2. Liquid crystalline solutions of cellulose acetate in phosphoric acid

Abstract
Cellulose derivatives form liquid crystalline solutions in various solvents. The subject of this chapter is mesophase formation of cellulose acetate in phosphoric acid. The influence has been studied of both the acid strength and the degree of substitution on the formation of an anisotropic phase. To that end solutions of cellulose acetate in phosphoric acid were prepared and characterized by determining the clearing temperature (the temperature at which the phase transition from an anisotropic phase to an isotropic one occurs), and the birefringence. Phosphoric acid may occur in various forms: as a monomer (orthophosphoric acid), a dimer (pyrophosphoric acid), and even a polymer. The solvent composition is expressed as a $P_2O_5$ concentration. It was found that the clearing temperature strongly increases with decreasing amount of water in the solvent. Once the $P_2O_5$ concentration was so high that no free water was left in the solvent, the clearing temperature was no longer influenced by the $P_2O_5$ concentration. Thus, it was demonstrated that water has a detrimental effect on the anisotropy of the solution. Therefore, the phosphoric acid should be free of water and the water binding capacity should be sufficient to even compensate for the moisture introduced with the polymer in order to achieve the highest clearing temperature.

The influence of the degree of substitution (DS) was studied on a series of samples with a DS ranging from 0.23 to 2.89. It was found that over the entire range good solubility occurred in anhydrous phosphoric acid. The degree of substitution hardly affected the clearing temperature in the process of dissolving a constant number density of polymer chains. The birefringence of the solution was strongly influenced by the degree of substitution, due to the intrinsic birefringence of the polymer chains. For cellulose acetate with a DS of 2.5 the solutions were hardly birefringent, although they were liquid crystalline.

2.1 Introduction
2.1.1 Liquid crystalline solutions of cellulose and cellulose derivatives
Cellulose and its derivatives have been the subject of extensive investigations. The first publication on a cellulose-based liquid crystalline solution dealt with hydroxypropyl cellulose in water although before this publication a DuPont patent application on lyotropic systems of various cellulose derivatives in a great variety of solvents had been filed. Since then many more systems, forming anisotropic solutions have been found. Gray has summarized the conditions for mesophase formation of cellulose-based systems: mesophase formation is promoted by making use of strongly polar or acidic solvents. Highly substituted cellulose in which the substituent is a large group forms nematic phases in many solvents. Cellulose with fewer or smaller substituents needs specific solvent interaction in order to form mesophases.
Lists of mesophases of solutions of cellulose and its derivatives have been given by Gray and Gilbert. Kamide and Saito state that, if cellulose acetate is dissolved in a highly polar solvent, the chain rigidity is enhanced. Also, the size of the solvent might be of importance, the larger solvent molecules inducing more steric hindrance than the smaller. Molecular dynamic simulations of cellulose and cellulose acetate in water and dimethylsulfoxide (DMSO) revealed that the influence of acetylation is strongly dependent on the solvent. Upon the degree of substitution being increased, in water the persistence length shows an increase and subsequent decrease. The reverse holds if DMSO is used as a solvent in the simulations.

As demonstrated by the above overview, to elucidate the rules in mesophase formation of cellulose-based systems, it is important to know the roles of both the solvent and the substituent. As an example we will regard the role of phosphoric acid as a solvent. Isotropic solutions of non-derivatized cellulose in phosphoric acid are known. Anisotropic solutions of some cellulose derivatives in phosphoric acid and other inorganic acids are mentioned by Kamide et al. in an Asahi patent application and a relevant paper. Mentioned are liquid crystalline solutions of cellulose acetate in phosphoric acid both with a high and a low H$_3$PO$_4$-concentration in the solvent. A Michelin patent application describes liquid crystalline solutions of cellulose formate in a mixture of phosphoric acid and formic acid. Finally, an anisotropic solution of non-derivatized cellulose in a specific mixture of sulfuric acid (SA), polyphosphoric acid (PPA) and water (W) is described in an Asahi patent application and a relevant paper. It was found that in the case of only one specific composition of the solvent, viz., SA/PPA/W is 1/8/1, an anisotropic solution is formed in a cellulose concentration higher than 16% w/w.

