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Analysis of the Hydrogen Bonding in (2-Hydroxypropyl)cellulose-Poly(acrylic Acid) Composites by Raman Spectroscopy

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SUMMARY: Novel anisotropic polymer composites obtained by the photopolymerisation of acrylic acid (AA) in lyotropic solutions of (2-hydroxypropyl)cellulose (HPC) were investigated. Raman spectroscopy was used in the study of hydrogen bonding formed by carboxylic groups of poly(acrylic acid) (pAA) between themselves and with the hydroxyl groups of HPC macromolecules. These investigations show that the supramolecular structure of pAA obtained by photopolymerisation contains mainly inner oligomeric forms and cyclic dimer forms, as a consequence of the "matrix polymerisation" of AA. The presence of HPC affects the process of the photopolymerisation of AA, by a redistribution of hydrogen bonding within the system, leading to a different supramolecular structure of pAA. With increasing amounts of HPC the inner oligomeric forms characteristic of bulk pAA disappear. In the composites, the pAA chains probably form the terminal oligomeric structure, with some free COOH groups, as well as hydrogen bonds with HPC.

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Introduction

(2-Hydroxypropyl)cellulose (HPC), similarly to many other cellulose derivatives, forms the cholesteric liquid crystal (LC) phase in wide a variety of solvents. The formation of the lyotropic mesophase is determined by several factors, such as the chemical structure of the cellulose derivative (flexibility of the cellulose backbone, size and polarity of the side-chains), physico-chemical properties of the solvent and the concentration of the solution and temperature1,2). Oriented LC materials are of considerable interest to many researchers because of both their interesting optical properties and potential practical application. Although the lyotropic solution can be oriented readily by shearing, the most important problem however is the poor thermal stability of the orientation of LC materials. After the cessation of the shearing, the metastable band texture is observed in a polarizing microscope, that converts back to the thermally stable polydomain chiral-nematic mesophase is seen as grain texture. The formation of such textures and the relaxation processes in lyotropic cellulose solutions are described in the literature3-6).

To obtain oriented, thermally stable material from the LC solution of cellulose derivatives, a novel method was introduced. It involves the photopolymerisation of vinyl monomers that are used as the solvent. Suitable solvents are, for example N,N-dimethylacrylamide7), 2-hydroxyethyl methacrylate8), methacrylic acid9), or acrylic acid (AA), which was used in this study9-11). For HPC/poly(acrylic acid) (pAA) composites, thermo-optical analysis has shown very high thermal stability of molecular orientation. The birefringence of this material remains practically unchanged up to 480 K, and the slight decrease at higher temperatures (even above the melting point of the HPC crystals at ca. 495 K) is fully reversible. The decline of the reversibility of the birefringence starts above 520 K, it is probably due to thermal degradation10). This means that the photopolymerised solvent (pAA) establishes the anisotropic matrix, imposing the orientation of the HPC molecules upon cooling. It also implies some orientation of the pAA macromolecules formed in the composite during the photopolymerisation4). Dielectric spectroscopy12) and dynamic mechanical investigations13) have confirmed this hypothesis. Most of the papers11,14-16) concerning LC anisotropic composites focus on the properties of cellulose derivatives. In view of the discussion above, it seems important to study additionally the structure and properties of non-mesogenic constituents in these composites, e.g. the polymerised solvent. Characterising the interactions between HPC and pAA macromolecules is especially interesting. We have postulated earlier that the hydrogen bonds between HPC and photopolymerised pAA macromolecules may play a crucial role in the formation and properties of the HPC - pAA composites10).

Many authors have presented analysis of hydrogen bonding in monocarboxylic acids and their solutions using Raman spectroscopy (see e.g. Refs.17-19)). The role of hydrogen bonding in the formation of AA aggregates in various solvents has been analysed in detail using Raman and IR spectra by Ansarian et al.19). In the case of pAA the situation is more complicated. Mobility is limited by the chemical structure of the macromolecules because of the large number of carboxylic groups situated along polymer chains. Theoretically three different connections by hydrogen bonding are possible in pAA. These lead to the supramolecular structures called by Dong et al.20) as: cyclic dimer, terminal oligomeric forms, and inner oligomeric forms (see Fig. 1). In this work we discuss the influence of HPC on the supramolecular structures of the pAA formed in the composites as seen by Raman spectroscopy.

