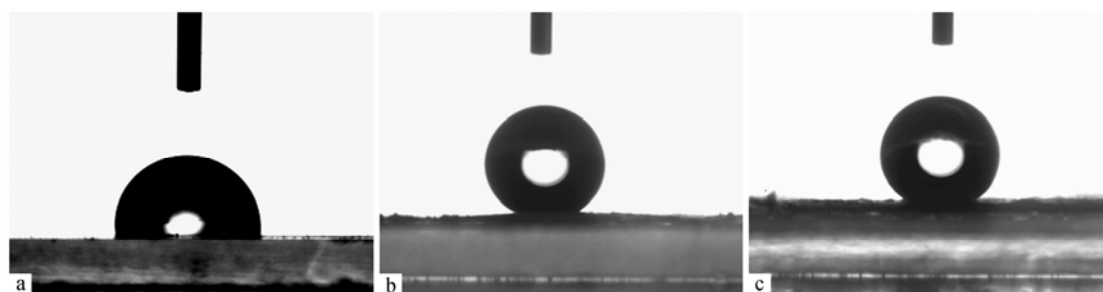


Fig. 4 Photographs taken during WCA measurements: (a) water droplet on the cast film of PSLG, (b) water droplet on the bead mat electrospayed from 2 wt% PSLG, (c) water droplet on the mat of microfibers electrospun from 22 wt% PSLG

The influence of surface morphology was further observed among the electroprocessed mats. It was found that the PSLG microfiber mats (3 – $4.7\ \mu\text{m}$ mean diameter) have WCAs ranging from 150° to 156° , while the bead mats (3 – $4.5\ \mu\text{m}$ mean diameter) display relatively high values ranging from 155° to 170° . This result is reasonably in agreement with the theoretical study by Ma and coworkers that droplet sitting on spheres has higher contact angle than that sitting on cylinders with comparable radii^[9].

Figure 5(A) shows the correlation between WCA on the bead mats and the mean diameter of the beads. It can be found that the WCA increases as the mean diameter of the beads decreases. This result indicates that the hydrophobicity of the PSLG bead mats could be enhanced by decreasing the bead dimension. Among the observed samples, the highest WCA value of 169.3° was displayed by the bead mat with mean diameter of $3.02\ \mu\text{m}$, which was electrosprayed from a 2 wt% PSLG solution.

The superhydrophobicity of the PSLG bead mats was further evaluated with tilt angle measurements. The bead mats displayed different tilt angles ranging from 4.2° to 16.5° , depending on the bead dimension, as shown in Fig. 5(B). Being consistent with the result of WCA investigation, the lowest tilt angle of 4.2° was observed on the bead mats with the WCA of 169.3° .

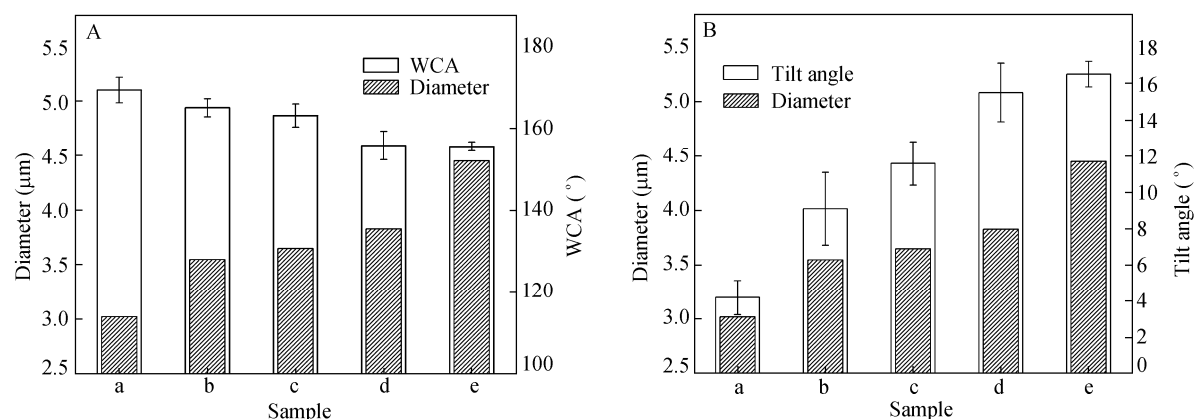


Fig. 5 The WCA (A) and tilt angle (B) on PSLG bead mats with different mean diameters of 3.02 μm (a), 3.55 μm (b), 3.65 μm (c), 3.83 μm (d) and 4.45 μm (e)

CONCLUSIONS

In summary, superhydrophobic surfaces of PSLG with WCAs and tilt angles in the ranges of 150° – 170° and 16.5° – 4.2° , respectively, were fabricated for the first time through electrospinning/electrospraying processes. Further studies concerning the surface biocompatibility and applications are undergoing.

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