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Some Aspects of the Reaction between Chitosan and Formaldehyde

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ABSTRACT

Reactions of chitosan (degree of deacetylation 67%, weight-average molecular weight 850,000) with formaldehyde were performed in a dilute aqueous acetic acid solution at a molar ratio of amino groups of the polymer to HCHO of 0.06:0.1 mol/L and at different temperatures (45, 60, and 75°C). In each case the pH of the reaction mixtures was 3.4 during the experiments. The process was investigated by measuring the kinetic changes of the free formaldehyde concentration and the sum of free formaldehyde and methylol groups produced. No gelation of the reaction product was observed. The experimental results led to the conclusion that the methylol groups formed by the addition of HCHO to chitosan functions take part in some intramolecular reactions with amino and/or hydroxyl groups of chitosan. Initially, the concentration of the resultant methylene bridges grows rapidly and then drops again until an equilibrium is established. This rather unusual decomposition of the methylene links once formed without changing the reaction conditions is ac-

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accompanied by a substantial growth of the amount of methylol derivative whose concentration at the beginning of the process increased rather slowly.

INTRODUCTION

Studies on the modification of urea-formaldehyde (UF) resins with chitosan [1, 2] showed that this polyaminosaccharide [3] did not bind formaldehyde emitted from the UF aminoplasts effectively. It was interesting to find that increasing the addition of chitosan to UF polycondensates resulted in an augmentation of the HCHO emission to a maximum level which was even higher than that for the control UF resin material. Further growth of chitosan content in the aminoplast led to some diminution of the formaldehyde release but never below an amount characteristic for the untreated resin sample. On the contrary, other polymeric ingredients containing $-NH_2$ groups, e.g., polyacrylamide, proved to be excellent HCHO-emission inhibitors [1, 2].

Various reactions of chitosan with aldehydes have been studied and the results reported in the literature [4-11]. However, their mechanisms are not always quite clear as, for example, in the case of formaldehyde. This paper provides more information about such a reaction of HCHO with the said polyaminosaccharide carried out in aqueous acetic acid solution at a relatively high dilution of the polymer.

EXPERIMENTAL

Chitosan

Chitosan used in the study was provided by Instytut Morski (Gdynia, Poland). It was produced by deacetylation of chitin which was extracted from Antarctic krill (*Euphasia superba*). Its weight-average molecular weight was 850,000, the degree of deacetylation was 67%, and the ash content was 0.9%.

Reaction of Chitosan with Formaldehyde

Chitosan (4.5 g) dissolved in 250 mL of an aqueous acetic acid solution (2%) was introduced to a 500-mL reaction flask provided with a thermometer and a magnetic stirrer. The flask was placed in a thermostated bath to maintain a selected constant temperature (i.e., 45, 60, and 75°C). After the desired temperature had been reached, aliquots of neutral formaline (38.2%) containing 1.2 g formaldehyde and water were preheated to the same temperature and added immediately to the chitosan solution so that the volume of the resultant mixture was 400 mL.

Once the reaction mixture was prepared, the measurement of time was started. Samples of 25 mL were taken at suitable intervals for analysis of the free formaldehyde and methylol groups.

Analysis of Free Formaldehyde

A 25-mL aliquot of the reaction mixture was cooled to 4°C and its pH was adjusted to pH 9.0 with 1 M Na_2CO_3 . Then 2 mL of 1 M Na_2SO_3 was added immediately and pH was lowered to 8.5 with a small quantity of 0.3 N HCl. The solution was left for 7 min and then acidified with 1 M CH_3COOH down to pH of 4.0. The excess sulfite was neutralized with a 0.1 N iodine solution using starch as an indicator. The formaldehyde-bisulfite product was decomposed with 25 mL 2 N aqueous Na_2CO_3 at pH 9.0, and the liberated sulfite was titrated with 0.1000 N I_2 until the blue color of starch was persistent.

Analysis of the Sum of Free Formaldehyde and Methylol Groups

To a 25-mL sample of the reaction mixture, 10 mL 2 N aqueous NaOH and 50 mL 0.1 N I_2 were added. It was then cooled in an ice-water bath for 1 h and acidified with 2 N H_2SO_4 . The excess iodine was titrated with a thiosulfite solution.

