BETA W7 MCT - NEW WAYS IN SURFACE MODIFICATION

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ABSTRACT

BETA W7 MCT is the first reactive cyclodextrin derivative manufactured on an industrial scale. It has a monochlorotriazinyl group as a reactive anchor well known from many reactive dyes. This derivative is able to form stable covalent bonds with nucleophilic groups and can be easily prepared in water in an effective one pot synthesis from cyanuric chloride and ß-cyclodextrin in a yield of approx. 90% based on the triazinyl group. The optimised degree of substitution of DS = 0.4 per anhydroglucose ensures a good complexation capacity even when this derivative is fixed to surfaces like textiles. This cyclodextrin derivative containing 2-3 reactive groups in the ring can be used as building block for new CD derivatives, as a crosslinking agent or as an excellent material for surface modification.

1. INTRODUCTION

Cyclodextrins and their derivatives are suitable for a wide variety of possible uses e.g. for stabilisation, masking or controlled release of hydrophobic substances [1,2]. With a cyclodextrin derivative bearing a reactive group it should be possible to incorporate these favourable properties of cyclodextrins permanently on a surface. Possible surfaces are e.g. cotton, paper or natural and synthetic polymers. For greatest stability the cyclodextrin should be fixed via a covalent bond. A reactive cyclodextrin would be also useful for the synthesis of new cyclodextrin derivatives. The selected reactive group in the new cyclodextrin derivative BETA W7 MCT (Fig. 1) is the monochloro-triazinyl group well known from many reactive dyes. This anchor is able to form the required stable covalent bond to nucleophilic groups.

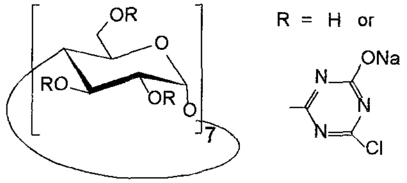

Fig. 1 Structure of BETA W7 MCT

2. MATERIALS AND METHODS

Beta-cyclodextrin is a product of Wacker-Chemie GmbH, Munich, Germany and cyanuric acid a product of SKW Trostberg AG, Trostberg, Germany. The synthesis of Beta W7 MCT was developed by Wacker-Chemie [3,4]. The degree of substitution of the reactive chlorine in the triazine group was calculated from ^{1}H-NMR after reaction of Beta W7 MCT with diethylamine in water [3,4]. The toxicological data have been carried out according to OECD guidelines. Measurements of the solubilisation capacity of MCT-derivatives with different degrees of substitution were carried out according to known methods from the literature.

3. RESULTS AND DISCUSSION

3.1. Synthesis

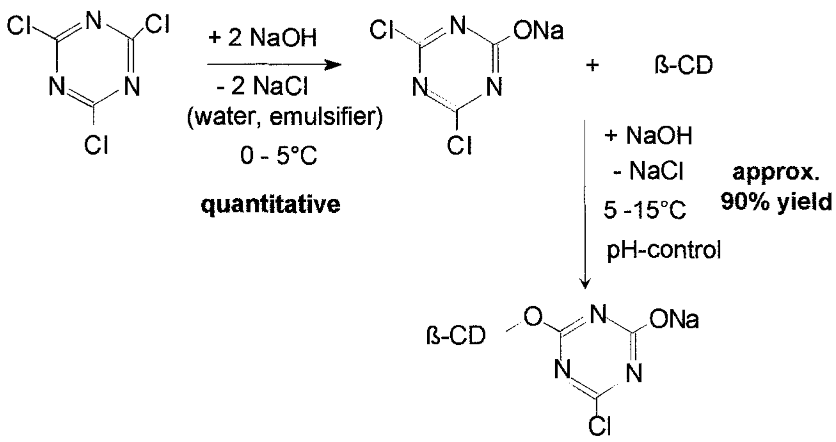

Fig. 2 Effective one pot synthesis of Beta W7 MCT

The first step in the effective one pot synthesis (Fig. 2) of BETA W 7 MCT is the preparation of a clear aqueous solution of dichlorotriazine sodium salt at low temperature starting from a dispersion of cyanuric chloride in water. Cyanuric chloride is an inexpensive chemical product available in very large quantities normally used for manufacturing e.g. agrochemical products or reactive dyes. It contains three chlorine atoms with different reactivity for nucleophiles. Under the chosen reaction conditions only one chlorine atom reacts with sodium hydroxide.