This chapter is concerned with the clarification of some phenomena regarding the effects of substitution and solvent on mesophase formation of cellulose acetate in phosphoric acid. The effect of the degree of substitution and the role of the acid strength will be examined systematically. As no commercial grades with low and intermediate degrees of substitution at a sufficiently high degree of polymerization were available, these samples were synthesized by partial saponification of cellulose acetate (DS of approximately 2.5) and cellulose triacetate. The samples were dissolved in phosphoric acids with varying strength, so that liquid crystalline solutions were formed. Upon being heated, the birefringent cellulose acetate solution becomes isotropic. The temperature at which this happens is called the clearing temperature.

2.1.2 Phosphoric acid

Phosphoric acid is a special acid in that it can form dimers, oligomers and even polymers. Orthophosphoric acid is the reaction product of phosphorus pentoxide and water:

Chapter 1 gives the distribution of the various acids as a function of P$_2$O$_5$ concentration. From the equilibrium distribution the amount of water in the acid system can be calculated. This is displayed in Figure 2.1. Here we can see that even above the concentration of the
composition of orthophosphoric acid there is still some water present in the system, which is due to dimerization. Orthophosphoric acid ($H_3PO_4$), pyrophosphoric acid ($H_4P_2O_7$) and polyphosphoric acid ($H_6P_4O_{13}$) correspond to $P_2O_5$ concentrations of 72.4, 79.6 and 84% w/w, respectively. Compositions between that of ortho- and pyrophosphoric acid are also referred to as superphosphoric acid$^{22}$.

![Figure 2.1: Water content as a function of $P_2O_5$-concentration in the solvent, open circles: apparent; solid circles: real, due to the equilibrium.](image)

In this chapter the solvent composition is defined by a $P_2O_5$ content, the solvent being given by the sum of all the phosphoric acid forms and water, including the equilibrium moisture of the polymer. Therefore, in all cases the moisture content of the cellulose acetate samples is measured. The polymer concentration is then corrected for this equilibrium moisture content, not by drying the polymer in advance but by considering the amount of water to form part of the solvent.

We therefore define a presolvent and a solvent as follows. The presolvent is described by the composition before the addition of the polymer, and is characterized by a $P_2O_5$ concentration in which the moisture of the polymer is not taken into account. After the addition of the polymer the solvent comprises all the phosphoric acid components and water. This means that the moisture of the polymer is incorporated in the calculation of the $P_2O_5$ concentration, which is illustrated with an example. To a presolvent with a $P_2O_5$ concentration of 75% w/w a polymer
is added with a moisture content of 5% w/w in an amount such that the dry polymer content in the solution is 20% w/w. The solvent then has a $P_2O_5$ concentration of 74.1% w/w $P_2O_5$.

By viewing orthophosphoric acid as part of the $P_2O_5$-water system, it is now possible to increase the acid concentration and study the effect on the clearing temperature. Phosphoric acid presolvents can be prepared by mixing two or more of the following components: orthophosphoric acid, pyrophosphoric acid, polyphosphoric acid, phosphorus pentoxide and water. Also other acids of pentavalent phosphorus can be used. The solid components will have to be melted, either before or after mixing them with the other substances. Moreover, the system should be allowed to assume its new state of equilibrium.

