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Peculiarities of linear and hyperbranched polyglycidols in water and aqueous surfactant solutions

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ABSTRACT

Linear and hyperbranched polyglycidol (LPGL and HPGL) with average molecular weight of a few thousands were studied in water and surfactant solutions. The employed surfactants are hexaethyleneglycol mono *n*-dodecyl ether ($C_{12}E_6$), cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). The working methods are surface tension, steady-state fluorescence, dynamic light scattering (DLS), electrokinetic potential and FTIR spectroscopy. The linear polyglycidols are weakly associative species, unlike the hyperbranched one which is more hydrophilic and harder associates. The linear polymers most efficiently interact with the anionic surfactant, followed by cationic and most weakly with the nonionic. The hydrodynamic diameters of the investigated polyglycidols depend on their structure and molecular weight. In the presence of SDS, the hydrodynamic diameters vary with surfactant concentration. The study reveals the solubilization of fluorescent probes (pyrene, naphthalene) inside the polyglycidol aggregates. Unlike the LPGL, the presence of cavities in HPGL macromolecule offers supplementary "pockets" for solubilization.

1. Introduction

Polyglycidol (PGL) is a highly flexible and hydrophilic polyether. The flexibility of macromolecules results from the free rotation around the single C—C bonds of the macromolecular backbone, whereas the hydrophilicity is due to the presence of methylhydroxyl group in each repeating unit. Previous results of water contact angle studies revealed that a thin layer composed of grafted polyglycidol chains is more hydrophilic than a comparable layer of poly(2-hydroxyethyl methacrylate) [1]. The high hydrophilicity of polyglycidol arises from inter- and intramolecular hydrogen bonds formed between water and the hydroxyl groups and the oxygen atoms of the PGL main chain. The feature favors polyglycidol over the famous poly(ethylene oxide) (PEO) that makes hydrogen bonds exclusively with water molecules. Calculations of energy of the most stable oligoglycidol and oligo(ethylene oxide) trimers have demonstrated that the free energy of polyglycidol hydration is lower (−26.14 kcal/mol) than of PEO (−16.05 kcal/mol) [1]. It was also unveiled that hyperbranched polyglycidol has better thermal and oxidative stability than poly(ethylene glycol) [2]. The above presented properties of polyglycidol suggest that the polymer is an attractive alternative to PEO in terms of a prospective broad

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spectrum of pharmaceutical and biomedical applications [3]. It is important to stress that, depending on the route of synthesis; one may obtain linear (LPGL) or hyperbranched polyglycidol (HPGL) [4]. The latter has a globular structure, which hampers the interaction with biomolecules. It is therefore assumed that adsorption of proteins onto HPGL in the blood stream is low [5]. Recently, it was established that cross-linked hydrogels of HPGL-PEO are useful scaffolds for tissue engineering [6].

Due to the large potential for applications of polyglycidol in medicine, especially in drug delivery and cell imaging [7,8], the study upon their interaction with biomimetic species, like the surfactants, is of high interest. To the best of our knowledge, there are no reports on this topic in the literature, which is in contrast with the largely studied PEO-surfactant systems [9–15]. However, a previous work of our group describes the fluorescent behavior of a DTAF-labeled poly(styrene-co-α-tert-butoxy-ω-vinylbenzyl-polyglycidol) in various surfactant media [16]. The paper reveals that, for surfactants with identical hydrocarbon tail, the polar head governs the solution properties of the fluorescently labeled copolymer. This is an enticing reason for studying the polyglycidol-surfactant systems.

