

Cellulose Derivatives – Organic Crystals and Liquid Crystals – Used the Longest, Known the Least*

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The basic characteristic of cellulose chemical constitution and its crystalline structure are presented. The LC-phases of cellulose derivatives were investigated by a series of techniques, which made possible to establish the specificity of chiral nematic mesomorphic structure and its transitions in correlation with intermolecular interactions of the side chains. The anisotropic composites, formed by stabilization of mesomorphic phase of LC-cellulose derivatives by photopolymerization of lyotropic solvent (acrylic acid), are characterized by thermo-optical analysis, dielectric spectroscopy, dynamic mechanical measurements, WAXS and Raman spectroscopy. These techniques show that the structure of the vinyl polymer within the composite is dependent on the oriented mesophase. The vinyl polymer phase in the glassy state counteracts the relaxation of LC-cellulose derivatives leading to its stabilization and reorientation in the heating and cooling cycles. These properties suggest such composites as materials of interesting from both fundamental and practical points of view.

Key words: cellulose, LC-cellulose derivatives, (hydroxypropyl)cellulose, composites, polymer networks

1. Introduction

In this review we wish to discuss some basic properties of cellulose in its crystalline and liquid crystalline (LC) state and the composites based on LC-cellulose derivatives. We are describing briefly the main lines of knowledge in that field, considering the work carried out in various laboratories and our results obtained during recent years.

It is commonly known that cellulose is the most abundant organic material on the earth, being the principal component of plants. The study and characterization of cellulose started in the 1830's. Cellulose was recognized as being composed of glucose units and isomeric with starch. However, even though cellulose technology developed rapidly during the XIX and early XX century, it was not until the basic development of principles of polymer structure that the true chemical structure of cellulose could be understood. It was shown that cellulose was a linear polymer consisting of glucose moieties joined by β -glucosidic bonds. Most of the finer details of cellulose

*Dedicated to the memory of Professor Krzysztof Pigoń.

chemical structure and properties were added mostly between the period 1930–1960 [1,2]. The concept that was finally emerged was that cellulose exists in an extended semirigid chain form with glucopyranose rings joined by β links. The anhydro-glucose units are almost in their lowest – energy chain form with all pendent groups equatorially disposed. The neighboring units are rotated through almost 180° relative to each other to achieve chain extension. This structure strongly favors the organization of individual cellulose chains in bundles with crystalline order held together by hydrogen bonds.

The chain length of cellulose in solution can be determined by various techniques, such as osmotic pressure, light scattering, viscosity measurements *etc.* It was shown that the degree of polymerization (DP) could range from less than 1000 for regenerated cellulose to 7000–10000 for wood pulp and as high as 15000 for the cotton long-chain cellulose molecules. They are frequently associated with smaller hydrocarbons. Its structure and functional groups influence chemical properties of cellulose. Reagents, which interact with hydroxyl groups, must first penetrate the fibrils (this type of morphology will be described later on) so accessibility or availability of the hydroxyl groups is an important factor of all cellulose reactions.

Derivatives of cellulose can be prepared by esterification, etherification, and xanthogenation and grafting. Cellulose esters of strong acids such as nitric, sulphuric and phosphoric acid may be prepared by a direct reaction with cellulose. Ethers of cellulose are formed in the presence of alkali, *e.g.* KOH with organic halides, sulphates *etc.* Some important ethers are methylcellulose, (carboxymethyl)cellulose, (hydroxyethyl)cellulose and (cyanoethyl)cellulose. Cellulose xanthate is the ester of dithiocarbonic acid. It is prepared as in the etherification by reaction of alkali cellulose with carbon disulphide. The resultant derivative is water-soluble and can be regenerated by coagulation in an acid medium. Graft copolymers, in which chains of monomer units of a different kind are attached to a backbone of cellulose, can be prepared by allowing vinyl monomers to polymerize on active free radicals or ionic sites on the cellulose. The initiating sites may be formed by *e.g.* peroxides or irradiation.

In this very short characteristics of chemical nature and reaction of cellulose we have left out many aspects of reactivity, solubility in new type of solvents, degradation *etc.* But we hope that it is sufficient to follow the next parts of this review devoted to crystalline structure and liquid crystalline properties.

