

MODIFICATION OF MICROCRYSTALLINE CELLULOSE BY A BINARY MIXTURE OF PYROMELLITIC DIANHYDRIDE AND PHOSPHORIC ACID

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UDC 547.458.81

The reactions involved in the esterification of microcrystalline cellulose with a binary mixture of pyromellitic dianhydride and phosphoric acid have been studied. By changing the molar ratio of dianhydride to acid it is possible to regulate the course of the reaction and to obtain products with required contents of phosphoric acid and carboxy groups.

In the esterification of cellulose with anhydrous phosphoric acid, the reaction takes place with the liberation of water and is an equilibrium-reversible process. It has been shown in [1, 2] that pyromellitic dianhydride (PMDA), by binding the water, can shift the reaction equilibrium to the right. In addition, pyromellitic dianhydride is an active esterifying agent. It appeared of interest to study the processes taking place on the interaction of cellulose with a binary mixture of PDMA and phosphoric acid.

Anhydrous phosphoric acid was obtained by dissolving P_2O_5 in DMSO and adding the amount of water necessary to hydrolyze the P_2O_5 to orthophosphoric acid. After the complete dissolution of the P_2O_5 and its hydrolysis, PMDA was added to the solution in the necessary proportion. PMDA may enter into chemical interaction with the $-OH$ groups of a weak inorganic (boric) acid [3]. The dissociation of the third stage of orthophosphoric acid is so slight that one can assume the possibility of its chemical interaction with PMDA in anhydrous media.

Because of the possible superposition of signals in the PMR spectrum, the study of the chemical processes between PMDA and phosphoric acid must be carried out with the use of deuterated solutions of dimethylphosphoramidate (DMPA). For this reason, and also with the aim of the greatest approach of the process under study to the technological conditions, the reaction was performed in DMSO, the signals of which in the PMR spectrum are not superposed on the signals of the benzene ring of PMDA and those of the $-OH$ groups both of water and of phosphoric acid.

It has been shown [4] that the dissolution of P_2O_5 in DMPA leads to the formation of a complex. In the PMR spectrum of a solution of P_2O_5 in DMSO no signals not characteristic of the latter were observed, which shows the absence of a complex between P_2O_5 and DMSO. In the PMR spectrum of such a solution there is only one signal, at 2.62 ppm, which is characteristic for DMSO. Consequently, this system is, in fact, a solution of P_2O_5 . No chemical shift of this signal was observed, which confirms this assumption.

When PMDA was added to a solution of P_2O_5 in DMSO, signals appeared in the 7.8, 8.2, and 8.7 ppm region that are characteristic for pyromellitic acid (PMAc), pyromellitic anhydride (PMAAn), and PMDA, respectively (Fig. 1, 1). The amounts of these components were 15.2, 50.4, and 34.4%, respectively, of the initial weight of the sample. After the mixture had been heated under the reaction conditions (90°C, 5 h), new signals, as compared with the PMR spectrum of the pure PMDA solution, appeared in this spectrum: in the 8.05 ppm region, a triplet of signals with a relatively intense one at 8.05 ppm, and in the 8.32 ppm region, a single signal (Fig. 1, 2). Their appearance confirmed the hypothesis of the possibility of a chemical interaction between PMDA and the least dissociated $-OH$ group of phosphoric acid. When water was added, these signals disappeared, which showed the instability of the compound formed between PMDA and phosphoric acid. It must be mentioned that some shift in the signal characteristic for PMAc, from 7.85 to 7.9 ppm, is apparently connected with structural differences from PMAc of the compound formed.

Tashkent Institute of Chemical Technology, 700034, Tashkent, ul. Shevchenko, 1. Translated from *Khimiya Prirodnykh Soedinenii*, No. 4, pp. 583-586, July-August, 1996. Original article submitted January 22, 1996.