2.2 Experimental

2.2.1 Raw materials

Cellulose acetate was obtained from Fluka. According to the Fluka specification the material had a DS of 2.47 and an $M_w$ of 61000. Three batches were used. The DS was determined analytically as described in Section 2.2.2 to be 2.74 for batch 1, 2.37 for batch 2, and 2.30 for batch 3. Cellulose triacetate was also received from Fluka. According to specification the DS was 3 and the $M_w$ 72000-74000. The material (batch 4) was analyzed to have a DS of 2.89 and was used for the preparation of samples for the DS-series. In all cases use was made of the analytically determined DS-values. Orthophosphoric acid was obtained from La Fonte Electrique SA, Bex Suisse (crystallized, 99% w/w $H_3P_0_4$). Polyphosphoric acid (84% w/w $P_2O_5$) was delivered by Stokvis.

2.2.2 Preparation and analysis of cellulose acetate with varying degrees of substitution

In order to study the influence of the degree of substitution it is desirable to have a wide variety of DS-values. Commercial grades of cellulose acetate are mostly highly substituted. Intermediate values were prepared by hydrolysis of the commercial grades.

For this purpose use was made of cellulose acetate (batch 2) and cellulose triacetate (batch 4). An amount of 100 g of cellulose acetate was brought into a 3 liter reactor to which a 75/25% v/v ethanol/water mixture was added. The suspension was heated to 60°C and stirred for 1 hour. A 1M NaOH-solution was added dropwise, the amount of which depended on the DS desired. The mixture was stirred for 30 minutes. After the suspension had been cooled it was filtered and washed with demineralized water and ethanol. The use of ethanol as a washing liquid is desirable in order to obtain a fine powder. The powder was dried in an oven at 45°C, milled in a Waring-blender and additionally dried. The equilibrium moisture content after 16h of conditioning and the degree of substitution were determined.

The degrees of substitution of the various cellulose acetate samples were determined by preparing a slurry of the dried cellulose acetate sample in 75% w/w ethanol and by deesterification with an excess amount of NaOH back titrated with HCl. A surplus of HCl is
added, which is again back titrated with NaOH\textsuperscript{23}. The results were compared with IR spectroscopy.

The equilibrium moisture content of the cellulose acetate samples was determined by using a balance equipped with an IR-drier or halogen-drier.

2.2.3 Dissolution of cellulose acetate in aqueous orthophosphoric acid and superphosphoric acid

For the influence of the acid strength to be studied solutions of cellulose acetate were prepared both in aqueous orthophosphoric acid (P\textsubscript{2}O\textsubscript{5} concentration in the solvent<72.4 \% w/w) and in superphosphoric acid (P\textsubscript{2}O\textsubscript{5-concentration in the solvent >72.4 \% w/w). The aqueous orthophosphoric acid solvents were prepared by mixing orthophosphoric acid and water in an IKA duplex kneader for 30 minutes at 45°C, to melt the solid component. The presolvent was cooled to approximately 15°C, after which the cellulose acetate (containing 3.9 \% w/w equilibrium moisture) was added in such an amount as resulted in a dry polymer content of 28.2 \% w/w in the solution. Use was made of batch 3 having a DS of 2.30. The system was kneaded for 30 minutes, during which the kneader was cooled. White, glossy, fiber forming solutions were obtained.

The solutions in superphosphoric were prepared in the same way as those mentioned above, albeit that polyphosphoric acid and water were used for the preparation of the presolvent. These components were mixed in the kneader for 30 minutes at 50°C and then cooled. Further, the same procedure was used as for the solutions with aqueous phosphoric acid.

Part of the solution was coagulated in water and thoroughly washed. On several of these precipitated polymers the degree of substitution was determined. It appeared that the DS decreased only slightly upon dissolution in phosphoric acid: a decrease of 0.17 in DS was observed. From IR measurements in the solutions it appeared that saponification became slightly more pronounced with a decreasing P\textsubscript{2}O\textsubscript{5 concentration\textsuperscript{24}.}

