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# Thermotropic Mesomorphism of (2-Hydroxypropyl)cellulose Systems-the Role of Hydrophilic and Lipophilic Segments

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# Thermotropic Mesomorphism of (2-Hydroxypropyl)cellulose Systems-the Role of Hydrophilic and Lipophilic Segments

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The (2-hydroxypropyl)cellulose (HPC) derivatives can be regarded as a system which is composed of poly(saccharide) main chain (hydrophilic segment) and aliphatic side chain as a hydrophobic (lipophilic) segment of the macromolecules. The influence of the hydrophobic effect on the thermotropic mesomorphism of HPC derivatives was investigated. The correlation between *d*-spacing of HPC-derivatives estimated from X-ray measurements and hydrophobic effect of the side chain was found. The relative hydrophobicity variation of the side chains of HPC-derivatives leads to an increase in the *d*-spacing between poly(saccharide) main chains. On the other hand, the increasing *d*-spacing in the HPC-derivatives shifts their transition temperatures to isotropic state and glass transition temperatures towards lower temperature range. It was suggested that the property/structure correlation of the HPC-derivatives is affected by the balance between hydrophilic and hydrophobic parts of the HPC-derivative macromolecules.

*Keywords:* liquid crystalline polymers; (2-hydroxypropyl)cellulose; hydrophobic effect

## INTRODUCTION

The thermotropic mesomorphism in the cellulose-based polymers is attributed to the rigidity of the anhydroglucose backbone [1]. The temperature, at which thermotropic mesophase exists, depends on the nature and degree of substitution of the cellulose [2,3]. Most cellulose polymers are chemically disordered and the substituent groups of different chemical composition are not

distributed uniformly along the chain. Flexible side chains appear to facilitate the orientation of the poly(saccharide) main chains by increasing its mobility and thus restricting crystallisation. Thermotropic mesomorphism is sensitive to the thermal history of the samples [4]. This implies that flexible side chains alone do not ensure sufficient polymer mobility for adequate thermotropic properties and that - in addition - the side chains should be chosen so as to minimise intermolecular interactions. A number of ester and ether derivatives of (2-hydroxypropyl)cellulose (HPC) form thermotropic cholesteric phase.

The aim of this study was to investigate the influence of the hydrophobic effect in the HPC-derivatives on their thermotropic mesomorphism. The HPC-derivatives are composed of the hydrophilic poly(saccharide) main chains and hydrophobic segments of the side chains.

The specific interactions such as hydrophobic effect are of great importance in biological systems[5]. However, the thermodynamics of these non-polar interactions is quite complex. As it has been shown for biological organic compounds, the hydrophobicity (often called lipophilicity) can be described by means of partition coefficient $P$ [5]. The prediction of a hydrophobic character, especially log $P$ value, was pioneered by Hansch development of the hydrophobic substituent constant $\pi$ [5,6]. Although log $P$ can be used as an index of the hydrophobicity of a whole molecule, in the case of a set of derivatives of a parent compound, in which a large portion of the structure remains constant, the hydrophobicity of substituents can be sufficient for correlation analysis.

## EXPERIMENTAL PART

(2-hydroxypropyl)cellulose (HPC) and methacrylic acid (MAA) were supplied by Aldrich Chemical Co. (Hexanoyloxypropyl)cellulose (HxPC) and (propionyloxypropyl)cellulose (PPC) were prepared from HPC according to the procedure described in the literature[7]. (Cyanoethylpropyl)cellulose (CEPC)

was obtained by the reaction of HPC and acrylonitrile[8]. X-ray diffractograms were recorded at room temperature using a Θ - 2Θ diffractometer with Cu-Kα radiation. The log *P* values for the substituents of HPC were calculated using PALLAS program[9]. The glass transition temperature $T_g$ of the investigated polymers was determined by DSC measurements. A polarising optical microscope equipped with the Mettler FP-82 hot stage and photomonitor was used for measuring both the transition temperature to the isotropic state $T_{ni}$ and the isothermal relaxation of the molecular orientation. The isothermal relaxation of the molecular orientation in the mechanically oriented (shearing) PPC and in the composite PPC/pMAA was estimated by monitoring the variation of the light transmission through the sample placed between crossed polarizers. The relative transmitted light intensity $I/I_o$ (where $I_o$ is the intensity at a reference initial stage) was recorded as a function of time at the constant temperature.

## RESULTS AND DISCUSSION

The chemical structure and characteristics of the HPC derivatives used in this study are shown in Figure 1 and Table 1, respectively.