2. The crystalline structure of cellulose

The structural features of cellulose materials such as crystallinity, crystallite size, the accessibility of the non-crystalline fraction have been studied over past 70 years [3]. Many different techniques to measure the crystallinity or accessibility have been employed, including physical and chemical sorption methods. The X-ray diffraction is still the principal reference method. Of the other techniques for cellulose crystallinity studies solid state ^{13}C nuclear magnetic resonance (NMR) has been shown very promising [4]. The ^{13}C NMR spectra acquired with cross – polarization, high

power proton decoupling and magic – angle spinning contain unique signatures corresponding to various recognized crystal forms. FTIR spectroscopy is relatively simple and fast method of determining cellulose crystallinity. The intensity of certain bands have been found to be sensitive to variation in crystallinity. We will focus our attention to X-ray diffraction because with modern equipment it is the most direct method of crystallinity measurement as well as of crystal structure determination [5]. It has been established that small crystallites are oriented parallel to the fibre axis of cellulose. The crystallites have a monoclinic unit cell with dimensions of about 10.3 Å (along the fibre axis), 8.2 Å and 7.9 Å with an angle of about 96°. These cells containing cellulose residues of two chains are considered as a good approximation of the structure of native cellulose although some uncertainty still exists about fine structure details.

Cellulose is polymorphic. The structure of native cellulose (cellulose I) is changed by strong alkali, as in mercerization or regeneration, to cellulose II, which is monoclinic with the same fibre axis repeating unit of 10.3 Å, but with other dimensions of 8.0 Å and 9.1 Å and an angle of 117°. Some other polymorphic forms have been suggested as cellulose III and cellulose IV, but now there exists the opinion that these are not the true polymorphic forms but rather disordered regions.

Cellulose contains not only higher ordered crystalline regions, but also amorphous regions. These different regions have not clearly defined boundaries. A two-phase fringe fibrillar model with ordered and disordered structural regions can describe the structure of cellulose. This can be quantitatively described by the degree of crystallinity from X-ray measurements and by data on dimensions and perfection of the ordered regions. The various crystallographic modifications differ in hydrogen bond structure. Superimposed on molecular ordering of macromolecules in crystallites there exists the hierarchically structured fibrillar morphology, covering a wide spectrum from elementary microfibrils in the nanometer range to the macrofibrils in the micrometer range in the case of native cellulose samples. The border line areas between these levels are still open questions, *e.g.* chain direction and chain conformation as well as the elementary fibrils of uniform dimensions.

The content of the non-crystalline fraction of cellulose can be in many cases more important than the crystallinity, due to accessibility for chemical reactivity. The “voids” in a disordered region are deduced from many measurements, but the direct method is positron (o-Ps) life time annihilation (PAL) spectroscopy. It has been used to determine the concentration and dimensions of free volume “holes” or pores in semicrystalline and amorphous materials [6]. From the PAL results using the parameter τ_3 (the o-Ps annihilation life time) it was found that the average radius of free volume decreases with increased degradation time (*e.g.* milling time). It may be due to generation of new “holes” and modification of the initial free volume. It seems interesting to note that the parameter I_3 (the intensity of the o-Ps annihilation) is also very useful in determination of fractional crystallinity in good correlation with deuteration and FTIR spectroscopy, particularly for cellulose samples with higher crystallinity [7]. These findings indicate that PAL is a useful probe for investigation the micro-

structure of cellulose in analogy to other semicrystalline polymers [8]. On the other hand, one has to remember that interpretation of the PAL results for oriented systems (like the cellulose fibrils) is difficult, because the “voids” can be also anisotropic.

3. Cellulose liquid crystals

Flory was the first to suggest that rigid polymers like cellulose could form a liquid crystalline solution [9]. Werbowyj and Gray [10] reported that cellulose derivatives form a highly iridescent and birefringent solution in many solvents at concentration 25–50 wt. % indicating the presence of lyotropic mesophase of chiral nematic nature. Presently, there is a large number of reports describing the cellulose derivatives that form lyotropic mesophases. It is not possible to enumerate all of them. Probably the most widely studied cellulose derivatives are (2-hydroxypropyl)cellulose (HPC) as the system HPC–H₂O is very tractable. The studies on this system stimulated numerous fundamental investigations in that field. Gray showed [11] that HPC forms ordered solutions in polar organic solvents like CH₃OH and C₂H₅OH too. It was found that the critical concentration is relatively independent of the molar mass.

