Synthesis of amphiphilic polysaccharides by micellar catalysis

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Abstract

Amphiphilic polymers are prepared by chemical modification of dextran, a neutral bacterial polysaccharide consisting of α-1,6 linked glucose units. Hydrocarbon groups are attached to the polysaccharide chains by reacting dextran with aliphatic or aromatic 1,2-epoxides in a basic aqueous medium. Because of the low water-solubility of the epoxides, the reaction medium is biphasic with the organic epoxide emulsified in the continuous aqueous phase.

It is shown that dextran modification is no longer possible with epoxides having very low water-solubility. The addition of a cationic surfactant appears to make chemical modification possible even with highly hydrophobic epoxides (1,2-epoxydodecane or 1,2-epoxyoctadecane). The reaction mechanism is discussed taking into account the characteristics of the reactants involved and especially the effect of surfactant (nature and amount).
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1. Introduction

Polymeric surfactants are an important class of compounds involved in aqueous formulations used in various industrial domains: food, cosmetics, pharmaceuticals, . . . These macromolecules exhibit unique properties such as: viscosifying behaviour in aqueous solutions at very low concentrations, surface active properties comparable to those of molecular surfactants, quasi-irreversible adsorption at interfaces, tuneable behaviour by controlling the synthesis conditions, . . . Amongst polymeric surfactants, hydrophobically modified polysaccharides are attracting more and more interest because they possess other important properties in addition to the previous ones like biocompatibility and biodegradability. The latter are becoming key-properties because of environmental concerns. Moreover, another serious advantage is that these compounds can be obtained from renewable resources. Polymeric surfactants from cellulose have been prepared, a long time ago, in a pioneering work by Landoll [1]. He first carried-out a controlled hydrophobic modification of cellulose ethers by reacting them with aliphatic epoxides. Since that time, many studies have been devoted to the field of amphiphilic polysaccharides and enlarged considerably the nature of the starting polysaccharide as well as that of the hydrocarbon groups grafted [2–8]. Generally, the starting polysaccharide is reacted with a hydrocarbon of fluorocarbon molecular reactant. Nevertheless, the modification reaction cannot generally be carried-out in pure water since the molecular reactant (fatty acid, aliphatic epoxide, . . .) is often poorly water-soluble. Up to now, authors used polar organic solvents able to dissolve both the polysaccharide and the molecular reactant [9] or mixtures of water and isopropanol, adjusting the proportions for complete dissolution of the feed [8]. The modification in pure water was limited to molecular reactants with relatively few carbon atoms (i.e. with a sufficient water-solubility) [8]. The ability to prepare hydrophobically modified polysaccharides in an aqueous mixture without any volatile organic compound (except the hydrocarbon reactant) is still a great challenge since it would favour their production at large scales and it is also required for their use in biomedical applications.

A formally similar topic is the preparation of amphiphilic polymers by copolymerization of a highly hydrophilic monomer with a hydrophobic one. The solubilities are so different that the reaction is difficult to carry-out in an aqueous medium [10]. The micellar copolymerization was introduced to solve that difficulty [11,12]. The low water-solubility of the hydrophobic compound was compensated by the use of a surfactant, which entrapped this monomer into micelles thereby increasing its apparent reactivity in copolymerization.

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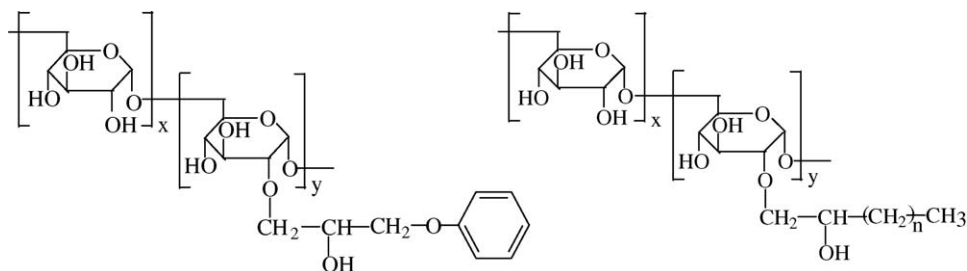
Scheme 1. Chemical structure of DexP$_\tau$ (left) and DexC$n+1_\tau$ (right), $n = 3, 5, 9$ or 15). The detailed study of the position modified by the epoxide (among the three possible ones) has not been performed yet. The substituent is thus attributed to the more reactive position [31].

