

## ACYLATION OF ACETYLCELLULOSE WITH PYROMELLITIC DIANHYDRIDE

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*The cross-linking reactions of acetylcelluloses having different levels of acetyl groups with pyromellitic dianhydride in homogeneous media have been investigated. A relationship has been established between the static exchange capacity (SEC) and the content of hydroxy groups in the acetylcellulose and the esterification conditions (homogeneous or heterogeneous-solid phase). It has been shown that on the interaction of acetylcellulose with pyromellitic dianhydride under homogenous conditions there is a uniform distribution of cross-linkages over the whole length of the acetylcellulose macromolecule, which enables products with high SEC values to be obtained.*

In the majority of cases, the esterification of native cellulose under heterogeneous conditions begins at the surface of the fibers. The introduction of transverse covalent bonds between the cellulose macromolecules on esterification with polyfunctional acids restricts their mobility and thereby inhibits the diffusion of an esterifying reagent into the depth of the cellulose fibers. Moreover, in cellulosic materials hydrogen bonds also act similarly to covalent bonds, leading to a powerful intermolecular interaction [1]. Consequently, in the heterogeneous esterification of cellulose with di- and polyfunctional acids an intrafibrillar, rather than an intermolecular, formation of bridge bonds takes place. What has been said above may substantially affect the degree of modification of cellulose and the properties of the product obtained. In this connection, it appears of interest to study the influence of the esterification of soluble cellulose derivatives by polyfunctional acids under homogeneous conditions where bridge bonds may be distributed uniformly over the whole length of a cellulose ester macromolecule.

Partially substituted esters of cellulose capable of dissolving in organic solvents are the most suitable objects and model compounds for studying features of the cross-linking of cellulose with polyfunctional acids. Under homogeneous conditions, the interaction of polyfunctional acids with partially substituted cellulose esters takes place through their free hydroxy groups. Therefore, in order to esterify partially substituted cellulose acetate with pyromellitic dianhydride a secondary acetylcellulose with a degree of substitution (DS) of 2.4—2.5 produced industrially and soluble in acetone was subjected to deep homogenous hydrolysis to different degrees of substitution.

Figure 1 presents kinetic curves of the change in the content of free hydroxy groups in acetylcellulose as a function of the time of hydrolysis. Saponification to low degrees of substitution (DS = 0.5—0.55) led to the appearance of free primary hydroxy groups in each pyranose unit. At such ratios of hydroxy groups and acetyl radicals, acetylcellulose is soluble in water [2]. With a further increase in the time of saponification the degree of substitution by acetyl groups in the acetylcellulose decreases. However, the reaction products again become insoluble in water, but, regardless of the degree of substitution by acetyl groups, they are soluble in DMFA. It has been shown by the tritylation method that the hydroxy groups of a water-soluble acetylcellulose, which are present on the sixth carbon atom, are unsubstituted; i.e., the acetyl groups in a water-soluble acetylcellulose are statistically distributed uniformly in the C<sub>2</sub> and C<sub>3</sub> positions [2]. It must be mentioned that the primary hydroxy groups in acetylcellulose are more accessible for further modification by polyfunctional acids.

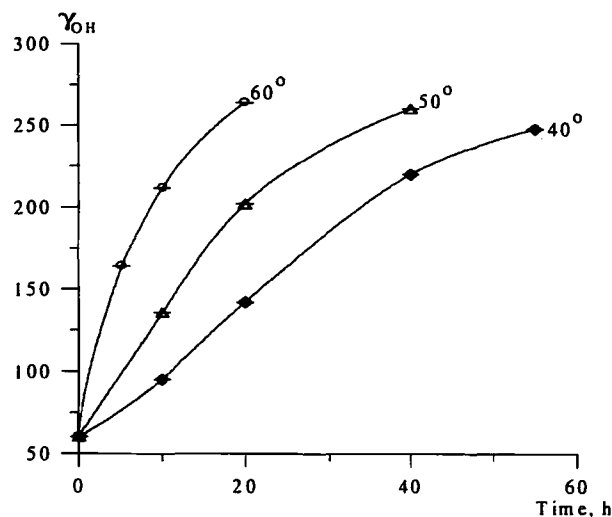
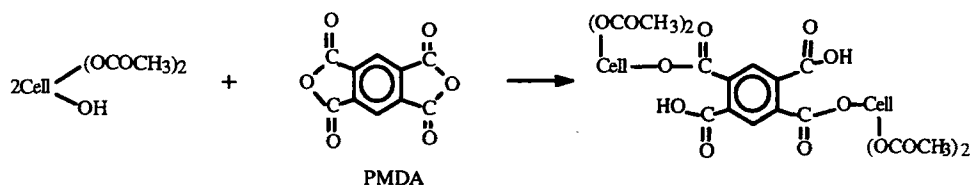


