SYNTHESIS AND CHARACTERIZATION OF NOVEL AMPHIPHILIC POLY(2-OXAZOLINE)-BASED COPOLYMERS FOR SURFACE MODIFICATION OF BIOMATERIALS

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Introduction

Poly(2-oxazolines) (POx) are an important class of polymers that have attracted substantial attention recently and are emerging as stabilizers, adhesives, surfactants and dispersants. Polymer synthesis from 2-oxazoline monomers is typically carried out via a cationic ring opening polymerization [1].
The aim of this study was to synthesize novel gradient amphiphilic poly(2-oxazoline)-based copolymers containing reactive allyl groups for further modification e.g. by peptides or drugs. To this end POx containing free allyl groups with different ratio of 2-ethyl-2-oxazoline (EtOx) to 2-(4-allyloxyphenyl)-2-oxazoline (AllPOx) were prepared.

Materials and Methods

AllPOx and methyl 4-nitrobenzenesulfonate were dried in a flask for 3 h. Then, EtOx and benzonitrile (2 mL) were added. Copolymerization was performed for 24 h at 110°C under argon and terminated with methanolic KOH (0.1 mol/dm^3, 1.2 mL) at room temperature for 2 h.
Gradient copolymers of EtOx with AllPOx were prepared in different molar ratios of both monomers (90:10, 80:20, 85:15, 75:25, 70:30 and 60:40) through one-pot cationic copolymerization at 110°C for 24 h in benzonitrile (c = 3 mol/dm^3). In all cases, cationic copolymerizations were initiated by methyl 4-nitrobenzenesulfonate ([M]/[I]=100). Prepared copolymers were purified by dialysis against ethanol, water/ethanol 70:30, and water.
The ^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature on a Varian VXR-400 using tetramethylsilane (TMS) as an internal standard. FTIR (Nicolet iS5-iD5spectrometer with the resolution of 4 cm^{-1}), in attenuated total reflection mode (ATR, with ZnSe crystal) was used. XPS studies were performed on K-Alpha high-performance Thermo Fisher spectrometer to study surface chemical composition. To evaluate molar mass and dispersity GPC was used (Agilent Technologies, trifluoroethanol, PMMA calibration).
Cytotoxicity of the obtained POx was assessed in contact with mice 3T3 fibroblast cell line by MTT assay at 560 nm and 750 nm.

Results and Discussion

Gradient copolymers of 2-ethyl-2-oxazoline (EtOx) with 2-(4-allyloxyphenyl)-2-oxazoline (AllOPhOx) were prepared in different molar ratios of both monomers through one-pot cationic copolymerization (FIG. 1).

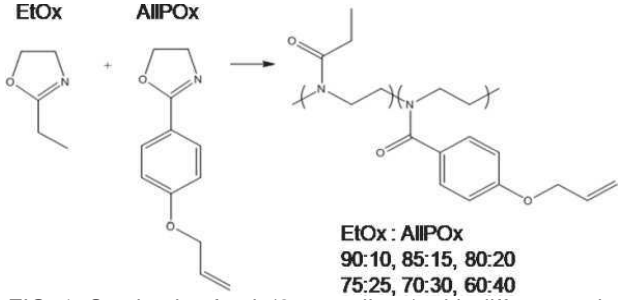

FIG. 1. Synthesis of poly(2-oxazolines) with different ratio of EtOx:AllPOx.

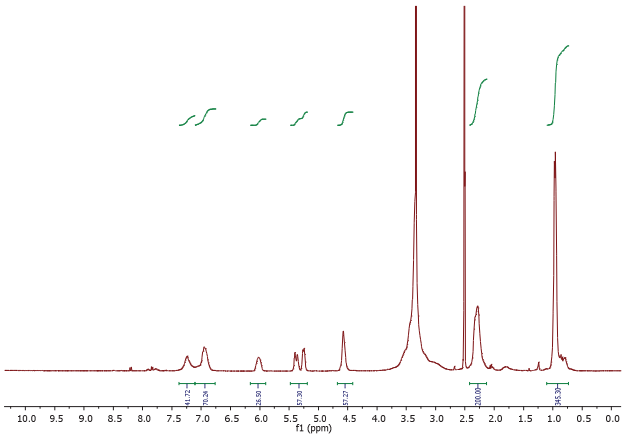

FIG. 2. ^{1}H NMR spectrum of POx with EtOx:AllPOx 80:20.

^{1}H NMR confirmed the composition of copolymers to be very close to feeding ratio of monomers (e.g. 78:22 for EtOx:AllPOx feeding ratio of 80:20). XPS showed presence of carbon, oxygen and nitrogen on the surface; atomic ratio was as expected. FTIR results showed the characteristic bands for POx: at 1130 cm^{-1} and 1620 cm^{-1}; the latter is characteristic for poly(2-oxazolines) and is due to stretching vibrations of C=O and C-N groups.
Molar mass for EtOx:AllPOx feeding ratio of 80:20 was 9700 g/mol, D=1.63. Obtained POx were found cytocompatible with model cells.

Conclusions

In this study, we obtained library of POx with defined structure and surface properties suitable for modification with peptides supporting cell adhesion.

Acknowledgments

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