DISCUSSION AND RESULTS

Since the degree of deacetylation of the used chitosan was 67%, its initial content in the reaction mixtures corresponded to molar concentrations of its amino, A_0 , and hydroxyl, H_0 , groups of 0.06 and 0.18 mol/L, respectively. With the initial molarity of formaldehyde in the solutions, $F_0 = 0.1$ mol/L, the experiments were carried out in aqueous acetic acid medium at pH of 3.4 and at various temperatures. The pH remained constant over the whole time of each reaction run.

The accompanying changes of the amount of free formaldehyde, F , and of the sum of unreacted HCHO and that bound in form of methylol groups, F_{1+h} , are illustrated in Fig. 1. Chitosan can react with formaldehyde through its hydroxyl and amine functions. In the former case hemiformal derivatives are produced and in the latter hydroxymethyl-amino groups are formed. Since the dilution of the polymer chains was rather high (more than 10^4 L/mol), intermolecular reactions were not likely to occur to a significant extent. No gelation was observed over

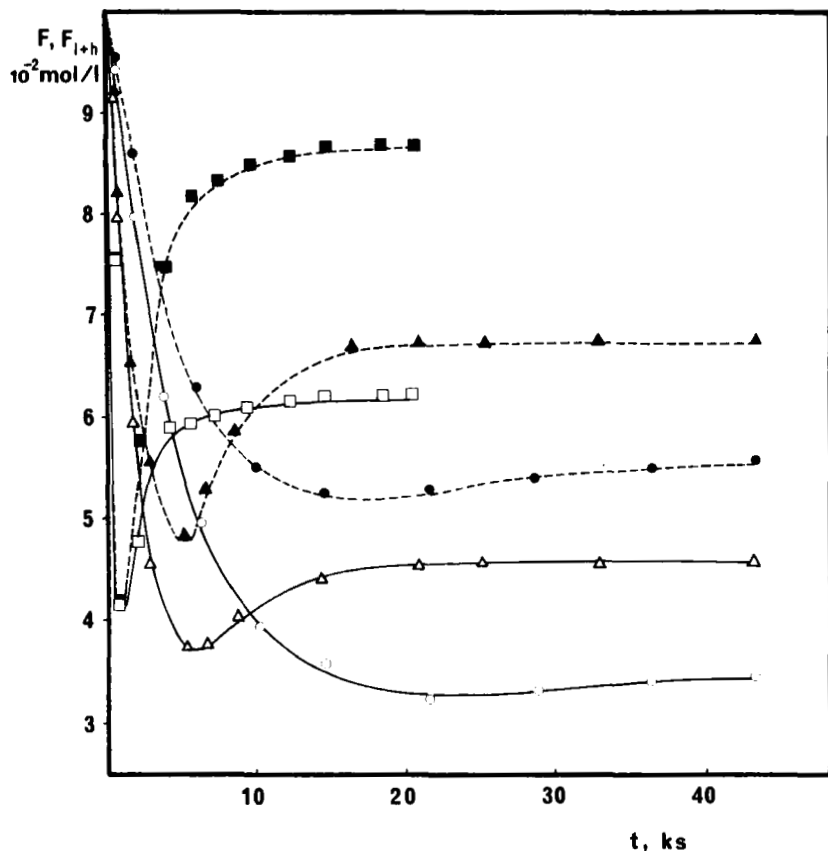
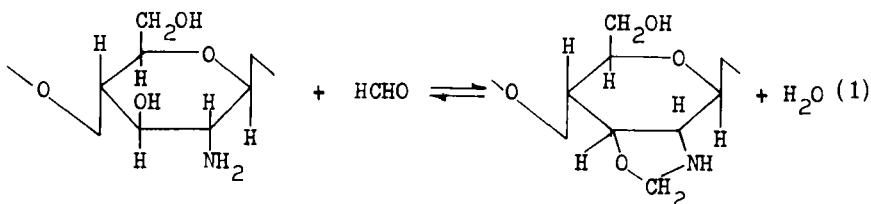


