INVESTIGATION OF THE STRUCTURE OF CELLULOSE ACETOPHTHALATE AND CELLULOSE ACETOSUCCINATE

Yu. I. Rumyantseva

Cellulose acetophthalate (CAP) and cellulose acetosuccinate (CAS) - mixed esters of cellulose (C) with acetic and dicarboxylic acids - have recently found wide use in polygraphy, the motion picture industry, and pharmacology. The physicochemical properties of CAP and CAS depend to a substantial degree on the conditions of their production and the degree of substitution [1-4]. According to the literature data [2, 3], CAP and CAS are usually produced under homogeneous conditions of esterification of the free OH groups of secondary cellulose acetate (CA) by phthalic or succinic anhydride. The course of the esterification of CAP and its properties depend on the distribution of OH groups between the 2-, 3-, and 6-carbon atoms of the glucopyranose unit in connection with the steric hindrances to phthalylation [2]. The use of CA with different contents of primary OH groups and the same degree of substitution with respect to acetic acid show that phthalylation of CA occurs primarily at the OH groups at C6, whereas succinylation is less selective [2].

The CAP and CAS used in this work were synthesized on the basis of Sericose brand CA, containing 44.2% bound acetic acid (YAC = 172, SP = 220). Samples of CAP with Yphth = 43, 63, 76, and 82 and CAS with Ysucc = 64, 68, and 77 were investigated. In the case of esterification, YAC and SP of AC are virtually unchanged. The samples were prepared in the form of films on a glass substrate from 15% filtered solutions of CAP and CAS in acetone and CA (YAC = 172) in DMF at room temperature. The polymers were preliminarily purified by reprecipitation in toluene. Films of CAP and CAS were dried at 40°C and a pressure of 0.15 Pa for 15 h, and films of CA at 80°C, pressure 0.15 Pa, for 30 h. Heat treatment of the samples was performed at 150°C under a pressure of 0.15 Pa. The IR spectra were recorded on a UR-20 spectrophotometer. The structure of CAP and CAS was also studied by the methods of molecular [5, 6] and "kinetic" [7, 8] probes. The probe substance (anthracene, scintillation grade) was introduced into the polymer solutions without additional purification in a concentration of 10^-4 M. The conditions of photooxidation of the anthracene impurity and the spectral methods of recording the process were outlined earlier [7]. The shift of the bands of the electronic absorption spectrum of anthracene that lie at the basis of the molecular probe method was followed on a Beckman UV-5270 spectrophotometer.

The introduction of phthalyl and succinyl substituents into CA should substantially change the energetics of the hydrogen bonds and the conformational structure of the macromolecules. Actually, with increasing degree of substitution with respect to dicarboxylic acids, a decrease in the half-width and the peak intensity of the band of the stretching vibrations of the OH groups included in H-bonds at 3485 cm⁻¹ is observed in the IR spectra of CAP and CAS. At the same time, a broad asymmetrical band in the region of 3130-3400 cm⁻¹ appears and increases in intensity with increasing degree of substitution (Fig. 1a). These changes are due to replacement of hydroxyl groups by phthalyl (CAP) and succinyl (CAS) substituents and an increase in the energy nonequivalence of the H-bonds as a result of association of the COOH groups of the phthalyl substituents. This may be due to conjugation of the COOH groups with the π-electrons of the benzene ring, as a result of which the electron density on the oxygen atom is somewhat increased. However, these differences can also be explained by specific conformational states of the phthalyl and succinyl groups. The participation of the C=O groups (proton acceptors) in H-bonds, as is well known, decreases the frequency ν(C=O). In comparison with CA, in the spectrum of CAP (Yphth = 82) the band ν(C=O) is shifted by 11 cm⁻¹ in the direction of short-
er frequencies, and in CAS ($\nu_{\text{succ}} = 77$) it is shifted by 4 cm$^{-1}$ (Fig. 1b). The substantial shift of the maximum $\nu(C=O)$ in the spectrum of CAP also indicates the formation of stronger H-bonds by the COOH groups of the phthalyl substituents. In the spectra of CAP and CAS the band $\nu(C=O)$ is substantially broadened on the short-frequency side; projections are noted at 1710 and 1690 cm$^{-1}$. In phthalic and succinic acids, the bands $\nu(C=O)$ of the COOH groups included in dimer-type H-bonds are situated at 1690 cm$^{-1}$ [9, 10]. Evidently, the observed changes in the long-wave edge of the band $\nu(C=O)$ in CAP and CAS are due not only to the energy difference of the H-bonds but also to the presence of different types of them — cyclic

$$-\text{C}^\circ\text{OH}... \text{O}^\circ\text{C}... \text{HO}-$$

and open $-\text{C}=\text{O}...\text{H}--\text{O}--$.