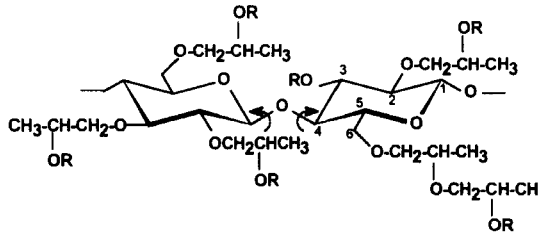


FIGURE 1 Repeating units of the investigated mesomorphic HPC-derivatives, where R = H (for HPC), $CH_2CH_2CN$ (CEPC), $COCH_2CH_3$ (PPC), $CO(CH_2)_4CH_3$ (HxPC).

These cellulose derivatives differ with respect to their polarity of the side chains (HPC, CEPC, PPC) or with respect to their side chain length (HxPC, PPC, HPC).

TABLE 1 Characteristics of cellulose derivatives ($T_g$ - glass transition temperature, $T_{ni}$ - isotropisation temperature)

| | R | $T_g$ [°C] | $T_{ni}$ [°C] | log $P$ | $d$ [nm] |
|---|---|---|---|---|---|
| **HPC** | -H | 15 | 205 | 0 | 1.04 |
| **PPC** | $-COCH_2CH_3$ | -20 | 135 | 0.77 | 1.29 |
| **HxPC** | $-CO(CH_2)_4CH_3$ | -50 | 100 | 2.3 | 1.53 |
| **CEPC** | $-CH_2CH_2CN$ | -20 | 194 | 0.54 | 1.17 |

The distributions of X-ray diffraction intensity for the investigated polymers at 25°C are shown in Figure 2. The narrow diffraction bands observed

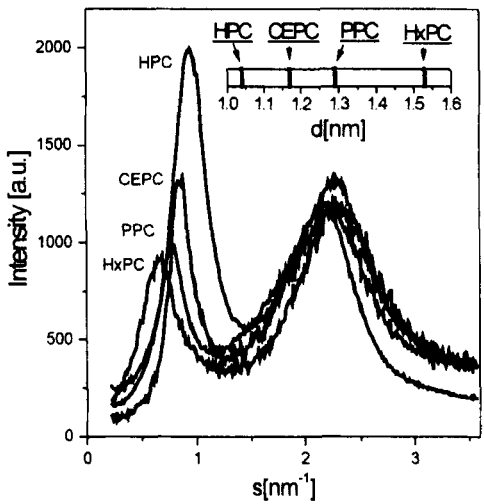


FIGURE 2 WAXS intensity distribution for HPC-derivatives measured at room temperature. The insert shows $d$-spacing calculated from the position of the first peak below s<1 nm$^{-1}$.

at s<1.0 $nm^{-1}$ are attributed to the backbone-backbone *d*-spacing of the poly(saccharide) main chains in the crystalline phase. The wide diffraction bands at s~2.3 $nm^{-1}$ are connected with slightly ordered amorphous phase. The analysis of the position and intensity of the peak below s=1$nm^{-1}$ can shed some light on physical and chemical changes of different HPC- derivatives. Considerable variation in the peak position indicates remarkable changes in the packing of the poly(saccharide) main chains (see insertion in Figure 2). On the other hand, decrease in the peak intensity suggests that the contribution of crystalline phase in the compounds under the investigation is being lowered. The *d*-spacing ranges approximately from 1.04 nm for HPC to 1.53 nm for the derivative with the longest side chains (HxPC). The values of relative hydrophobicity log*P* of propionyloxy, hexanoyloxy, and cyanoethylo substituents of HPC, estimated from Hansch coefficients, are listed in Table 1.

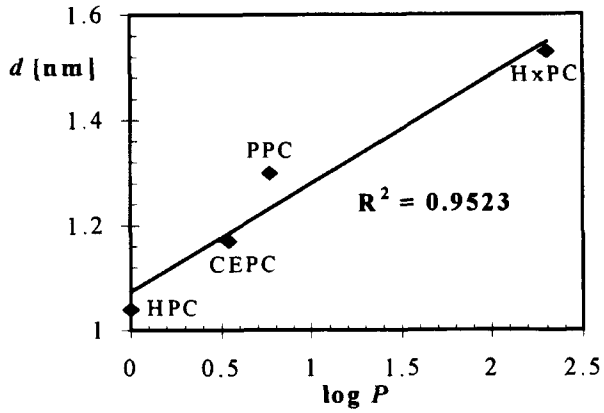


FIGURE 3 Relationship between *d*-spacing and the hydrophobicity index log *P* for HPC-derivatives.

Figure 3 illustrates an effect of hydrophobicity of substituents, expressed here as index log $P$, on the $d$-spacing for HPC and its derivatives. The linear relationship between the $d$-spacing of the poly(saccharide) main chains and the hydrophobicity of substituents indicates that property/structure correlation of HPC-derivatives is determined by the hydrophilic-hydrophobic balance between poly(saccharide) main chains and hydrophobic side chains. The chemical modification of HPC macromolecules, which is presented here, leads to the LC-polymers exhibiting the thermotropic mesomorphism even at room temperature (PPC, HxPC). At the same time, the glass transition temperature $T_g$ and isotropisation temperature $T_{ni}$ of the mesomorphic phases for HPC-derivatives are shifted to lower temperature range (Table 1). One can expect that – in the mesomorphic state of HPC-derivatives – the poly(saccharide) main chains (hydrophilic segments) tend to separate into network stabilised by hydrophobic side chain system.

