

Analysis of the Nature of the Self-Assembly Phenomenon of Nano-fibers for Tissue Engineering and Drug Delivery

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INTRODUCTION

Nanotechnology is an emerging field which uses the principles of science and engineering to fabricate materials or structures with dimensions in the nanometer scale [1]. The great interest in nanoscale materials stems from the unusual and unique property profile these materials exhibit compared to macromaterials. Novel physical, chemical and biological properties such as unique shape, orientation, surface chemistry, topology and reactivity exhibited by these materials originate from their small dimensions. These material properties translate into unusual electrical, optical, magnetic, mechanical, thermal and biological properties for these materials. Some of the nanostructures or nanoscale materials currently under investigation include quantum dots and wires, nanoscale self-assemblies and thin films, nanocrystals, nanotubes, nanowires, nanorods, nanofoams, nanospheres and nanofibers.

This project deals primarily with “*Molecular self-assembly*”. This is a complex strategy for nanofabrication that involves designing molecules and super molecular entities so that propensity to shape complement causes them to aggregate into desired structures. Self-assembly exhibits many advantages as a strategy, as it carries out many of the most difficult steps in nanofabrication particularly the ones involving atomic-level modification of structure using very highly developed techniques of synthetic chemistry. In the direction of producing and controlling self assembly structure, block copolymers or segmented polymeric are interesting because they can microphase separate and organize to form periodic nanostructures.

During the second phase of this proposal we continued with the synthesis and characterization of the poly(ethylene oxide)-co-poly(caprolactone) and poly(teramethylene glycol) co-poly(caprolactone) block copolymers as a key component in molecular self-assembly. (*See section 1- Multiblock Copolymer Synthesis and Characterization*). We also evaluated the structural and physical characteristics of fibers formed during electro-spinning process. We designed an electro spinning machine and started with the study of the effect of the polymer concentration and electric field on fiber diameter and distribution. (*See section 2- Electro-spinning process*). The main accomplishments made during this period are presented below.

RESULTS AND DISCUSSION

Materials

ϵ -Caprolactone, stannous octoate (SnOct₂), poly(ethylene glycol) (PEG) (M_w= 1500, 8000 gr/mol), Polyteramethylene glycol (PTMG) (M_w= 650, 2000, 2900 gr/mol) and anhydrous toluene were used as received from Aldrich.

1- Multiblock Copolymer Synthesis and Characterization

Five PCL-b-DIOL-b-PCL (PCL: poly caprolactone) triblock copolymers with different DIOL/PCL ratios were synthesized by ring-opening polymerization, which was carried out in a reactor flask containing a Teflon-coated stirring bar. Predetermined amounts of PEG or PTMG, ϵ -caprolactone, SnOct₂ (0.1 g) and dried toluene were put into the reactor flask. The reaction sample was heated using an oil bath at 120 °C for 48 h. The triblock copolymers were prepared by coupling the hydroxyl end groups of the diol to the resulting open molecule formed during the ring-opening polymerization of the ϵ -caprolactone. The synthetic scheme is shown in Figure 1.

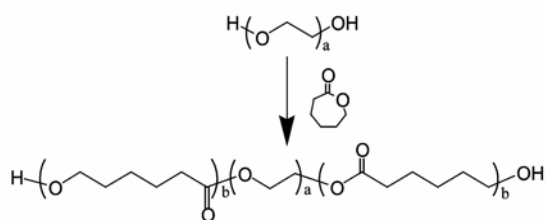


Figure 1 Synthetic scheme of a triblock copolymer PCL-b-DIOL-b-PCL

After completion of the reaction, the resulting polymers were dissolved in methylene chloride and then precipitated into excess diethyl ether and dried in a vacuum oven. These procedures were repeated three times. The compositions and characteristics of the resulting triblock copolymers are shown in Table 1.

During this phase, we also prepared samples with different PCL block length and constant PEG or PTMG amounts. The results are also included in table 1.

The molecular weights of the PCL-DIOL-PCL triblock copolymers, determined by gel permeation chromatography (GPC) are included in Table 1. The progress of reaction was also followed by GPC.

