

Synthesis and Characterization of Acryloyloxystarch

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ABSTRACT: By Schotten–Bauman's esterification of amylose with acryloyl chloride, a new ester derivative of starch—acryloyloxyamylose—was prepared, which contains double bonds. The effects of the reagent ratio, KOH concentration, and reaction time on the degree of amylose esterification were examined. The original amylose and acryloyloxyamylose were characterized by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, GPC, and DSC. Acryloyloxyamylose was polymerized in solution by the free-radical process and by photopolymerization in a solid state to obtain a crosslinked product. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2123–2129, 1997

Key words: acryloyloxyamylose; characterization; polymerization; crosslinking

INTRODUCTION

Starch is a known carbohydrate in which, regardless its origin, there are two polysaccharides composed of 1,4- α -D-glucopyranosyl units. One of them is linear amylose, and the second one, amylopectin containing a branched chain. Owing to its properties, starch has found application in pharmacy, cosmetics, therapeutics, papermaking, and textile industry. The development of application possibilities of this natural polymer is connected with the modification of its properties, among other things, by chemical modification.

Literature reports^{1–8} described mainly the ester derivatives of starch. The preparation of these derivatives with a high substitution degree is not easy, mainly due to the insolubility of starch granules in a suitable medium without a significant degradation of starch. Among the various procedures of starch ester preparation attempted to overcome this difficulty are the gelatinization pretreatment of starch¹ and the dispersion in inert solvents at elevated^{2,3} as well as at room temperatures.⁴ The addition of the ester group is carried out by employing the appropriate acid chloride or the acid anhydride in the presence of pyridine.

The aim of the present article was to prepare a new starch derivative—acryloyloxyamylose—by amylose esterification with acryloyl chloride by Schotten–Bauman's method, as well as the physical and chemical characterization of the esterification products. For the purpose of the application of acryloyloxyamylose as a multifunctional crosslinking agent, the ability of the acrylate double bond connected to the polysaccharide chain to radical polymerization and photopolymerization was also examined.

EXPERIMENTAL

Materials

Amylose (AM), a commercial product (POCh, Gliwice, Poland), with $[\eta] = 0.08$ dL/g (in DMSO at 25°C), was dried prior to use at a temperature of 80°C under a vacuum. Acryloyl chloride (ACl) was prepared by reacting acrylic acid with benzoyl chloride by following the procedure of Stampel et al.⁹ Organic solvents, methyl ethyl ketone (MEK), dioxane, and dimethyl sulfoxide (DMSO), were purified by generally known procedures.

Synthesis of Acryloyloxyamylose

To a three-necked flask, provided with a stirrer and a thermometer, 2 parts by vol of aqueous AM

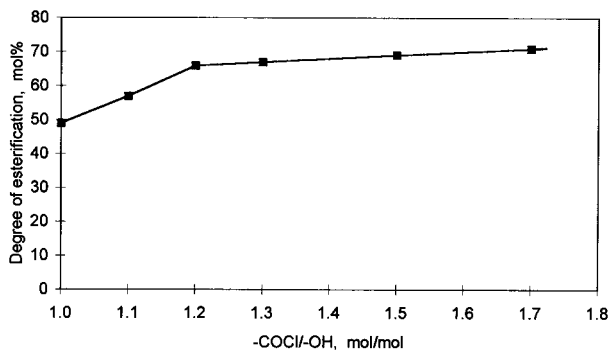


Figure 1 Dependence of the esterification degree on the $-\text{COCl}/-\text{OH}$ ratio. Reaction conditions: $[\text{AM}] = 0.15 \text{ mol/L}$, 40 mL; $[\text{KOH}] = 3 \text{ mol/L}$, 20 mL; MEK 42 mL; toluene 4 mL; temperature -7°C ; time 40 min.

solution with a concentration equal to 1.5 mol/L ($[\text{AM}]$ calculated per D-glucopyranosyl unit; with three hydroxyl groups per unit), 1 part by vol of aqueous KOH solution ($[\text{KOH}]$ from 1.0 to 5.0 mol/L), and 1 part by vol of MEK were added and cooled down to -7°C . Then, ACl in a mixture of 1.1 parts by vol of MEK and 0.2 part by vol of toluene were added dropwise. The reaction was run for some scores minutes with intensive stirring and then the reaction mixture was left for separation. The upper organic layer (esterification product, toluene, MEK) was separated from the aqueous lower one in which remained the unreacted amylose. Then, the organic layer was dried over anhydrous Na_2SO_4 . 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.