Cellulose like other natural polymers is chiral. The above mentioned characteristic iridescent colors and circular polarization of the reflected light were at first observed for concentrated solution of HPC in water indicating that the concentration dependent chiral nematic pitch correlates with the wavelength of the reflected visible light.

The handedness of the helical structure can be determined by several optical and electron microscopic techniques. Since in general only the cellulosic backbone contributes to the molecular chirality of these phases, it might be expected that the same handedness would be observed for all cellulose derivatives. Based on optical studies of lyotropic mesophases of HPC in water and other solvents, it was generally found that HPC and its esters and ether derivatives have a right handed chiral nematic sense, with a pitch increasing with the increase of temperature and decreasing with polymer concentration. However, it was observed that a lefthanded chiral nematic mesophase exists in ethylcellulose dissolved in glacial acetic acid. There are a number of known examples, which show that chemical modification of side chain substituents may change the twist. Chiral nematic twist is also solvent dependent.

Chiral nematic liquid crystalline phases are fluids, in which chiral nematic order is readily destroyed by shear and reforming in some situations. The chiral structure is of course destroyed by dilution below the critical concentration or by heating above the critical temperature of mesophase formation. The chiral nematic order of liquid crystalline phases can be trapped by different techniques, the simplest being the casting films from mesophase solution. The nematic order can be inferred from transmission electron micrographs (TEM) images of thin cross-sections of solvent cast films, which show periodicity, corresponding to half of the nematic pitch along with some disclinations associated with discontinuities of the chiral nematic structure. The chiral nematic order of a thermotropic cellulose derivatives with unsaturated side-

chain may be also trapped by photocross-linking. Anisotropic gels have also been prepared by cross-linking of lyotropic (hydroxypropyl)cellulose and its derivatives solutions. These films can swell but do not dissolve in water. Concluding these remarks on chirality of cellulose derivatives one should say that the origin of chiro-optical properties observed for liquid crystalline derivatives with a common chiral chains and different but achiral substituents or solvents is not at all understood. The links between molecular structure and chiral nematic handedness and pitch remain a challenge.

The studies of optical anisotropy, thermal properties as well as relaxation phenomena of the series of substituted HPC allow for systematic conclusions on formation and properties of lyotropic and thermotropic mesophases. The objects of our intensive complex studies were (propionyloxypropyl)cellulose (PPC), (hexanoyloxypropyl)cellulose (HxPC) and (cyanoethylpropyl)cellulose (CEPC) – see Fig. 1 [12]. The increase of the size of substituents or their polarity, *e.g.* cyanoethyl group, results in a decrease of glass transition temperature T_g (Table 1). The size of substituents can also be correlated with *d* spacing (packing density), which can be derived from X-ray diffraction maximum of crystalline phase (Fig. 2). The decrease of temperature at which isotropic phase appears (T_{ni}) is also dependent on substituents (Table 1) [12,13]. The correlation of these properties is not fully clear without taking into consideration the hydrophobicity index ($\log P$) of side chain substituents (Fig. 3). The hydrophilic polysaccharide main chains are in equilibrium with lipophilic side groups, which determine the stability of mesophase and the transition to isotropic phase [14].

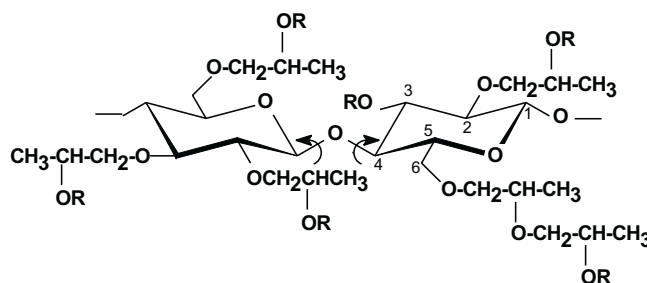


Figure 1. Repeating units of the investigated mesomorphic HPC-derivatives, where R = H (for HPC), $\text{CH}_2\text{CH}_2\text{CN}$ (CEPC), COCH_2CH_3 (PPC), $\text{CO}(\text{CH}_2)_4\text{CH}_3$ (HxPC).

Table 1. Characteristics of cellulose derivatives (T_g – glass transition temperature, T_{ni} – isotropization temperature, $\log P$ – hydrophobicity, index (*d*) – *d*-spacing [12]).