FIG. 1. Changes of F (\circ, Δ, \square) and of F_{1+h} ($\bullet, \blacktriangle, \blacksquare$) during the studied reaction of chitosan with formaldehyde at 45 (\circ, \bullet), 60 (Δ, \blacktriangle), and 75°C (\square, \blacksquare).

the course of the process. However, from Fig. 1 it follows that after the beginning of the experiments, $F_0 - F_{1+h} > 0$, so some part of the hydroxymethyl groups undergo further transformations. They probably involve certain intramolecular condensation reactions between methylols and amino or hydroxyl functions which are favored by the acid pH of the mixture. With regard to the steric arrangement of the functional groups in chitosan pyranosic rings [12], it seems possible that some formation of methylene bridges between nitrogens and oxygens on C_3 takes place:



The hypothesis that intramolecular reactions may occur is supported by applying Flory's theory of gelation [13]. According to it, if such reactions had not been involved, a gel would have appeared at the critical point defined by [13]

$$p_c = \sqrt{\frac{\alpha_c}{r}} \quad (2)$$

where p_c is the extent of reaction of amino and hydroxyl groups of chitosan at the moment of gelation, in this case, α_c is the corresponding critical value of the branching coefficient [13], and r is the ratio of the sum of molar concentrations of the chitosan amine and hydroxyl functions to the normality of formaldehyde. Since HCHO behaves in the described process as a bifunctional reagent, $r = 1.2$. The value of α_c is calculated from the expression

$$\alpha_c = \frac{1}{f - 1} \quad (3)$$

f being a functionality of chitosan with regard to its group reactivity toward formaldehyde. The average functionality of an aminoglucoside unit of the chitosan used (deacetylation degree 67%) is 2.67 (2 -OH groups and statistically 0.67 amino group per unit) if we neglect acetal-amino groupings which in general are relatively much less reactive. Then the mentioned f parameter may be calculated as a product of multiplication of the number-average degree of polymerization of chitosan by a factor of 2.67. According to the reported results [14], for chitosans of various origins and extracted by different methods, the ratio of weight-average, M_w , to number-average, M_n , molecular weights was always less than 10. Hence, if the above given value for M_w is taken, it may be suggested that α_c should not exceed 5.6×10^{-4} . The corresponding critical value for p_c will then theoretically be equal to 2.2×10^{-2} or less. The extent of reaction for the amino and hydroxyl groups of chitosan, p_e , was found experimentally from

TABLE 1. Extent of Reaction, p_e , of Amino and Hydroxyl Groups of Chitosan in the Studied Reaction with Formaldehyde at the Stage of Equilibrium

Temperature (°C)	p_e
45	0.44
60	0.36
75	0.21

$$p_e = (2F_o - F_{1+h} - F)/(A_o + H_o) \quad (4)$$

where F_{1+h} and F were measured at equilibrium. The results are summarized in Table 1. Although p_c was calculated in an approximate way, such substantial differences between its value and those for p_e probably result from the occurrence of intramolecular reactions.

In the equilibrium stage in the reaction mixture there are hydroxymethyl derivatives linked with nitrogen and oxygen atoms on C_3 and C_6 as well as products of some intramolecular reactions on one side, and on the other side reagents, i.e., formaldehyde and unreacted chitosan functional groups. From the graphic illustration presented in Fig. 2, it is seen that at the beginning of the examined process there occurs a very slow formation of methylols whose concentration, F_h , was determined as a difference: $F_h = F_{1+h} - F$. Presumably, in this initial period fast reactions of intramolecular condensation take place, as for instance in Eq. (1). On the other hand, the addition product of HCHO to $-OH$ on C_6 , which for steric reasons does not react as easily with the nearby hydroxyl or amine functions, is not stable. Therefore, at the beginning of the process practically no or little formation of hemiformal (O-methylol) groups is observed. It is interesting to note that initially the overall concentration of hydroxymethyl derivatives increases slower at higher temperatures. Then, after some time the temperature begins to have an opposite effect on the growth rate of the amount of methylol until equilibrium is achieved. As far as the final concentration of hydroxymethyl groups is concerned, it increases with an increase in the temperature of the process. As F_h begins to grow rapidly (Fig. 2) in Fig. 1, at the same time it is observed that the loss of free formaldehyde attains a certain extreme value during the course of the reaction. At this moment the quantity of reacted HCHO which is not bound in the form of methylols is a maximum. If Eq. (1) is valid,