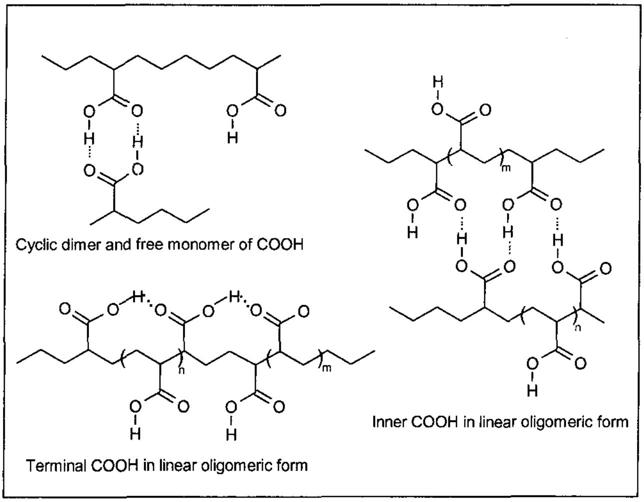

Fig. 1: Supramolecular structures of pAA formed by hydrogen bonding (redrawn after Ref.[20])

Experimental

The HPC (M.W.=100000) was obtained from Aldrich Chemical Co. The pAA was synthesised by radical photopolymerisation of pure AA using Erasure 651 (Ciba-Geigy) as a photoinitiator, and a UV-lamp (365 nm) as a light source. The composites were obtained by the photopolymerisation of mechanically oriented thin films (c.a. 180 μm) of the suitable liquid crystalline solutions of HPC in acrylic acid under the same conditions as for pAA. Composite materials with different molecular ratios of HPC to pAA were investigated. It should be emphasised that pAA and HPC are not miscible. However, by the method used here one can obtain material with components dispersed on a molecular level[7]. A detailed description of the preparation of the composites is presented elsewhere[4,10-12].

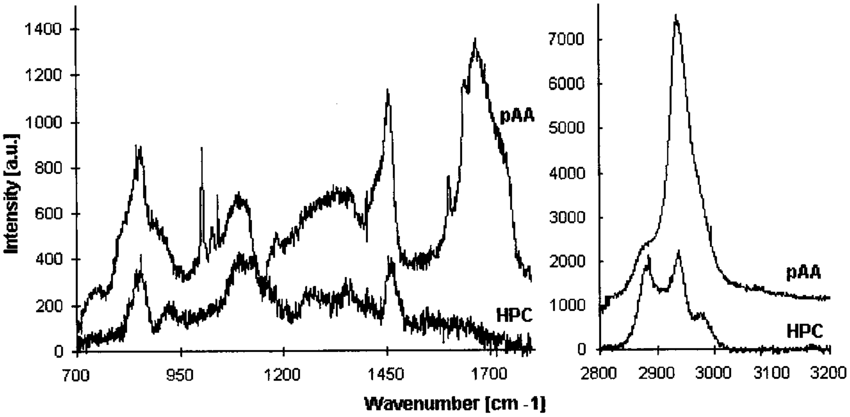

Fig. 2: Raman spectra of pAA and HPC.

Table 1. Observed frequency and assignments of Raman bands of pAA (Refs.[20,21]).

Frequency [cm^{-1}]		Assignments
Our investigations	Refs. [20,21]	
2943 s, 2880	2927 s, 2877	CH_2 or CH stretching
1660	1698	C=O stretching
1456	1457	CH_2 deformation
1330	1333	CH_2 twisting
1187	1191	C-O stretching coupled with O-H in-plane bending
1100	1105	C-CH_2 stretching or CH_2 rocking
866	846	C-COOH stretching

s = streng

Table 2. Observed frequency and assignments of Raman bands of HPC (data from Refs.[22-24]).