2.2.4 Dissolution of cellulose acetate with various degrees of substitution and step by step dilution

The influence of concentration and degree of substitution were studied simultaneously. To that end highly concentrated solutions of three grades (DS of 2.74, 0.77, and 0.23) of cellulose acetate were prepared and diluted step by step. The former cellulose acetate was a commercial sample (batch 1), the other two were partially deacetylated. Highly concentrated solutions of the three grades (35.7, 26.4, and 23.5 \% w/w, respectively) were prepared by dissolving the cellulose acetate in a presolvent of phosphoric acid with a P\textsubscript{2}O\textsubscript{5 concentration of 74.4 \% w/w, which was prepared by mixing orthophosphoric acid and polyphosphoric acid in an IKA Duplex-kneader at a ratio of 80/20. The mixture was heated and kneaded under nitrogen until a homogeneous solvent was obtained. The mixture was cooled to room temperature and the
polymer was added. Dissolution generally occurred within 5-15 minutes. However, the components were mixed for 60 minutes, the last 15 minutes of which in vacuo. During kneading the mixture was maintained between 10-25 °C by cooling. When the polymer was completely dissolved, a sample was taken for analysis and then the solution was diluted by adding the same presolvent dropwise. The mass of the sample that was taken was corrected for. This procedure was repeated several times.

2.2.5 Dissolution of cellulose acetate with a varying degree of substitution at a constant number density of monomeric units

The role of the substituent was examined more closely in a series at a constant number density of polymer chains. Solutions were prepared by dissolving cellulose acetate in a presolvent of 74.4 % w/w P$_2$O$_5$ in an IKA Duplex kneader under nitrogen. To that end ortho- and polyphosphoric acid were mixed, heated to 50 °C and allowed to equilibrate for 30 minutes in the kneader. The orthophosphoric acid concentration has been determined by means of a density measurement. The density measurement had titrimetrically been calibrated in advance. After the solvent had been cooled, the polymer was added. Cellulose acetate was added in a quantity equivalent to 15 % w/w cellulose, the equivalent cellulose concentration $c_{\text{cell, eq}}$. The weight fraction of cellulose acetate $c_{\text{CA}}$ therefore depended on the DS as follows:

$$c_{\text{CA}} = c_{\text{cell, eq}} \cdot \frac{162}{162 + DS \cdot 42} \quad (2.1)$$

The equilibrium moisture content of the polymers had been determined beforehand. The amount of material added was corrected for the water content. The solutions were kneaded for 1 hour, the last 15 minutes of which in vacuo.

2.2.6 Determination of clearing temperature and birefringence

The anisotropic cellulose acetate solutions display a bright and occasionally colorful image when viewed under a polarization microscope. Upon heating the colors start to fade until in the end a dark field appears. At the higher degrees of substitution the solutions of cellulose acetate are birefringent but hardly any colors are observed under the polarization microscope. But a clearing temperature could still be determined. Use was made of a Jenaval polarization microscope (amplification 100x). Approximately 100 mg of the solution was applied between two slides. The sample was introduced into a Mettler FP 82 Hot stage and heated at a heating rate of 5°C/min. When the image had turned almost black, the temperature was recorded. This temperature was taken to be the clearing temperature $T_c$. $^{19}$
The birefringence $\Delta n$ was determined by making use of a type B Abbe refractometer type B$^{19,25}$. Measurements were performed at room temperature. Use was made of a polarizer in the ocular of the refractometer to select the parallel and perpendicular refractive index. By measuring the angles of total reflection the two refractive indices were determined. The difference found between the two values was the birefringence.

2.3 Results and discussion

2.3.1 Influence of phosphoric acid concentration

The clearing temperatures of the solutions with varying orthophosphoric acid concentration are displayed in Figure 2.2. The acid strength is expressed as the $P_2O_5$ concentration in the solvent, as defined in Section 2.1.2. Orthophosphoric acid corresponds to a $P_2O_5$ concentration of 72.4 % w/w. So the aqueous phosphoric acid compositions are below this concentration. In this range of compositions a large influence of acid strength is observed. This is probably related to the amount of water present in the solutions. The polymer and the orthophosphoric acid always contain some water. Therefore a way was sought of working under absolutely anhydrous conditions. It was mentioned in section 2.1.2. that orthophosphoric acid can be considered to form part of the $P_2O_5$-water system. Anhydrous conditions can be reached by increasing the $P_2O_5$ content in the solvent, as was observed in Figure 2.1. To obtain these concentrations use was made of mixtures of polyphosphoric acid and water. The results for $P_2O_5$-concentration in the solvent above 72.4 % w/w are also displayed in Figure 2.2.

