

# Thermotropic Mesomorphism of Selected (2-hydroxypropyl)cellulose Derivatives

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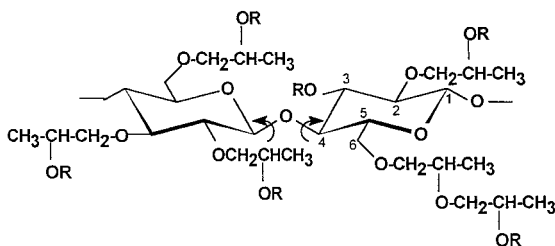
**ABSTRACT:** The thermotropic mesomorphism of some cellulose derivatives (CD) based on the (2-hydroxypropyl)cellulose (HPC) was investigated. Three types of derivatives: two esters (PPC, HxPC) and cyanoethyl derivative (CEPC) were prepared. The X-ray diffraction patterns of CDs were compared with the differential scanning calorimetry, thermo-optical, and mechanical measurements within a broad range of the temperature. Two relaxation processes  $\alpha_a$  and  $\alpha_m$ , observed in the solid state of HPC, are also exhibited by all CDs, however, at lower temperatures. The  $\alpha_m$  relaxations, which indicate the transition from frozen anisotropic phase to mobile liquid crystalline (LC)-phase, are shifted towards the lower temperatures with a corresponding increase in the  $d$ -spacing of the poly(saccharide) main chains of CDs (as seen in the X-ray measurements). The transition temperature to isotropic phase  $T_{ni}$  as well as glass transition temperature  $T_g$  ( $\alpha_a$ -relaxation) of the investigated CDs depend on the interactions between the lipophilic side chains and the hydrophilic poly(saccharide) main chains of CDs. These interactions are determined by the length and polarity of the lipophilic side chains. The observed changes in the transition temperature to isotropic phase  $T_{ni}$  for CDs is consistent with the assumption that LC-organization of the poly(saccharide) main chains is stabilized by the lipophilic side-chains system. A significant increase in the length of the lipophilic side chains leads to nonlinear conformation, thus reducing the influence of van der Waals forces, and consequently lowering  $T_{ni}$ . The polymer with high polarity lipophilic side chains (CEPC) exhibits higher  $T_{ni}$  in comparison to the ester derivative PPC with the same length of the side chains but having lower polarity. The stabilization effect of the lipophilic side-chains system on the LC-organization of the poly(saccharide) main chains is determined by the dynamic balance between length and polarity of the lipophilic side-chains system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 837–844, 2000

**Key words:** LC cellulose derivatives; phase transition; thermotropic mesomorphism; (2-hydroxypropyl)cellulose

## INTRODUCTION

Cellulose is a semirigid polymer whose glass transition temperature  $T_g$  can be drastically lowered by introducing suitable side chains. Such cellulose derivatives (CD) often form lyotropic liquid

crystalline (LC) phases, which are of the cholesteric type and originate essentially from semirigidity and chirality of the cellulose main chain.<sup>1,2</sup> The mesophase formation is observed in the concentrated solution of CDs at a volume fraction of polymer ( $v'$ ) higher than that predicted by Flory's theory. It should be also emphasized here that  $v'$  is often strongly solvent dependent.<sup>1</sup> These effects might be attributed to solvent interactions, dras-



R = H (for HPC), CH<sub>2</sub>CH<sub>2</sub>CN (CEPC), COCH<sub>2</sub>CH<sub>3</sub> (PPC), CO(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> (HxPC)

**Figure 1** Chemical structure of the repeating units of the investigated LC-CDs.

tically affecting the polymer chain flexibility. Several studies have appeared in the literature concerning the solid-state properties of CDs proving that the CDs can exhibit the LC-phases even in the absence of solvent.<sup>1,3–5</sup> Recent studies on the dielectric and mechanical properties of (2-hydroxypropyl)cellulose (HPC)<sup>6</sup> as well as its cyanoethylated derivative<sup>7,8</sup> have shown that these CDs in the solid state are characterized by a complex morphology, consisting of crystalline, amorphous, and intermediate phases.

The primary objective of this work is to find the relation between thermotropic mesomorphism of CDs and their molecular structure. For this purpose CDs were investigated in the quiescent state and under influence of mechanical deformation (shearing). The behavior of CDs in the quiescent state was investigated using X-ray, differential scanning calorimetry (DSC), and thermo-optical analysis (TOA). The LC-phases of CDs were investigated by means of dynamic mechanical measurements at the broad range of temperature as well as by analysis of the properties observed after the mechanical shearing. Our research was focused mainly on HPC, as a parent material, and its three derivatives.