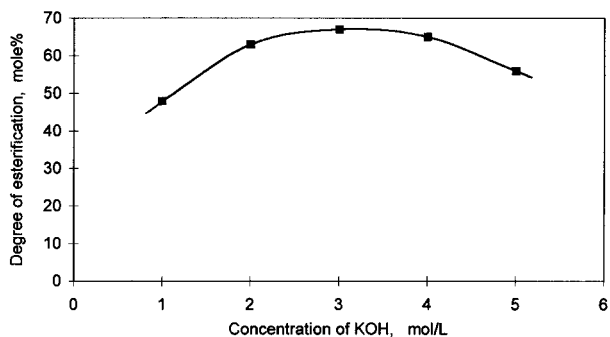


Figure 2 Dependence of the esterification degree on the KOH concentration. Reaction conditions: $[\text{AM}] = 0.15 \text{ mol/L}$, 40 mL; ACl 1.2 mol-equiv (to the hydroxyl groups of AM); MEK 42 mL; toluene 4 mL; temperature -7°C ; time 40 min.

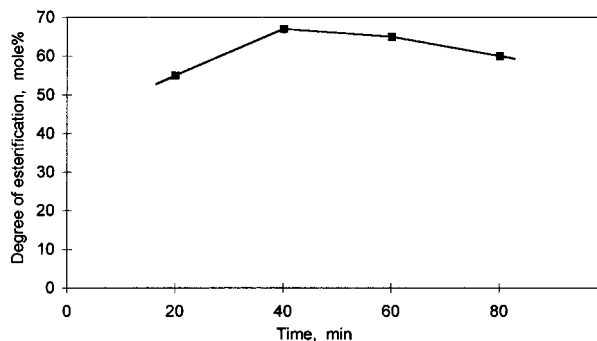


Figure 3 Dependence of the esterification degree on time. Reaction conditions: $[\text{AM}] = 0.15 \text{ mol/L}$, 40 mL; $[\text{KOH}] = 3 \text{ mol/L}$, 20 mL; ACl 1.2 mol-equiv (to the hydroxyl groups of AM); MEK 42 mL; toluene 4 mL; temperature -7°C .

Measurements

Infrared spectra were recorded using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. ^{13}C - and ^1H -NMR spectra were obtained using a Bruker DPX 250 MHz spectrometer with $\text{DMSO}-d_6$ and CDCl_3 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 and Mallatt.¹⁰

Chromatograms were performed in a Hewlett-Packard HP-1050 in a PLgel 5 μm mixed-C column at 80°C , with an eluent flow rate of 0.8 mL/min injection volume of 20 μL . An RI detector HP 1047A was used. The average molecular weight was calculated from a polystyrene standard calibration curve.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 instrument with a heating rate of $10^\circ\text{C}/\text{min}$ from 40 to 250°C in a nitrogen atmosphere. The sample of about 5 mg was placed in an aluminum pan and an aluminum cover was crimped on. The intrinsic viscosity $[\eta]$ of AM and acryloyloxyamylose was measured in DMSO at a temperature of 25°C , using a Ubbelohde viscometer.

Polymerization

The polymerization of acryloyloxyamylose 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 acryloyloxyamylose ranged from 120 to 26 g/L. The polymeriza-

