

# PREPARATION AND CHARACTERISATION OF (METH)ACRYLOYLOXYSTARCH

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## Abstract

*By Schotten-Bauman's esterification of starch with (meth)acryloyl chlorides, an ester derivative of starch – (meth)acryloyloxystarch – was prepared, which contains double bonds. The original starch and (meth)acryloyloxystarch were characterised by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, GPC and TGA. (Meth)acryloyloxystarch was polymerised in solution by the free-radical process and by photopolymerisation in a solid state to obtain a crosslinked product.*

## Keywords

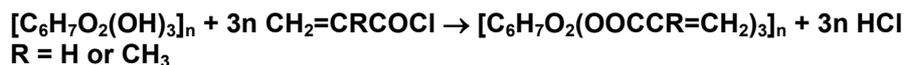
*Starch, modified starch, (meth)acryloyloxystarch, characterisation, polymerisation, thermal stability*

## Introduction

Starch is a known carbohydrate in which, regardless of its origin, two polysaccharides are found, namely amylose and amylopectin. Amylose is essentially a linear polymer consisting of 1,4- $\alpha$ -D-glucopyranosyl units. On the other hand, amylopectin is a highly branched polymer containing 1,4- $\alpha$ -D-glucopyranosyl units with 1,6 links at branch points. Amylose is soluble in water, whereas amylopectin is only sparingly soluble [1]. Owing to its properties, starch has found application in pharmacy, cosmetics, therapeutics, papermaking, and **the textile industry**. The development of the possibilities for applying this natural polymer is connected with the modification of its properties, among other things, by chemical modification.

Literature reports [2-8] have mainly described the ester derivatives of starch. The preparation of these derivatives with a high degree of substitution is not easy, mainly due to the insolubility of starch granules in a suitable medium without significant degradation of the starch. Among the various procedures of starch ester preparation which have attempted to overcome this difficulty, the gelatinisation pretreatment of starch and the dispersion in inert solvents at elevated and 100m temperatures are applied [2-4]. The addition of the ester group is carried out by employing the appropriate acid chloride or acid anhydride in the presence of pyridine.

The aim of the present paper was to prepare a starch derivative – (meth)acryloyloxystarch – by starch esterification with acryloyl chloride and methacryloyl chloride by Schotten-Bauman's method (Scheme 1), as well as the physical and chemical characterisation of the esterification products. The ability of the double bond connected to the polysaccharide chain to cause radical polymerisation and photopolymerisation was also examined.



Scheme 1.

## Experimental

### Materials

Starch (ST), a commercial product (POCh, Gliwice, Poland), with  $[\eta] = 0.08 \text{ dL/g}$  (in DMSO at 25°C), was dried prior to use at a temperature of 100°C under a vacuum. Acryloyl chloride (ACI) and methacryloyl chloride (MCI) were prepared by reacting acrylic acid or methacrylic acid with benzoyl

chloride by following the procedure of Stampel et al.[8]. The organic solvents, methyl ethyl ketone (MEK), dioxane, and dimethyl sulphoxide (DMSO), were purified by generally known procedures.

### **Synthesis of Acryloyloxystarch (AST) and Methacryloyloxystarch (MST)**

AST and MST were prepared by Schotten-Bauman's esterification of ST with ACI or MCI. The optimum process parameters were found experimentally:

#### *Solution A*

Solution of ST (3:2 by vol. H <sub>2</sub> O:THF) 0.5 mol/L groups OH	1 vol.
Aqueous solution of KOH 3.0 mol/L	1 vol.
MEK	1 vol.

#### *Solution B*

(meth)acryloyl chloride 1.2 mole-equiv. (to the hydroxyl groups in ST)	
MEK	1.1 vol.
Toluene	0.2 vol.

Solution A was introduced into a three-necked 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 30 min, and then the mixture was left for separation. The upper organic layer was separated from the lower one, in which only the ST esterified to a low extent remained. Next, the organic layer was dried with anhydrous MgSO<sub>4</sub>. The product of esterification was precipitated with heptane, and purified by dissolving in chloroform and reprecipitating with heptane. It was dried at room temperature under a vacuum.

