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ORIGINAL PAPER

# Preparation and cross-linking properties of methacrylated sucrose

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**Abstract** By interfacial esterification of sucrose with methacryloyl chloride, an ester derivative of sucrose—methacryloyloxysucrose was prepared, which contains vinyl side groups. The structure of methacrylated sucrose (MS) was determined by means of FTIR, $^{1}$H NMR, and $^{13}$C NMR spectra. The MS was used as new cross-linker to cross-link poly(2-hydroxyethyl methacrylate). The influence of the amounts of cross-linking agent on the swelling behavior of these hydrogels was studied. Differential scanning calorimetry (DSC) was used for measuring the different states of water in hydrogel materials. DSC date showed that the content of freezing water in hydrogel decreased with growth of MS percentage.

**Keywords** Sucrose · Methacrylated sucrose · Cross-linker · Hydrogels · Freezing water

## Introduction

Sucrose and its derivatives are of interest as potentially useful substrates in the chemical and biological fields [1]. Due to its low price and high production, sucrose could be particularly important for this purpose. To develop new applications of sucrose and its derivatives, chemical modifications of sucrose have been investigated. Sucrose esters are very interesting compounds because the properties of sucrose can be modified to extend the use of this sugar by incorporating different

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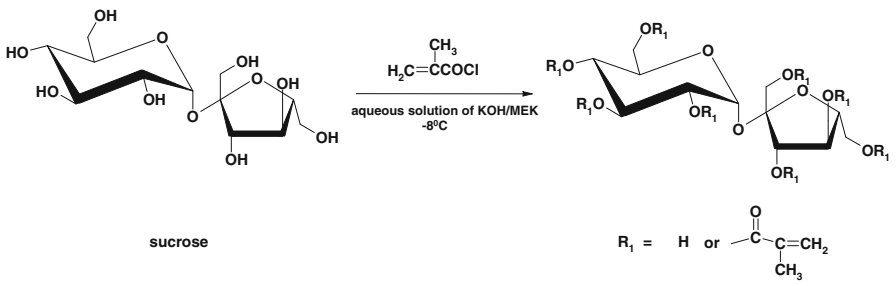
groups into the sucrose molecule. They are used in the industries of detergents, cosmetics, pharmaceuticals, as well as in the food sector as non toxic emulsifiers [2]. In early studies, a number of authors [3–6] have demonstrated the suitability of the method for the esterification of unprotected sucrose of acid chlorides. The possibility of using water as an alternative solvent for the esterification of sucrose instead of organic solvents such as *N*,*N*-dimethylformamide, dimethylsulfoxide, or pyridine has been studied [5]. In some cases, an aqueous solution of NaOH was used [6]. Enzymes have been also used as catalysts in the synthesis of carbohydrate (in particular sucrose) esters. The enzymatic regioselective synthesis of sucrose-1′-methacrylate from sucrose and vinyl methacrylate using subtilisin Carlsberg, a readily available bacterial serine protease, has been described in article [7]. Also Potier et al. [8] have obtained sucrose monomethacrylate in the reaction between sucrose and trifluorethyl methacrylate using Proteinase N enzyme as catalyst. The nonselective synthesis of methacrylated sucrose (MS) proposed in article [9] consisted of transesterification of sucrose with glycidyl methacrylate in DMSO in the presence of 4-(*N*,*N*-dimethylamino)pyridine as catalyst. Polymerizable or amphiphilic sucrose esters have been obtained regioselectively with a good yield [10, 11]. Schotten–Baumann's interfacial esterification is commonly known in organic chemistry as a method for the preparation of esters from alcohols and acid chlorides. Thus, it seems to be of interest to use this method to prepare sucrose esters.

Synthetic hydrogels based on poly(2-hydroxyethyl methacrylate) (PHEMA) have been tested for their use as suitable synthetic materials because of their superior biocompatibility, high permeability to small molecules (i.e., tissue metabolites) and hydrophilic properties [12]. The cross-linkers, which remain in the resulting hydrogels, usually show high toxicity. Therefore, it was necessary to develop an alternative, biodegradable, and low-toxicity cross-linker. In order to overcome these obstacles, we developed a novel cross-linker of sucrose with side vinyl groups.

The aim of this study was to prepare a sucrose derivative, containing reactive double bonds—methacryloyloxysucrose, by Schotten–Baumann's esterification of sucrose with methacryloyl chloride (Scheme 1) and to characterize the obtained product and its use as biodegradable cross-linker for cross-linking of poly(2-hydroxyethyl methacrylate).