## EXPERIMENTAL

### Materials

HPC ( $M_w = 100,000$ ) and acrylic acid (AA) were supplied by Sigma Aldrich (Poland) (Hexanoyloxypropyl)cellulose (HxPC) and (propionyloxypropyl)cellulose (PPC) were prepared from HPC, according to the procedure given in the literature.<sup>9</sup> (Cyanoethylpropyl)cellulose (CEPC) was obtained by the reaction of HPC and acrylonitrile.<sup>10</sup> The chemical structure and characteristics of the LC cellulose derivatives (LC-CDs) used in this

study are shown in Figure 1 and Table I, respectively. These CDs differ in polarity (HPC, CEPC, PPC) or the length of their side chains (HxPC, PPC, HPC). At room temperature, HPC is a crystalline polymer having strong intramolecular hydrogen bonds.<sup>11</sup> Due to the high dipole moment of the 2-cyanoethyl groups, the polarity of CEPC is much higher than that of other LC-CDs. The dielectric permittivity of CEPC is 15.<sup>12</sup> PPC and HxPC are semisolid derivatives of HPC, their low polarity results from the presence of carbonyl group in the ester side chains. The films of CDs for thermo-optical investigations were obtained by casting from dichloromethane solution (10 wt %).

### Measurements

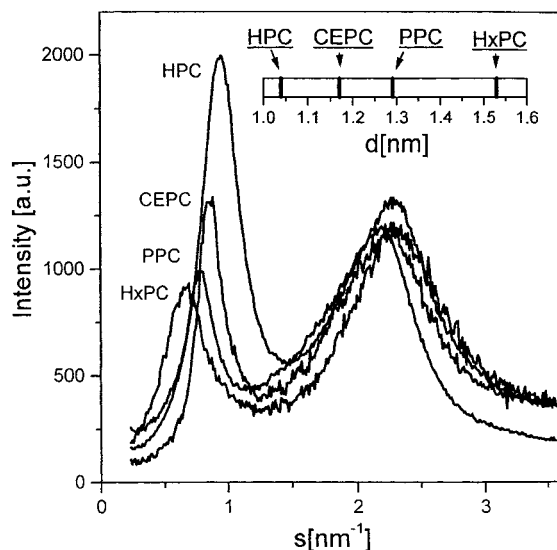
Dynamic mechanical measurements were performed using the (Rheometric Sci. Instr., USA) RMS 800 mechanical spectrometer. Shear deformation was applied under the condition of controlled deformation amplitude, varied between  $\Delta\gamma = 0.0001$  and  $\Delta\gamma = 0.05$  at low and high temperatures, respectively, always remaining, however, in the range of the linear viscoelastic response of the studied samples. Plate-plate geometry was used with plate diameters of 6 mm and 25 mm, for the temperatures below and above 50°C, respectively. The gap between plates (sample thickness) was approximately 1 mm. The experiments were performed under a dry nitrogen atmosphere. Results are presented as temperature dependencies of storage ( $G'$ ) and loss ( $G''$ ) shear modulus measured at a constant deformation frequency of 10 rad/s. The results collected below 50°C were obtained at a cooling rate of 2°C/min and those above 50°C at a heating rate of 2°C/min.

X-ray diffractograms were recorded at room temperature by means of a  $\theta$ - $\theta$  diffractometer with Cu-K $\alpha$  radiation. DSC measurements were

**Table I** Characteristics of Cellulose Derivatives

Cellulose Derivatives	$T_g$ [°C] <sup>a</sup>	$T_{ni}$ [°C] <sup>a</sup>
HxPC	-50	100
PPC	-20	135
CEPC	-20	194
HPC	15	205

<sup>a</sup>  $T_g$  (glass transition temperature) and  $T_{ni}$  (isotropization temperature) of CDs are determined from DSC and TOA measurements.



**Figure 2** Wide-angle X-ray scattering (WAXS) intensity distributions for HPC, PPC, HxPC, and CEPC measured at room temperature. The insert shows  $d$ -spacing calculated from the position of the first peak below  $s < 1 \text{ nm}^{-1}$ .

made using the Mettler DSC 30 calorimeter (Mettler Toledo, Switzerland) at constant heating rate of  $10^\circ\text{C}/\text{min}$ .