Previously, chemical modification of polysaccharides with organometallic compounds using an interfacial process was reported with or without phase transfer catalyst [13–17]. A similar procedure has not been applied to the preparation of amphiphilic polysaccharides. Nevertheless, molecular surfactants based on sucrose hydroxyalkyl ethers have been prepared using a biphasic reaction medium [18–21].

In that work, we report the synthesis of hydrophobically modified polysaccharides in water by grafting aliphatic hydrocarbon chains (containing between 6 and 16 carbon atoms) onto dextran, a neutral bacterial polysaccharide. The biocompatibility of dextran has been established previously and amphiphilic dextran derivatives can be used for the preparation of dextran-covered nanoparticles for biomedical applications [22,23]. Thus dextran appears to be an attractive starting material. Moreover, the relative simplicity of its repeat unit (only hydroxyl groups) renders it convenient for studying new conditions of chemical modification.

The reaction procedure involves a biphasic mixture. The reaction used is a nucleophilic addition of hydroxyl groups (partly ionized) onto the ring of hydrocarbon epoxides. The ability of water-soluble surfactants to promote polysaccharide modification is investigated. Several reaction parameters are examined like the structure and amount of surfactant or the nature of the epoxide.

2. Experimental

2.1. Materials

The native dextran was obtained from Pharmacia (Uppsala, Sweden) and is commercially named T40©. The other chemicals were from Aldrich (St. Quentin Fallavier, France) and were used as received. MilliQ water was used for all the experiments.

2.2. Hydrophobic modification of dextran

2.2.1. Modification procedure

A standard procedure can be depicted as follows. To 2 g of dextran T40© (0.0123 mol of glucose units), 20 mL of sodium hydroxide solution (1 M) are added as well as the required amount of surfactant. The mixture is stirred at room temperature during approximately 4 h to allow a complete dissolution of the reactants. Afterwards, the required amount of epoxide (0.0123 mol) is added dropwise and the biphasic mixture is stirred at room temperature for several days. The reaction mixture is added dropwise to 300 mL of ethanol. The precipitate is washed with 300 mL of ethanol and dissolved in 70 mL of pure water. The solution is dialyzed against an ethanol/water mixture (50:50, v/v) and finally water. The obtained aqueous solution is freeze-dried to recover the modified polymer.

Five different epoxides were used, one aromatic 1,2-epoxy 3-phenoxy propane and four aliphatic molecules: 1,2-epoxyhexane, 1,2-epoxyoctane, 1,2-epoxydodecane and 1,2-epoxyhexadecane.

A control reaction has been performed with pure water instead of sodium hydroxide solution. With 1,2-epoxy-hexadecane, which is a solid at room temperature, the reaction was carried-out at 55 °C.

For all the reactions, the amount of attached epoxide has been determined by ^{1}H NMR and expressed as the degree of hydrophobic substitution (see Section 2.2.2). The yield of each reaction has been calculated as the ratio of the weight of freeze-dried final material to the theoretical weight corresponding to the initial amount of native dextran plus the corresponding amount of attached epoxide (as indicated by ^{1}H NMR). The yield defined in that way is essentially indicative of the efficiency of polymer recovery and does not give any indication about the completion of the reaction. The latter can be evaluated by the comparing the amount of attached epoxide to the composition of the feed (see Section 2.2.2).