The hydrophilic-hydrophobic balance in the HPC-derivatives can be changed by introducing to HPC-derivatives the macromolecules of well defined hydrophilic properties, such as poly(acrylic acid) (pAA) or poly(methacrylic acid) (pMAA). The miscibility of HPC with flexible polymers was studied by Wang *et.al.*[10]. The miscibility of HPC with its flexible counterparts such as pAA or poly(vinylpirolidon) was investigated using solvent cast bland films. Solution blending of HPC with flexible polymers resulted in the phase separation films or mutual precipitation in the case of HPC and pAA. In order to overcome phase separation *via* $\Delta\chi$ effect, the blends investigated by us (polymer composite) were prepared by *in situ* photopolymerisation of the monomer containing dissolved HPC-derivatives in the liquid crystalline phase[11].

The dielectric spectroscopy measurements showed [12] that intermolecular interactions in the composites affect the $\alpha$-relaxation of both HPC-derivatives and pAA. The $\alpha$-relaxation of the compounds can be presented in the following sequence:

HPC/pAA>CEPC/pAA>PPC/pAA>HxPC/pAA

For the HxPC/pAA and PPC/pAA composites the α-relaxation of HPC-derivatives is disturbed only slightly. In the case of HPC/pAA composites the α-relaxation of HPC is not visible at all. The influence of pAA on the α-relaxation process of HPC-derivatives in the composite is correlated with hydrophobicity of the side chain of the poly(saccharide) main chains. With increasing hydrophobicity of the side chain of HPC-derivatives, the influence of pAA on the α-relaxation process of HPC-derivatives is quenched.

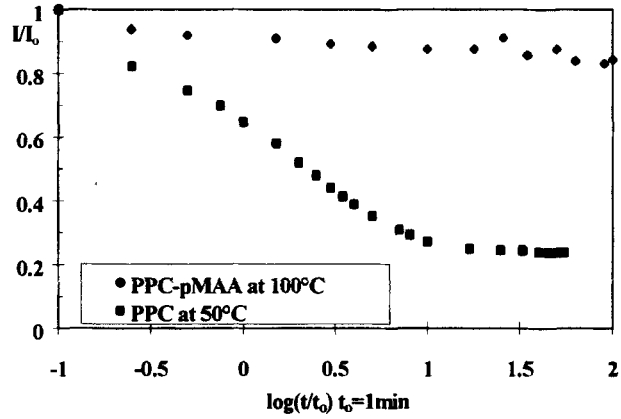


FIGURE 4 The isothermal relaxation of the molecular orientation of PPC and PPC/pMAA.

The composites of HPC-derivatives, prepared by photopolymerisation of the oriented lyotropic liquid crystalline solution of HPC-derivatives in the liquid monomers (acrylic or methacrylic acid), maintain mesomorphic organisation above isotropisation temperature of pure HPC-derivatives[11,13]. Figure 4 shows relaxation of the molecular orientation in the mechanically oriented (shearing) PPC at the temperature of 50° C and that of PPC composites PPC/pMAA at

the higher temperature (100° C). The relaxation of the molecular orientation of PPC in the composite PPC/pMAA is strongly hampered in comparison to pure PPC. The pAA and pMAA belong to the hydrophilic polymers as the indices log *P* for these polymers are equal to -4.07 and -1.3, respectively, at pH=7.0[9].

The results of this study show that hydrophilic-hydrophobic balance is an important factor which determines the mesogenic behaviour of the investigated polymers.

## CONCLUSIONS

The thermotropic mesomorphism of the HPC-derivatives is related to the hydrophobic effect of the side chains of the poly(saccharide) main chain. The hydrophobicity of the side chains ensures the sufficient packing (*d*-spacing) of the poly(saccharide) main chain. On the other hand, increasing *d*-spacing in the HPC-derivatives shifts the transition temperature to isotropic state towards the lower temperature range. This way, the property/structure correlation of the HPC-derivatives is affected by balance between hydrophilic and hydrophobic parts of the HPC-derivative macromolecules. This implies that the hydrophilic segments of the HPC-derivatives form mesomorphic organisation, which is stabilised by interactions of the hydrophobic side chain system. When hydrophilic polymers, such as poly(acrylic acid) or poly(methacrylic acid), are properly introduced into HPC-derivatives, the stabilisation effect of the mesomorphic state can be significantly improved.

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