With increasing degree of substitution with respect to dicarboxylic acids, a redistribution of the relative intensity of the components of the doublet band in the region of 2940-2970 cm$^{-1}$ is observed — a decrease in the intensity of the long-wave component and an increase in the intensity of the short-wave component (Fig. 1a). From theoretical calculations of the vibrational spectrum of CTA [11] it follows that the short-wave component at 2963 cm$^{-1}$ with a substantial contribution to the RPE of $\nu(CH)$ of the CH$_3$ groups of the acetate substituents at C$_2$ and C$_3$ is most sensitive to a change in the steric arrangement of these groups. If we consider that the contribution of the vibrations $\nu(CH_3)$ of the succinyl group at 2980 cm$^{-1}$ to the short-wave component of the band in CAS is negligible and is manifested in a broadening of the short-wave edge, while $\nu(CH)$ of the phthalyl groups are situated at 3040 and 3080 cm$^{-1}$ [9], we can consider that the changes in the relative intensity of the components of the doublet band are due to conformational transformations of the acetate groups at C$_2$ and C$_3$ when phthalyl (CAP) or succinyl (CAS) substituents are introduced into the macromolecule. The decrease in the intensity and broadening of the band $\delta_{\text{as}}(\text{CH}_3)$ at 1430 cm$^{-1}$ can be explained, as was done in [12], by a decrease in the homogeneity of the conformational states of the acetate groups, considering the interference of the bands of the deformational vibrations of the OH groups of the phthalyl substituent (1405 cm$^{-1}$) and of the CH$_2$ and OH groups of the succinyl substituent (1415 cm$^{-1}$) (Fig. 1b). The conformational changes in the acetate groups at C$_2$ and C$_3$ when phthalyl substituents are introduced are also confirmed by a decrease in the peak intensity of the band at 840 cm$^{-1}$ (Fig. 1b), which is assigned [11] to the vibrations of the C-O bond of the acetate groups at C$_2$ and C$_3$. In [13] the high sensitivity of the band 840 cm$^{-1}$ to changes in orientation, plasticizing, and temperature influences on CA is associated with a change in the steric arrangement of the groups at C$_2$ and C$_3$.

When substituents of dicarboxylic acids are introduced, the peak intensity decreases and the half-width of the asymmetrical band 900 cm$^{-1}$ increases; a shoulder appears at 920 cm$^{-1}$, the intensity of which increases with increasing degree of substitution (Fig. 1b). Analogous changes in the band 900 cm$^{-1}$ observed in the orientation of CTA and CDA films are explained by conformational transformations of the CH$_2$OAc groups [14]. Evidently such changes in the steric arrangement of the CH$_2$OAc and CH$_2$OSuc groups (since phthaloylation and succination proceed predominantly at C$_6$ [2]) occur when the numbers of phthalyl and succinyl substituents are increased. The formation of a new system of H-bonds also suggests the realization of the corresponding conformational states. A narrowing and redistribution of the intensity of the band due to a complex set of delocalized vibrations with the greatest contribution of $\nu(C-O)$ and $\nu(C-C)$ of the framework of elementary units to the RPE, is observed in the region of 1000-1100 cm$^{-1}$. This band is sensitive to rotamers of the ester side groups as a result of rotation around the C-O bond [11]; therefore, the indicated spectroscopic differences should be explained by a change in the ratio of rotational isomers of the ester groups. These changes are most appreciable in the spectra of CAP, which suggests more substantial conformational transformations when phthalyl groups are introduced into the polymer.

An analysis of the data obtained permit us to conclude that when phthalyl or succinyl groups are introduced into CA, the system of hydrogen bonds is complicated as a result of association of the COOH groups and the appearance of dimer-type H-bonds, the energy variety of the H-bonds is increased, the uniformity of the conformational states of the acetate groups at C$_2$ and C$_3$ is decreased, and the steric arrangement of the CH$_2$OAc and CH$_2$OSuc groups is changed with increasing degree of substitution with respect to dicarboxylic acids.

In the case of heat-treatment of CAP, a decrease in the absorption is observed in the region of 3130-3400 cm$^{-1}$ and a simultaneous small increase in the intensity of the band 3485 cm$^{-1}$ (Fig. 1a). Moreover, new bands appear at 1853 and 536 cm$^{-1}$, and on the edges of the bands 1738 and 1420 cm$^{-1}$, shoulders appear at 1780 and 1471 cm$^{-1}$ (Fig. 1b). The peak in-