	R	T_g [°C]	T_{ni} [°C]	$\log P$	<i>d</i> [nm]
HPC	-H	15	205	0	1.04
PPC	- COCH_2CH_3	-20	135	0.77	1.29
HxPC	- $\text{CO}(\text{CH}_2)_4\text{CH}_3$	-50	100	2.3	1.53
CEPC	- $\text{CH}_2\text{CH}_2\text{CN}$	-20	194	0.54	1.17

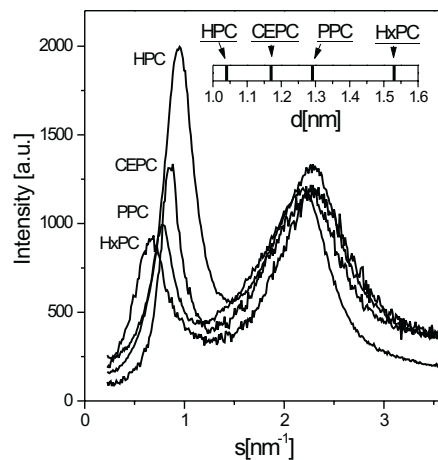


Figure 2. WAXS intensity distribution for HPC-derivatives measured at room temperature. The insert shows d-spacing calculated from the position of the first peak below $s < 1 \text{ nm}^{-1}$ [12].

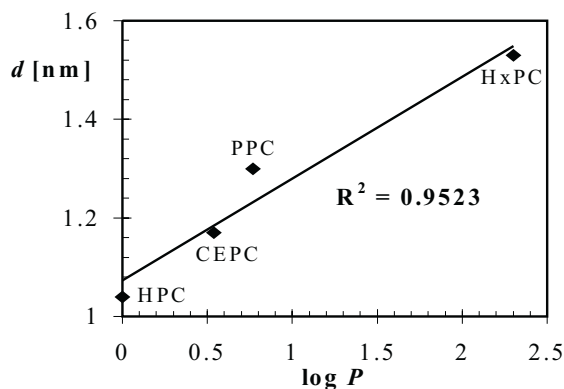


Figure 3. Relationship between d-spacing and the hydrophobicity index ($\log P$) for HPC-derivatives [14].

The studies of thermo-optical properties (TOA) of oriented thin films of LC cellulose derivatives furnish also important information on the stability of “band” structure. Such fine equidistant lines seen under crossed polarizers develop in polymer LC layers upon shearing. The decrease of the normalized intensity of transmitted polarized light as function of time (at constant temperature) well reflects the interactions of side groups in competition with hydrogen bonding, see *e.g.* [15].

The determination of phase transitions to liquid crystalline state of mesomorphic cellulose derivatives is not as simple as in the case of low molecular weight LC. Analyzing the DSC thermograms, one can detect the glass transition temperature T_g and the isotropization temperature, but the transition to the liquid crystalline state is not observed. It is not a singularity of these LC cellulose derivatives. This is the reason why dielectric spectroscopy and dynamic mechanical analysis (DMA) were used to elucidate this phenomenon. The results will be discussed in the next part devoted to composites of LC cellulose derivatives.

The investigation of cellulose LC of both lyotropic and thermotropic mesophases has evidently also several purposes from the technological viewpoint in preparing high strength/high modulus fibres of regenerated cellulose using less energy consuming and friendlier environmentally processes. Until now such use of liquid crystalline cellulose has not been particularly developed. Another potential uses of lyotropic cellulosic liquid crystals are chiroptical fibres and various composites prepared mainly by photopolymerization of the oriented cellulose derivatives in polymerizable solvents – monomers, *e.g.* acrylic acid (AA). Also thermotropic cellulose derivatives were considered for preparation of chiroptical fibres. However, they are unlikely to find such application, as essentially they are ethers of cellulose and the desubstitution would be difficult. It is possible for some derivatives for which substituents can be removed under rather middle condition, but it is really far from practical use.

4. Composites of liquid crystalline cellulose

Recent trends in studies of lyotropic and thermotropic liquid crystalline cellulose derivatives are concentrated on: (i) characterization of particular properties of such systems and (ii) on composites consisting of oriented LC-phase of cellulosic component and a polymer, which stabilizes this orientation.

