Mechanical properties and morphology of electrospun mats made of poly (ω-pentadecalactone)

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Abstract. Electrospinning of biodegradable poly(ω-pentadecalactone) (PPDL) is poorly investigated. In the present work, PPDL homopolymers of different molecular weight were synthesized by ring-opening polymerization of ωPDL, and then electrospun. Mixtures of PPDL with hexafluoro-2-propanol (HFIP) and with HFIP-chloroform blend were used for electrospinning. Since PPDL is poorly soluble in HFIP at high concentrations, the PPDL-HFIP mixture was turbid and its electrospinning led to heterogeneous mats. Addition of 30% of chloroform to the PPDL-HFIP mixture turned it into a transparent solution. After electrospinning, the PPDL-HFIP-chloroform mixtures yielded mats, which consisted of flat and round fibers with a wrinkled surface. The flat fibers (ribbons) were observed more frequently when the PPDL sample with the highest molecular weight was electrospun. All the obtained electrospun mats demonstrated high elongation at break (from 150% to 350%). In our future research, these mats will be examined as biomaterials.

1. Introduction
Electrospinning is a versatile method that uses electrostatic field to produce fibrous materials. A great variety of polymers from synthetic polyesters to proteins and polysaccharides could be used to produce electrospun nanometer-scale fibers and, finally, polymer mats and scaffolds with regulated surface area, morphology, porosity and mechanical properties [1]. Electrospun mats attract significant attention as scaffolds for cell culturing [2], tissue engineering [3] and wound healing [4], because of the similarity between the electrospun fibers and the extracellular matrix morphology.

Mechanical properties of electrospun mats are highly important for biomedical applications. Cells adhesion, differentiation, shape and cytoskeleton structure depend on the physical properties of the cell substrate, such as stiffness, roughness and elasticity [5].

Mechanical properties of electrospun mats might differ favorably from the properties of the same polymer materials fabricated by others methods [6]. They strongly depend on mat structure and vary greatly with the changing fiber diameter [7], morphology [8] and alignment [9]. Moreover, mechanical properties of electrospun mats could be enhanced or tuned either physically or chemically.
by heat treatment [10], solvent vapor treatment [11], crosslinking [12], and by adding new components [13] or plasticizers [14].

To date, electrospun materials based on widely-used polymers like polylactide (PLA) [10,15], polylactide-co-glycolide (PGLA) [16], poly(ε-caprolactone) (PCL) [6] and poly(trimethylene carbonate) (PTMC) [17] are intensively studied. Electrospun products of ω-pentadecalactone (ωPDL) (co)polymerization [18] and homopolymerization have been far less investigated, despite the fact that they demonstrate promising shape memory effect [19] and increase neurite outgrowth in comparison with traditional PLA fibers [20].

In the present paper, we report an effective method of controlled ring-opening polymerization of ωPDL, which yielded PPDL homopolymers of different molecular weight. The main purpose of the work was to determine the effect of molecular weight and electrospinning conditions on morphology and mechanical properties of the electrospun material.

2. Materials and methods

2.1 Materials

CDCl₃ (99.8% atom D), 2,6-di-tert-butyl-4-methylphenol (>99%), Bu₂Mg (1.0 M solution in heptane) and ω-pentadecalactone (>98%) were purchased from Sigma-Aldrich (USA). [(BHT)Mg(OBn)(THF)]; was prepared according to the literature [21]. Chloroform (99.8%) and 1,1,1,3,3,3-hexafluoroisopropanol (99%) were purchased from Component-Reagent (Russia) and P&M-Invest (Russia) respectively.

2.2 Polymer characterization

PPDL samples were characterized by ¹H and ¹³C Nuclear Magnetic resonance (NMR) spectroscopy, by Differential Scanning Calorimetry (DSC), by Size Exclusion Chromatography (SEC) and by X-ray diffraction (XRD). NMR spectroscopy studies were performed on a Bruker AV400 instrument. DSC thermograms were recorded on a DSC823 Mettler Toledo system at a rate of 10°C·min⁻¹ under an argon atmosphere. SEC measurements were carried out on an Agilent PL-GPC 220 chromatograph equipped with a PLgel Oxelis column (eluent: tetrahydrofuran, 1 ml·min⁻¹, 40°C). The X-ray diffraction studies were carried out at a Rigaku Rotaflex RU-200 instrument with a rotating copper anode, equipped with a wide-angle horizontal goniometer Rigaku D/Max-B and a scintillation point detector.