2.2.2. Polymer structural characterization and nomenclature

The degree of hydrophobic substitution, τ (%), is defined by: $\tau = 100 \times (y/(x + y))$ (see Scheme 1). Considering that there are three hydroxyl groups in each glucose unit, the degree of substitution, as defined above, can reach values as high as 300%. The obtained polymers were characterized by ^{1}H NMR in deuterated dimethylsulfoxide, using a Bruker spectrometer (300 MHz). Before dissolution in deuterated dimethylsulfoxide, the solid polymers were dried overnight in an oven at 110 °C. The modified polymer samples will be named DexP$_\tau$, DexC4$_\tau$, DexC6$_\tau$, DexC10$_\tau$ and DexC16$_\tau$ according to the epoxide used: 1,2-epoxy 3-phenoxy propane, 1,2-epoxyhexane, 1,2-epoxyoctane, 1,2-epoxydodecane and 1,2-epoxyoctadecane (respectively).

The amount of epoxide added in the reaction medium is always such that the molar ratio epoxide:sugar unit is unity. As a result, the maximum degree of hydrophobic substitution could be 100%. Consequently the extent of the reaction between dex-

Table 1
Dextran modification carried-out with various epoxides, without surfactant and at room temperature

Reaction no.	Aqueous phase	Epoxide	Reaction time (h)	Yield[a] (%)	τ[b] (%)
1	Water	1,2-Epoxyoctane	142	75	0
2	1 M NaOH	1,2-Epoxyoctane	142	82	1
3	1 M NaOH	1,2-Epoxyhexane	117	82	19
4	1 M NaOH	1,2-Epoxy 3-phenoxy propane	117	61	35

The molar ratio of epoxide to glucose unit is 1.0.

[a] Ratio of the weight of recovered polymer to the maximum weight of polymer having the degree of substitution determined experimentally (for details see Section 2.2.1).

[b] Determined by ^{1}H NMR in deuterated dimethyl sulfoxide.

tran and the considered epoxide can be evaluated by the degree of hydrophobic substitution of the final product.

2.3. Size exclusion chromatography

The unmodified dextran samples were characterised by size exclusion chromatography (SEC). The eluent was 0.1 M NaNO$_3$ at 40 °C. The flow rate was 0.7 mL/min and obtained by a Waters 590 pump. The series of column was of Shodex type (SB-806, 805, 804 HQ) and the SEC detection system combined a differential refractometer Waters 410 and a light scattering device miniDawn (Wyatt Tech. Corp.).

The commercial sample of dextran T40$^©$ has been characterized: $\overline{M}_n = 26,000$ g/mol, $\overline{M}_w = 40,000$ g/mol and $I_p = 1.6$.

3. Results and discussion

3.1. Results

The hydrophobic modification of dextran in aqueous medium has been previously carried-out in water with an epoxide having a limited water-solubility, 1,2-epoxy 3-phenoxy propane (phenylglycidylether). The targeted application was the preparation of polysaccharide-covered poly(styrene) nanospheres [24–26].

In that work, we tried to apply the same procedure with different aliphatic epoxides and with phenylglycidylether for comparison. Dextran was dissolved in a basic aqueous medium. The presence of the base in the aqueous phase was necessary for the reaction between the epoxide and the polysaccharide. Indeed, no signals from the epoxide could be detected in the absence of sodium hydroxide (Table 1, entries 1 and 2). A similar result has been obtained with cellulose [27]. The effect of sodium hydroxide concentration was not investigated here and all the experiments were carried-out with a 1 mol/L NaOH solution as the aqueous phase. After characterizing the unmodified dextran resulting from reaction no. 1 (Table 1) by size exclusion chromatography, we found that its average molecular weights were identical to those of the native polysaccharide. Hence, no dextran degradation could be evidenced within the reaction time. The epoxide (in such amount that the molar ratio of epoxide to glucose unit is unity) was emulsified into the aqueous phase under stirring. The progressive dissolution of the hydrocarbon reactant allowed the reaction to proceed. When applying this procedure to aliphatic epoxides, the resulting modification of dextran was drastically lowered as the number of carbon atoms in the epoxide increased (Table 1, entries 2–4).

