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STRUCTURAL AND POLYMER-ANALOGOUS TRANSFORMATIONS IN CELLULOSE ON ESTERIFICATION WITH POLYFUNCTIONAL ACIDS

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Structural transformations of cellulose in ethylenediamine and in liquid ammonia and on subsequent esterification with polyfunctional organic and inorganic acids have been studied.*

As is known, structural transformations of cellulose under the action of active liquid media exert a substantial influence on its reactivity. We have studied the influence of the conditions of performing the reaction on possible further transformations and also on the properties of the products obtained.

Ethylenediamine penetrates into the crystal lattice of microcrystalline cellulose (MCC), forming inclusion compounds analogous to native cellulose [1]. Pronounced swelling of the MCC and an increase in the mobility of the molecular chains are observed, which should increase the reactivity of the cellulose. Ethylenediamine neutralizes the reactivity of a dianhydride [2], and, therefore, to perform an esterification reaction, after the swelling of the cellulose the ethylenediamine was eliminated from it by displacement with another solvent. The displacement of ethylenediamine with propyl alcohol led to MCC III (Fig. 1). Alcohols form esters with polyfunctional acids and their anhydrides [3] and, therefore, before esterification the alcohol was eliminated from the MCC III by drying. We also subjected to esterification a sample of MCC that had been treated with ethylenediamine and from which the ethylenediamine had been displaced with dimethyl sulfoxide, without subsequent drying (Fig. 1). An x-ray diffractogram of such a sample has reflections in the 2θ regions of 12 and 21°, which are characteristic of cellulose III, and at 15, 17, and 22°30′, which are characteristic of cellulose I. On the basis of these facts, it may be assumed that the disruption of the cellulose-ethylenediamine complex by dimethyl sulfoxide does not lead to the complete "reconstruction" of the crystal lattice of cellulose either in cellulose III (as in the case of the disruption of the complex by propyl alcohol) or in cellulose I (as when ethylenediamine is displaced by water and various ketones [4]).

Figure 2 shows kinetic curves of the change in the content of carboxy groups in MCC as a function of the reaction time. The nature of the curves is similar for all the samples. Two sections can be seen. In the first section, the number of carboxy groups rises linearly, practically approaching its limiting value in 1-2 h, which is characteristic for cross-linking reactions. In spite of the fact that the esterification of all the samples was performd under identical conditions (temperature, time, molar ratio), the limiting values were different. The highest number of carboxy groups and the highest rate of the reaction (K_c = 3.06) were observed for MCC that had not been subjected to drying after the displacement of the ethylenediamine with DMSO. The carboxy group content increased 1.9-fold in comparison with the initial MCC (K_c = 1.7) and 1.8-fold in comparison with MCC III (K_c = 1.74). Substantial changes were also observed in the structures of these samples. The x-ray diffractograms after esterification differed from the original state of the cellulose with a mixed I + III structure. This indicated that the esters obtained had the structure of cellulose I (Fig. 1). Reversion to the crystal lattice in cellulose I apparently takes place when cellulose having the mixed structure is subjected to high-temperature (90°C) treatment with a solution of pyromellitic dianhydride (PMDA) in DMSO followed by the washing of the samples with water. In this case, the DMSO plays an important role. In spite of the elimination of ethylenediamine from the crystal lattice of the cellulose, the presence of DMSO apparently ensures a high mobility of the macromolecules as compared with a dried sample. Furthermore, DMSO, entering

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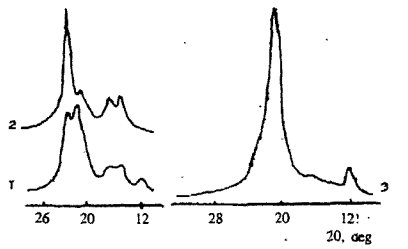

Fig. 1

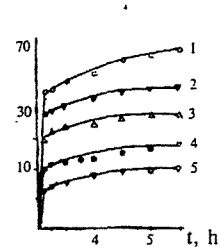

Fig. 2

Fig. 1. X-Ray diffractogram of MCC after treament with ethylenediamine and displacement of the latter with DMSO (*1*), after the esterification of I with pyromellitic anhydride (*2*), and after the esterification of MCC III with pyromellitic anhydride (3).

Fig. 2. Dependence of the change in the number of COOH groups in MCC on the time of esterification with pyromellitic anhydride: *1-3*) total number of COOH groups; *4,5*) number of free COOH groups; *1, 4*) MCC with a I + III structure; *2, 5*) MCC III; *3*) MCC I.

into donor–acceptor interaction with the hydroxy groups of the cellulose, forms hydrogen bonds with them, which leads to some weakening of the intermolecular hydrogen bonds even in the still unformed crystal lattice of cellulose III.