**Scheme 1** Esterification of sucrose with MCl

## Experimental

### Materials

Sucrose trade product (available on the market) was used without additional purification. 2-Hydroxyethyl methacrylate (HEMA, Aldrich Chem., Co.) was purified by distillation under reduced pressure and the fraction of by 87–89 °C/5 mmHg was collected. Methacryloyl chloride (MCl) was prepared by treating methacrylic acid with thionyl chloride, b.p. 98–99 °C/760 mm Hg. Organic solvents: methyl ethyl ketone (MEK and toluene, Aldrich Chem., Co.) were dried and purified by common methods.

### Synthesis of MS

The MS was prepared according to a previously reported modified procedure for synthesis of methacrylated starch [13].

Solution A
Aqueous solution of sucrose: 0.5 mol $dm^{-3}$ groups OH: 1 vol.
Aqueous solution of KOH: 3 mol $dm^{-3}$: 1 vol.
Methyl ethyl ketone: 1 vol.

Solution B
Methacryloyl chloride: 1.5 mol equiv. (to the hydroxyl groups in sucrose).
Methyl ethyl ketone: 1.1 vol.
Toluene: 0.2 vol.

Solution A was introduced into a three-neck flask provided with a stirrer and a thermometer, cooled down to −8 °C, and then solution B was added dropwise. The process was carried out with intensive stirring for 40 min and then the reaction mixture was left for separation. The upper organic layer was separated from the aqueous lower one in which only sucrose esterified to a low degree remained. Next, the organic layer was dried over anhydrous $MgSO_4$. The product was precipitated with heptane and purified by dissolving in THF and reprecipitating with heptane. It was dried for a short time under vacuum at room temperature, protected against day light. The obtained MS has degree of substitution (DS) equal to 6.5. Yield was 49% based on DS equal to 6.5.

### Synthesis of cross-linked PHEMA

The free-radical polymerization of HEMA in the presence of AIBN as initiator and variable amounts of the cross-linking agent was carried out for 24 h, gradually raising the process temperature from 40 to 75 °C. Typical course of this process was as follows: 4.4 $cm^3$ of HEMA, 0.02 g AIBN, and the cross-linking agent in amounts ranging from 0.5 to 5.0 wt% in relation to the monomer were placed by means of a syringe between two glass plates separated by a silicon spacer

(120 × 50 × 0.9 mm). The glass plates were siliconized with a dimethyldichlorosilane. The polymerization was carried out in a laboratory drier under the following conditions: 2 h at 40 °C, 4 h at 55 °C, and 18 h at 75 °C. The gradual temperature raising prevented blister formation in the cross-linked PHEMA samples. After removal of the glass plates, the films obtained were dried at 75 °C. The samples were cut out from the films with the dimensions 15 × 10 × 0.9 mm for investigating their swelling behavior.

Before the examination of all, the samples were immersed in a large excess of ethanol for about 48 h at 25 °C to remove the noncross-linked material and then were dried at room temperature for about 24 h, and further dried in a 60 °C under vacuum to a constant weight.

## Photopolymerization

A thin layer of MS was applied onto a KBr plate by evaporation of the solvent from the MS solution in chloroform and then dried at room temperature under vacuum. The layer obtained was irradiated with a L6/58 quartz tube (37.5 W) without filter from a distance of 20 cm. The conversion of double bonds in MS during UV irradiation was investigated by FTIR spectroscopy. The absorption peak of the >C=C< at 1638 $cm^{-1}$ was used to calculate its conversion while the absorption peak of the carbonyl group at 1728 $cm^{-1}$ was used as standard. The conversion of double bonds was calculated according to Eq. 1

$$\% \text{ Conversion} = \frac{(A_{1638}/A_{1728})_0 - (A_{1638}/A_{1728})_t}{(A_{1638}/A_{1728})_0} \times 100 \quad (1)$$

where $(A_{1638}/A_{1728})_0$ and $(A_{1638}/A_{1728})_t$ are the ratio of absorbance at 1638 $cm^{-1}$ to that of 1728 $cm^{-1}$ before and after different irradiation times, respectively.

## Measurements

Infrared spectra were recorded using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. $^1$H-NMR and $^{13}$C-NMR spectra were obtained using a Bruker DPX 250 MHz spectrometer with DMSO-$d_6$ (for sucrose) or $CDCl_3$ (for MS) as solvent and TMS as an internal reference.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 instrument with a heating rate of 20 °C $min^{-1}$ from −30 to 200 °C in nitrogen atmosphere. The MS sample of about 5 mg was placed in an aluminum pan and aluminum cover was crimped on.