The addition of a surfactant into the aqueous phase led to an increase of the dextran modification but the effect strongly depended on the surfactant used (Table 2). For the three surfactants used, the concentration in the aqueous phase was always higher than the critical micelle concentration (cmc) in pure water at room temperature. Since sodium hydroxide acted to decrease the cmc, the surfactant molecules were mainly included in micelles. Adding a cationic surfactant (dodecyltrimethylammonium bromide, DTAB), in the aqueous phase brought about a significant increase of dextran modification by epoxyoctane as compared to the same reaction carried-out in the absence of

Table 2
Dextran modification carried-out with 1,2-epoxyoctane and various surfactants

Reaction no.	Surfactant	Surfactant/dextran (w/w)	Reaction time (h)	Yield[a] (%)	τ[b] (%)
5		0.05	136	75	7
6	DTAB	0.1	120	73	4
7		0.2	136	78	16
8		0.4	136	72	16
9	SDS	0.1	120	52	1
10		0.4	117	75	1
11	Tween 80$^©$	0.1	120	76	2
12		0.4	136	64	4

The aqueous phase is 1 M sodium hydroxide and the reaction occurs at room temperature. The molar ratio of epoxide to glucose unit is 1.0.

[a] Ratio of the weight of recovered polymer to the maximum weight of polymer having the degree of substitution determined experimentally (for details see Section 2.2.1).

[b] Determined by ^{1}H NMR in deuterated dimethyl sulfoxide.

Table 3
Dextran modification carried-out with DTAB and various epoxides

Reaction no.	Epoxide	Reaction time (h)	Yield[a] (%)	τ[b] (%)
13	1,2-Epoxyoctane	96	72	12
14	1,2-Epoxydodecane	96	87	16
15	1,2-Epoxyoctadecane	96	—	n.d.[c]

The aqueous phase is 1 M sodium hydroxide and the reaction temperature is 55 °C. The weight ratio of DTAB to dextran is 0.4. The molar ratio of epoxide to glucose unit is 1.0.

[a] Ratio of the weight of recovered polymer to the maximum weight of polymer having the degree of substitution determined experimentally (for details see Section 2.2.1). For reaction no.15, this yield cannot be calculated but the weight of recovered material was comparable to that of reactions nos.13 and 14.

[b] Determined by ^{1}H NMR in deuterated dimethyl sulfoxide.

[c] The solubility of the product in deuterated dimethyl sulfoxide was too low.

surfactant. Furthermore, a higher amount of surfactant led to a higher dextran modification (Table 2, entries 5–8). With an anionic surfactant (sodium dodecyl sulphate, SDS) or a neutral one (Tween 80©), the increase of dextran modification was much more limited than that observed with DTAB at the same relative amount of surfactant (Table 2, entries 6, 8 and 9–12). For all the recovered products, no surfactant signal could be detected in the NMR spectra.

The reaction was extended to other aliphatic epoxides: epoxydodecane and epoxyoctadecane. Because of the melting temperature of epoxyoctadecane, the reaction was carried-out at 55 °C instead of room temperature. Dextran modification was performed in all cases, even with highly hydrophobic epoxides (Table 3) and the yields were comparable.

3.2. Discussion

The reaction between dextran and epoxide is a base-catalysed ring-opening reaction. With a basic catalyst, the major product is that resulting from the addition on the less substituted carbon atom of the epoxide ring (Scheme 1) [28,29]. No detailed study has been performed about the reactivity order of the various hydroxyl groups toward the reaction studied here. The position indicated on Scheme 1 is the more reactive toward acetylation [30] or silylation [31].

When the epoxide is emulsified in the aqueous phase containing the base and the polysaccharide, the reaction is mainly limited by the solubility of the epoxide in the aqueous phase. Indeed, the basic catalyst used in this work is sodium hydroxide, which is insoluble in the organic phase as well as the native polysaccharide. Moreover, a partial hydrolysis of the epoxide is likely to compete with dextran modification in the aqueous phase. These two limitations significantly reduce the degree of modification of the polysaccharide that can be obtained [32–34]. In the case of phenylglycidylether, we showed previously that performing the reaction in dimethylsulfoxide (where both epoxide and dextran are soluble) allowed obtaining degrees of substitution of 100% and even higher [26]. A similar conclusion holds for the reaction of sucrose with aliphatic epoxides [19,35].