2.3 Mats preparation by electrospinning

Electrospinning was carried out for PPDL-HFIP (100 mg/ml) and PPDL-HFIP-chloroform mixtures using Nanofiber Electrospinning Unit (China). Electrospinning of both compositions (PPDL-HFIP with and without chloroform) was performed under the same conditions: the accelerating voltage was 30 kV; feed rate was 1 mL; the distance between the needle (inner diameter 0.7 mm) with the polymer solution and the counterelectrode (metallic plate) was 20 cm.

2.4 Scanning electron microscopy (SEM)

The PPDL electrospun mats were covered by 10 nm gold-palladium alloy using Sputter Coater Q150T (Quorum Technologies, UK) and examined with a Zeiss Merlin microscope equipped with Gemini II Electron Optics (Zeiss, Oberkochen, Germany). SEM imaging was done at 1 kV accelerating voltage and 50–70 pA probe current.

2.5 Mechanical tests

Mechanical tests were carried out on a TiraTest-2200 tensile machine (movement speed: 5 mm/min, the sample geometry: 10×3×0.03 mm).

3. Polymer synthesis and characterisation

Different methods and catalysts have been applied in ωPDL polymerization. The use of non-toxic coordination catalysts based on "biometals" such as Mg [22] is attractive for the synthesis of polymers
for biomedical applications. Recently we demonstrated that heteroleptic BHT-Mg catalysts (BHT = 2,6-di-tert-butyl-4-methylphenoxy) are highly effective in ωPDL ROP [23].

In this work we used a BHT-Mg single-component catalyst of the formula [(BHT)Mg(μ-OBn)(THF)]2 [21]. Before polymerization, ωPDL was heated at 90–95 °C in vacuum (0.01 Torr) with stirring for 1 hour. Reactions were performed under an argon atmosphere in flame-dried glass vials. Calculated amount of Mg catalyst (1M toluene solution) was injected into well-stirred ωPDL melt at 100 °C, ωPDL/Mg molar ratios were 100, 150 and 200. After 2 hours of stirring, the product was dissolved in minimal volume of boiling toluene, and precipitated by methanol containing 5 eq. of acetic acid. This operation was repeated without addition of AcOH; ωPDL polymer (PPDL) was filtered off and dried in vacuo at room temperature for 8-12 hours (0.01 Torr) to constant mass. The yields were 93% (PPDL-100), 95% (PPDL-150) and 96% (PPDL-200).

Molecular weights of PPDL were determined by SEC and by end-group analysis of 1H NMR spectra (Table 1) by comparative integration of signals of PhC=O– group of BHT-Mg initiator and –CH2OH end group with signals of –OC₂H₅ and –C(O)C₂H₅ fragments in PPDL chain (Figure 1).

Table 1. PPDL samples obtained by [(BHT)Mg(μ-OBn)(THF)]2 catalyzed ROP of ωPDL in bulk at 100 °C (2 h reaction). \( M_n^{\text{theo}} \), \( M_n^{\text{NMR}} \) and \( M_n^{\text{SEC}} \) are number average molecular weights that are (a) theoretically calculated, found by (b) NMR 1H and by (c) SEC measurements. \( D_M \) is the polydispersity index defined as \( M_w^{\text{SEC}} / M_n^{\text{SEC}} \), where \( M_w^{\text{SEC}} \) is the mass average molecular weight found by SEC. Crystallinity was estimated based on DSC and XRD data; the estimated melting enthalpy for 100% crystalline PPDL is 220 J g⁻¹.