About 2–4 mg hydrogel sample which had been preswollen at room temperature was quickly cooled to −60 °C and equilibrated for 10 min. The sample was slowly heated at a program rate of 10 °C $min^{-1}$ up to 40 °C.

The DS of the MS was determined by titration method. The procedure in detail is as follows: 0.2 g of the sample was weighed accurately and placed in 250 $cm^3$ flask. Twenty milliliters of distilled water was added to flask and stirred overnight at room temperature. Thirty milliliters of 0.1 M NaOH was added and heated at 60 °C for

2 h under reflux condenser. After cooling to room temperature, titration was conducted with 0.1 M HCl using phenolphthalein as indicator [14].

The swelling of cross-linked PHEMA versus time was examined by determining the amount of absorbed swelling agent (water). About 0.18 g samples were immersed in excess water at 25 °C for various periods of time. The swollen samples were dried with a filter paper and weighed. The degree of swelling was calculated using the following expression:

$$\text{Degree of swelling } = [(W_t - W_0)/W_0] \quad (2)$$

where $W_t$ and $W_0$ are weights of the sample at time $t$ and zero (the dry state), respectively.

## Results and discussion

The FTIR spectra of sucrose and MS (DS = 6.5) are shown in Fig. 1a, b. In the spectrum of the esterification product, one can observe a strong absorption band at 1728 $cm^{-1}$ which can be ascribed to the valence vibration of >C=O. An absorption band corresponding to >C=C< appears at 1638 $cm^{-1}$. In addition, there is also a distinct absorption band within the range from 3640 to 3150 $cm^{-1}$ derived from hydroxyl groups, which indicates an incomplete esterification of sucrose.

Figure 2a, b shows the $^1H$ NMR spectra of sucrose and the MS. In spectrum (Fig. 2b) one can observe multiplets derived from methacryloyl group at 1.94 ppm (methyl proton, $H_b$) as well as at 5.45 and 6.14 ppm (protons at the double bond, $H_a$).

