Colloids and Surfaces A: Physicochem. Eng. Aspects 436 (2013) 744–750

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Hydrophobic modification of dextran with 1,2-epoxyalkanes in aqueous micellar medium: Competition between interfacial and bulk reactions and consequences on polymer properties

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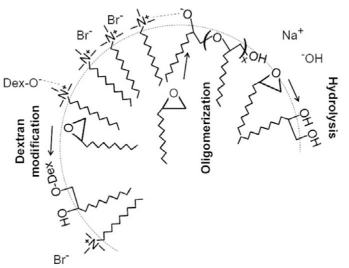
HIGHLIGHTS

- Dextran was modified by 1,2-epoxydodecane in aqueous micellar medium.
- The importance of using a cationic surfactant was underlined.
- The role of epoxide structure on formation of oligomeric by-products was detailed.
- The influence of micellar medium on properties of modified dextrans was evidenced.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 June 2013
Received in revised form 28 July 2013
Accepted 30 July 2013
Available online 7 August 2013

Keywords:
Dextran
Amphiphilic polysaccharide
Micellar catalysis
Epoxide

ABSTRACT

Hydrophobic modification of dextran (degree of polymerization around 125) by reaction with 1,2-epoxydodecane was investigated in micellar aqueous medium in which epoxide was dispersed under magnetic stirring in the presence of a cationic surfactant. A base catalyst, sodium hydroxide, was added in water. Dextran derivatives with degrees of substitution up to 10% were prepared. Apart from dextran modification, epoxide molecules underwent interfacial oligomerization which led to by-products that had to be extracted by dialysis followed by Soxhlet extraction. Two main reaction parameters influenced the amount of oligomeric by-products, i.e. temperature and surfactant structure. Adsorption of these compounds at air/water interface was studied by surface tension and dilational rheology measurements and compared to that observed with amphiphilic dextrans prepared in homogeneous conditions.

1. Introduction

Dextran is a non ionic bacterial polysaccharide consisting of a main chain with α-(1→6) linked D-glucose units that can represent between 50 and 97% of total glucosidic bonds and some branches found in positions α-(1→2), α-(1→3) and α-(1→4), depending on the bacterial strain [1]. The α-(1→3) links forming short branches represent about 5% in commercially available dextran T40© [2]. Dextran T40© comes from a bacterial strain called *Leuconostoc*

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http://dx.doi.org/10.1016/j.colsurfa.2013.07.045

mesenteroïdes [3] and is used in many applications in food, pharmaceutics and medicine [1,4–7].

The covalent attachment of hydrocarbon chains along dextran backbone has been investigated since the 70s. In that way amphiphilic polymers were obtained that combined the chemical properties brought by the native polysaccharide to those coming from the amphiphilic character: self organization in aqueous or organic solution as well as at liquid–liquid and liquid–solid interfaces. The main structural parameters controlling the self-organizing behavior are the number of carbon atoms contained in hydrocarbon tails, number of hydrophobic groups attached along polysaccharide backbone and the degree of polymerization of polysaccharide (DP). In addition, the nature of covalent bonds between hydrocarbon tails and sugar units modifies the chemical stability in the conditions of application. For about 15 years, polymeric stabilizers based on dextran have been synthesized in our laboratory for preparing nanoparticles [8], stabilizing submicronic oil-in-water emulsions [9–11] and more recently submicronic water-in-oil emulsions [12].

Covalent attachment of hydrocarbon groups onto polysaccharides generally raises important difficulties related to the selection of the solvent of reaction. In the case of neutral polysaccharides like dextran, starch or inulin, polar organic solvents (dimethylsulfoxide, N-methylpyrrolidone, etc.) and mixtures of water and polar organic solvents (water-isopropyl alcohol, etc.) were found to dissolve both native polysaccharide, hydrophobic reactant and modified polysaccharide, leading to significant reaction yields [13–15]. Nevertheless, it would be of great interest to reduce the use of such solvents and even to be able to carry out polysaccharide hydrophobic modification in mainly aqueous reaction media. Although etherification of dextran in water with sodium hydroxide (1 M) and a water-soluble epoxide was reported more than 30 years ago, this topic received little attention over the past 15 years [16]. A series of investigations appeared about the synthesis of non ionic surfactants by esterification or etherification of unprotected sugars molecules in aqueous medium containing cationic surfactants [17–22]. These results supported the idea of applying micellar catalysis to polysaccharide modification by water-insoluble epoxides. The feasibility of that strategy was first demonstrated for modification of dextran (DP $\approx$ 125) with epoxides (mainly epoxyoctane) [23] and further extended to modification of inulin (DP $\approx$ 25) by epoxides and alkenyl succinic anhydrides [24,25]. Using epoxyalkanes has the advantage of providing alkyl ethers that do not restrict the stability in alkaline conditions as compared to native polysaccharide. In addition, the presence of a hydroxyl group in β position for each attached hydrocarbon tail, significantly improves water solubility of amphiphilic polysaccharides as compared to ester derivatives. Nevertheless, epoxyalkanes may undergo oligomerization in the conditions used for polysaccharide modification, which can limit reaction efficiency and produce undesirable secondary products [26].