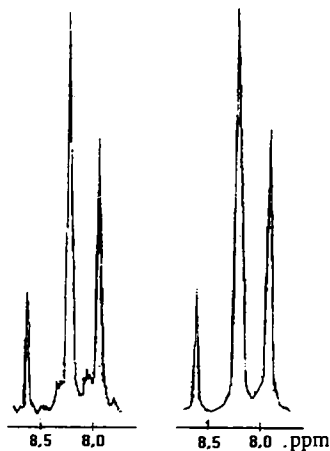


Fig. 1. PMR spectrum of a solution of P_2O_5 in DMSO after the addition of PMDA (1) and after the heating of the reaction mixture at $90^\circ C$ for 5 h (2).

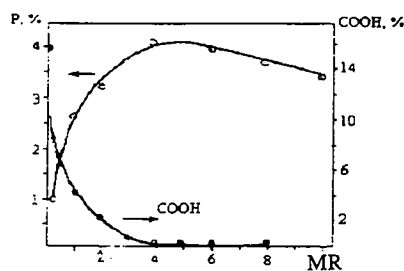


Fig. 2. Dependence of the levels of phosphorus in the MCC phosphate on the MR H_3PO_4/MCC (P) and of COOH groups on the MR $H_3PO_4/PMDA$ (COOH).

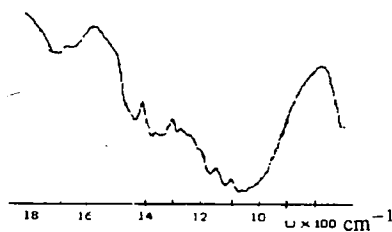


Fig. 3. IR spectrum of the phosphorus derivative of MCC.

The kinetic curves of the esterification of cellulose by a binary mixture of PMDA and phosphoric acid were typical for reactions of cellulose accompanied by cross-linking of the molecules. The rate of the reaction was high in the first 1-2 h and then fell sharply. The degree of modification of the cellulose reached a limit after about 6 h. The number of added cross-linking reagents depended on the temperature and had a definite limit for each temperature. Increasing the time of the reaction did not enable it to reach the limit corresponding to a higher temperature.

The influence of the temperature on the rate of the reaction and the magnitude of the limiting modification of the cellulose was apparently due to the increase in the mobility of the macromolecules with a rise in the temperature. However, a temperature above $90^\circ C$ ($110-130^\circ C$) no longer had much influence on these indices. This is perhaps connected with the fact that the liberation of water as a result of the reaction and the additional hydrolysis of the MCC to oligomers soluble in

water and organic solvents progresses at elevated temperatures. Phosphoric acid, in addition to esterifying cellulose, may catalyze the dehydration and degradation (hydrolysis) of the polymer.

Figure 2 shows the dependence of phosphorus content of the MCC phosphate on the molar ratio (MR) of phosphoric acid to MCC at the MR $\text{H}_3\text{PO}_4:\text{PMDA} = 1/1$. As can be seen from Fig. 2, with an increase in the MR the amount of phosphorus introduced rose, reaching a maximum at an MR of (4-5):1. With a further increase in the MR there was some fall in the phosphorus content of the cellulose and an increase in the hydrolysis (degradation) of the cellulose macromolecule, which apparently took place as far as the formation of soluble oligomers. This led to a loss of the highly substituted fraction during the washing process.

At first glance, because of the absence of water from the reaction medium, hydrolysis of the cellulose macromolecules is impossible. However, the esterification of phosphoric acid takes place with the liberation of water. In addition, the reaction mixture contained a strong water-abstracting reagent — PMDA — which can dehydrate cellulose with a C1-1C conformational transition of the pyranose unit through the formation of 3,6-anhydro rings [4].

This hypothesis was confirmed by IR spectroscopy (Fig. 3) showing the appearance of a band at $850\text{-}860\text{ cm}^{-1}$ relating to 2,3-anhydro rings [5]. There were bands of vibrations of pyranose units in the $700\text{-}900\text{ cm}^{-1}$ region. Individual absorption bands are sensitive to the spatial position of the C1- $\text{H}_{\alpha(\text{o})}$ bond. In particular, a band at $844 \pm 8\text{ cm}^{-1}$ is an indication of the presence of a C1- H_o bond, i.e., it is specific for a glucopyranoside with an equatorial H atom at C₁ [5, 6], which confirms the possibility of dehydration as a result of C1-1C conformational transitions.