In the second reaction step of the synthesis the prepared dichlorotriazine compound reacts with ß-cyclodextrin in water at higher temperature under alkaline conditions and pH-control. When the degree of substitution of the reactive group decreases from DS = 1.0 to DS = 0.4 the achieved yield according to the triazine moiety increases from 78% to 88% due to a pre-complexation effect. After purification and spray drying BETA W7 MCT has an appearance of a stable white powder. Comparable Alpha- or Gamma-MCT derivatives are also available.

3.2. Properties

BETA W7 MCT is good soluble in water (> 30% (g/g)) and as a dry powder it is stable for a minimum of one year. In water hydrolysis occurs, the degree of hydrolysis and its reaction velocity mainly depends on temperature and pH-value. An aqueous solution of BETA W7 MCT e.g. is stable at pH = 8-9 and room temperature for at least 2 months. The hydrolysis becomes faster at higher temperature or at lower pH-value due to an autocatalytic effect of the released hydrogen chloride. The solubilisation capacity of BETA W7 MCT depends on the degree of substitution. With decreasing DS-value the solubilisation capacity increases. On the other hand a high fixation yield affords a high degree of substitution. Table 1 summarises these general properties:

Table 1 Beta W7 MCT - General properties

properties	benefit
reactive group	covalent bonding
Degree of substitution DS = 0.4	ensure high fixation yields ensure good complexing capacity
good water solubility (>30%)	easy handling

Table 2 reports a short overview of toxicological data known up to now. BETA W7 MCT has no irritating or sensitising effect according to OECD tests. Therefore no irritating or sensitising effect e.g. of MCT finished textiles is expected.

Table 2 Beta W7 MCT - Toxicological data

Test	System	Result
Acute Toxicity, oral (OECD No 401)	rat	LD50 > 2000 mg/kg
Primary skin irritation (OECD No 404)	rabbit	not irritating
Skin sensibilisation (OECD No 406)	guinea pig	not sensitising
Amestest (OECD No 471)	Salmonella typhimurium	not mutagenic

3.3. Possible applications of BETA W7 MCT

3.3.1. as building block

The formation of new cyclodextrin derivatives for special applications is readily achieved with this multifunctional agent. BETA W7 MCT reacts under slightly alkaline conditions with molecules bearing nucleophilic groups such as OH-, NH- or SH-groups. Fig. 3 shows as one example the reaction of BETA W7 MCT with amines. With this reaction it is e.g. possible to fix a hydrophobic anchor with a high affinity to hydrophobic surfaces covalently to the cyclodextrin. Potential applications could be the modification of synthetic textiles (e.g. polyester, polyamides, polyacrylics).

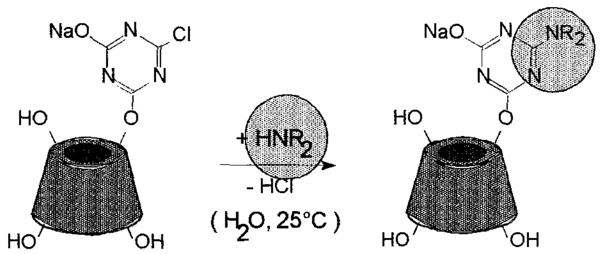

Fig. 3 Beta W7 MCT - Building block for new derivatives

3.3.2. as crosslinking agent

With a degree of substitution of DS = 0.4 BETA W7 MCT contains 2 -3 reactive triazine groups per cyclodextrin molecule. This is why this cyclodextrin derivative can also be used as a new formaldehyde free crosslinking agent with complexing capacity e.g. for the synthesis or modification of natural or synthetic polymers like starch, cellulose, polyallylamine or gelatine. With a higher degree of substitution BETA W7 MCT forms an insoluble cyclodextrin polymer by reacting with itself. Possible applications could be new chromatography materials or membranes for extraction purposes.