In this work, linear and hyperbranched polyglycidol are investigated, in the absence and presence of surfactants, by surface tension (ST), FTIR, steady-state fluorescence (SSF), DLS and electrokinetic measurements. Hexaethylene glycol mono *n*-dodecyl ether ($C_{12}E_6$), cetyl trimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS) are the surfactants employed. They belong to different surfactant classes (*i.e.*, nonionic, cationic, and anionic) and have critical micellar concentrations which increase by one order of magnitude from one surfactant to another. In this way, a wide range of surfactant concentrations will be investigated. Moreover, $C_{12}E_6$ and SDS are well-known biocompatible species while CTAB is a largely used disinfectant, so all three deserve academic and medical applicative interest in combination with polyglycidols. The study reveals that LPGL is more favorable to surfactant interaction than HPGL. Among the surfactants, only SDS interacted with both LPGL and HPGL. Like pyrene probe, SDS was able to access the holes in the globular PGL. The work is important as it sheds light on polyglycidols as biomedical materials and surfactant micelles, which well-mimics the cellular membranes. The acquired information is valuable for designing novel materials, with better drug delivery and imaging applications than those currently available on the market.

2. Experimental

2.1. Materials

The following reagent grade chemicals from Aldrich were used without purification: ethyl vinyl ether, 2,3-epoxypropanol, p-toluenesulfonic acid monohydrate, aluminium chloride hexahydrate, methanol, potassium *tert*-butoxide, hexadecyl-trimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS), pyrene (Py) and naphthalene (Np). Hexaetheleneglycol mono *n*-dodecyl ether ($C_{12}E_6$) was a Nikko Chemicals product and was used as received.

2.2. Methods

The methods of synthesis, purification and characterization of LPGL and HPGL are described in Supplementary Information. There were investigated two linear polyglycidols with molecular weights of 3250 (LPGL32) and 9610 (LPGL96) and a hyperbranched polyglycidol with molecular weight 4040 (HPGL40).

Fig. S1 in the Supplementary Information presents the FTIR spectra of LPGL32 and HPGL40 which contain characteristic strong absorption bands at 3443 cm^{-1} and respectively, 3355 cm^{-1}. The bands are related to stretching vibration of O—H. For both polymers, the stretching vibration of C—H was observed in a 2870–2950 cm^{-1} region and the bending vibration of C—H appeared in the 1300–1460 cm^{-1} region. Stretching vibration of C—O—C ether group is observed in the 1066–1111 cm^{-1} region. The results are in accordance with those previously observed for polyglycidol by Wesolek et al. [17].

Surface tension measurements were carried out using a Krűss K11 MK3 tensiometer, by the Du Noüy ring method.

Steady-state fluorescence data were collected on a Horiba Jobin Yvon FluoroMax 4P spectrofluorimeter. The slits were set at 2 nm for excitation and 1 nm for emission. The excitation was at 335 nm for pyrene and at 290 nm for naphthalene. A Krűss digital Abbe refractometer AR2008 was used for measurements of refractive index.

Dynamic light scattering (DLS) measurements were carried out with a Nano ZetaSizer from Malvern Instruments. The apparatus was equipped with a laser emitting at 633 nm and the intensity of scattered light was detected at 173°. The experiments were performed at 25 °C and after 24 h from the preparation of polymer solutions, without and with surfactant. In surfactant-free systems the concentration of linear polyglycidols was of 1×10^{-1} M, in order to have a reliable size comparison between the two polyglycidols with low and high molecular mass. The hydrodynamic diameter, d_h, was determined with the Stokes-Einstein equation ($d_h = k_BT/3\pi\eta D$), where k_B is the Boltzman constant, T is the absolute temperature, η is the viscosity of the environment and D is the diffusion coefficient.

The electrokinetic measurements were done with the same Nano ZetaSizer from Malvern Instruments. The ζ-potential is an index of the stability of colloidal particles and was obtained from the electrophoretic mobility, by using the Smoluchowsky model.

FTIR spectra were collected on a Thermo Scientific Nicolet iN10 spectrometer. The spectra resolution was 4 cm^{-1} and 32 scans were registered for each spectrum in the range from 400 to 4000 cm^{-1}.

The structure of linear polyglycidol macromolecules was confirmed by ^{1}H NMR spectra (Bruker, 200 MHz). The structure of hyperbranched polyglycidol was estimated based on ^{1}H NMR and ^{13}C NMR spectra (Bruker, 500 MHz).

The molecular weights of polymers and their dispersity factors were analyzed by SEC. Detailed information are given in Supplementary Information.