A polarizing optical microscope equipped with the Mettler FP-82 at stage and photomonitor was used to measure the light transmission changes through the sample placed between crossed polarizers (TOA). The relative transmitted light intensity  $I/I_0$  (where  $I_0$  is the intensity at a reference initial state and  $I$  is the intensity at a given temperature) was recorded as a function of temperature at heating rate of  $2^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### X-ray Investigations of Cellulose Polymers in the Quiescent State

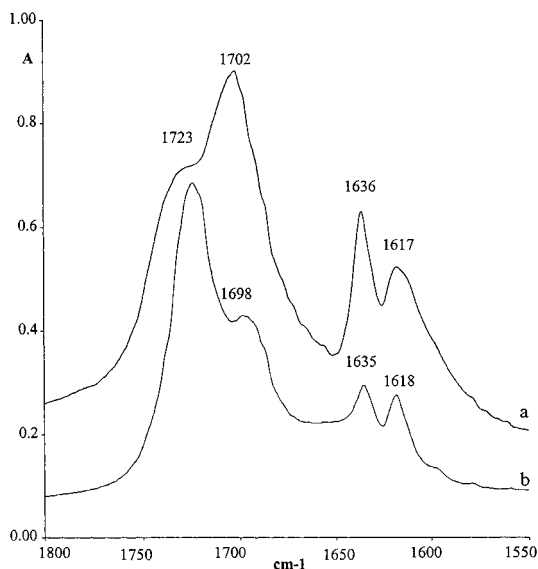
The X-ray diffraction intensity distribution for the investigated polymers at the  $25^\circ\text{C}$  is discussed below. The diffractogram of HPC, presented in Figure 2, is in accordance with results published by Samuels.<sup>11</sup> The narrow diffraction band observed at  $s = 0.96 \text{ nm}^{-1}$  ( $2\theta = 8^\circ$ ), corresponding to the  $d$ -spacing of 1.04 nm, is attributed to backbone-backbone  $d$ -spacing of the poly(saccharide) main chains in the crystalline phase of HPC. The broad diffraction band at  $s = 2.28 \text{ nm}^{-1}$  ( $2\theta = 20^\circ$ ) is related to slightly ordered

amorphous phase of HPC. The diffractogram of HPC is similar to those observed for LC-poly(siloxanes) and poly(phosphazenes) discussed by Godowski.<sup>13</sup> However, these polymers have quite different molecular structure as compared with HPC. These synthetic polymers show a narrow and intensive diffraction band at the range of  $2\theta = 8\text{--}12^\circ$  and second broad band at  $2\theta = 16\text{--}25^\circ$ . The LC-phases of poly(siloxanes) and poly(phosphazenes) originate from stiffness of the main chains of the macromolecules, similar to LC-CDs.<sup>1</sup>

The changes in the intensity and peak position below  $s = 1 \text{ nm}^{-1}$  for various derivatives of HPC, shown in Figure 2, indicate remarkable changes in the packing of the poly(saccharide) main chains as well as the decreasing contribution of the crystalline phase. The  $d$ -spacing ranges approximately from 1.04 nm for the HPC to 1.53 nm for the derivative with the longest side chains (HxPC).

The increase of  $d$ -spacing between poly(saccharide) main chains can be obtained not only by chemical modification of the side groups of HPC, but also by dissolution of HPC in the lyotropic low molecular solvent, for example AA.<sup>14,15</sup> The HPC-AA system forms lyotropic LC-phase with long cholesteric pitch  $P^{15}$  at room temperature. The molecular interactions of AA with HPC are relatively strong in the HPC-AA system. The evidence for these interactions are provided by the observed changes in the IR absorption of carbonyl groups of the pure AA and AA in the mesomorphic environment of HPC, (see Fig. 3). From the analysis of the spectra and the absence of any additional bands in HPC spectrum in this range, one can conclude that the presence of HPC induces the effect of the dilution of AA. The band near  $1700 \text{ cm}^{-1}$  due to hydrogen bonds of AA dimers is diminished. This phenomenon was discussed in the previous paper<sup>16</sup> and it was explained on the basis of the Raman spectroscopy investigations. The X-ray diffraction intensity distribution for the HPC-AA system is shown in Figure 4. The intensity of the narrow low-angle diffraction band at  $s < 1 \text{ nm}^{-1}$  of the lyotropic system HPC-AA practically disappears as compared with pure HPC (see Fig. 2).

