

Combining oligothiophene with oligo-(D,L-lactide) into a complex, branched topology toward a functional interface aimed at biomedical applications

•Anca-Dana Bendrea^{1*}, Natalia Simionescu¹, Elena-Gabriela Hitruc², Luminita Cianga¹, Ioan Cianga¹ and Mariana Pinteala¹

¹Centre of Advanced Research in Bionanoconjugates and Biopolymers “Petru Poni” Institute of Macromolecular Chemistry 41 A, Grigore-GhicaVoda Alley, 700487 Iasi, Romania; e-mail: anca.bendrea@icmpp.ro (A.-D. B.); ioanc@icmpp.ro (I.C.); lcianga@icmpp.ro (L.C.); natalia.simionescu @icmpp.ro (N.S.); pinteala@icmpp.ro (M.P.)

²Department of Physics of Polymers and Polymeric Materials, “Petru Poni” Institute of Macromolecular Chemistry, 41 A, Grigore-GhicaVoda Alley, 700487 Iasi, Romania; e-mail: gabihit@icmpp.ro (E.-G. H.)

INTRODUCTION & AIM

The last decades have witnessed an increasing interest in advanced electroactive biomaterials based on conducting, π -conjugated polymers with a “rod-graft-coil” architecture, for use in different biomedical applications. Such topology offers, in addition to the freedom of various combinations of chemistries, also the opportunity to program, optimize and control, from the molecular design stage, the processing-structure-properties relationship and the self-assembly pathway. The present report focus on the study of those properties of an oligothiophene grafted with oligo-(D,L-lactide) (OTH-PDLLA) that allow to establishing its suitability as a biomaterial. Thus, its capability for forming thin films, on either rigid or flexible supports, using for processing solvents with different polarities and variable concentrations and films surface properties were explored employing dynamic laser-scattering (DLS), contact-angle measurement and atomic force microscopy (AFM). The results of the OTH-PDLLA interactions with normal human gingival fibroblasts (NHGF) cells proved the oligomer's biocompatibility, this being the first that advocate for OTH-PDLLA potential as electroactive biointerface or as active layer in flexible and/or implantable transient electronics.