3.3.3. for surface modification

Surfaces like textiles or paper with nucleophilic groups can be modified with BETA W7 MCT using well established methods known from the textile industry. BETA W7 MCT has only a very low affinity to cotton, therefore it is impossible to finish cotton at high temperature in an exhausting process like some textile dyes. In this case the cyclodextrin derivative would react mainly with water and not with the textile. A possible way for textile finishing using BETA W7 MCT would be the so-called pad / roll process. Therefore an alkaline aqueous MCT solution is padded on the textile and squeezed. Fig. 4 shows this general procedure for textiles like cotton in a schematic representation. After drying the fixation of the reactive cyclodextrin takes place at elevated temperature. Final washing removes unreacted cyclodextrin.

In lab-trials using a drying oven a fixation time of 3-5 min at 150 °C was found to be suitable. Using contact heat this fixation time decreases to less than 1 min at 145°C or 10 - 20 sec. at 175°C. By this method a gravimetric fixation yield of approx. 80-90% could be reached.

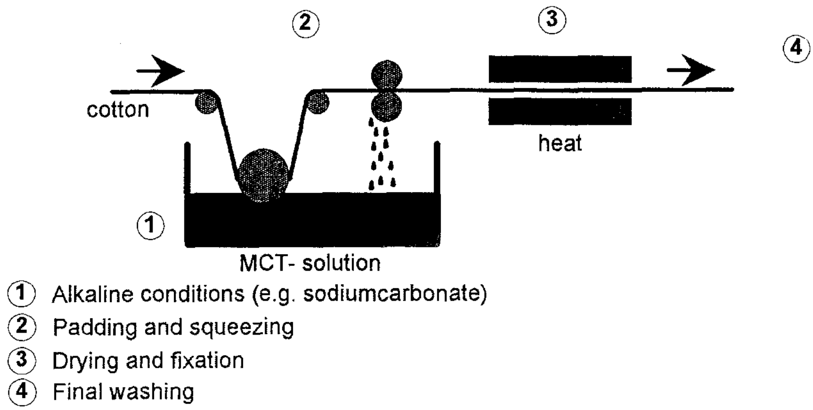

Fig. 4 Schematic representation for textile finishing with BETA W7 MCT

Measurements of the complexing capacity of MCT-finished cotton with hydrophobic substances like toluene indicate that the cavity of the bonded cyclodextrin is freely available and can be used for complexations. Increasing amounts of BETA W7 MCT on the textiles correspond to increasing amounts of complexed guest substances. The finishing is washfast and the components can be re-loaded after a washing step.

The cavity of the cyclodextrin can be utilised in a variety of ways. Active ingredients can be included in the cyclodextrin and released again in a controlled manner. A few possible applications of MCT-finished textiles are listed in table 3. For laundry odoring these textiles are able to complex fragrances. These components are released over a period of time after rewetting the textile. Simultaneously sweat absorption takes places when these textiles are worn. Another possible application of these textiles with new interesting properties would be an antimicrobial textile finishing for hospital hygiene.

Table 3 Possible applications of MCT-finished textiles

applications	examples
fragrance release	laundry odoring
odor absorption	sweat absorption
controlled release	antimicrobial finishing
stabilisation	active ingredients

4. CONCLUSION

With BETA W 7 MCT a new cyclodextrin derivative is commercially available in technical scale for a variety of possible uses (Fig. 5). The future will show the potential of this new derivative and its main application areas.

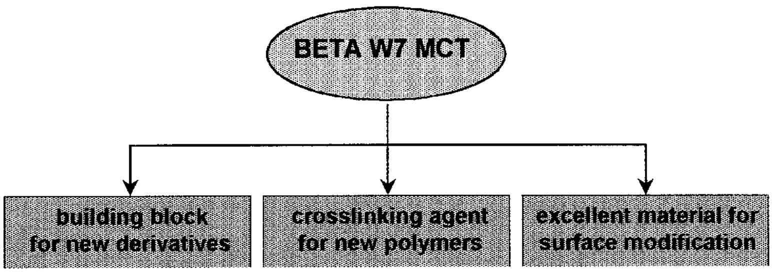

Fig. 5 Possible uses of BETA W7 MCT

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