With phenylglycidylether, the solubility in the aqueous phase is enough for the reaction to occur with a sufficient rate. Hydrophobically modified polysaccharides are formed and start to act as surfactants in the reaction medium. Consequently, the size of epoxide droplets decreases progressively. This increases the contact surface between the two phases and speeds up dextran modification. A visual observation of the reaction medium confirmed that interpretation. Initially the reaction medium was cloudy and it became completely white after 24 h reaction. Later, the reaction medium became translucent (after 96 h reaction). This could be attributed both to the consumption of epoxide and to the production of amphiphilics dextran derivatives. As for the reactions carried-out with epoxyhexane and epoxyoctane, the reaction medium remained cloudy over the whole reaction time (117 h or more). Even if a significant degree of substitution is obtained with epoxyhexane, we can assume that the modified dextran has no sufficient surface activity to efficiently increase epoxide emulsification. Results about saccharide surfactants are consistent with that suggestion [36] and similar observations have been reported in the case of the synthesis of sucrose hydroxyalkyl ethers in dispersed aqueous medium [20]. With epoxyoctane, water solubility is too low for obtaining a significant degree of substitution (Table 1).

Using a group contribution method, the water solubilities of phenylglycidylether, epoxyhexane and epoxyoctane were estimated [37]. The ratios of the estimated solubilities to that of phenylglycidylether (taken as a reference) are: 1.00, 0.31 and 0.01 (respectively). Consequently, water-solubility seems to be one parameter controlling the observed extent of reaction, especially in a homologous series of compounds like the aliphatic epoxides used in this work. For phenylglycidylether, the presence of the phenoxy group could eventually induce a difference in chemical reactivity itself and thus, a difference in the rate of the chemical processes. The limitation resulting from a low water-solubility has been generally overcome by the use of various organic co-solvents [9,38]. Here, we chose to avoid the use of organic co-solvent and tried to favour the reaction between epoxide and dextran in the aqueous phase by the use of a surfactant so as to keep a mainly aqueous reaction medium. The added surfactant may act by at least two ways. First it helps the emulsification of the epoxide under stirring and thus increases the contact surface between the two phases. Secondly it is able to dissolve epoxide molecules into micelles and thus to increase the amount of epoxide in the aqueous phase [39,40]. Nevertheless, since it is known that native dextran has no affinity for oil/water interfaces [41], it is necessary that the surfactant could induce interactions with the polysaccharide backbone. Glucose units can be assumed to be more or less ionised in the presence of sodium hydroxide because of the weak acidity of the hydroxyl groups of dextran

[42–46]. Thus, we theorised that the use of a cationic surfactant could be efficient to promote the reaction between epoxide and polysaccharide glucose units, leading to dextran hydrophobic modification. Indeed, the addition of limited amounts of DTAB in the aqueous phase brought about a significant hydrophobic modification of dextran by epoxyoctane, which was not possible in the absence of surfactant (Table 2). The comparison with a neutral (Tween80$^{©}$) or an anionic surfactant (SDS) shows that the charge of the surfactant has a strong influence on its ability to promote polysaccharide modification. With the last two surfactants, the degrees of substitution obtained are only slightly higher than those obtained without surfactant. We must notice that SDS was only partly soluble in the aqueous phase giving either cloudy solution (reaction no. 9, Table 2) or partial precipitation (reaction no. 10, Table 2) before the addition of epoxide. In the same conditions, DTAB and Tween80$^{©}$ gave clear solutions. This lack of solubility could explain the low efficiency of SDS but the comparison of DTAB and Tween80$^{©}$ confirms the importance of the head group. An interesting comparison can be done with the synthesis of sucrose hydroxylalkyl ethers in dispersed medium by reaction between sucrose and epoxydodecane [20]. While a cationic surfactant like cetyl trimethylammonium bromide is efficient in promoting the targeted reaction, non-reactive neutral surfactants or anionic surfactants are unable to promote the synthesis of sucrose hydroxyalkyl ethers. In the case of neutral surfactants (Brij 58 and Brij 30), the authors suggest a low emulsifying ability in the sucrose-rich aqueous phase. As for the anionic surfactant tested (potassium stearate) it is observed that its effect is mainly to promote the hydrolysis of the epoxide instead of its reaction with sucrose.