### **Measurements**

Infrared spectra were recorded using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were obtained using a Bruker DPX 250 MHz spectrometer with DMSO-d<sub>6</sub> and CDCl<sub>3</sub> as solvents and TMS as an internal reference. The extent of the esterification was determined from the carbon and hydrogen content of the product, as measured by elemental analysis, as well as by the alkali saponification procedure described by Genung & Mallatt [9].

The values of the number average molecular weight ( $M_n$ ), the weight average molecular weight ( $M_w$ ) and the polydispersity ( $M_w/M_n$ ) of the AST were determined by gel permeation chromatography (GPC). A chromatogram in THF were obtained in the Waters modular system using an Ultrastaygel Linear Column (mixed pore size, bed diameter 7 μm) and a Waters 410 RI-detector under the following conditions: column temperature of 35°C, eluent flow rate of 0.8 ml/min, and an injection volume of 25 μL. The average molecular weight was calculated on the basis of a polystyrene standard calibration curve. The intrinsic viscosity ( $\eta$ ) of ST, AST and MST were measured in DMSO at a temperature of 25°C, using a Ubbelohde viscometer.

Thermogravimetric measurements were carried out using a TGA-7 thermobalance from Perkin-Elmer under nitrogen (heating rate of 20°C min<sup>-1</sup>).

### **Polymerisation**

The polymerisation of AST and MST was carried out in a dioxane solution under nitrogen at 75°C in the presence of AIBN as an initiator (0.9 g/L). The concentration of AST and MST ranged from 120 to 26 g/L. The polymerisation process was carried out for about 0.5 h to produce homogeneous gels. These gels were collected by filtration, carefully washed with warm chloroform, and dried to a constant weight at 60°C under a vacuum.

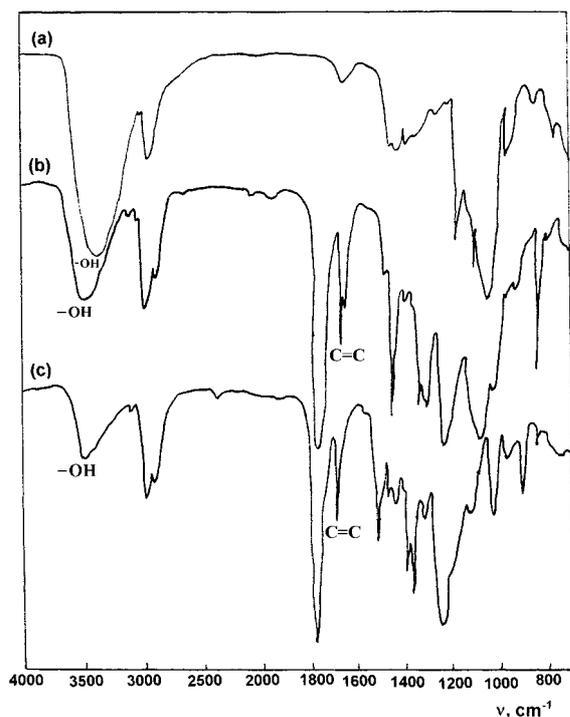
### **Photopolymerisation**

A thin layer of AST and MST was applied onto a NaCl plate by the evaporation of the solvent from the chloroform solution, and then dried at room temperature under a vacuum. The resultant films were irradiated with an L6/58 quartz tube (37.5 W) without a filter from a distance of 30 cm. The rate of disappearance of the absorbance of >C=C< ( $\nu = 1635 \text{ cm}^{-1}$ ) in AST and MST after various irradiation times was recorded using an FTIR spectrophotometer.