Table 1 Compositions and characteristics of the PCL-b-DIOL-b-PCL triblock copolymers

Sample Name	Diol	Diol Molecular mass gr/mol	Theoretical molecular mass gr/mol	Calculated Molecular mass (GPC) gr/mol
PCL(5000)-b-PEG(1500)-b-PCL(5000)	PEG 1500	1500	11500	5621
PCL(5000)-b-PEG(8000)-b-PCL(5000)	PEG 8000	8000	18000	16555
PCL(5000)-b-PTMG(650)-b-PCL(5000)	PTMG 650	650	10650	
PCL(5000)-b-PTMG(2000)-b-PCL(5000)	PTMG 2000	2000	12000	
PCL(5000)-b-PTMG(2900)-b-PCL(5000)	PTMG 2900	2900	12900	11552
PCL(10000)-b-PEG(1500)-b-PCL(10000)	PEG 1500	1500	21500	
PCL(10000)-b-PEG(8000)-b-PCL(10000)	PEG 8000	8000	28000	
PCL(10000)-b-PTMG(650)-b-PCL(10000)	PTMG 650	650	20650	
PCL(10000)-b-PTMG(2000)-b-PCL(10000)	PTMG 2000	2000	22000	
PCL(10000)-b-PTMG(2900)-b-PCL(10000)	PTMG 2900	2900	22900	

Differential scanning calorimeter (DSC) analysis of the PCL- DIOL-PCL triblock copolymers was performed. Table 2 shows the melting transition and the enthalpy of melting for the different copolymers. During the cooling curve, larger enthalpy of crystallization was observed for the different copolymers. The hysteresis of the melting peak and the crystallization peak comes from the slower crystallization rate than melting rate during the DSC experiment with the heating/cooling rate of 10 °C/min.

Table 2 Differential scanning calorimeter analysis of the triblock copolymers

Sample Name	Melting Temperature °C	Enthalpy of melting J/gr
PCL(5000)-b-PEG(1500)-b-PCL(5000)	52.1	101.4
PCL(5000)-b-PEG(8000)-b-PCL(5000)	98.8	160.3
PCL(5000)-b-PTMG(2900)-b-PCL(5000)	28.7	66.0

2- Electro-spinning process

During the second phase of this proposal we designed an electro spinning machine (See Figure 2). Electrospinning is a spinning process which uses high voltage electrostatic field in order to produce fibers with diameter range from several microns down to 100nm or less. After the set-up of electrospinning machine we started with the study of the effects of the polymer concentration and electric field on fiber diameter and distribution.



Figure 2 - Electro spinning machine designed in the Polymer Nanocomposite Center/Polymer and Fiber Engineering Department at Auburn University.

The following images obtained from the scanning electron microscope (SEM) show the effects of the polymer concentration on fiber diameter and distribution. Under the fixed conditions of voltage (10 KV), flow rate and work distance (10 cm) between the target and syringe, an increase in diameter was observed as the concentration was increased from 10 to 20 wt%. However, the opposite effect was observed when voltage (from 10 to 20 KV) was increased under fixed conditions of concentration, flow rate and work distance. A higher voltage reduced the diameter of electrospun fibers.

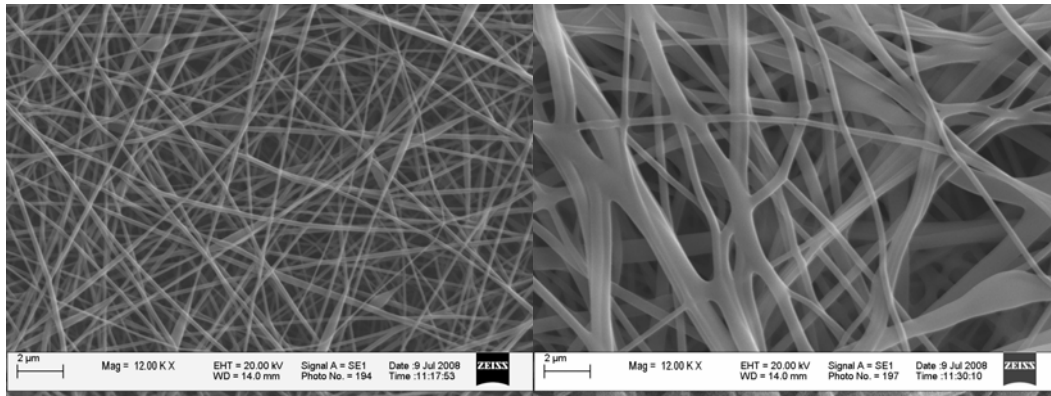


Figure 3 - Electrospun fibers

Future work

During the third phase of this project, we will continue with the evaluation of the block length on the morphology of solid films. The compositions and characteristics of the resulting triblock copolymers will be analyzed. Different techniques will be used in order to understand the phase separation effect and the organization/assembly of the final structures (e.g. Atomic Force Microscopy, Light Scattering and Optical Microscopy).

REFERENCES

1. Nalwa, H.S., Handbook of nanostructured materials and nanotechnology, Academic Press, San Diego, 2000.
2. Whitesides G. M., Self Assembly and Nanotechnology, paper presented in the Fourth Foresight Conference on Molecular Nanotechnology, held November 9-11, 1995, in Palo Alto, California.