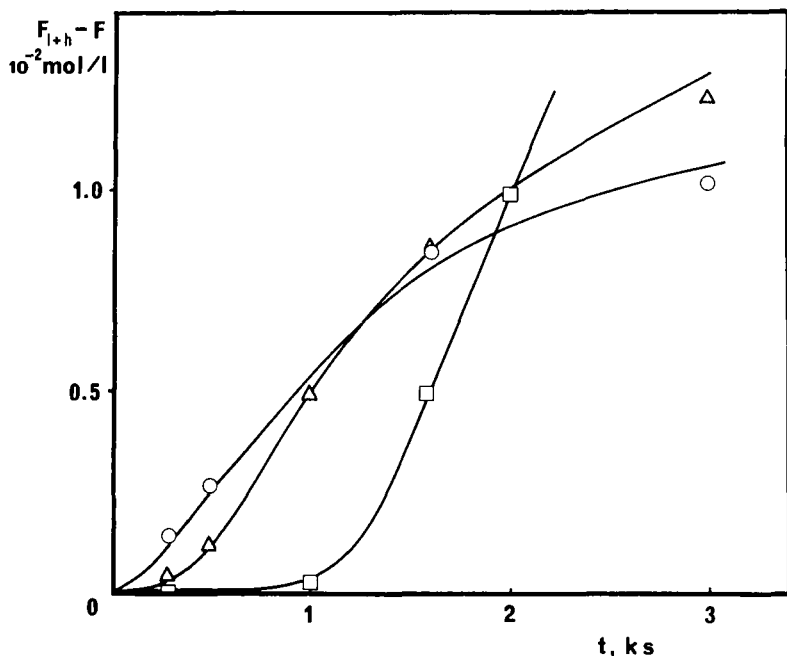
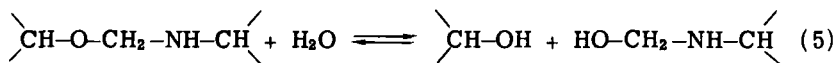


FIG. 2. Changes of methylol concentration ($F_{1+h} - F$) during the studied reaction of chitosan with formaldehyde at 45 (○), 60 (△), and 75°C (□).

this may be, for instance, a cyclic product containing a methyleneoxyamine bridge. The shape of the kinetic curves in Figs. 1 and 2 indicates that after reaching some critical extent of reaction, such intramolecular methylene links probably begin to decompose partially. This disruption is accompanied by a rapid increase of methylol concentration in the reaction system which may be due, for instance, to the following hydrolysis:



Although the N-methylol groups generated can dissociate further to liberate free formaldehyde, they are more stable than the hemiformal derivatives. Therefore, possibly they are mainly responsible for the final hydroxymethyl concentration level at equilibrium.

The qualitative observations made above on the course of changes of free formaldehyde, of methylol, and of methylene concentrations in the system studied lack a clear explanation. Perhaps some irreversible changes of the chitosan macromolecule conformation during the reaction are involved here, which result in a destabilization of

intramolecular methylene cross-links or cyclization products as in Eq. (1). A certain instability of chitosan-formaldehyde combinations, which seems to be relatively high, is the reason why the examined polysaccharide abundant in amino groups was not only inefficient in reducing formaldehyde emission from UF resins but even stimulated such a release if used in some critical amount.

SUMMARY AND CONCLUSIONS

The reaction of chitosan with formaldehyde carried out in aqueous acetic acid solution at relatively high dilution of the polyaminosaccharide chains probably involves some intramolecular cyclizations between the amino and hydroxyl groups of the polymer. Initially, the quantity of methylene links thus formed attains a maximum and then drops until an equilibrium is established. A hydrolytic scission of methylene bridges results in a rapid generation of methylol groups which are likely to be attached mainly to nitrogen atoms. Such unusual kinetic changes of the concentrations of both reagents and the reaction products are perhaps associated with some deformations of chitosan chains as they react with formaldehyde in the studied system.

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