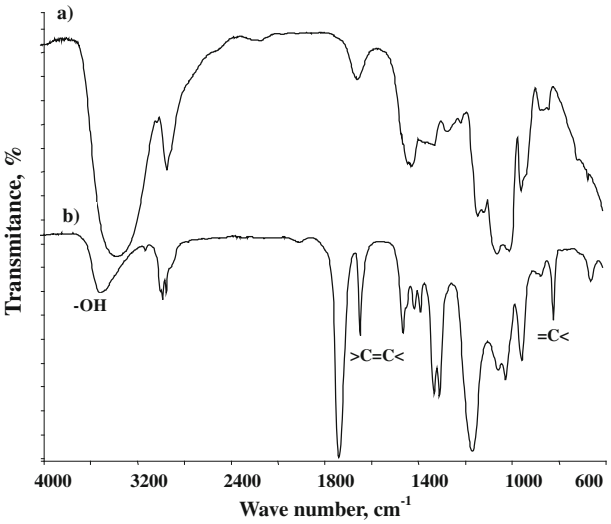



**Fig. 1** The FTIR spectra of **a** sucrose and **b** MS

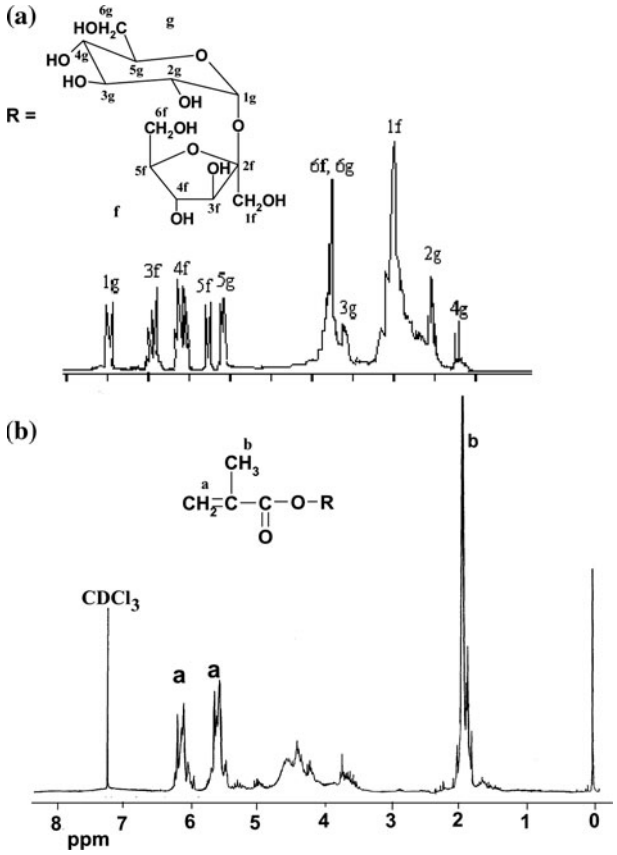



**Fig. 2** The $^{1}$H NMR spectra of **a** sucrose and **b** MS

The formation of the MS is also confirmed by the respective $^{13}$C NMR spectrum (Fig. 3b). Here, the signals of methacryloyl group are detected at 166.5 ($C_{16}$), 135.2 ($C_{14}$), 126.8 ($C_{13}$), and 19.0 ($C_{15}$) ppm.

The sucrose has eight hydroxyl groups, the maximum possible DS is 8.0. The determination of DS by titration involved complete basic hydrolysis of the ester linkages and titration of the excess alkali. DS for MS is 6.5 was determined by means of the method for starch esters.

Preliminary observation shows that MS is susceptible to the action of UV radiation. After irradiation of the sample under investigation, one can observe a broadening of the absorption band of the carbonyl group at 1728 cm$^{-1}$ (the area of this band is approximately constant) while the intensity of the absorption band of $CH_2$=C< ($\nu$ = 1638 cm$^{-1}$) is decreased. This is probably due to cleavage of double bonds by UV radiation and the formation of cross-linking in the molecule which results in a product insoluble in organic solvents. This process is illustrated in Fig. 4 showing the conversion of $CH_2$=C< versus irradiation time.

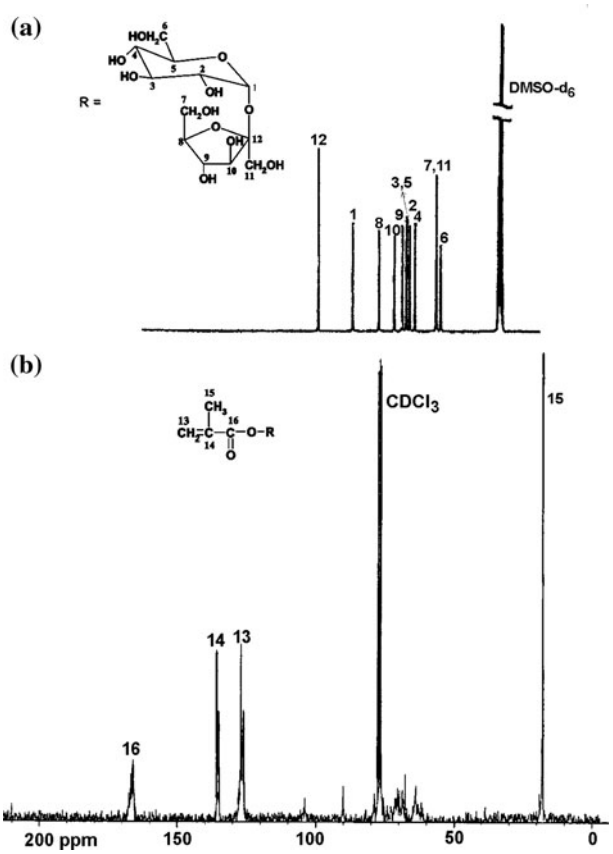



**Fig. 3** The $^{13}C$ NMR spectra of **a** sucrose and **b** MS

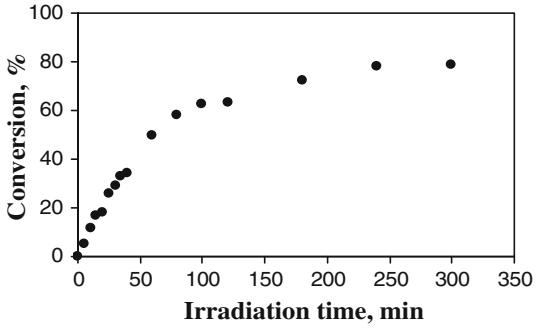



**Fig. 4** The conversion of $CH_2$=C< versus irradiation time

Figure 5 shows the curves illustrating the swelling of PHEMA networks in water obtained with various amounts (0.5–5.0 wt%) of MS. As can be seen, the equilibrium swelling is reached after about 24 h. Its value decreases with increasing amount of MS used in the initial reaction mixture.