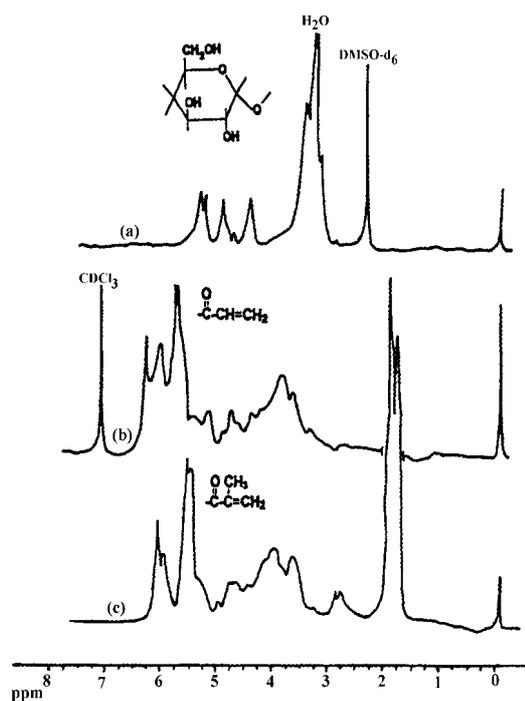
## Results and Discussion

### Spectral Characterisation of Starch Esters

Figure 1 (a-c) shows the FTIR spectra of the original ST (Figure 1a), AST (Figure 1b) and MST (Figure 1 c). As can be seen, in the spectrum of AST and MST, as compared to the ST, the additional absorption bands appear at  $1730\text{ cm}^{-1}$  and at  $1635\text{ cm}^{-1}$  which can be ascribed to the bonds  $>\text{C}=\text{O}$  and to  $>\text{C}=\text{C}<$  respectively. In addition, there is also a distinct absorption band within  $3700\text{-}3140\text{ cm}^{-1}$  corresponding to the hydroxyl group, which testifies to the incomplete esterification of ST.



**Figure 1.** FTIR spectra of (a) ST (b) AST and (c) MST



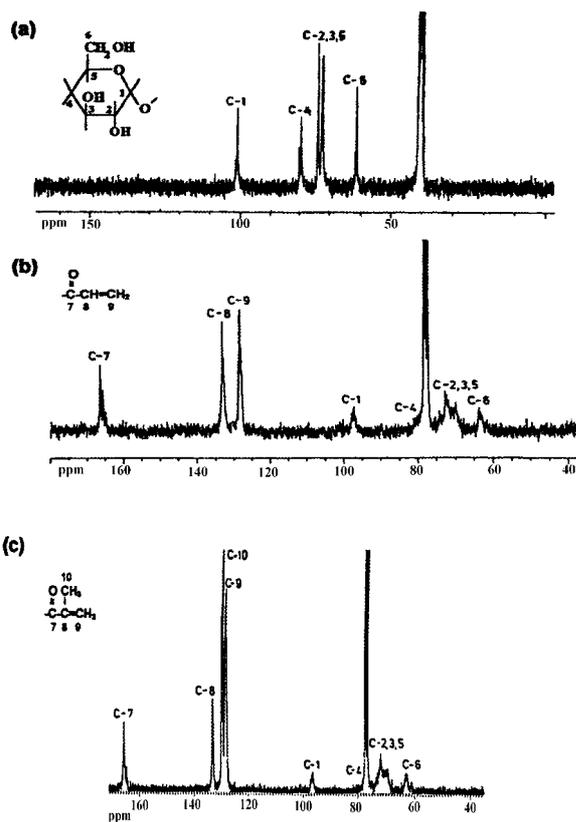
**Figure 2.**  $^1\text{H-NMR}$  spectra of (a) ST, (b) AST and (c) MST

In the  $^1\text{H-NMR}$  spectrum of AST and MST (Fig. 2b,c), in comparison with the spectrum of ST (Fig. 2a) there are weakly developed bands within the range of  $5.65\text{-}6.73\text{ ppm}$ , which can be ascribed to the protons of vinyl groups. For the MST, an additional new peak appears at  $1.62\text{-}2.43\text{ ppm}$  due to the protons of  $\alpha\text{-CH}_3$