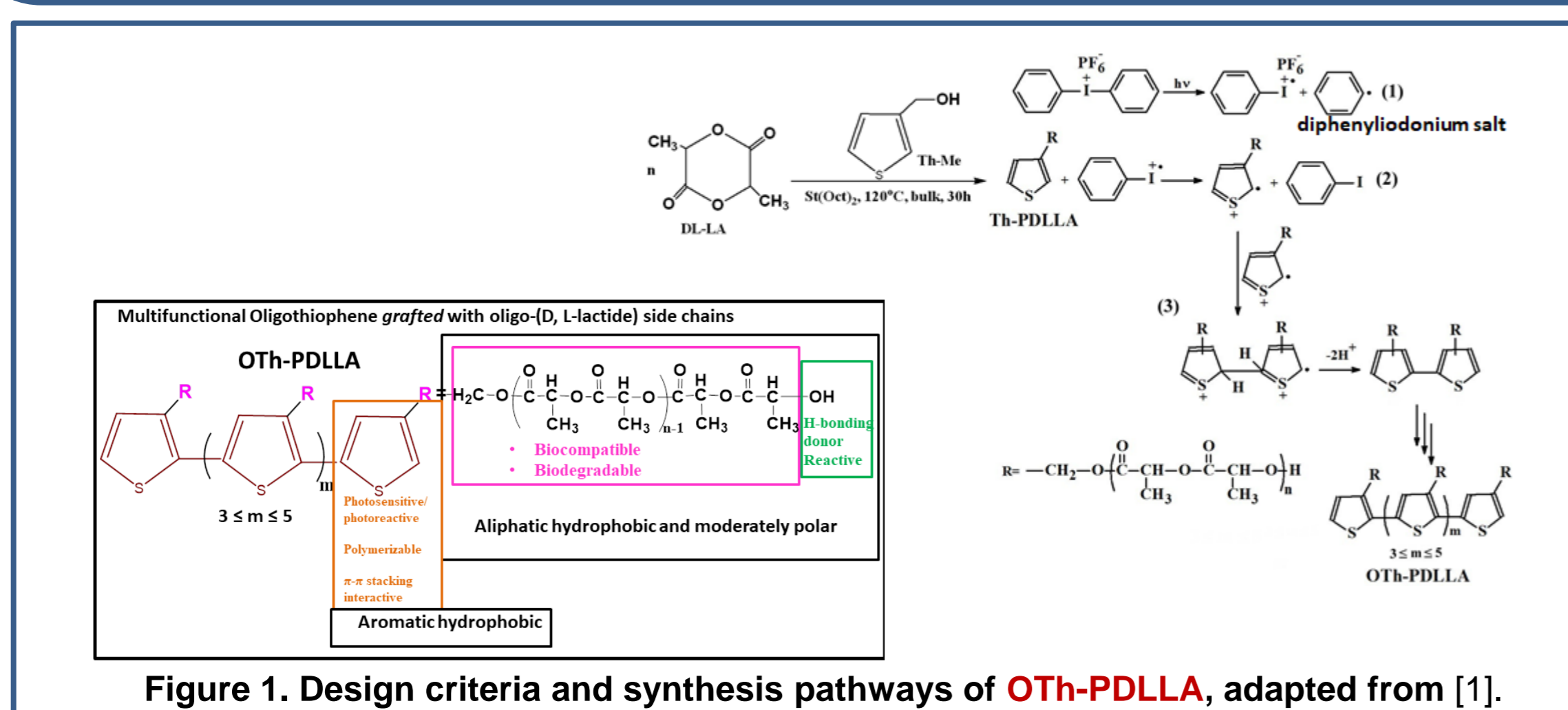


Figure 1. Design criteria and synthesis pathways of OTH-PDLLA, adapted from [1].

Table 2. Hydrodynamic radii, water contact angle, surface roughness of OTH-PDLLA films and particles size in dry state measured by AFM

Sample	Particle size by DLS(nm)	Water Contact angle (degree) of oligomer's films deposited on		Roughness by AFM (nm)		Particle size by AFM (nm)
		Glass ¹ (78)	PLA ¹ (82)	Glass (2.55)	PLA (36.5)	Glass
OTH-PDLLA DMSO,10mg/ml	600;5100	83	80	53	73	width=600, height=40
OTH-PDLLA CHCl ₃ ,10mg/ml	947	85	-	15	-	600
OTH-PDLLA CHCl ₃ ,1mg/ml	934	74	-	41	-	450

¹Values of water contact angle for uncovered supports; ² Calculated for 10x10 μ m² area scanning;

Figure 4. Size distribution by intensity of particles formed by OTH-PDLLA in DMSO and Chl