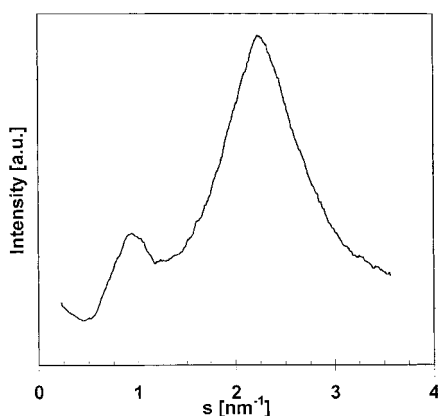
Comparison of the diffractograms of HPC and its derivatives as well as lyotropic LC-system of HPC-AA leads to the conclusion that the physical or chemical modification of HPC macromolecules result in the increase in  $d$ -spacing of the poly(saccharide) main chain. The  $d$ -spacing of the poly-



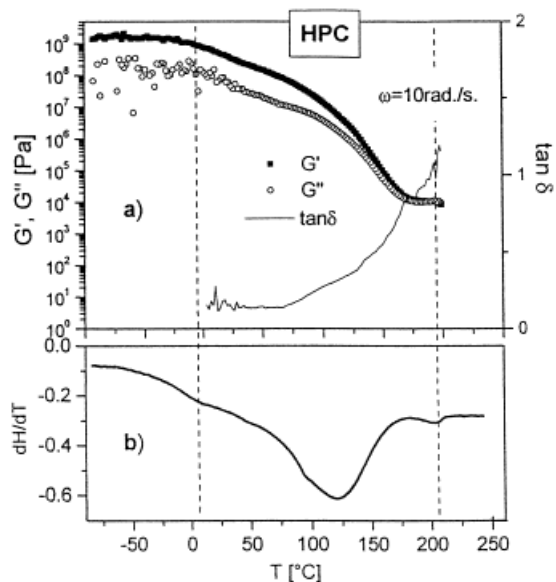
**Figure 3** IR absorption of carbonyl groups of the pure AA (a), and AA in the lyotropic LC-phase of HPC-AA system (b).

(saccharide) main chains has an influence on the intensity of the low-angle diffraction band attributed to crystalline phase. Increasing the  $d$ -spacing either by lyotropic solvent or by chemical modification of HPC reduces the intensity of low-angle crystalline bands.

The thermotropic LC-phase of HPC was observed above 160°C with transition temperatures to isotropic state at 205°C.<sup>17</sup> The cyanoethylated derivative CEPC forms lyotropic LC-phases,<sup>10</sup> however, DSC and thermo-optical characteristics<sup>8</sup> suggest the presence of the thermotropic LC-phase at the elevated but lower temperatures in



**Figure 4** Wide-angle X-ray scattering (WAXS) intensity distributions for LC-lyotropic HPC-AA system (50 : 50 wt %).

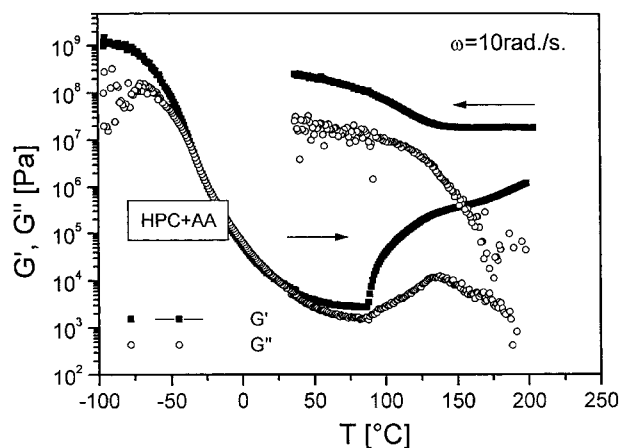


**Figure 5** Temperature dependencies of  $G'$ ,  $G''$ , and  $\tan \delta$  (a), and DSC thermogram (b) for HPC. The vertical dashed lines indicate temperatures assigned as  $T_g$  (glass transition) and  $T_{ni}$  (isotropization temperature).

comparison with HPC. The ester derivatives PPC and HxPC form well-defined thermotropic LC-phase at room temperature.<sup>9,14</sup> It suggests that there is a correlation between the  $d$ -spacing of the poly(saccharide) main chain and the thermotropic mesomorphism of the investigated polymers. The transition temperature to the thermotropic phase seems to decrease with an increase of the  $d$ -spacing.