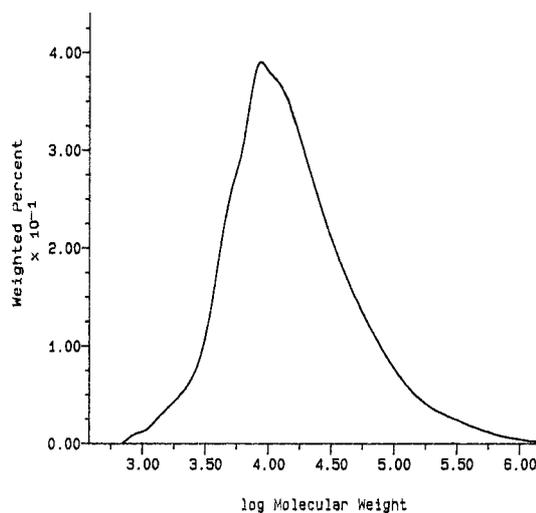
The  $^{13}\text{C-NMR}$  spectra of the original ST, AST and MST are shown in Figure 3(a-c). For the ST, C-1, C-4, and C-6 have chemical shifts at  $101.6$ ,  $80.9$ , and  $61.2\text{ ppm}$  respectively, while C-2, C-3, and C-5 have chemical shifts at  $68.2 - 71.3\text{ ppm}$ . For the AST, the new peaks appearing at  $171.3$ ,  $146.1$ , and  $135.8\text{ ppm}$  are assigned as C-7, C-8, and C-9 on the acryloyloxy moiety. Moreover, for the MST, the additional new peak which appears at  $140.0\text{ ppm}$  is assigned as C-10 on methacryloyloxy moiety.

The elemental analysis of sample AST resulted in C,  $53.76\%$ , and H,  $5.32\%$ . The theoretical values calculated for diacryloyloxy starch  $\text{C}_6\text{H}_8\text{O}_5(\text{CH}_2=\text{CHCO})_2$  ( $270.24$ ) are C,  $53.33\%$ , and H,  $5.22\%$ . For the sample MST we obtained in C,  $57.06\%$ , and H,  $6.24\%$ . The theoretical values calculated for dimethacryloyloxystarch  $\text{C}_6\text{H}_8\text{O}_5[\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}]_2$  ( $298.24$ ) are C,  $56.33\%$ , and H,  $6.22\%$

The analysis of the above FTIR,  $^1\text{H}$ ,  $^{13}\text{C-NMR}$  spectra and the results of the elemental analysis confirm the structure of the modified ST



**Figure 3.**  $^{13}\text{C}$ -NMR spectra of (a) ST, (b) AST and (c) MST



**Figure 4.** The molecular weight distribution of AST

Molecular weights and molecular weight distribution measurements by GPC made on the sample of AST gave  $\overline{M}_n = 8900$  and  $\overline{M}_w = 24,300$  with a polydispersity value of  $\overline{M}_w/\overline{M}_n = 2.73$ . For example, the molecular weight distribution of this starch ester is shown in Figure 4.

Similar values of the intrinsic viscosities of AST, MST and ST samples ( $[\eta] = 0.09$  dL/g,  $[\eta] = 0.07$  dL/g and  $[\eta] = 0.08$  dL/g, respectively) testify to the fact that there is no degradation of the polysaccharide chain under the esterification conditions.

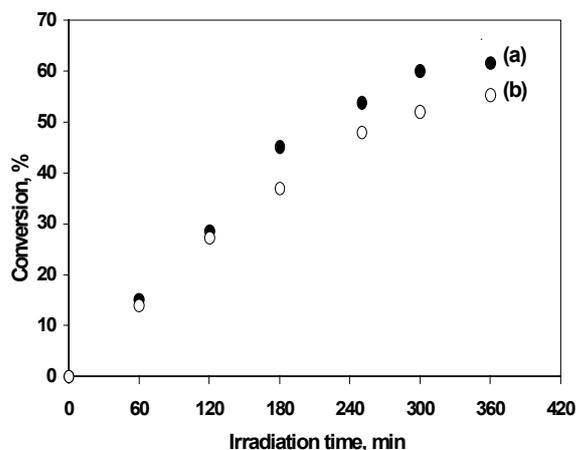
Difficulties in obtaining a complete substitution of AST and MST can, among other things, be due to the considerable steric effects of the (meth)acrylate groups combined with the polysaccharide chain. All the esterification products obtained in the reaction between ST and ACl or MCl are readily soluble in solvents such as chloroform, tetrahydrofuran, dioxane, acetone, and DMSO, but they are insoluble in alcohols, heptane, and water.