| Sample | ωPDL/Mg molar ratio | \( M_n^{\text{theo}} \), a) kDa | \( M_n^{\text{NMR}} \), b) kDa | \( M_n^{\text{SEC}} \), c) kDa | \( D_M \) | DSC peak, °C | Estimated crystallinity, % |
|--------|----------------------|-----------------|-----------------|-----------------|----------|----------------|--------------------------|
| PPDL-100 | 100 | 24.2 | 28.5 | 35.1 | 3.3 | 96.1 | 95.3 | 73±5 |
| PPDL-150 | 150 | 36.2 | 37.3 | 48.2 | 3.3 | 97.3 | 96.1 | 72±5 |
| PPDL-200 | 200 | 48.2 | 43.9 | 59.0 | 3.4 | 99.8 | 98.9 | 70±5 |

Figure 1. 1H NMR spectrum (CDCl₃, 20 °C) of PPDL-100
The found \( M_n^{\text{SEC}} \) values are systematically overestimated by ca. 30% compared to \( M_n^{\text{NMR}} \) due to calibration with a polystyrene standard within SEC measurements. In general, good agreement of \( M_n \) values obtained by NMR and by SEC confirms the living character of \( \omega \text{PDL} \) polymerization initiated by the BHT-Mg benzyloxy complex. Broadening of Molecular Weight Distribution (MWD) may be addressed to possibility of binuclear and mononuclear coordination mechanisms proposed for heteroleptic magnesium complexes \([21]\), and immortal character of the reaction mixture that allows transesterification reactions after full monomer consumption \([22]\).

4. Electrospinning
All PPDL-HFIP mixtures at 100 mg/ml concentration and room temperature were unstable and turbid that resulted in heterogeneous electrospun fibers morphology. To avoid this, the chloroform was added to PPDL-HFIP mixtures until they became transparent. The minimal volume fraction of chloroform, which transformed all PPDL-HFIP mixtures into stable homogeneous phases, was 30%. The same effect was reached if PPDL-HFIP mixtures were heated up to 40 °C. We think that the PPDL-HFIP system demonstrated a behavior with the upper critical solution temperature.

Electrospun mats fabricated from the unstable PPDL-HFIP mixtures consisted of heterogeneous fibers of different sizes and forms: mainly flat (ribbons) and cylindrical fibers with transverse and longitudinal wrinkles (Figure 2). Such variety in morphology could be associated with the heterogeneity of the solutions. Addition of chloroform allowed us to fabricate homogeneous electrospun mats (Figure 3). It turned out, that wrinkles are a common feature for all the electrospun PPDL fibers, regardless of the polymer molecular weight and the solvent used.

![Figure 2. Mats fabricated from PPDL-HFIP mixtures: (A) PPDL-200; (B) PPDL-150; (C) PPDL-100.](image)

![Figure 3. Electrospun mats fabricated from PPDL-HFIP-chloroform mixtures: (A,B) PPDL-200; (C,D) PPDL-150; (E,F) PPDL-100.](image)
In our case, wrinkled fiber surface took place for all polymers mixtures; this effect could be associated with features of the charging process of PPDL jet during electrospinning and the following buckling instability [24]. Moreover, fiber shapes changed with molecular weight of PPDL: flat fibers (ribbons) were prevalent for > 45 kDa PPDL (PPDL-200), round fibers – for 25–35 kDa (PPDL-100 and PPDL-150), but ribbons could be found more likely in mats formed from PPDL-150 than on mats prepared from PPDL-100.

All the electrospun PPDL mats demonstrated high elongation at break (Table 2), unlike the electrospun mats made of PLA [20]. While PPDL-100 and PPDL-200 gave the similar value of elongation at break for different mixtures, elongation at break for PPDL-150 electrospun from HFIP-chloroform blend was two times exceeded the elongation at break value for PPDL-HFIP mixture.

5. Conclusion
We present the controlled synthesis of PPDL using a non-toxic BHT-Mg catalyst. By the selection of electrospinning conditions, we obtained homogeneous fibrous materials with uniform morphology and promising mechanical characteristics. We found, that the shape of the electrospun fibers (cylindrical fibers or ribbons) depended on the molecular weight of the polymers: more ribbons were observed for a polymer with a higher molecular weight. All the electrospun PPDL fibers had a wrinkled structure regardless of the mixture type. The highest elongation at break value was approximately 350% for PPDL-150 electrospun from HFIP-chloroform mixture.

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