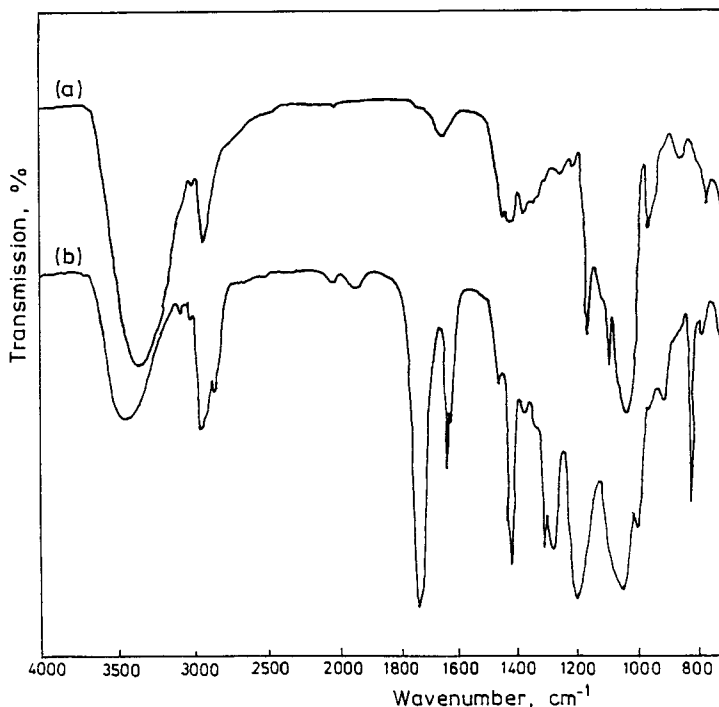


Figure 4 FTIR spectra of (a) amylose and (b) diacryloyloxyamylose.

tion process was carried out for about 0.5 h to produce a homogeneous gel. The gel was collected by filtration, carefully washed with warm chloroform, and dried to a constant weight at 60°C under a vacuum.

Photopolymerization

A thin layer of acryloyloxyamylose 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 film was 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 $\text{CH}_2=\text{CH}-$ ($\nu = 1635 \text{ cm}^{-1}$) in acryloyloxyamylose after various irradiation times was recorded using an FTIR spectrophotometer.

RESULTS AND DISCUSSION

Preparation of Acryloyloxyamylose

The results of the examined dependence of AM esterification with ACl on the $-\text{COCl}/-\text{OH}$ molar ratio, concentration of KOH, and reaction time are shown in Figures 1–3. As seen in Figure 1, once the $-\text{COCl}/-\text{OH}$ ratio exceeds 1.2, there

is already observed a slight increase in the substitution degree of hydroxyl groups in AM. The optimal concentration of KOH in the reaction is about 3.0 mol/L; its further increase results in a decreased esterification degree, which is likely to be associated with the intensification of acid chloride hydrolysis (Fig. 2). After about 40 min of the process duration, there is no further increase in the esterification degree (Fig. 3).

From the presented experimental data, it follows that the described method, despite the modification of some reaction parameters, can provide products only with esterification degrees from 49 to 71% (the degree of substitution [DS] from 1.47 to 2.11). Difficulties in obtaining a complete substitution of AM can be due, among other things, to considerable steric effects of the acrylate groups combined with the polysaccharide chain. All the esterification products obtained in the reaction between AM and ACl are readily soluble in solvents such as chloroform, tetrahydrofuran, dioxane, acetone, and DMSO, but they are insoluble in alcohols, heptane, and water.

Characterization of Diacryloyloxyamylose

A detailed physical and chemical characterization was performed for the sample with a DS of about