The progress in preparation of composites containing liquid crystalline polymers and in determination their various properties would be not possible without the intensive investigation of some low molecular weight LC systems. Twenty years ago the main objects of basic and applied studies were the dispersions of low molecular weight liquid crystalline substances in polymeric matrices – Polymer Dispersed Liquid Crystal (PDLC). In this case polymer is a continuous phase for LC inclusions of spherical symmetry and diameter of several microns (for review see *e.g.* [16,17]). A number of advantages and deficiencies have been found for these systems. The most important deficiency is the nonideal spherical shape of the inclusions, which results in non-homogeneous light scattering under various angles. The interactions of LC inclusions with polymers matrix (surface effects) and slow response time to electric field limit now such displays from wide use.

More recently Polymer Stabilized Liquid Crystals (PSLC) have created a specific interest [17]. The main components in these systems are LC of various molecular weights. The PSLC systems are prepared mainly by the photopolymerization. When the polymerization occurs in oriented LC phase, polymer exists as a complementary solid network, which stabilizes the system. The morphology of PSLC systems may be generally described as two-phases systems, in which isotropic phase consists mainly of polymer and anisotropic phase is rich in LC.

The interest in anisotropic network with liquid crystalline organization increases dynamically in the recent years. It is primarily concerned with production of oriented thin solid films based on self-assembling properties of low molecular weight liquid crystals for various applications. Photoinitiated transformations of oriented LC monomers with multifunctional groups to the solid state are particularly interesting

owing to the fact that low temperature of photopolymerization does not change LC organization.

Very versatile method of preparation of highly anisotropic networks containing LC cellulose derivatives is the use of solvents which can be photopolymerized, *e.g.* vinyl monomers. Preparation and properties of reversible anisotropic polymer networks based on lyotropic LC solutions of cellulose derivatives in polymerizable solvents such as acrylic or methacrylic acids were the object of several our studies [15,18–20]. Usually, shearing induced orientation of the system before polymerization. The mechanically oriented lyotropic solutions after cessation of shearing form a “band” texture visible under crossed polarizers. This “band” structure shows relaxation phenomena and the grain texture observed before shearing recovers with time [15,18].

The relaxation time of band structure is much longer than that of texture formation because of reorientation of greater molecular systems. The photopolymerization of vinyl monomers in oriented lyotropic liquid crystalline solution leads to birefringent polymer composite. These systems show reversible anisotropic optical properties as examined by thermo-optical analysis (TOA) thus they can be classified as reversible anisotropic networks. Such type of networks has thermal stability of birefringence at the room temperature mainly determined by the molecular mobility of the polyacid directly connected with its glass transition [15,20].

Molecular relaxation of these anisotropic composites was investigated by dielectric and mechanical spectroscopies [21–23]. The molecular relaxation process characteristic of pure cellulosic component are modified in the composites due to strong intermolecular interactions between the macromolecules. These interactions are also responsible for stabilization of the structure and the optical properties of the composites. The TOA, dielectric relaxation and DMA techniques reveal the differences between HPC in poly(acrylic acid) – poly(AA) – and HPC in poly(methacrylic acid) – poly(MAA) [22]. The temperature dependences of electric modulus M'' for HPC–poly(AA) and HPC–poly(MAA) systems are presented in Fig. 4 and Fig. 5. The

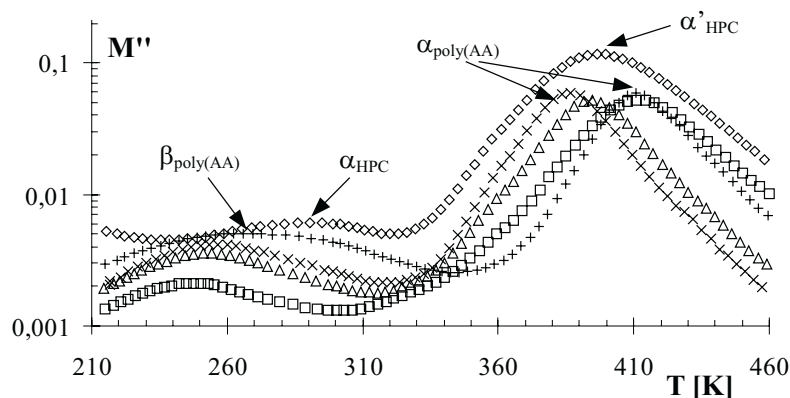


Figure 4. Temperature dependences of electric modulus (M'') at 1 kHz for HPC–poly(AA) systems with different composition: (\diamond) pure HPC, (\square) 60:40, (Δ) 40:60, (\times) 20:80 and ($+$) pure poly(AA) [22].