Fig. 1. Change in the content of free hydroxy groups in acetylcellulose with the time of hydrolysis.

Homogeneous reactions with pyromellitic dianhydride (PMDA) of cellulose acetates having the low degree of substitution  $DS = 0.5$  were conducted in DMFA solution. The reaction of diacetylcellulose with PMDA takes place in accordance with the following scheme:



The course of the reaction was followed from the change in the SEC. Under homogeneous conditions, PMDA begins to react with acetylcellulose at room temperature. Keeping an acetylcellulose—PMDA mixture in DMFA for two days was accompanied by the formation of a clear gel. Raising the reaction temperature to 50—90°C shortened the time of formation of a gel to 5—10 h. In order to exclude gel formation in the esterification process and with the aim of performing the reaction under homogeneous conditions in the liquid phase, esterification was conducted with constant stirring. Then, with a rise in the temperature and an increase in the time of the reaction the viscosity of the solution rose greatly.

Figure 2 shows the dependence of the change in the SEC of the reaction product on the  $\gamma_{OH}$  value of the initial acetylcellulose. The molar ratio of acetylcellulose to PMDA was 1:4, the reaction temperature 90°C, and the time 8 h. As can be seen from Fig. 2, with an increase in  $\gamma_{OH}$  the SEC rose. Attention is attracted by the high value of the SEC, reaching 12.5 meq/g. By esterifying di- and monosubstituted acetylcellulose ( $\gamma_{OH} < 210$ ) it was possible to obtain products with SECs of 2.5—14.5 meq/g. These materials were insoluble in water both in the initial state and after modification. The esterification products precipitated well in water. With an increase in the concentration of free hydroxy groups ( $\gamma_{OH} = 230$ —250), the acetylcellulose swelled greatly or dissolved in water. Its precipitation from acetic acid solution required a mixture of water and acetone or pure acetone. In spite of the high value of its degree of substitution, after the esterification of such an acetylcellulose with the dianhydride, because of their pronounced swelling the reaction products precipitated poorly in water. Again, a mixture of water and acetone was necessary for their precipitation.

Figure 3 shows the dependence of the change in SEC on the reaction time for samples of acetylcellulose with different concentrations of free hydroxy groups. The curves obtained are typical for cross-linking reactions of cellulose. In the first stages, the cellulose esterification reaction progressed in dependence on an increase in the concentration of free hydroxy groups. With an increase in  $\gamma_{OH}$  from 60 to 110 the SEC rose approximately threefold, and from 110 to 160 approximately twofold. However, a further increase in the concentration of free hydroxy groups raised the SEC only slightly. With an increase in  $\gamma_{OH}$  from 160 to 210 and from 210 to 260 the SEC rose 1.1- and 1.2-fold, respectively. The sharp increase in the degree of modification with a rise in  $\gamma_{OH}$  from 60 to 160 was connected with the "voluminousness" of the PMDA molecule.