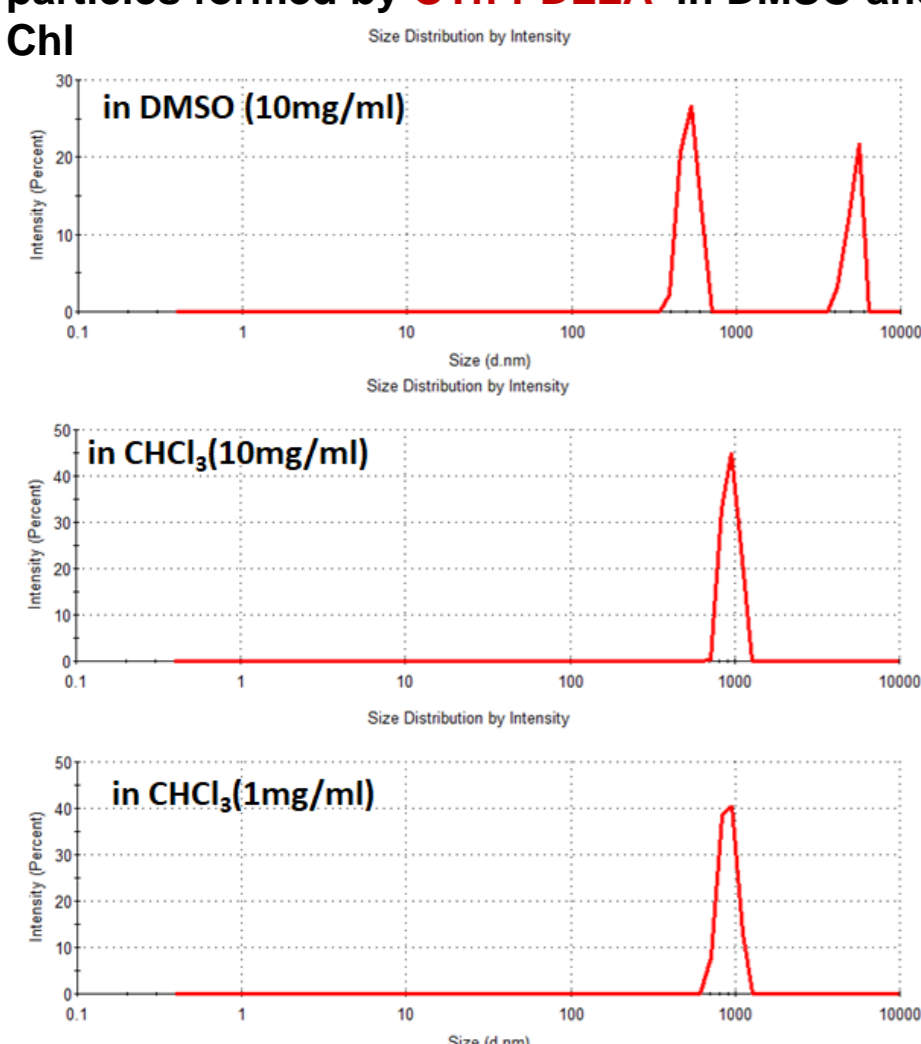


Table 1. Several physical properties of the used solvents for investigations and those of the OTH-PDLLA oligomer's constitutive parts

Compound (e) ^k	Hansen Solubility parameters (MPa ^{1/2})				Solvent-Polymer interaction parameters (χ)		
	δ_D	δ_P	δ_H	δ_T	Chl	DMSO	CH ₂ Cl ₂
PDLLA	18.6	9.9	6	22/20.5	0.32	0.28	0.99
Thiophene;(2.86)	18.9	2.4	7.8	20	miscible ^a		
P3HT	18.5	2.8	4.51				
Chl (4.81)	17.8	3.1	5.7	19			
nonpolar in accord with its dielectric constant value							
DMSO (46.68)	18.2	6.3	6.1	20.3			
Polar solvent with high dielectric constant							

^a- experimentally noticed; ^k- dielectric constant

REFERENCES

Bendrea, A. D.; Cianga, L.; G6en Colak, D.; Constantinescu, D.; Cianga, I. Thiophene End-Functionalized Oligo-(D,L)-Lactide as a New Electroactive Macromonomer for the “Hairy-Rod” Type Conjugated Polymers Synthesis. *Polymers*. **2023**, *15*, 1094

Figure 1. AFM images for OTH-PDLLA films obtained from its dispersion in Chl at c=10mg/ml (a) and c= 1mg/ml (b)