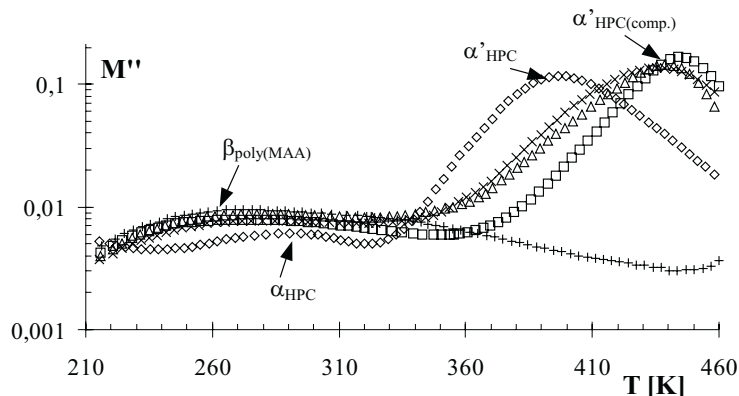


Figure 5. Temperature dependences of electric modulus (M'') at 1 kHz for HPC–poly(MAA) systems with different composition: (\diamond) pure HPC, (\square) 60:40, (Δ) 40:60, (\times) 20:80 and (+) pure poly(MAA) [22].

complex electric modulus is defined by $M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2)$, where ε' and ε'' are real and imaginary part of complex dielectric permittivity ε^* . The differences in the position of the maxima related to various relaxation processes of the composite components are clearly seen and can be explained by different properties of poly(AA) and poly(MAA) [22]. It is interesting to note, that in HPC–poly(AA) composites, where strong hydrogen bonds are present, the anisotropy is stable and the isotropization cannot be observed in the temperature range up to 500 K. In HPC–poly(MAA) composites, the decrease of birefringence is observed at lower temperatures because of thermal degradation of poly(MAA). Anisotropic composites based on PPC and HxPC, which are characteristic on various side chain length, exhibit also differences in molecular relaxation process [23].

All the characteristic phenomena occurring in LC cellulose derivatives when the temperature increases: glass transition of amorphous phase, transition from rigid anisotropic phase to mobile LC mesophase and the transition from mesophase to isotropic liquid, are also seen in the composites with poly(AA), although they are more or less modified by the presence of the second more rigid component depending on the concentration of the cellulosic component. Generally in the composites with higher contents of cellulosic component the α relaxation of this component dominates, while for the lowest concentration of cellulose derivatives the relaxations descended from poly(AA) (β and α relaxations) are mostly visible [23].

The effect of reversibility of optical anisotropy in these composites is demonstrated for the PPC–poly(AA) composite in Fig. 6. The anisotropic banded structure reappear during cooling after isotropization in the same form as before. This is most probably caused by the fact that orientation of cellulose derivatives in the lyotropic solution induces the orientation of polyacid network grown during photopolymerization. After isotropization such oriented polyacid network can induce the reorientation of LC component.

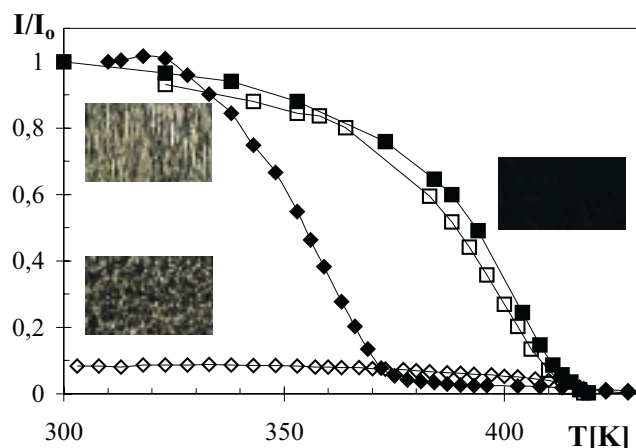


Figure 6. TOA characteristics of pure PPC (diamonds) and composite PPC–poly(AA) in the heating (full symbols) and cooling (open symbols) cycles; where I/I_0 express transmission of the polarized light normalized to the room temperature. The photomicrographs show textures of the samples at the room temperature and after isotropization.

