A STUDY OF MESOMORPHOUS PROPERTIES OF *O*-(2-HYDROXYPROPYL)CELLULOSE DERIVATIVES

Iva SROKOVA[a], Gabriel CIK[b,]* and Pavel HODUL[a]

[a] *Department of Fibers and Textile,*
Slovak Technical University, 812 37 Bratislava, The Slovak Republic
[b] *Department of Environmental Sciences,*
Slovak Technical University, 812 37 Bratislava, The Slovak Republic

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O-(2-Hydroxypropyl)cellulose has been used for synthesis of *O*-decyl-*O*-(2-hydroxypropyl)cellulose (DHPC; DS = 2.2) and *O*-stearoyl-*O*-(2-hydroxypropyl)cellulose (SHPC; DS = 2.1). Both compounds show mesomorphous properties of liquid polymeric crystals. DHPC in the form of highly viscous liquid has a lyotropic character. SHPC as solid has thermotropic properties with two phase transitions in the interval of 40 – 70 °C.

Introduction of flexible substituents into a cellulosic chain changes the polymer into a thermotropic liquid crystal with cholesteric arrangement[1,2]. Highly concentrated aqueous and aqueous-alcoholic solutions of hydroxypropylcellulose exhibit lyotropic properties of liquid crystals[3]. The cholesteric structure was also observed with the solid film of hydroxypropylcellulose[4].

The present paper describes some mesomorphic properties of *O*-stearoyl-*O*-(2-hydroxypropyl)cellulose (SHPC) and the newly synthesized *O*-decyl-*O*-(2-hydroxypropyl)cellulose (DHPC).

EXPERIMENTAL

The synthesis started from commercial *O*-(2-hydroxypropyl)cellulose (HPC) Klucel G (Hercules) with the substitution degree DS = 3 and $\overline{M}_w$ = 300 000.

SHPC was synthesized according to refs[5,6]. The ester obtained had DS = 2.1 (calculated from the elemental analysis: 70.82% C, 11.07% H). The characteristic wavenumbers of IR spectrum ($\tilde{\nu}$, cm^{-1}): C=O 1 736, COC 1 176, OH 3 493, CH_2 2 853, CH_3 2 922. ^{13}C NMR analysis (δ, ppm): C6 62.1, C=O 173.1, C2′ 68.9, C3′ 34.5, C4′ – C17′ 31.9 – 22.7, C18′ 14.1.

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* The author to whom correspondence should be addressed.

DHPC was synthesized on the basis of a modified procedure known for cellulose, i.e. a reaction with decyl bromide in a mixed solvent medium dimethyl sulfoxide–SO_2–diethylamine[2]. During 30 min, 1 g HPC was added to 20 ml dimethyl sulfoxide. The mixed solvent (1.4 g diethylamine, 1.2 g SO_2, 10 ml dimethyl sulfoxide) prepared in advance was added to the suspension obtained with stirring whereupon a yellow solution was formed. The reaction mixture was treated with 9.7 g (0.24 mol) NaOH added portionwise and then stirred at 50 °C 1 h. After adding 10 g decyl bromide, the reaction proceeded 20 h at 70 °C, and then the reaction mixture was poured to 200 ml chloroform. The insoluble portion was filtered off, and the chloroform solution was washed three times with water. After drying the solution and evaporating the solvent, 2.1 g highly viscous yellow liquid was obtained; DS = 2.2 (calculated from the elemental analysis: 70.02% C, 11.35% H). Characteristic wavenumbers of IR spectrum: COC 1 124, OH 3 497, CH_2 2 856, CH_3 2 924. ^{13}C NMR analysis (δ, ppm): C6 69.5, C2′ 71.0, C3′ 31.6, C4′ – C9′ 30.3 – 22.7, C10′ 14.1.

The IR spectra were measured in chloroform, using a PU 9800 FTIR apparatus (Philips Analytical). The electronic absorption spectra were measured using a PU 8800 apparatus (Philips Analytical). The samples were applied in the form of a film spread on glass. The ^{13}C NMR spectra were measured with an XL-300 apparatus (Varian) in $CDCl_3$.

The DSC curves were obtained with a differential scanning calorimeter DSC 7 (Perkin–Elmer) in the temperature interval of 30 – 190 °C; the heating rate was 10 °C per min.

The thermal stability was measured on a derivatograph Pavlik–Pavlik–Erdey (Hungary) in the temperature interval of 20 – 600 °C.

The photographs of the compounds investigated were obtained with a polarization microscope Amplival (Zeiss).

The limit viscosity numbers were determined in dioxane in the concentration interval of 0.001 – 0.008 g ml^{-1} at 20 °C. $[\eta]_{HPC}$ = 501 ml g^{-1}, $[\eta]_{DHPC}$ = 30.5 ml g^{-1}, $[\eta]_{SHPC}$ = 735 g ml^{-1}.