#### Thermotropic Mesomorphism of the CDs

Figure 5 shows temperature dependencies of the shear storage ( $G'$ ) and loss ( $G''$ ) modulus for HPC as well as DSC thermogram. At low temperatures the polymer is in a glassy state with the  $G'$  modulus higher than  $10^9$  Pa. The first softening of the polymer appears at about 10–20°C and it is correlated with a weak change of the specific heat (Fig. 5b). This can be attributed to the glass transition of the amorphous polymer. Above this temperature there is a broad range of temperature, which extends over approximately 200°C. The mechanical properties of HPC in this range are strongly dependent on water content and can vary within 3–4 orders of magnitude of the modulus. The isotropization occurs at about 205°C but around 120°C one can observe indications of an



**Figure 6** Temperature dependencies of  $G'$ ,  $G''$ , for HPC-AA (50 : 50 wt %) at the heating and cooling scans.

additional relaxation process, which can be interpreted as  $\alpha_m$  relaxation.

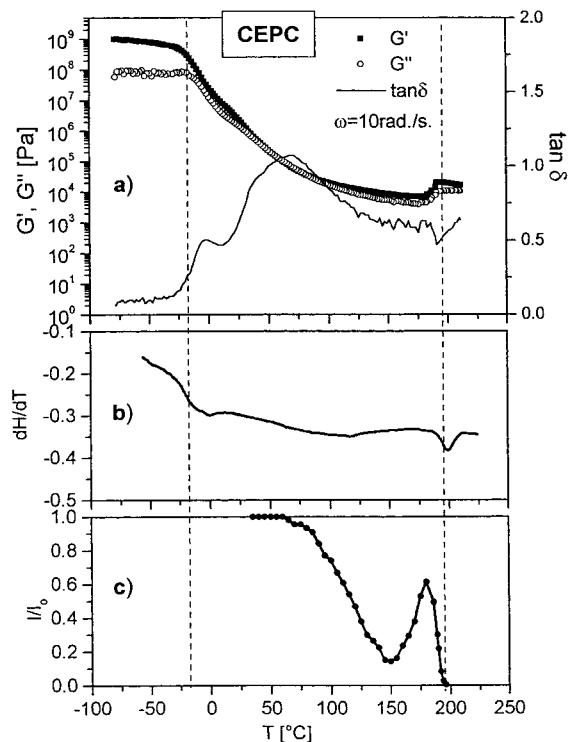
The investigations of the dielectric and dynamic mechanical properties of HPC published by Pizzoli et al.<sup>6</sup> have indicated the existence of four relaxation regions  $\gamma$ ,  $\beta$ ,  $\alpha_a$ , and  $\alpha_m$  in order of increasing temperature, over the temperature range  $-150$ – $150$ °C. Two relaxation  $\alpha_a$  and  $\alpha_m$  are associated with large-scale molecular motion. The  $\alpha_a$  relaxation occurs at the same temperature range as the glass transition in the DSC and mechanical measurements and thus it is associated with devitrification process of the disordered phase of HPC. The  $\alpha_m$  relaxation, observed above  $100$ °C, is associated with a large decrease of elastic modulus and signifies the mobility of a glassy cholesteric mesophase. Considering  $\alpha_a$  and  $\alpha_m$  relaxations, the modulus of HPC shows two drops, the steeper one being associated with the  $\alpha_m$  relaxation (Fig. 5a).

Below isotropization temperature of HPC one can observe the narrow “plateau” on the temperature dependence of the modulus. This “plateau” was not mentioned by Pizzoli et al.<sup>6</sup> because their investigations were conducted over the temperature range  $-150$ – $150$ °C.