In these composite systems hydrogen bonding is very important. The role of hydrogen bonding in the formation and stabilization of LC phases has been extensively discussed considering several classes of compounds including amphiphilic molecules and their mixtures [24]. Structural aspects of some mesomorphic cellulose derivatives in the crystalline and liquid crystalline state have been studied by Zugenmaier, explaining correlation between pitch of the cholesteric mesophase and crystalline structure [25]. This is the reason why analysis of hydrogen bonding in HPC–poly(MAA) systems was performed by Raman spectroscopy. Raman spectra (Fig. 7) show that carboxylic groups of poly(MAA) form hydrogen bonds between themselves and also with the hydroxyl groups of HPC macromolecules. It was concluded that supramolecular structure of poly(MAA) after photopolymerization contains mainly cyclic dimer forms (band 1660 cm^{-1}) as a consequence of the matrix polymerization of MAA. The presence of HPC affects the process of photopolymerization by the redistribution of hydrogen bonding system in the lyotropic solution (Fig. 8) and leads to a different supramolecular structure of poly(MAA). When the amount of HPC increases the inner oligomeric forms characteristic of bulk poly(MAA) disappear [26].

The low-frequency Raman scattering (LFRS) was used in order to determine the orientation of poly(AA) in anisotropic composite with liquid crystalline PPC. The comparison of the LFRS of the pure poly(AA) and PPC–poly(AA) composites, obtained for different relative configurations of the polarizers and the oriented sample at various temperatures, shows clearly that the anisotropy of this network is stable even at temperatures higher than the temperature of isotropization (Fig. 9) [27]. The comparison of the LFRS and thermo-optical analysis data proves that the reversibility of optical birefringence can be explained by the model of anisotropic poly(AA) network

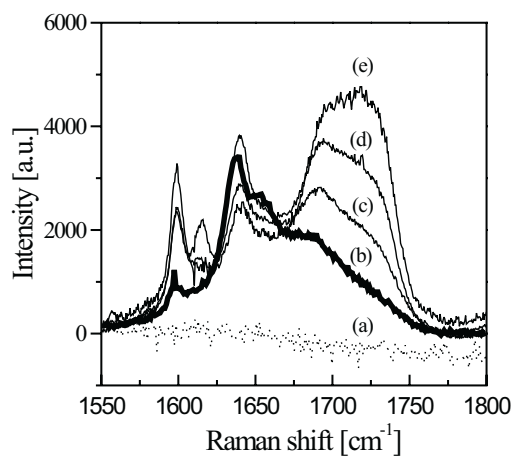


Figure 7. Raman spectra of poly(MAA) in the composite with HPC, with different ratio poly(MAA)/HPC: (a) 100:0, (b) 80:20, (c) 60:40, (d) 40:60, (e) 0:100.

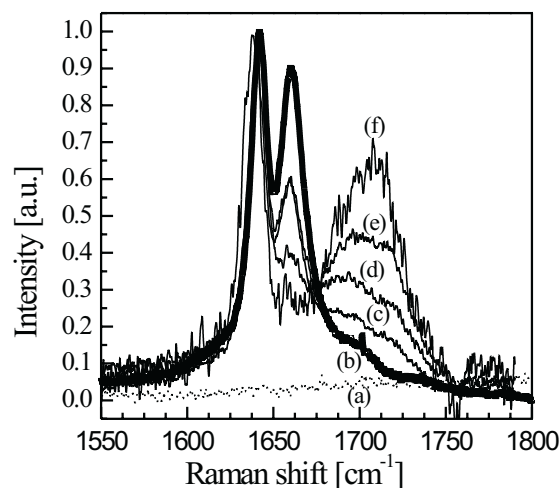


Figure 8. Raman spectra of MAA in the solution with different ratio MAA to HPC: (a) 100:0, (b) 65:35, (c) 55:45, (d) 40:60, (e) 15:75, (f) 0:100.

penetrating the PPC phase. These remarks show that the application of Raman spectroscopy for studies of systems containing cellulose derivatives yield very interesting results concerning the structure of such composites.