### Polymerisation and Photopolymerisation of (Meth)acryloyloxystarch

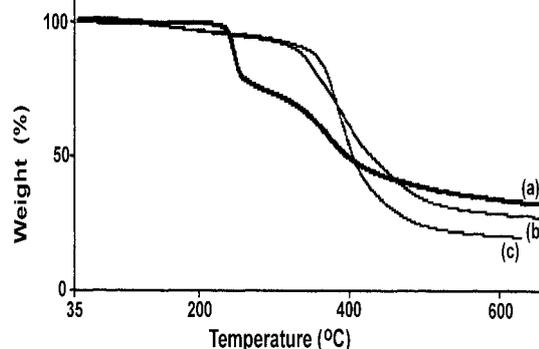
The examination performed of the polymerisation of AST and MST showed that – with AST and MST concentrations from 120 to 26 g/L,  $[\text{AIBN}] = 0.9$  g/L, temperature of  $75^\circ\text{C}$ , time of about 0.5 h, and in dioxane as the solvent, already at double bond conversion degrees numbering a dozen or so – crosslinked products (gels) are formed which are insoluble in organic solvents. Probably the main kind of reactions which take place under these process conditions are intermolecular. The FTIR analysis of the polymerisation products obtained showed that all of them contain unreacted double bonds connected to the polysaccharide chain.

Preliminary observations showed that AST and MST is susceptible to the action of UV radiation. After the irradiation of the samples under investigation, one can observe a broadening of the absorption band of the carbonyl group at  $1730\text{ cm}^{-1}$  (the surface area of this band is approximately constant), while the intensity of the absorption band of  $>\text{C}=\text{C}<$  is decreased ( $\nu = 1635\text{ cm}^{-1}$ ). This is probably due to the cleavage of double bonds by UV radiation and the formation of crosslinkages in the polymer, which results in a product insoluble in organic solvents. This process is illustrated in Figures 5a and 5b, which shows the disappearance rate of  $>\text{C}=\text{C}<$  vs. irradiation time. As seen, the double

bonds in AST disappear slightly faster. This may be associated with most reactivity acrylic groups. The cast films of AST and MST on glass or metal, after UV irradiation, show low adhesion to the base and are brittle.



**Figure 5.** The rate of disappearance of  $>C=C<$  vs. irradiation time for (a) AST and (b) MST



**Figure 6.** TGA curves of (a) ST (b) AST and (c) MST

### Thermal Analysis of (Meth)acryloyloxystarch

The thermograms of initial ST, AST and MST are shown in Figure 6 (a-c). The thermal decomposition of initial ST occurred in three stages. The first stage was observed at 230-265°C, the second stage at 265-435°C and the third stage at 435-656°C. In the case of the MST, thermal decomposition starts at 350°C, its maximum rate occurring at 390°C. In addition, a gradual weight decrease is observed at the beginning in AST and MST samples, which could be due to the evaporation of residual impurity. The results obtained clearly point to the higher thermal stability of ester starch in relation to ST.

### Conclusions

The studies performed showed that the esterification of starch with acryloyl chloride or methacryloyl chloride by Schotten-Bauman's method results in a new derivative of starch – (meth)acryloyloxystarch – in which double bonds are combined with the polysaccharide chain. Under optimal esterification conditions, one can obtain products with only a substitution degree of about 2. The free-radical polymerisation of (meth)acryloyloxystarch in solution and its photopolymerisation in the solid state result in crosslinked products. The results obtained from DSC and TG measurements show an increase in the thermal stability of (meth)acryloyloxystarch when compared with the original starch.

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