Frequency [cm^{-1}]	Assignments
3020-2850	symetric and asymmetric stretching of CH_2 andCH_3
1460	deformation of COH group
1410	CH_2 deformation
1340	wagging CH_2; deformation OH
1235	deformation OH
1150-1000	C-O stretching, rings modes
750-950	CH_2 group-skeletal modes

The Raman spectra were obtained using the Jobin Yvon Raman microscope T64000 with a He-Ne laser (λ=632.8 nm; power = 35 mW), and also the DILOR Ramis Raman microscope with an Ar laser (λ=514.5 nm; power = 150 mW). In both cases the essentially similar spectra were obtained. During the curve fitting, a multi-Lorentzian function was found to be adequate to resolve the bands.

Results

Raman spectra of pure pAA and HPC in two regions of the spectrum 700-1800 cm^{-1} and 2800-3200 cm^{-1} are shown in Fig. 2. The major vibration modes are listed in Table 1 for pAA, and in Table 2 for HPC. These spectra are very complex in the 700-1500 cm^{-1} and 2800-3200 cm^{-1} regions, because many bands are related to different vibration modes in HPC as well as in pAA macromolecules. In the 1600-1800 cm^{-1} region, one can observe modes due to the stretching of the C=O groups of pAA: the 1660 cm^{-1} band with a shoulder at a higher frequency, and the 1730 cm^{-1} band. The Raman line with a maximum at 1640 cm^{-1} corresponds to the vibration of the C=C group, due to residual monomer, and the 1600 cm^{-1} band is probably due to a small amount of water absorbed by pAA.

Fig. 3 presents the Raman spectra in the 1600-1800 cm^{-1} range for the composites with different concentrations of HPC: 20, 40 and 60 %. The Raman bands at 1600 and 1640 cm^{-1}, attributed to impurities as described above, were removed mathematically. Using a multi-Lorentzian function, it was possible to resolve the spectrum of pAA (Fig. 3a) into several bands with maxima at 1640, 1660, 1715 and 1740 cm^{-1}, which correspond to the bands identified by Dong et al.[20)] (see Table 3). An additional band at 1730 cm^{-1} was observed in the spectra of the composites. With increasing concentration of HPC, one can observe a pronounced change in the ratio of the intensity of the 1680 cm^{-1} Raman line to the intensity of the 1660 cm^{-1} band, compared with that for the spectrum of pure pAA. Also, the new band at 1730 cm^{-1} appears. In the spectrum of the composite with 60 % of HPC, the 1730 cm^{-1} band is the most intense, while the 1660 cm^{-1} band is very weak.

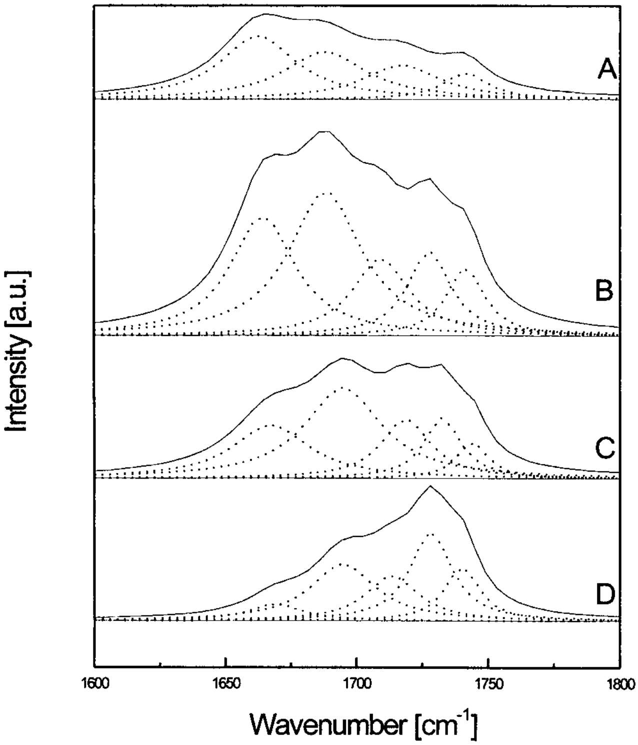

Fig.3: Computer-resolved Raman spectra of the carbonyl stretching modes of pure pAA (a) and HPC/pAA composites:20/80 (b), 40/60 (c), 60/40 (d).