It was the aim of this work to examine the hydrophobic modification of dextran by 1,2-epoxydodecane in aqueous medium containing surfactant. Epoxide oligomerization was especially investigated with regard to influences of temperature, surfactant and epoxide nature. Finally, consequences of micellar modification on solution and interfacial properties of amphiphilic dextrans were analyzed.

2. Materials and methods

2.1. Materials

All chemicals were from Aldrich with the highest purity available. MilliQ water was used in all experiments. A commercial dextran sample, T40® from Amersham Pharmacia was used. Its weight-average and number-average molar masses were characterized by size exclusion chromatography and found equal to 40,000 g/mol and 33,000 g/mol, respectively.

2.2. Dextran modification in aqueous micellar medium

Dextran (5 g) was dissolved in 50 mL 1 M sodium hydroxide solution during 16 h at room temperature. 5.71 g of dodecyltrimethylammonium bromide (DTAB) were added. If necessary, the reaction medium was heated to 50 °C with an oil bath. After temperature stabilization, the required amount of epoxide (1,2-epoxydodecane, 1,2-epoxyoctane, or 1,2-epoxyhexane) was added. The mixture was maintained under stirring during 96 h. The crude reaction medium was transferred to a dialysis bag and dialyzed against water/ethanol mixtures (50/50, v/v) and finally water. The aqueous solution recovered after dialysis was freeze-dried and sampled for analysis by ^{1}H NMR. The solid product was put in a Soxhlet extractor and washed with absolute ethanol during 24 h. The recovered ethanol was fully evaporated and the resulting solid was analyzed.

2.3. Epoxide oligomerization in the absence of dextran

The same reaction and purification procedures as the ones used for dextran modification were followed but without addition of dextran.

2.4. Structural analyses

^{1}H and ^{13}C NMR spectra were obtained with a Brücker Avance 300 spectrometer (300.13 MHz and at 300 K).

Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-ToF) spectra were acquired on a Voyager-DE STR instrument (Applied Biosystems) equipped with a nitrogen laser (337 nm) to desorb and ionize the samples. The instrument was operated in linear mode. The matrix was obtained from a mixture of tetrahydrofuran/dithranol/NaI, 50/45/5 (v/v/v).

Size exclusion chromatography analyses were performed with a system comprising a Merck L6200A pump (0.7 mL/min), a Degazys DG 1310, Uniflow unit, a 200 μL injection loop, a PL aquagel-OH Guard pre-column followed by 2 PL aquagel-OH 40 and PL aquagel-OH 50 columns (Polymer Laboratories). The detection system was a miniDawn (Wyatt Technology Corporation) photodiffusiometer (wavelength 690 nm and detection at 41.6°, 90° and 138.4°) followed by a Merck RI-71 differential refractometer. The eluent was 0.1 mol/L $NaNO_3$ with 0.2 g/L NaN_3.

2.5. Capillary viscometry

Viscometric measurements with aqueous polymer solutions were carried out using an Ostwald-type capillary viscometer (0.46 mm diameter). The temperature was regulated by a circulating bath. Prior to measurements, the aqueous solutions were filtered through 0.2 μm filters. Polymer concentration was checked by weighting dry extracts obtained after letting the solutions 24 h in an oven at 110 °C. The found values were always about 90% of the calculated ones. No kinetic corrections were required since we verified that the flow time was proportional to the kinematic viscosity. The densities of the polymer solutions were assumed to be identical to that of pure water within the concentration range explored (up to 50 g/L).