AN INVESTIGATION OF THE ADDUCT OF POLY(VINYL FURFURAL ACETAL) AND MALEIC ANHYDRIDE BY IR SPECTROSCOPY

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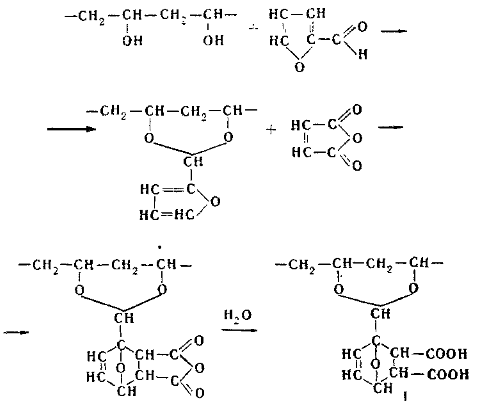
The IR spectra of films of PVA subjected to acetalation with furfural and to coupling with maleic anhydride by the diene synthesis have been obtained, and an assignment of absorption bands is given. The alkali treatment of the adduct of poly(vinyl furfural acetal) with maleic anhydride is apparently accompanied by the epimerization of one carboxyl group.

One of the methods of imparting cation-exchange properties to fibers and films of poly(vinyl alcohol) (I) is their acetalation with furfural and subsequent treatment with maleic anhydride by the Diels-Alder reaction [1]



In this work, we have investigated samples of films of I and also the products of its conversions through furfurylation and through the diene synthesis (II and III) by IR spectroscopy. The spectrum of heat-stabilized films of I (Fig. 1, a) shows only an increase in the intensity of the crystallinity bands at 1147 cm^{-1} as compared with the initial film of I. The spectrum of the product of the acetalation of I with furfural (II, Fig. 1, b) shows absorption bands at 745, 793, 885, 895, 930, and 955 cm^{-1}, corresponding to the nonplanar deformation vibrations of the C—H bond of the furan ring [2] and absorption bands at 820, 1005, and 1067 cm^{-1} corresponding to the vibrations of the rings of an acetal of I [3]. It is not excluded that the absorption at 1005 cm^{-1} is also due to the pulsation vibrations of the furan ring [4]. The disappearance in the spectrum of II of the band at 915 cm^{-1} corresponding to the $\gamma_r(CH_2)$ vibrations in the amorphous phase [5] and the invariability of the intensity of the crystallinity band shows that the acetalation reaction takes place mainly in the amorphous part of the polymer.

The change in the shape of the band and the intensity of absorption in the 1430-1450 cm^{-1} region and the decrease in intensity of the absorption band at 3340 cm^{-1} in the spectrum of II as compound with that of I shows a decrease in the number of hydroxyl groups in the process of furfurylation as a consequence of blockage with acetal bonds. The bands at 1227, 1375, 1430, and 1445 cm^{-1} (CH and CH$_2$ groups; δ_{CH} and δ_{OH}) [6,7] present in the spectrum of the initial I are retained in the spectrum of II. In the IR spectrum of III (Fig. 1, c), the absorption bands due to the vibrations of the furan ring have disappeared. The absorption bands at 820 and 1067 cm^{-1} corresponding to the vibrations of the acetal ring remain, and the absorption band at 1005 cm^{-1} is shifted toward the shortwave region of the spectrum, 985 cm^{-1}. A change in the frequency of the absorption bands of the acetal ring according to the nature of the radical attached to the ring has been observed previously [3]. All this confirms the correctness of the scheme given above for the reaction of poly(vinyl furfural acetal) with maleic anhydride.

The absorption band at 1090 cm^{-1} probably relates to the ν_{C-O} absorption in I. The absorption in the 1170-1300 cm^{-1} region corresponds to the interaction between the planar deformation vibrations of C—O when a hydrogen bond is present [8] and, probably, the absorption due to the oxygen bridge of the ring of the ad-