Table 3. The position of the maxima of the Raman bands due to the vibration of C=O groups for different supramolecular structures of pAA[20].

Band position [cm^{-1}]	Assignment
1742	free COOH groups
1715	terminal COOH groups in oligomeric forms
1680	cyclic dimers
1660	inner COOH groups in oligomeric forms

Discussion

In this study we have focused our interest on the 1600-1800 cm^{-1} range of the Raman spectrum. because it is a suitable region for investigating the influence on the vibration modes of the C=O group of possible hydrogen bonding interactions between carboxylic and hydroxyl groups in the composites. Additionally, the absence of any bands in the HPC spectrum in this range facilitates the analysis of the modification of the C=O vibration modes in the composites.

As seen for pure pAA in Fig. 3a the broad feature centered at about 1660 cm^{-1} is composed of several bands, indicating the existence of several complex supramolecular structures of pAA, as suggested by Dong et al.[20] (see Fig. 1, and Tab. 3). By analysing the spectrum, one can conclude that in pure pAA obtained by photopolymerisation, the inner oligomeric forms and cyclic dimers dominate. The formation of such structures requires that some segments of the two polymer chains be parallel. The probability of such a configuration is relatively high in the case of pure photopolymerised pAA, especially if one assumes a model of "matrix polymerisation" of AA in bulk[19,25,26]. In this model, the molecules of AA are bound via hydrogen bonds along the already grown chain of pAA, which plays a role similar to that of the matrix in classical matrix polymerisation.

In the HPC/pAA composites, the presence of the HPC induces a dilution effect on the pAA. In addition to the different supramolecular structures of pAA,one can expect the formation of hydrogen bonds between the carbonyl groups of pAA, and the hydroxyl groups of HPC. The HPC macromolecules bind both the AA molecules and the growing pAA chains by hydrogen bonds. Therefore one can also expect some kind of "matrix polymerisation". With increasing concentration of HPC the effect of HPC-AA interactions on the formed pAA chains becomes stronger. The supramolecular structures formed by the interaction between the segments of different pAA chains, which exist in pure pAA (inner oligomeric forms, see Fig. 1), disappear at high concentration of HPC. This results in the diminishing of intensity of the 1660 cm^{-1} line. Simultaneously, the intensity of the 1730 cm^{-1} band increases, suggesting that the terminal oligomeric forms of the supramolecular structures of pAA (which are formed by intramolecular hydrogen bonding, see Fig. 1) coexist with free COOH groups. Another possible reason for the increasing intensity of the 1730 cm^{-1} band is the formation of hydrogen bonds between pAA and HPC molecules27).

The presence of the relatively strong intermolecular interactions in the HPC/pAA composites was postulated previously by us, on the basis of thermooptical investigations and dielectric spectroscopy, to explain the high thermal stability and reversibility of optical anisotropy10), as well as the observed modification of molecular relaxations in the composites12). Recently it was also found that the anisotropy of the mechanical storage modulus in these composites increases with increasing temperature in the range of the β-molecular relaxation of pAA13). This effect can be explained only if one assumes that in these oriented systems, the transverse strength is partially determined by intermolecular interactions.

Conclusions

Raman spectroscopy investigations show that the supramolecular structure of pAA obtained by photopolymerisation contains mainly inner oligomeric forms and cyclic dimer forms, as an effect of the “matrix polymerisation” of AA. The presence of HPC affects the process of the photopolymerisation of AA, due to the redistribution of hydrogen bonding in the system, and leads to a different supramolecular structure of pAA. With an increasing amount of HPC, the inner oligomeric forms characteristic of bulk pAA disappear. In the composites, the pAA chains probably form the terminal oligomeric structure with some free COOH groups, as well as hydrogen bonds with HPC.

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