RESULTS AND DISCUSSION

Figure 1 presents the electronic absorption spectra of thin films of the HPC derivatives synthesized which were spread on a microscopic glass. The spectra measured show qualitative differences: whereas DHPC exhibits a weak absorption maximum at 860 nm, no such maximum is present in the spectrum of SHPC. However, SHPC shows absorption

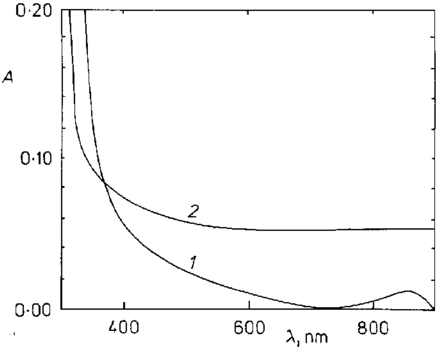

FIG. 1
Electronic absorption spectra of polymeric films: *1* DHPC, *2* SHPC

throughout the visible spectral range. These differences indicate the presence of different structural groupings of the macromolecules of modified HPC. Figures 2 and 3 present photographs taken in polarized light with samples of thin films obtained after evaporation of solvent (chloroform). From Fig. 2 it follows that in DHPC one can observe a biphase structure of the derivative synthesized. The presence of typical hexagonal crystal structures indicates lyotropic liquid-crystal properties in the case given. On the other hand, the SHPC sample (Fig. 3) exhibits a dense structure of long rods separated by dark fields. Such structure can be ascribed to a smectic-cholesteric arrangement of thermotropic character[7]. Similar structures are predicted by the authors of ref.[1] for various alkyl derivatives of cellulose, too.

In order to confirm our presumption that DHPC and SHPC represent lyotropic properties and thermotropic liquid crystals, respectively, we carried out measurements of DSC and thermal stability of these derivatives. Figure 4 presents the DSC curve of SHPC. Its course shows a weak exothermic peak with the maximum at 43.6 °C and a strong endothermic peak at 62.9 °C. The value calculated for the endothermic transition is 121 J g^{-1}.

In order to confirm the presumption that the extremes given are connected with phase transitions, we monitored the thermostability of the derivative. The decomposition of SHPC in oxygen atmosphere does not start until 170 °C; the mass decrease at 330 °C is 59%, and at 518 °C the sample is decomposed to 96%. The DSC record of DHPC has monotonous character. These facts allow the statement that SHPC exhibits thermotropic properties of a liquid crystal. The phase transition at 43.6 °C can be ascribed to the transition solid–anisotropic phase, and the endothermic peak at 62.9 °C corresponds to the phase transition anisotropic phase–isotropic phase[1].

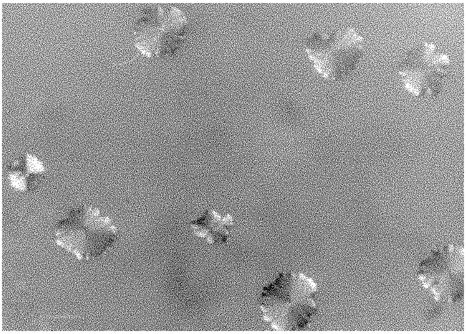

FIG. 2
Photograph of surface of DHPC film in polarized ligth (magnification 450×)

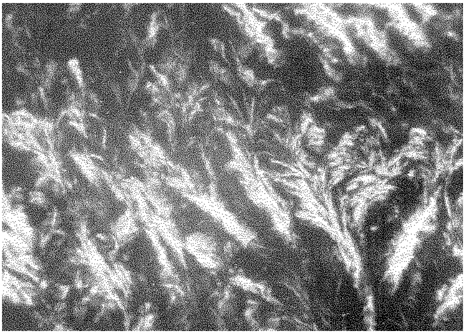

FIG. 3
Photograph of surface of SHPC film in polarized ligth (magnification 320×)

The measurements of limit viscosity numbers of DHPC and starting HPC unambiguously show that the strongly alkaline reaction medium has caused a degradation of macromolecular chain, which in the given case is manifested by the almost one order decrease in [η]. This fact also results in the reaction product exhibiting properties of highly viscous liquid: the latter, alone without the presence of solvent, exhibits lyotropic properties of a liquid crystal.

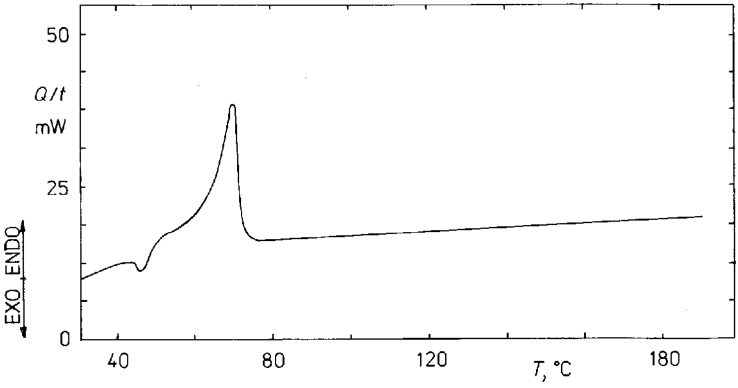

FIG. 4
DSC curve of *O*-stearoyl-*O*-(2-hydroxypropyl)cellulose

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