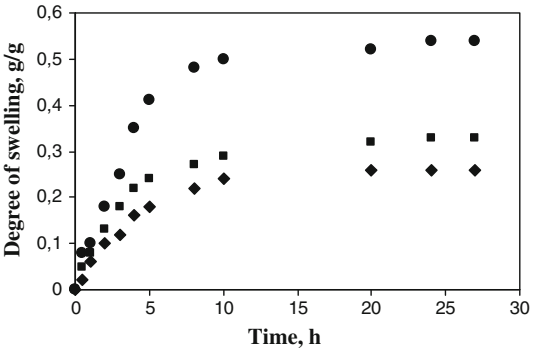



**Fig. 5** Swelling curves of PHEMA cross-linked with various amounts of MS: *circle* 0.5 wt%, *square* 3.0 wt%, *diamond* 5.0 wt%

The MS was characterized by DSC analysis. In the first heating cycle of MS an exothermic peak can be observed within the temperature range 63–165 °C. This exotherm probably results from the thermal polymerization of double bonds of the MS leading to cross-linked product what is confirmed by the disappearance of the peak in the MS sample during the second cycle of heating.

Differential scanning calorimetry can provide information about the states of water in the swollen hydrogels. In general, the state of water in the polymer hydrogel can be divided into free water, freezing bound water, and nonfreezing bound water [15, 16]. Free water is the freezing water, which does not take part in hydrogen bounding with polymer chains and shows a similar transition temperature and enthalpy of fusion in the DSC curves, as pure water does. Freezing bound water is the water which interacts weakly with polymer molecules and has a melting endotherm below 0 °C. Bound water is the nonfreezing water as it is immobilized from hydrogen bounds with polymer chains. These water molecules are immobilized and show no freezing peak. The water structure data of the hydrogels are listed in Table 1.

It can be seen from Fig. 6 that for the hydrogel with 0.5 wt% of cross-linker the endothermic peak was separated into two peaks, one remaining at close to 0 °C, and the other shifting to about −40 °C. These two peaks indicate the existence of the two types of water in the hydrogel, the free water and the freezing bound water.

It has been found that the hydrogel with 0.5 wt% of cross-linker contain more freezing water including the free water and the freezing bound water, while the hydrogels with 3.0 and 5.0 wt% of MS, respectively are occupied mainly by the nonfreezing bound water.

**Table 1** Calculated freezing water and nonfreezing bound water in swollen hydrogels from DSC results

| Hydrogels | Mass % MS in the gel | g-water/g-swollen gel | | | Freezing water/ total water (%) | Nonfreezing bound water/total water (%) |
|---|---|---|---|---|---|---|
| | | Total water | Freezing water | Nonfreezing bound water | | |
| Gel1 | 0.5 | 0.490 | 0.231 | 0.259 | 47.14 | 52.86 |
| Gel2 | 3.0 | 0.257 | 0.060 | 0.197 | 23.35 | 76.65 |
| Gel3 | 5.0 | 0.215 | 0.022 | 0.193 | 10.23 | 89.77 |

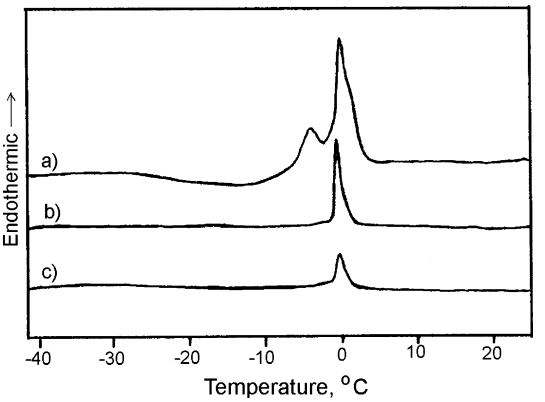



**Fig. 6** DSC heating scans of the hydrogels with different amounts of MS: **a** 0.5 wt%, **b** 3.0 wt%, **c** 5.0 wt% swollen in deionised water

## Conclusions

The studies performed have shown that the esterification of sucrose with MCl by Schotten–Baumann's method results in formation of MS. The MS was used as new cross-linker to cross-link poly(2-hydroxyethyl methacrylate). DSC date showed that the content of freezing water in hydrogel decreased with growth of MS percentage. It has been found that the high-hydration hydrogel contain relatively more freezing water, while the low-hydration hydrogels are occupied mainly by the nonfreezing bound water. The differences between the DSC results were explained by a structural transformation during cooling. There are two states of water in the unfrozen hydrogel, i.e., unfrozen water and disordered water which is mainly formed in narrow apertures in the hydrogel. The degree of equilibrium swelling of the hydrogels prepared depends on the quantity of the cross-linker used.



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