This short review of our work on liquid crystalline cellulose derivatives and their composites presents only the main results obtained recently. The compactness of the text does not allow the detailed description of some other interesting composites, *e.g.*

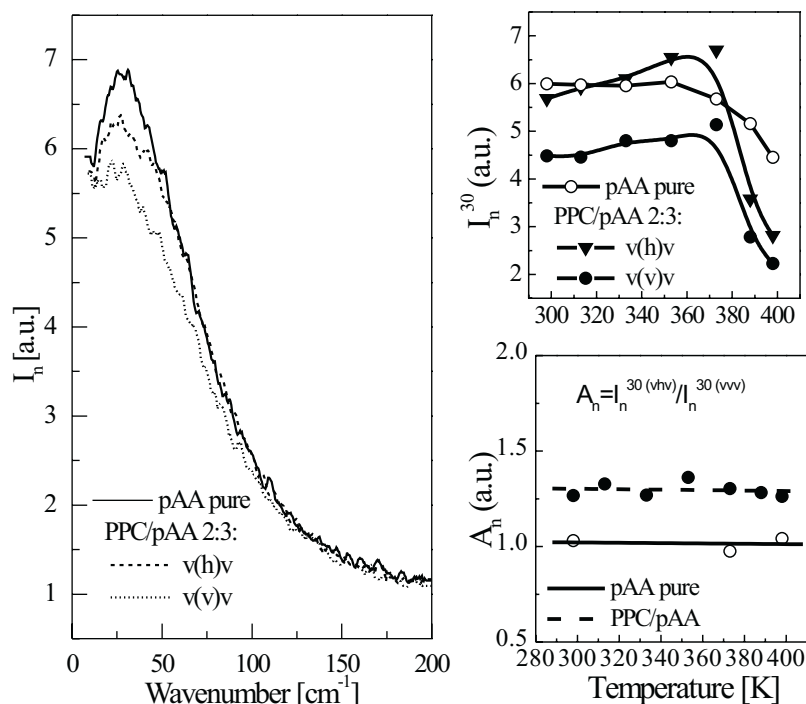


Figure 9. Low-frequency Raman scattering of the poly(AA) and its composite with PPC (details see ref. 25).

with polyacrylonitrile. The reader may find detailed results and discussion in the habilitation thesis of Wojciechowski [20] and PhD thesis of Okrasa [28] and/or in the papers quoted therein.

5. Conclusions and outlooks

The high number of lyotropic derivatives, which could be used for formation of anisotropic networks stabilized by *in situ* polymerization of mesogenic phase in a polymerizable solvent (monomer), allows for expectation that such systems will be still of great interest. Non-covalently bonded reversible anisotropic networks form interesting new area with many potential applications such as in information storage, orientation layers and as polymer blends with LC-organization. Until now, approaches to such system utilize mixtures of low-molar-mass LC-s with one or two ionizable terminal groups and the corresponding polymers like poly(acrylic acid) [29]. Most reversible anisotropic networks take advantage of the non-covalent hydrogen bond as the reversible cross-linking unit.

This article illustrates the actual situation existing with regard to LC-s of the cellulose derivative and reversible anisotropic networks (composites) based on the LC-cellulose derivative and non-mesomorphic polymer. These networks have supra-

molecular architecture and tend to preserve the LC organization of the cellulose derivative efficiently and are made by photopolymerization of monomers dissolved in an ordered phase of the LC-cellulose derivative. As the polymerization proceeds, the non-mesogenic polymer tends to phase separate, forming phase coexisting with an ordered phase of LC-cellulose derivative. Theoretical description of this process must comprise the polymerization kinetics, phase separation and phase ordering. This is a difficult task because these three processes are interconnected. The polymerization rate depends on the local concentration, which is related to the kinetics of phase separation of the LC-cellulose derivative. These composites were subjects of several experimental studies of the effects of various factors on the morphology, architectures and molecular movement of the networks.

There are new trends appearing in the literature showing that these systems can be used for preparation of novel functional systems with specific properties. Networks based on LC (hydroxypropyl)cellulose containing cellulose microcrystals complexed with ions has been described [30]. Nanocrystallites of cellulose prepared by the method described by Reval *at al.* [31] were complexed with Fe(III) ions and incorporated in the form of dispersion into anisotropic networks, based on liquid crystalline (hydroxypropyl)cellulose. The orientation (anisotropy) of such systems, fixed by polymerization of lyotropic solvent, is stable in the wide temperature range. This organization is reversible like it was shown by us previously. The decomposition and/or orientation of these metal complexes in oriented systems, basing on liquid crystalline cellulose, leads to anisotropic systems of iron oxides or ion particles implying new application of liquid crystalline cellulose for preparation interesting nanocomposites.

Acknowledgment

It is our honor to dedicate this work to Professor Krzysztof Pigoń, distinguished scientist in the field of organic solids. He was the closest and unforgettable friend of one of us (M. Kryszewski), and scientific and moral authority to all of us.

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