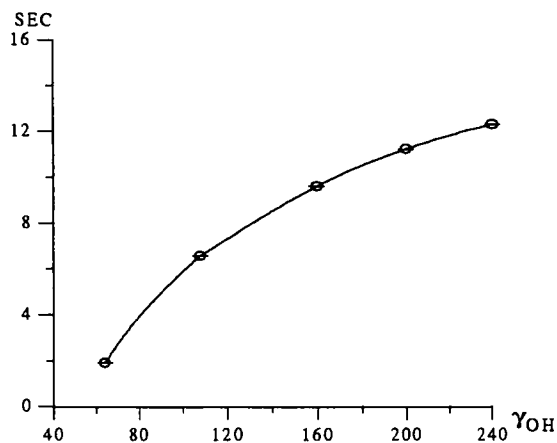


Fig. 2. Dependence of the change in SEC on  $\gamma_{OH}$  in the esterification of acetylcellulose by PDMA. Reaction time 8 h.

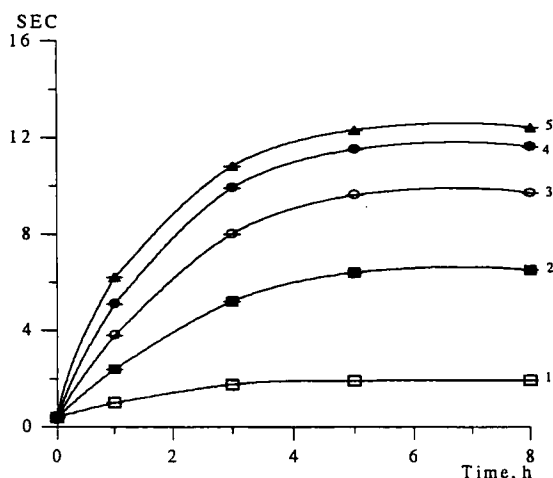


Fig. 3. Dependence of the SEC on the reaction time for specimens with various  $\gamma_{OH}$  values: 1) 60; 2) 110; 3) 160; 4) 210; 5) 260,

As already mentioned, in the acid saponification of acetylcellulose it is mainly the primary acetyl groups (at the  $C_6$  atoms) that are hydrolyzed. In the first stages of the reaction of feebly substituted cellulose with the dianhydride it was just these groups that were esterified, and then a substantial increase in the degree of modification was observed. With an increase in the time of hydrolysis of acetylcellulose, the secondary (on the  $C_2$  and  $C_3$  atoms) acetyl groups were gradually saponified. However, the secondary hydroxy groups are sterically less accessible for the voluminous PMDA molecule. Because of this, in spite of the homogeneity of the reaction conditions, the rate of modification decreased. The hypothesis put forward above is in harmony with literature statements on the accessibility and reactivity of the hydroxy groups of cellulose [4]. In the cross-linking of acetone-soluble cellulose acetates with dimethylethyleneurea it was shown that even with a slight change in the concentration of hydroxy groups in the cellulose the accessibility of the remaining ones for  $D$ -exchange was far lower than in the initial sample [5].

Together with the esterification of the free hydroxy groups of acetylcellulose by the dianhydride, a transesterification reaction also took place. The content of bound acetic acid in the reaction product decreased by a factor of approximately 1.2—1.4 in comparison with the initial acetylcellulose. The transesterification of the acetyl groups is explained by a peculiarity of the reaction studied. In the first stages of the reaction the PMDA esterifies the free hydroxy groups of the acetylcellulose, with the predominant substitution of the primary hydroxy groups. In view of its limited mobility and steric factors, the

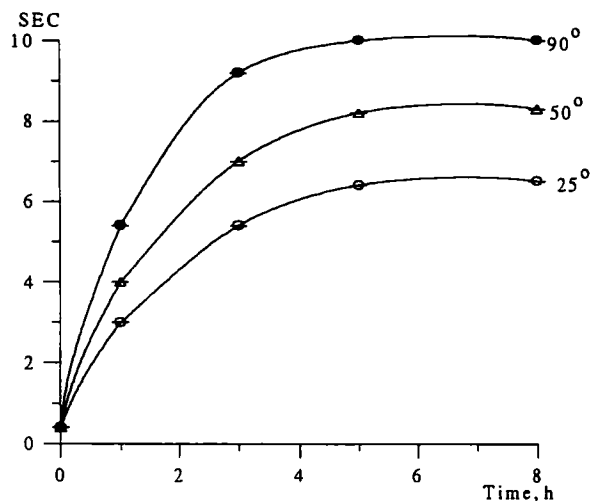


Fig. 4. Kinetic curves of the esterification of diacetylcellulose with pyromellitic dianhydride in the solid phase.

pyromellitic dianhydride bound with the cellulose can interact only with accessible functional groups. When there are no free hydroxy groups, the displacement of adjacently located acetyl groups — i.e., transesterification — also takes place, with the intermolecular or intramolecular cross-linking of the cellulose molecule.