The esterification of MCC III that had been subjected to drying after intracrystalline swelling led to products with a lower carboxy group content than for a sample of cellulose that had not been subjected to drying, although it did increase the number of carboxy groups in comparison with the initial MCC I. When cellulose is dried, as a result of elimination of the solvent complete fixation of the lattice takes place through the formation of the new intermolecular hydrogen bonds that are characteristic for this structure. This restricts the mobility of the macromolecules. The formation of intermolecular hydrogen bonds also leads to a densification of the structure, which, in its turn, restricts the accessibility of the hydroxy goups of the cellulose.

High-temperature treatment of cellulose III with a solution of PMDA in DMSO followed by water washing did not lead to reversion of the crystal lattice in cellulose (I) (Fig. 1). This, at first sight extraordinary, fact is explained by the specificity of the reaction under study. PDMA reacts with MCC on the surface of the crystallites, linking individual chains disrupted as a result of hydrolysis. The esterification of MCC III, which has a completely fixed structure and strongly established hydrogen bonds, with a solution of PDMA in DMSO begins at the surface and proceeds fairly rapidly with the most accessible hydroxy groups. The cross-links formed in this way on the surface of the crystallites block and consolidate the crystal lattice, which prevents its reversion to cellulose I. When there is no or only slight cross-linking, a change in the crystal lattice is possible even for cellulose III. It must be mentioned that we have observed such a change on the esterification of cellulose III with phosphoric acid.

The results given above were obtained on esterifiction under mild conditions, i.e., the esterifiction process exerted no significant effect on the crystal lattice of the cellulose. To study the structural transformations of cellulose during esterification under severe conditions we chose the phosphorylation of cotton cellulose with a mixture of orthophosphoric acid and urea.

The treatment of cellulose with an 18% solution of sodium hydroxide gives cellulose II [5]. The treatment of both native cellulose and of cellulose II with liquid ammonia leads to a polymorphic transformation with the production of cellulose III. IR spectroscopy has shown that cellulose III obtained from cellulose I (cellulose III_I) differs from cellulose III obtained from cellulose II (cellulose III_{II}) [6]. The results of the esterification of cellulose III_I and cellulose III_{II} with a mixture of orthophosphoric acid and urea showed that cellulose III_{II} has a considerably greater reactivity than cellulose III_I. The cotton cellulose was obtained by boiling cotton lint at a high temperature under excess pressure, which, however, does not replace the classical method of activating cellulose with sodium hydroxide.

X-Ray structural analysis showed that the cotton cellulose III_{II} had a lower degree of crystallinity than the cellulose II. The esterification of both samples under severe conditions led to complete amorphization (Fig. 3). Subsequent activation of the cellulose with sodium hydroxide and liquid ammonia opened up the crystal structure, which, at first sight, should have occasioned a marked increase in the degree of substitution of the cellulose and, accordingly, of the ionic capacity of the reaction products. However, the results of the phosphorylation of various modifications of cellulose showed that, under otherwise identical conditions, the phosphorus content depended little on the degree of activation. On the phosphorylation of cellulose

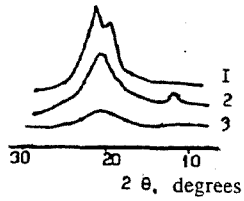

Fig. 3. X-Ray diffractogram of cellulose after treatment with sodium hydroxide (*1*) and with liquid ammonia (*2*), and after phosphorylation (*3*).

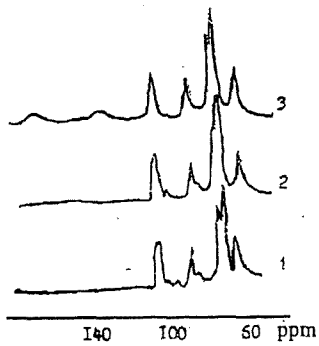

Fig. 4

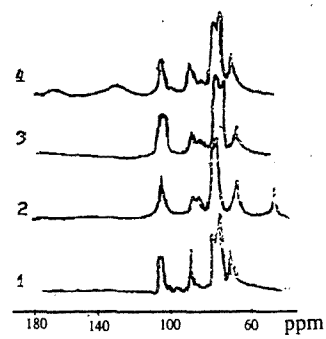

Fig. 5

Fig. 4. Solid-phase ^{13}C NMR spectra of MCC I (*1*), MCC III (*2*), and the pyromellitate of MCC III (*3*).