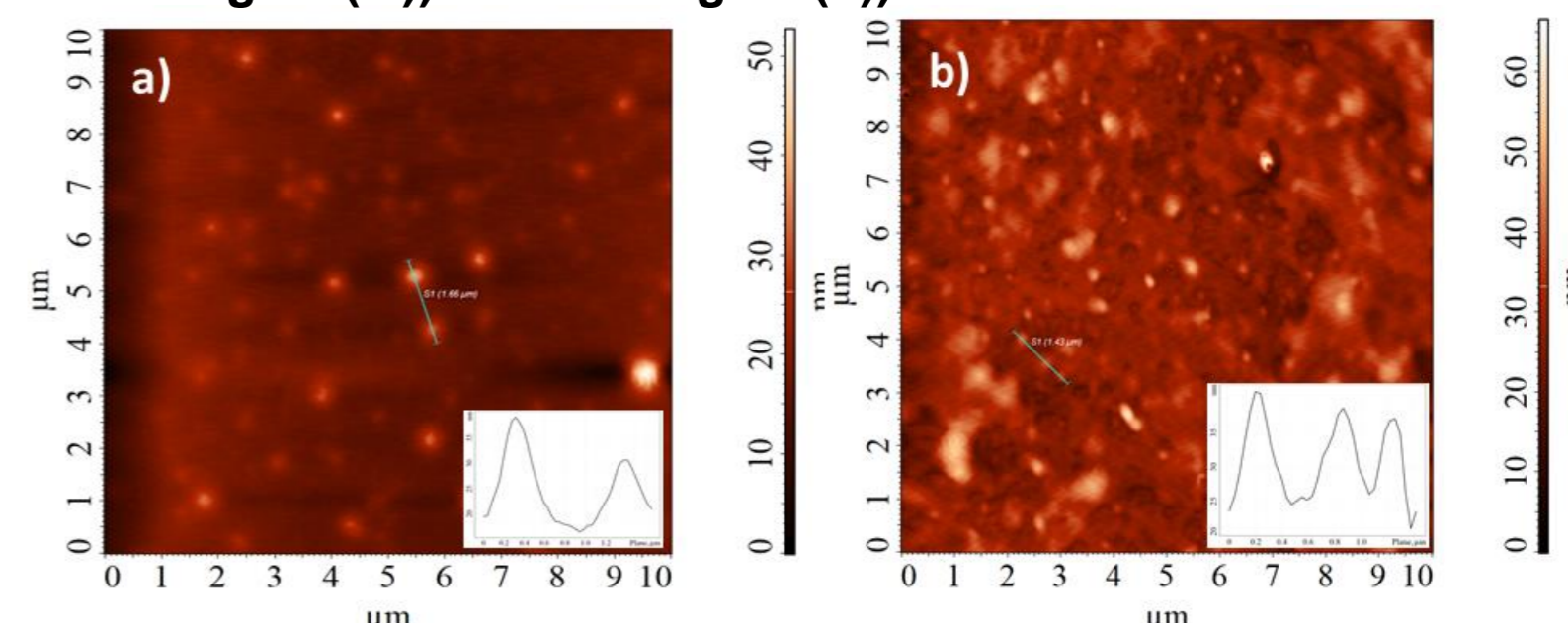


Figure 2. AFM images for OTH-PDLLA films obtained from its dispersion in DMSO at c=10mg/ml deposited on glass (a) and PLA film (b)