Figure 4 shows kinetic curves of the esterification of feebly substituted acetylcellulose. The SECs of the products of a reaction under homogeneous—solid phase conditions were lower than those of products obtained in solution. This is explained by the sharp decrease in mobility both of the cellulose macromolecules and of the esterifying reagent — the dianhydride. However, the SEC was approximately twice that of a sample obtained by the esterification of a highly substituted cellulose, i.e., diacetylcellulose [6]. This increase was apparently connected with the presence of a large number of free hydroxy groups in the cellulose ( $\gamma_{OH} = 210$ ).

The heterogeneous solid-phase reaction has its peculiarities. When films of acetylcellulose were kept for five minutes in a dimethylformamide solution of PMDA, after subsequent esterification the maximum level of bound PMA in the cellulose was reached. And for obtaining of insoluble films by means of cross-linking with dianhydride is enough to keep the films in a solution of PMDA for 0.5—1 minute. With the same amount of bound PMA in the cellulose the solubility of the films obtained by the heterogeneous method was far lower than that of films cross-linked by the homogeneous solid-phase method. However, in the heterogeneous solid-phase method a surface localization of the functional groups was achieved which permitted a rise in the rate of ion-exchange when the films were used as ion-exchangers and in membrane technology. This method also permits insoluble films with high SECs to be obtained with the minimum consumption of the dianhydride.

The sorption properties of cellulose and its derivatives are very important in both the theoretical and the practical respects. The abundance of highly polar hydroxy groups in cellulose causes its considerable attraction for additional water molecules. However, the hygroscopicity of cellulose is connected not only with the presence of hydroxy groups in its molecule but also with the peculiar nature of its submicroscopic structure. Even the complete replacement of the hydroxy groups by hydrophobic groups such as acetyl does not lead to an appreciable change in the amount of water retained in its submicroscopic capillaries (in MCC, also in the intercrystallite space).

Water can be retained mechanically through capillary (intercrystallite) condensation. We have observed such retention in a study of the swelling of MCC in polar solvents and on activation with nitrogen-containing reagents [7, 8]. On the other hand, at certain degrees of substitution of the hydroxy groups by hydrophobic (even acetyl) groups, cellulose has pronounced hydrophilic properties (for example, water-soluble acetylcellulose). The replacement of the hydroxy groups of cellulose by more hydrophilic groups may also enhance the sorption properties of the polymer. Thus, under ordinary laboratory conditions N-carboxymethylcellulose contains about 11.5% of moisture, in an atmosphere with 70% humidity it adsorbs about 42% of water, and in an atmosphere saturated with water vapor absorption reaches 200% of moisture by weight [1].

## EXPERIMENTAL

Feebly substituted acetylcellulose was obtained by a known method involving the hydrolysis of a 12.5% solution of secondary (DS = 2.50—2.55) acetylcellulose dissolved in 75% acetic acid [9]. After predetermined intermediate times of hydrolysis, a definite amount of solution was taken and precipitated in water. The amount of bound acetic acid in the precipitate was determined. Highly hydrolyzed samples and water-soluble samples were precipitated in acetone. Cellulose acetates with different degrees of substitution (from 2.0 to 0.5) were obtained, and these were dissolved in DMFA. Samples with DS = 0.5 also dissolved in water.

The reaction of the cellulose acetates with pyromellitic dianhydride was conducted at a molar ratio of acetylcellulose to PMDA of 1:4, at 90°C for 8 h with constant stirring in a homogenous medium (dissolved in DMFA). The course of the reaction was monitored from the change in the SEC [10].

The SECs of the samples of acetylcellulose after reaction with PMDA were determined by a known procedure [11].

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