Increasing the amount of added surfactant leads to higher degrees of substitution (Table 2, entries 5–8) and values around 16% were reached. It has been demonstrated that dextran modified samples with such amounts of C6 groups exhibit emulsifying properties [25,47]. It is not possible to comment further the influence of the amount of surfactant at this stage of the work. Indeed, a precise control of the stirring rate would be necessary since it is of primary importance in a heterogeneous reaction medium [13]. The aim of that preliminary study was to evidence the role of DTAB in promoting the chemical modification of dextran. The establishment of a detailed correlation between reaction conditions (amount of surfactant, stirring rate, amount of epoxide, . . .) and dextran modification will be the topic of a future work.

It is known that the nature of the hydrocarbon moieties attached to the polysaccharide backbone has a strong influence on the solution behaviour of the resulting polymer [48]. In the presence of DTAB, dextran modification by epoxydodecane and epoxyoctadecane was possible (Table 3). Because of the melting point of epoxyoctadecane (26 °C) the reaction was carried-out at 55 °C. The obtained polymers exhibited much lower solubility in dimethylsufoxide than native dextran or DexC6$_\tau$ derivatives. This demonstrates that rather hydrophobic dextran derivatives can be prepared in a mainly aqueous reaction medium by the use of an appropriate surfactant.

For the synthesis of surfactants based on sucrose hydroxyalkyl ethers, the authors identified three side-reactions produc-

ing by-products from epoxide: homogeneous oligomerisation in the organic phase, interfacial hydrolysis and nucleophilic attack of the epoxide ring by the base in the organic phase [20]. Moreover, the formation of polysubstituted sucrose ethers in the organic phase was evidenced. With the conditions used here for dextran modification, the base is not soluble in the organic phase and thus, cannot induce either the formation of epoxide oligomers or a ring-opening reaction. As a result, the side reaction of hydrolysis should be limited to the interface and to the aqueous phase involving either individual epoxide molecules or epoxide molecules surrounded by surfactant micelles (especially in the case of cationic surfactant). As for the formation of polysubstituted units, it was not possible to investigate that point with the DexC6$_\tau$ samples produced here because of the relatively low content of etherified hydroxyl groups. This remains an important point to clarify.

4. Conclusion

The preliminary experiments presented here demonstrate the possibility of preparing amphiphilic polysaccharides in a mainly aqueous reaction medium with the organic reagent being emulsified under stirring. The addition of a cationic surfactant promotes polysaccharide modification in the case of poorly soluble reagents. Physico-chemical parameters like the nature and amount of surfactant are found to have a significant effect on the extent of modification. A micellar catalysis is suggested to account for the effect of the cationic surfactant used, DTAB.

Starting from these results, more work will be carried-out concerning the relation between the structure of the modified polysaccharide and the physico-chemical parameters of the reaction procedure (amount of surfactant, rate of stirring, molecular weight of polysaccharide, . . .). Moreover, the structural characteristics of the modified polymer have to be further examined: mono-or polysubstituted units, presence of unreacted chains in the final product, . . .

This mainly aqueous procedure is a promising method of preparation of amphiphilic polysaccharides, avoiding the use of organic solvents. In addition, its applicability to reactions mixtures containing highly hydrophobic epoxides is an important point for the development of modified polysaccharides with valuable properties for aqueous formulations.

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