In the IR spectra of the product of the phosphorylation of MCC with a H_3PO_4 -PMDA mixture there was an increase in absorption in the $1200\text{-}1280\text{ cm}^{-1}$ region relating to the stretching vibrations of a $\text{-P}\leftarrow\text{O}$ group, a band at $1200\text{-}1220\text{ cm}^{-1}$ relating to the stretching vibrations of a $\text{P}=\text{O}$ group involved in a $\text{P}=\text{O}\cdots\text{HO}-$ hydrogen bond, and one at $1250\text{-}1280\text{ cm}^{-1}$ to the stretching vibrations of a $\text{P}=\text{O}$ group not involved in a hydrogen bond [5, 7]. Changes in the $1650\text{-}1700\text{ cm}^{-1}$ region attract attention. Adsorbed water and double carbon-carbon bonds may absorb here, and so may $\text{P}=\text{O}$, -OH groups, which give a broad (sometimes 200 cm^{-1}) absorption region with a maximum at 1660 cm^{-1} . Direct identification of $\text{C}=\text{C}$ bonds from the IR spectra is difficult, although in [5] this band is assigned just to such groups since it disappeared after the bromination of a phosphorus derivative of MCC. $\text{C}=\text{C}$ bonds may have various locations — for example, between C₂ and C₃ and between C₅ and C₆.

We may also note the presence in the IR spectrum of a diffuse band at 1740 cm^{-1} relating to the carboxy groups of bound PMA. This can be explained by the presence of acetyl phosphate groups in the reaction product.

Figure 2 (COOH curve) shows the dependence of the level of carboxy groups on the MR $\text{H}_3\text{PO}_4:\text{PMDA}$ (MR MCC:PMDA = 1/2). When phosphoric acid was absent from the reaction mixture, PMDA esterified cellulose with a yield of 16% of bound COOH groups in the reaction product. However, on the addition of even a very small amount of phosphoric acid at a MR $\text{H}_3\text{PO}_4:\text{PMDA} = 1/1$ the level of bound COOH groups in the reaction product fell to 4%. This is explained by the occurrence of another reaction — the phosphorylation of the cellulose by the phosphoric acid.

The phosphorus content of the reaction product reached 2.5%. The water liberated in the phosphorylation reaction hydrolyzed the PMDA to PMA and PMAc. In contrast to the esterification of cellulose with a binary mixture of PMDA and sulfuric acid [2], phosphoric acid is not a water-abstracting agent and does not stimulate the esterification of cellulose by PMA and, particularly, PMAc. With a further increase in the MR $\text{H}_3\text{PO}_4:\text{PMDA}$ the level of COOH groups in the reaction products slowly fell and reached practically zero at the MR $\text{H}_3\text{PO}_4:\text{PMDA} = 8/1$. This value corresponded to the MR $\text{H}_3\text{PO}_4/\text{MCC} = 4:1$. As has been noted above, the practical maximum of the phosphorus content of the reaction product is reached at this MR.

The results given above show that by changing the MRs $\text{H}_3\text{PO}_4:\text{MCC}$ and $\text{H}_3\text{PO}_4:\text{PMDA}$ it is possible to obtain mixed cross-linked acid esters of cellulose with pyromellitic and phosphoric acids that may be of interest as ion-exchange materials.

EXPERIMENTAL

The esterification of MCC by a mixture of PMDA with phosphoric acid was conducted in a round-bottomed flask fitted with a reflux condenser closed at the top and with a stirrer having a glycerol seal in a 0.9 M solution of PMDA in DMSO at 90°C .

The necessary amount of P_2O_5 was dissolved in DMSO and the calculated amount of water to hydrolyze the anhydride to phosphoric acid was added at 10-15°C. Then the PMDA was added, and after this had dissolved completely the esterification process was started by the addition of the MCC.

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