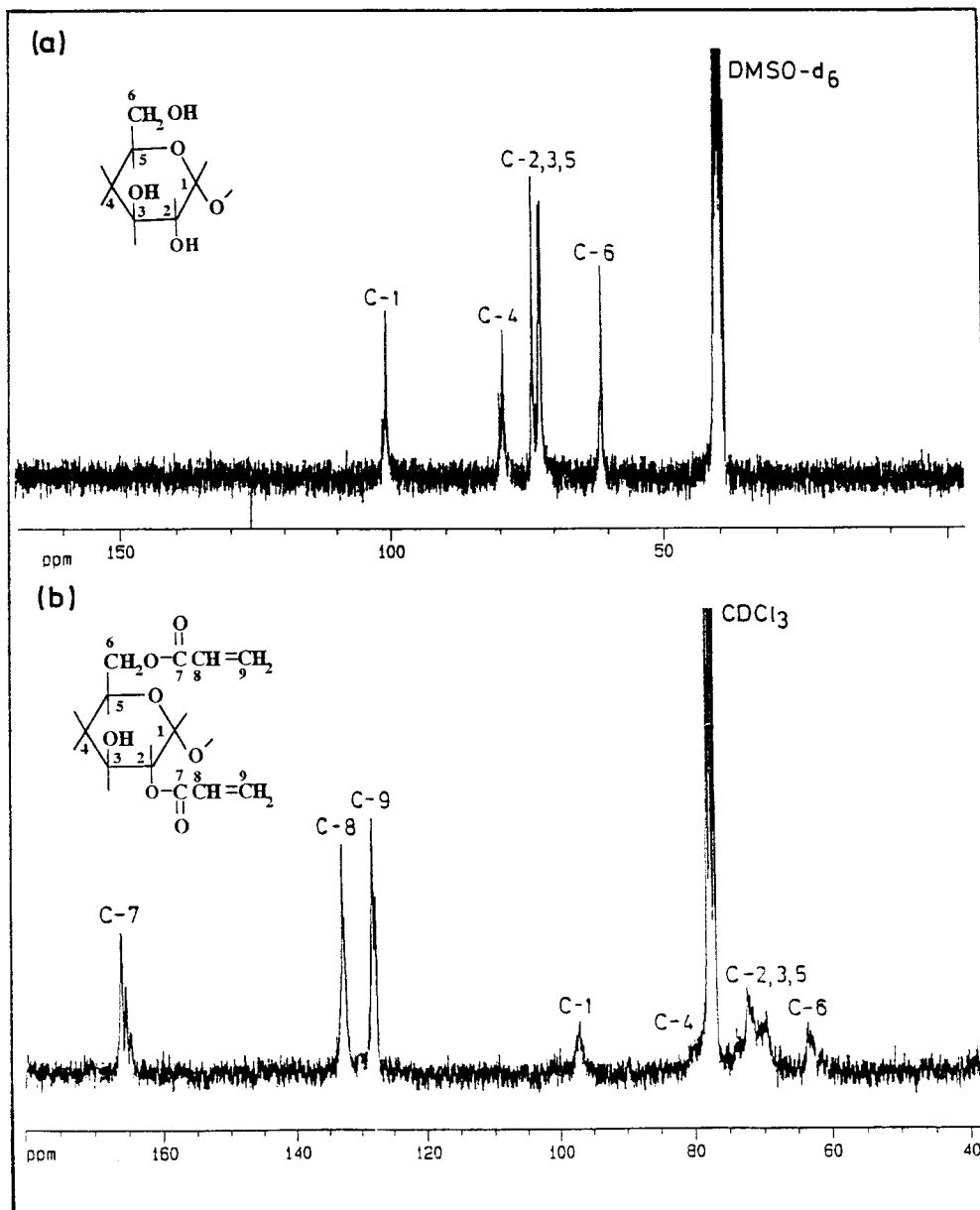


Figure 5 ^{13}C -NMR spectra (62 MHz) of (a) amylose at $\text{DMSO-}d_6$ and (b) diacryloyloxyamylose at CDCl_3 .

2—diacryloyloxyamylose (DAAM). The elemental analysis of this sample resulted in C, 53.76%, and H, 5.32%. The theoretical values calculated for diacryloyloxyamylose $\text{C}_6\text{H}_8\text{O}_5$ $(\text{CH}_2=\text{CHCO})_2$ (270.24) are C, 53.33%, and H, 5.22%.

The FTIR spectra of DAAM and AM are shown in Figure 4(a) and (b). In the spectrum of the esterification product, as compared with that of AM, one can observe a strong absorption band at 1730 cm^{-1} which can be ascribed to the valence vibration of $\text{C}=\text{O}$. An absorption band corre-

sponding to $\text{CH}_2=\text{CH}-$ appears at 1635 cm^{-1} . In addition, there is also a distinct absorption band within $3700\text{--}3140\text{ cm}^{-1}$ corresponding to the hydroxyl group, which testifies to an incomplete esterification of AM.