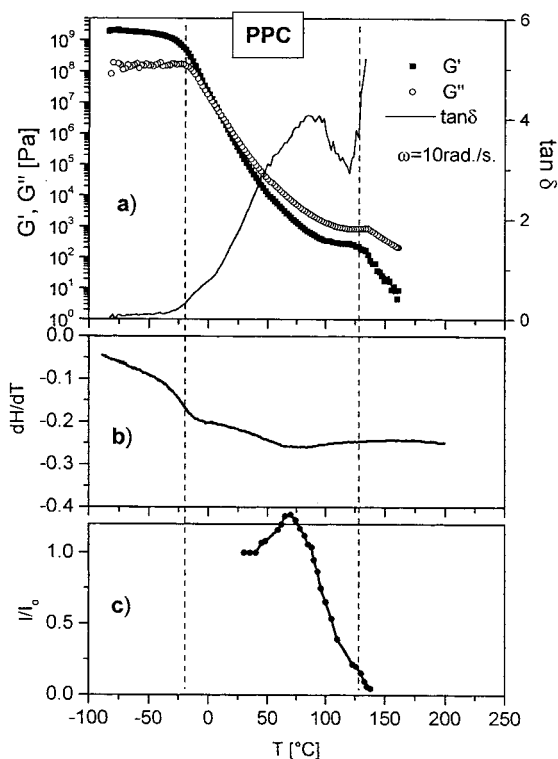
Figure 6 shows temperature dependencies of the shear storage ( $G'$ ) and loss ( $G''$ ) modulus for lyotropic HPC-AA system. The lyotropic solvent in the HPC environment results in the significant changes of thermomechanical behavior. The glassy state of HPC-AA system is shifted towards lower temperature, approximately equal to  $-100$ °C, with the  $G'$  modulus of the order of  $10^9$  Pa. The modulus of HPC-AA system above the glassy state can vary over 6 orders of magnitude

( $\alpha_m$  relaxation). At temperature above  $85$ °C, the modulus increase is related to thermal polymerization of AA in the HPC-AA mesophase. The increase of the  $d$ -spacing of HPC main chains by lyotropic solvent shifts the  $\alpha_m$  relaxation to lower temperatures.

Figures 7a, 8a, and 9a show temperature dependencies of the shear storage and the loss modulus ( $G'$  and  $G''$ ) and the loss tangent,  $G''/G'$ , for the remaining thermotropic CDs CEPC, PPC, and HxPC. The dynamic mechanical results are compared with the DSC (Figs. 7b, 8b, & 9b) and TOA characteristics (Figs. 7c, 8c, & 9c) of the samples. For all cases, two characteristic temperatures can be distinguished. The first one corresponds to the glass transition temperature and the second one is attributed to the isotropization. Between these temperatures, the systems are in LC states. The glass transition temperatures,  $T_g$ , and the isotropization temperatures,  $T_{ni}$ , are listed in Table I. Above the glass transition temperatures  $T_g$  of the investigated polymers as well as lyotropic HPC-AA system, two regimes are easily noticed on the shear storage modulus vs temperature curve. The



**Figure 7** Temperature dependencies of  $G'$ ,  $G''$ , and  $\tan \delta$  (a), DSC (b), and TOA characteristics (c) for CEPC. The vertical dashed lines indicate temperatures assigned as  $T_g$  (glass transition) and  $T_{ni}$  (isotropization temperature).



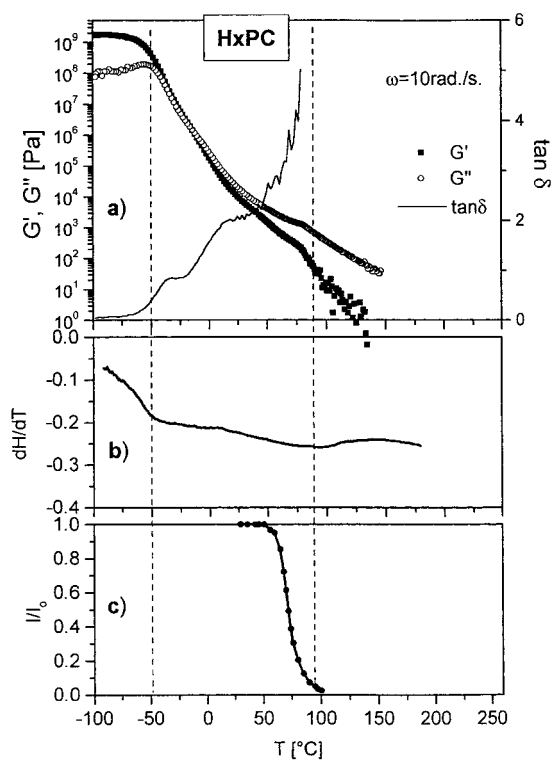
**Figure 8** Temperature dependencies of  $G'$ ,  $G''$ , and  $\tan \delta$  (a), DSC (b), and TOA characteristics (c) for PPC. Meaning of the vertical dashed lines is the same as in Figure 7.

first regime is related to the sharp drop ( $\alpha_m$ -relaxation) and the other to the gradual changes of  $G'$  with temperature. CEPC plot shows a broad "plateau" on the temperature dependence. The region with low rate of  $G'$  changes can be interpreted as a region of the mobile LC phase after termination of  $\alpha_m$ -relaxation.