Although the effect of the phosphoric acid concentration on the clearing temperature was very pronounced for concentrations below 72.4 % w/w $P_2O_5$, hardly any influence of the acid strength is found above that level. This can be attributed to the amount of water in the solvent, which is visualized in Figure 2.1. As water is a small molecule, the molar quantities are rather large as compared with the molar amount of polymer in the solution. The molar ratio of water and glucose units was calculated as a function of the acid strength by making use of Figure 2.1 and the clearing temperature is plotted as a function of this molar ratio in Figure 2.3. Now it is more apparent why only a small amount of water is of such a large influence on the clearing temperature, considering that polar groups from the cellulose (either hydroxyl or carbonyl) and water have to compete for the interaction with phosphoric acid.

The importance of water in mesophase formation of solutions of cellulose in a mixture of N-methylmorpholine N-oxide (NMMO) and water was also recognized by Chanzy et al., who used a molar ratio of NMMO and water to characterize the solvent$^{26}$. However, in this system a defined amount of water is necessary to dissolve the cellulose.
Figure 2.2: Influence on clearing temperature of P$_2$O$_5$-concentration in the solvent. Orthophosphoric acid corresponds to P$_2$O$_5$ content of 72.4 % w/w. The DS was 2.30 and the cellulose acetate concentration 28.2 % w/w.

Figure 2.3: Clearing temperature of solutions of cellulose acetate (DS=2.30, 28.2 % w/w cellulose acetate) in phosphoric acid as a function of molar ratio of water and monomer units.
2.3.2 Influence of cellulose acetate concentration and degree of substitution

It was demonstrated that at acid concentrations above the composition of orthophosphoric acid the clearing temperature is unaffected by the phosphoric acid concentration. In this range of compositions solutions of cellulose acetate were prepared at several cellulose acetate concentrations by step by step dilution of initially highly concentrated solutions. In addition, the influence of the degree of substitution was studied. Therefore, a series of concentrations were prepared and analyzed at various degrees of substitution. The IR-spectra of the various samples of cellulose acetate are shown in Figure 2.4. It appears that a broad range of degrees of substitution can be covered by partial saponification.

Figure 2.4: Infra-red spectra of cellulose acetate samples with the acetate peak at 1735 cm\(^{-1}\) for DS-values of 0.23, 0.96, 1.53, and 2.37 (increasing height of the acetate peak)

The clearing temperatures of the solutions in the three series of concentrations were determined. They are plotted as a function of cellulose acetate concentration in Figure 2.5. All lines show a moderate influence of concentration on clearing temperature, with the slope decreasing at increasing concentration, probably due to degradation. Thus plotted, there seems to be a large influence of the degree of substitution. However, at a constant polymer concentration the number of chains decreases with increasing degree of substitution. This can be taken into account when calculating an equivalent cellulose concentration \(c_{\text{cellulose}}\) by compensating for the molecular weights of the monomeric units, as defined in Equation 2.1. In Figure 2.6 the clearing temperature is plotted versus this equivalent cellulose concentration.
Figure 2.5: Clearing temperature as a function of cellulose acetate concentration (crosses: $DS=0.23$; open circles: $DS=0.77$; solid circles: $DS=2.74$) using a presolvent with a $PZO_5$ concentration of 74.4 % w/w

Now the curves for the various grades coincide perfectly. Thus it seems to be that the influence of the degree of substitution will almost vanish when using the equivalent cellulose concentration. The clearing temperature is hardly affected by the degree of substitution when considering equimolar quantities. This is very remarkable and deserved closer examination.