Fig. 5. Solid-phase ^{13}C NMR spectra of: *1*) MCC; *2*) after treatment with ethylenediamine and washing with DMSO; *3*) after elimination of the DMSO by drying; *4*) sample 2 esterified with a dianhydride.

II and cellulose III_{II}, products with relatively close phosphorus contents were obtained, although the phosphorus content was somewhat higher for cellulose II. This is apparently connected with the formation of a chemical bond beween the terminal aldehyde groups of the cellulose and ammonia during the activation process [1], which undoubtedly lowers the number of accessible active centers in the cellulose. However, in spite of this, substantial differences were observed in the selective properties of the phosphocelluloses obtained after different activation processes. The best selectivity was found in the phosphocellulose obtained from celluose III_{II}.

The results of the x-ray structural investigations of the samples were confirmed by their solid-phase ^{13}C NMR spectra. Figure 4 shows the solid-phase ^{13}C NMR spectra of MCC (cellulose I); of MCC treated with ethylenediamine, after the displacement of the latter with propyl alcohol and drying (cellulose III); and also of cellulose III after esterification with PMDA. The spectrum of the MCC after treatment with ethylenediamine differed substantially from the spectrum of cellulose I in the chemical shifts of the C_2, C_3, and C_6 atoms (signals in the 72-74 ppm region), which showed a different (as compared with cellulose I) conformation and (or) a different molecular environment [7]. Particularly appreciable was the change in the chemical shift of the C_6 atom, i.e., the change in the surface-isomeric structure of the hydroxymethyl groups. Thus, in cellulose I an isomer having a signal in a higher-field region (δ = 66 ppm) predominated, and in celluloses III one in a lower-field region (δ = 62 ppm).

There is also a difference in the solid-phase ^{13}C NMR spectra for these samples at C_4 (δ = 84-88 ppm). In the spectrum of cellulose III obtained by treating MCC with ethylenediamine there is a weak signal in the 66 ppm region. In combination with a signal at 74 ppm, this shows that some part of the cellulose had retained the structure of cellulose I. For cellulose III treated with PMDA no appreciable changes were observed in the spectra as compared with untreated cellulose III, which confirmed the results of the x-ray structural investigation. Signals in the 131 and 166.55 ppm regions of the spectrum

of this sample were assigned to the carbons of the benzene ring and to carboxylic carbon and confirmed the presence of bound PMA in the cellulose.

Figure 5 shows the solid-phase ^{13} NMR spectra of MCC (*1*); of the same material that had been treated with ethylenediamine, after the displacement of the ethylenediamine with dimethyl sulfoxide (*2*), and after the elimination of the DMSO by drying (*3*); and that of the cellulose pyromellitate (*4*) obtained from sample (*2*). After the displacement of the ethylenediamine with dimethyl sulfoxide, signals characteristic for cellulose III (C_6 — 62.33 ppm, C_2—C_3—C_5 — 73.55 ppm with a weak shoulder at 74 ppm) predominated, although a weak signal at 65.32 from the C_6 atom, characteristic for cellulose I, was also retained. On drying (elimination of DMSO) the crystal lattice partially reverted to cellulose I, as was shown by an intensification of the signal at 65 ppm from the C_6 atom. At the same time, the signal in the 73.55 ppm region disappeared and two new signals characteristic for cellulose I appeared (δ 72 and 74 ppm). A signal at 40.47 ppm in the spectrum of the second sample, which disappeared on drying, related to the methyl groups of DMSO and confirmed its presence and its elimination on drying. These facts showed the subsequent reversion of the structure to cellulose I on the elimination of DMSO and confirmed the results of x-ray structural analysis. The solid-phase ^{13}C NMR spectra of cellulose pyromellitate obtained after the displacement of the ethylenediamine with dimethyl sulfoxide were similar to the spectrum of cellulose I, and signals in the 131.71 and 166.65 ppm regions confirmed the presence of bound PMA in the cellulose.

EXPERIMENTAL

Cotton cellulose and MMC obtained by hydrolyisis of the cotton cellulose with 2.5 N aqueous HCl were used. Activation was effected with a 17-18% aqueous solution of NaOH [5]; with ethylenediamine by complete immersion of the MMC at 35-50°C for 50 h [1]; and with liquid ammonia. Esterification of the MMC with PMDA was carried out in DMSO in a round-bottomed flask with constant stirring at 90°C for 6 h [8]. For phosphorylation, the cellulose was saturated with an aqueous solution of phosphoric acid and urea. The reaction was conducted at 135-150°C for 60 min, with the passage of air through the cellulose. After the end of the reaction, the cellulose was washed with water and dried. The x-ray diffractograms and solid-phase ^{13}C NMR spectra were obtained as decribed in [8].

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