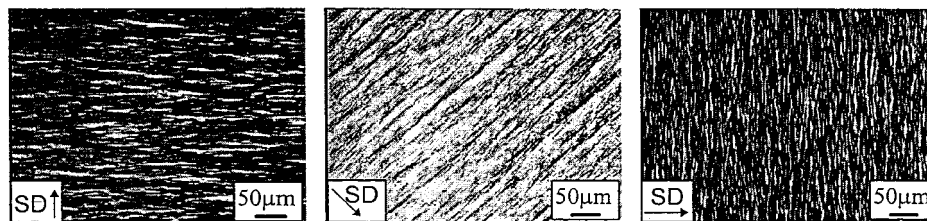
The data, which are given in Table I, indicate that the glass transition temperatures of HPC and its derivatives are determined by the length of the side chains. The increasing length of the side chains of the poly(saccharide) macromolecules shifts the glass transition temperature from 10–20°C for HPC to –50°C for HxPC.

The property/structure relationship of the investigated polymers is similar to recently published results on the homologous series of the LC-n-alkyl-substituted monosaccharides.<sup>18</sup> It was shown that transition temperature to the thermotropic state  $T_n$  of the substituted monosaccharides is determined primarily by interactions between monosaccharide cores of the molecules.  $T_n$  shows insignificant increase with increasing chain length of the n-alkyl group. The situation is

quite different for clearing temperature  $T_{ni}$ , which increases with chain length, reaching a maximum and then decreases gradually, as the chain becomes longer. For the homologous series there will be an increase of van der Waals forces of attraction leading to a higher values of  $T_{ni}$ . The temperature  $T_{ni}$  increases reaching its maximum, and then decreases due to chain-folding of long alkyl chains leading to nonlinear conformation and lower  $T_{ni}$ . The increasing length of the side chain in the polymer series HPC, PPC, and HxPC leads to a decrease in the clearing temperature from 205°C for HPC, 135°C for PPC, to 100°C for HxPC. The clearing temperature depends not only on the length of side chains but also on their polarity. Two polymers, which have the same side-chain length CEPC and PPC, exhibit different clearing temperatures. More polar CEPC has higher isotropization temperature ( $T_{ni} = 194^\circ\text{C}$ ) than less polar PPC ( $T_{ni} = 135^\circ\text{C}$ ). Finally, taking into account the  $T_{ni} = 205^\circ\text{C}$  of polar HPC, one can conclude that  $T_{ni}$  of the investigated HPC derivatives depends on the balance between length and polarity of the side



**Figure 9** Temperature dependencies of  $G'$ ,  $G''$ , and  $\tan \delta$  (a), DSC (b), and thermo-optical characteristics (c) for HxPC. Meaning of the vertical dashed lines is the same as in Figure 7.



**Figure 10** Microphotograph of banded texture for the 20  $\mu\text{m}$  film of PPC in diagonal and two orthogonal positions of shearing direction (SD) with respect to optical axis (OA) of polarizers.

chains of the poly(saccharide) main chain. The transition temperature to the thermotropic state  $T_n$  of the investigated polymers will be discussed in the next section.

### Shear-Induced Textures of Cellulose Polymers

The shear-induced textures (banded texture) observed after the cessation of shearing belong to unusual phenomena occurring in the mesogenic state of main chain of nematic or cholesteric LC polymers.<sup>19</sup> This kind of phenomenon has not been reported for isotropic polymers. The banded texture can be used for identification of the thermotropic as well as lyotropic mesophases. In contrast to the well investigated shear-induced textures observed in the lyotropic LC-phases of HPC,<sup>20–23</sup> the shear-induced texture that appears in the thermotropic LC-phases of CDs have never been investigated.