The ^{13}C -NMR spectra of the original AM and DAAM are shown in Figure 5(a) and (b). For the AM, C-1, C-4, and C-6 have chemical shifts at 101.6, 80.9, and 61.2 ppm, respectively, while C-2, C-3, and C-5 have chemical shifts at 68.2–71.3 ppm. For the DAAM, new peaks appearing at

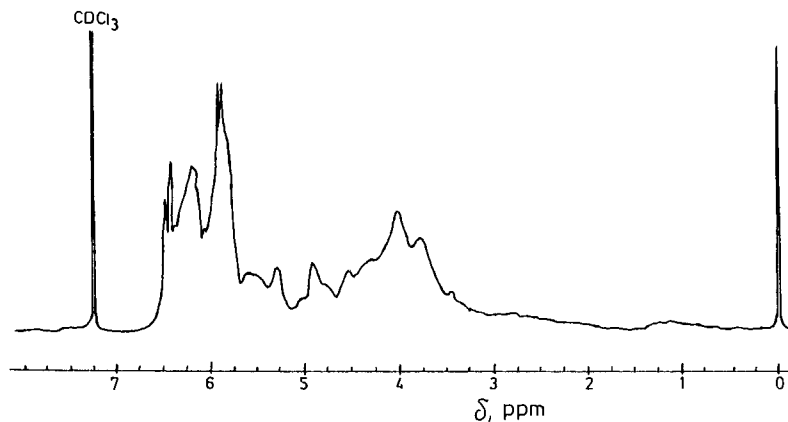


Figure 6 $^1\text{H-NMR}$ spectrum (250 MHz) of diacryloyloxyamylose at CDCl_3 .

171.3, 146.1, and 135.8 ppm are assigned as C-7, C-8, and C-9 on the acryloyloxy moiety. In the $^1\text{H-NMR}$ spectrum of DAAM (Fig. 6), there is, among other things, a weakly developed band within the range 5.65–6.73 ppm which can be ascribed to the protons of $\text{CH}_2=\text{CH}-$.

Molecular weights and molecular weight distribution measurements by GPC made on the sample of DAAM gave $\bar{M}_n = 18,920$ and $\bar{M}_w = 93,290$ with a polydispersity value of $\bar{M}_w/\bar{M}_n = 4.95$. The molecular weight distribution of this modification product is shown in Figure 7. Similar values of the intrinsic viscosities of DAAM and AM samples ($[\eta] = 0.09$ 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.

Polymerization and Photopolymerization of Diacryloyloxyamylose

The performed examination of the polymerization of DAAM showed that with DAAM concentrations

from 120 to 26 g/L, $[\text{AIBN}] = 0.9$ g/L, temperature of 75°C , time about of 0.5 h, and in dioxane as the solvent, already at double-bond conversion degrees amounting to a dozen or so, there are formed crosslinked products (gels) which are insoluble in organic solvents. Probably, intermolecular reactions are the main ones which take place under these process conditions. The IR analysis of the obtained polymerization products showed that all of them contain unreacted double bonds connected to the polysaccharide chain.

Preliminary observations showed that DAAM is susceptible to the action of UV radiation. After the irradiation of the sample under investigation, one can observe a broadening of the absorption band of the carbonyl group at 1730 cm^{-1} (the surface area of this band is approximately constant), while the intensity of the absorption band of $\text{CH}_2=\text{CH}-$ 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

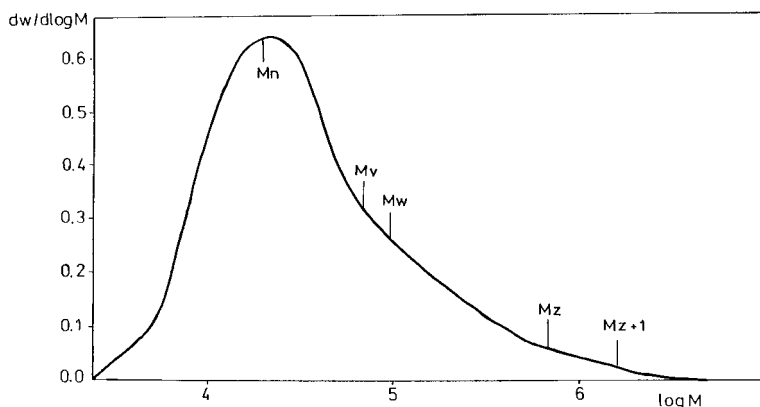


Figure 7 The molecular weight distribution of diacryloyloxyamylose.

illustrated in Figure 8, which shows the disappearance rate of $\text{CH}_2=\text{CH}-$ vs. irradiation time. The cast films of DAAM on glass or metal, after UV irradiation, show a low adhesion to the base and are brittle.