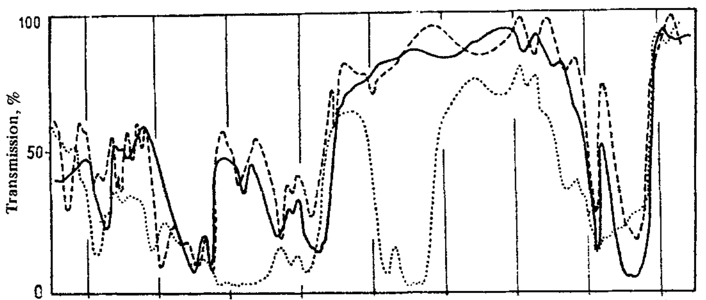


Fig. 1. Spectra of films of PVA (NaCl prism): a) after heat stablization (I, thickness ≈ 10 mμ); b) after furfurylation (II, thickness ~ ~ 10 μ); c) after the diene synthesis reaction (III, thickness ~ 15 mμ).

duct. The absorption bands at 1363 and 1410 cm^{-1} are probably connected with the fan-like vibrations of the CH and CH_2 groups and the deformation vibrations of the OH groups [6]. The absorption frequency at 1630 cm^{-1} corresponds to the stretching vibrations of the C=C bond of the adduct. The absorption bands in the 1700-1750 cm^{-1} region correspond to $\nu_{C=O}$ of carboxyl groups. The presence of the latter is also confirmed by the presence in the spectrum of a series of bands in the 2500–3000 cm^{-1} region. The decrease in the intensity of the ν_{OH} absorption band at 3340 cm^{-1} as compared with the spectrum of II may be caused by processes accompanying the diene synthesis reaction (for example, dehydration or oxidation).

In view of the possibility of the occurrence of isomerization of the carboxyl groups in the adduct III, it appeared of interest to carry out a more detailed spectroscopic study in the 1600–1800 cm^{-1} region of the films investigated previously. With this aim the spectrum of III was taken after the film had been treated with 0.1 N sodium hydroxide solution and subsequent conversion of the ion-exchange product into the H-form. A comparison of the spectra (Fig. 2a and b) shows that this treatment causes a change in the structure of the adduct III. The absorption bands at 1680 and 1742 cm^{-1} in the IR spectra disappear and only the bands at 1710 and 1728 cm^{-1} remain, their intensity rising considerably. This can apparently be regarded as a confirmation of the passage of the carboxyl groups of the adduct after treatment with alkali from the cis form into the trans form which has been detected previously by chemical methods.

The results obtained are in full agreement with modern ideas on the strict spatial directivity of the diene synthesis [9] and with the results of investigations [10,11] in which it was shown that the alkaline hydrolysis of esters of cis-1,2-dicarboxylic acids in the bicyclic systems of 3,6-endoxocyclohexane is accompanied by the epimerization of one of the carboxyl groups with the formation of the corresponding trans acid.

The spectra given in the figure also show that in III even before treatment with alkali there was a certain number of carboxyl groups in the trans position. It is most likely that this is connected with the action of heat to which the film was subjected in the process of its treatment with water and extraction with acetone.

EXPERIMENTAL

The spectra were taken on H-800 and IKS-14A spectrophotometers. The spectrophotometric investigations were performed with samples of PVA of Japanese manufacture of type FF-2 having a degree of polymerization of 1500 (content of acetate groups 0.2%; sodium acetate absent).

The method of obtaining the films has been described previously [12]. The films were subjected to heat stabilization in the free state at 220° C for 6 min, after which they were acetalated with furfural under the conditions described for the treatment of fiber [13] using a high-ratio bath of the following compositon: furfural 4%, H_2SO_4 20%, sodium sulfate 20%. The reaction temperature was 70° C and the time 40 min. The films were then washed with water and extracted with ethanol for a day.

The furfurylated films (II) were subjected to coupling with maleic anhydride by the Diels-Alder reaction at 120° C for 3 hr, using a 10% solution of maleic anhydride in toluene. The reaction was carried out in sealed tubes, and after the end of the process the films were washed with distilled water (temperature 50–60° C) and extracted with acetone for 24 hr.

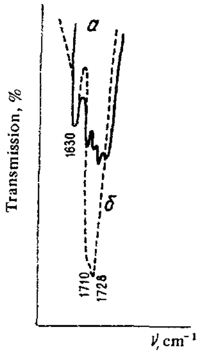


Fig. 2. Spectrum of a film of PVA in the 1600–1800 cm^{-1} region (NaCl prism): a) after the diene synthesis reaction; b) after treatment with 0.1 N sodium hydroxide solution and conversion into the H-form.

The treatment of the films after the Diels-Alder reaction with 0.1 N sodium hydroxide solution was carried out for 48 hr.

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