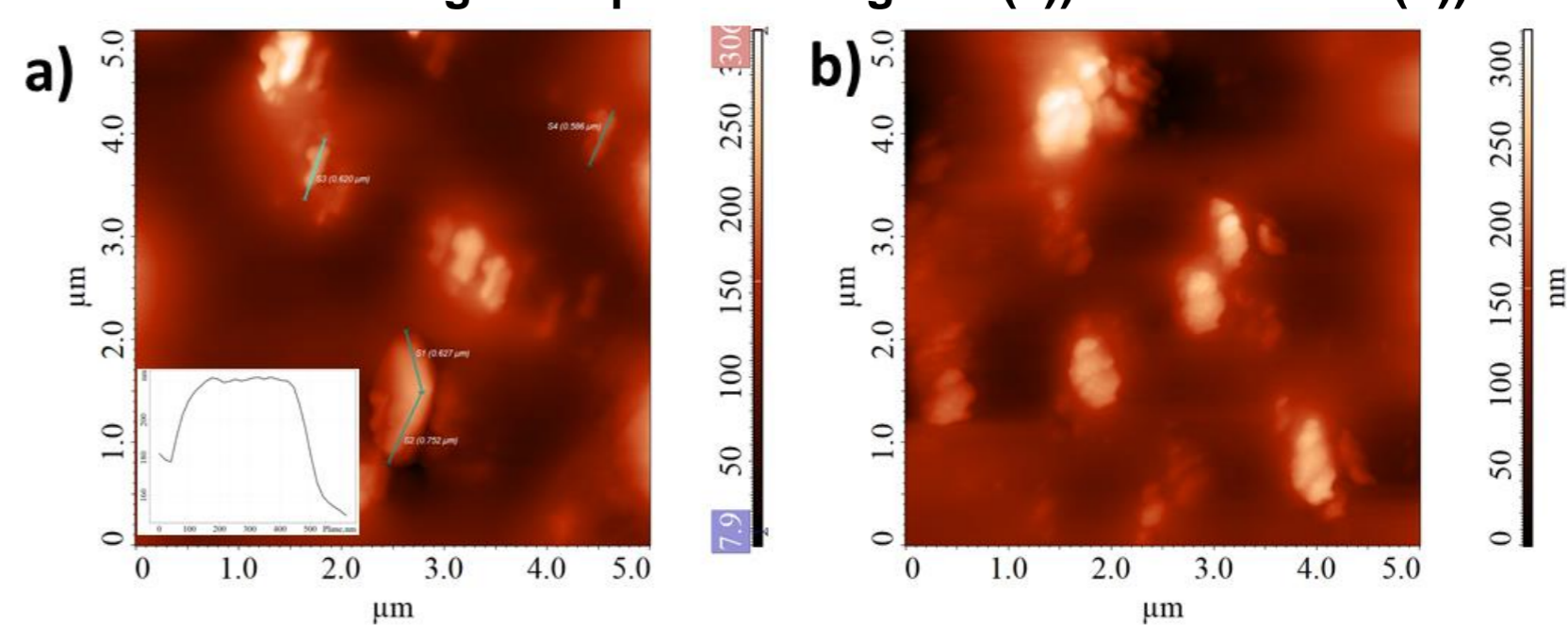
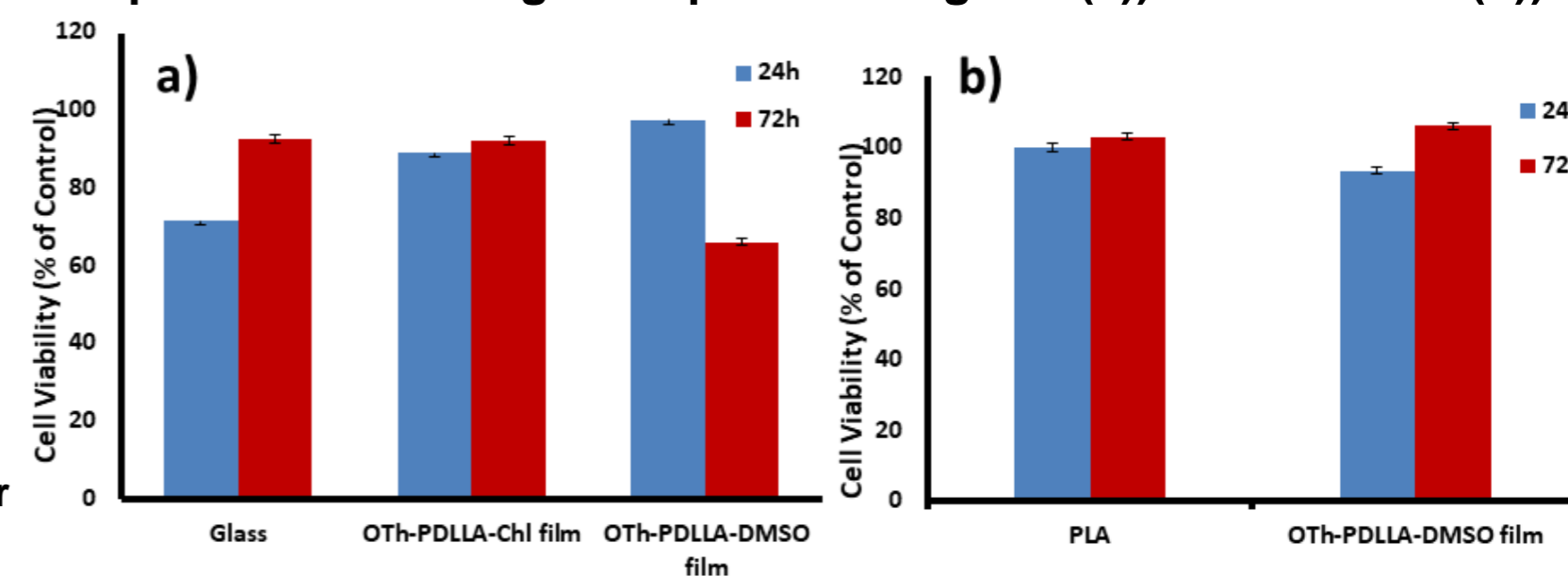


Figure 3. In vitro cell viability of NHGF seeded on OTH-PDLLA films obtained from its dispersion at c=10mg/ml deposited on glass (a) and PLA film (b)



CONCLUSION

The present study showed that OTH-PDLLA offer several ways to modulate films surface topography properties in order to adjust their interactions with biological entities as proteins or cells. Employing techniques like dynamic laser-scattering (DLS), contact-angle measurement and atomic force microscopy (AFM) changes in the in particle's size, in wettability and films surface topography were investigated. Notably, keeping constant the nature of solvent but varying solution's concentration the films roughness can be varied, while solvent polarity has more influence in films morphology than in their wettability. Using MTS assay the oligomer's biocompatibility was also confirmed. These are important aspects that advocate for OTH-PDLLA potential use as biocompatible bioelectronic interface or, based on its structural potential for biodegradation, for transient electronics.