The investigated cellulose polymers were subjected to shear deformation at temperatures between  $T_g$  and  $T_{ni}$ . The banded texture in the PPC, HxPC, and lyotropic HPC-AA films appears immediately after the cessation of the shearing at room temperature. Figure 10 shows the banded texture of PPC film visible under cross polarizers. Formation of the banded texture in CEPC and HPC immediately after the cessation of the shearing requires higher temperatures during shearing: 80–100°C for CEPC and 170–180°C for HPC. The temperature of the banded texture formation corresponds to the termination of  $\alpha_m$ -relaxation of CDs and to the temperature at which the significant variations of  $G'$  with temperature are either diminished (PPC, HxPC, HPC-AA) or achieve “plateau” (HPC, CEPC). The thermomechanical characteristics of the cellulose polymers permits to estimate a temperature above which the shear-induced texture (banded texture) can be obtained immediately after the cessation of the

shearing. One can assume that the temperatures of the formation of shear-induced textures are correlated with transition temperature to thermotropic LC-phase  $T_n$  of the CDs. In the case of LC-monosaccharides<sup>18</sup> the temperature  $T_n$  decreases with a decrease of the interactions between monosaccharide cores of the molecules. Similarly to the LC-n-alkyl substituted monosaccharides,<sup>18</sup> transition temperature  $T_n$  of CDs, estimated from shear experiments, is determined primarily by interactions of the poly(saccharide) main chain and should be affected by their separation.

Taking into account the results of X-ray investigations, increasing separation ( $d$ -spacing) between the poly(saccharide) main chains of the investigated polymers, changing in order of HPC < CEPC < PPC < HxPC, leads to the lowering of transition temperatures  $T_n$  from 180°C for HPC, 80°C for CEPC, to room temperature for PPC and HxPC.

It may be assumed that the thermotropic LC states of CDs are composed of the poly(saccharide) backbones that form LC-network accomplished by their intermolecular interactions, whereas the aliphatic side chains form a complementary network held together by van der Waals forces. It is microscopic separation of the hydrophilic and lipophilic parts of the CDs that determines the absolute values of their transition temperatures.

### CONCLUSIONS

The thermotropic mesomorphism of the investigated CDs is related to its molecular structure. Two relaxation processes,  $\alpha_a$  and  $\alpha_m$ , observed in the solid state of HPC, are also found in case of other CDs, but at the lower temperatures. The  $\alpha_m$  relaxation, which is indicated by a remarkable

decrease of modulus with temperature, is associated with the transition from frozen anisotropic state to mobile thermotropic LC phase. It was found that the  $\alpha_m$  relaxation, hence, the transition to LC-phase of CEPC, PPC, and HxPC occurs at lower temperatures than that of HPC. The mobile thermotropic LC-phases of CDs are observed in the shearing experiments at the temperature correlated with  $d$ -spacing of the hydrophilic poly(saccharide) main chains. The larger the  $d$ -spacing of CDs (for the investigated range of 1.0–1.5 nm), the lower the temperature of the mobile thermotropic LC-phases formation. This transition temperature varies between the highest 180°C for HPC (smallest  $d$ -spacing) and the lowest room temperature for PPC and HxPC (largest  $d$ -spacing), assuming the intermediate value of 70–80°C for CEPC. Therefore, it is suggested that the  $\alpha_m$  relaxation processes and the temperatures of the formation of the mobile thermotropic LC-phases depend on the interactions of the hydrophilic poly(saccharide) main chains of CDs. The weaker interactions between the poly(saccharide) main chains separated by larger  $d$ -spacing shift the  $\alpha_m$  relaxation processes to the lower temperature.

The transition temperatures to the glass state  $T_g$  ( $\alpha_a$  relaxation processes) of CDs are dependent mainly on the length of side chains.

The transition temperatures of CDs to isotropic phase  $T_{ni}$  depend, on the other hand, on the length and polarity of the side chains of the poly(saccharide) main chain. Higher polarity polymers, such as HPC and CEPC, exhibit higher isotropisation temperature  $T_{ni}$  than less polar ester derivatives PPC and HxPC.

The trend of the mesomorphic behavior of CDs is consistent with the assumption that thermotropic phase of CDs is composed of two subsystems. The first one is formed by poly(saccharide) main chains with the LC-organization and the second one, complementary system of the lipophilic side chains, stabilizes the LC-organization of the poly(saccharide) main chains. The structure and molecular interactions of the lipophilic side-chains system have a significant influence on the LC-organization.

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