DSC Studies

Figure 9(a)–(d) shows DSC thermograms of AM, DAAM, and the product of free-radical polymerization of DAAM. The DSC thermogram of amylose [Fig. 9(a)] shows an endothermic peak within the temperature range from 175 to 190°C, which is probably connected to water evaporation. Water is commonly found in polysaccharides.¹¹ The thermal decomposition of AM under nitrogen begins at a temperature of about 227°C. In the case of DAAM [Fig. 9(b)], the exothermic peak, noticeable in the DSC thermogram within 129–171°C, results probably from the thermal crosslinking of double bonds. This is confirmed by the disappearance of the absorption band of $\text{CH}_2=\text{CH}-$ in the IR spectrum ($\nu = 1635 \text{ cm}^{-1}$) of the sample after its heating up to 171°C, as well as by the course of the DAAM thermogram in the second cycle of DAAM heating [Fig. 9(c)]. Within the examined temperature range for this sample, one can observe only an increase in $\Delta H/\Delta t$ with temperature. This is consistent with the results obtained by Vera-Graziano et al.¹² for poly(dimethyl siloxane) crosslinked to various extents. In the case of the polymerization product of DAAM, the DSC curve [Fig. 9(d)] shows also an exothermic peak which can be ascribed to the thermal crosslinking of the double bonds unreacted in the free-radical polymerization.

The presence of acrylate double bonds capable of polymerization in DAAM makes it possible to use DAAM as a multifunctional crosslinking agent in the preparation of hydrogels or in graft-

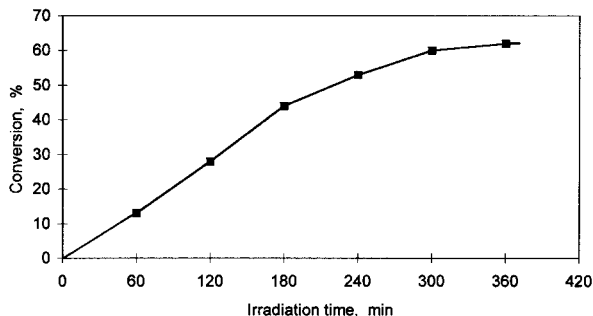


Figure 8 The rate of disappearance of $\text{CH}_2=\text{CH}-$ vs. irradiation time.

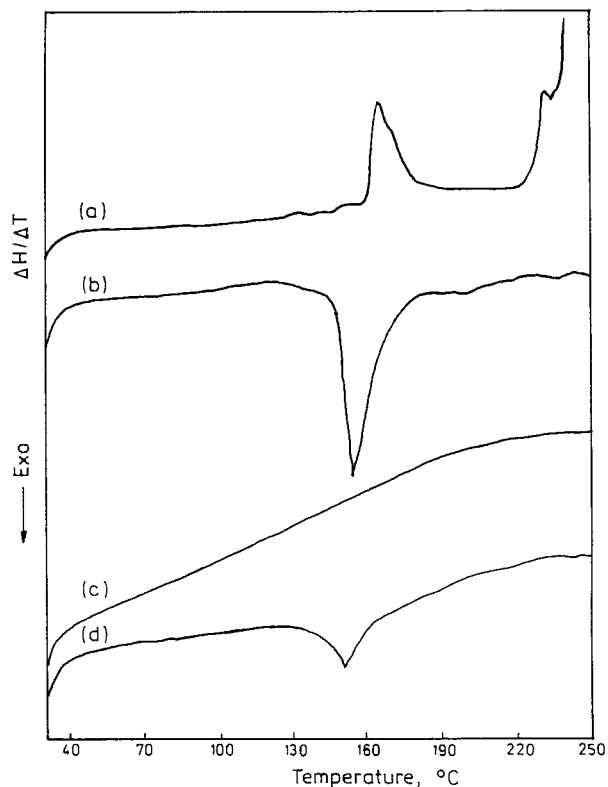


Figure 9 DSC thermograms of (a) amylose, (b) diacryloyloxyamylose, the first heating, (c) diacryloyloxyamylose, the second heating, and (d) product of free-radical polymerization.

ing vinyl monomers onto DAAM. This issue will be the subject of further studies.

CONCLUSIONS

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

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