Use was made of the experience that a description using molar quantities is preferred to that using weight fractions. Therefore, the influence of the degree of substitution was studied using equimolar quantities corresponding to an equivalent cellulose concentration of 15 % w/w. In Figure 2.7 the clearing temperature is plotted as a function of the degree of substitution. It is demonstrated that cellulose acetate can be dissolved in this particular solvent, even when the degree of substitution is as low as 0.23. This in itself is amazing; for it is known that the solvent to be chosen depends on the degree of substitution of cellulose acetate. At the same equivalent cellulose concentration the clearing temperatures compare favorably, which justifies the use of the equimolar quantities. The clearing temperature increases only slightly upon varying the degree of substitution from 0.23 to 2.89, although the polymer concentration will increases from 15.9 to 26.3 % w/w.
Figure 2.6: Clearing temperature as a function of equivalent cellulose concentration (crosses: DS=0.23; open circles: DS=0.77; solid circles: DS=2.74) using a presolvent with a $P_2O_5$ concentration of 74.4 % w/w

Figure 2.7: Influence of degree of substitution on clearing temperature at an equivalent cellulose concentration of 15 % w/w and $P_2O_5$ concentration in the presolvent of 74.4 % w/w
Figure 2.8 shows the parallel and perpendicular refractive indices of the solutions of cellulose acetate with varying degrees of substitution.

The birefringence of the solutions is strikingly low. At the lowest degree of substitution the birefringence is 0.005, which is much lower than the birefringence of aramid solutions (0.06 for a 10 % w/w solution of DABT)\textsuperscript{27}. The low birefringence of the cellulose acetate solutions is due to the low intrinsic birefringence of the polymer itself. Furthermore, the birefringence strongly depends on the degree of substitution, with hardly any birefringence being left in the highly substituted samples. Therefore, when viewed under a polarization microscope, the image is not spectacular, no colors are observed for the higher degrees of substitution. However, a phase transition can still be observed upon heating, indicating that the solutions are really liquid crystalline. The degree of substitution has a marked influence on the birefringence, but has hardly any effect on the clearing temperature. The decrease of the birefringence is therefore not related to a decrease of orientation in the solvent, but to a decrease of the maximum birefringence of the chains in solution. By substitution the electron density is changed and hence the interaction with light in both directions, which corresponds to the birefringence. This difference in birefringence can also be seen in the fibers of cellulose, cellulose acetate (DS=2.5) and cellulose triacetate, viz. +0.05, +0.005 and -0.003, respectively\textsuperscript{28}. Hence, for cellulose triacetate the birefringence is even negative. The same trend is now observed for the solutions in phosphoric acid. In that case a change in birefringence is
therefore not related to a change in orientation but is caused by a change in internal structure of the molecule.

Another solvent often used for cellulose acetate is trifluoroacetic acid, from which highly oriented cellulose acetate yarns were spun, which were saponified to very strong cellulose yarns\(^{29,30}\). In Figure 2.9 a comparison is made between cellulose triacetate dissolved in phosphoric acid and cellulose triacetate dissolved in trifluoroacetic acid\(^{31}\). It is shown that when dissolved in phosphoric acid cellulose triacetate displays anisotropy at much lower mass concentrations than when dissolved in trifluoroacetic acid. Part of the difference can be ascribed to a difference in density of the solvent, viz., 1900 kg/m\(^3\) for phosphoric acid and 1540 kg/m\(^3\) for trifluoro acetic acid, if an excluded volume approach is used for explaining the occurrence of a liquid crystalline phase. However, even when using volume fractions rather than weight fractions, cellulose triacetate still forms an anisotropic phase in superphosphoric acid at lower polymer concentrations than in trifluoro acetic acid. This offers interesting opportunities for the use of such solutions, e.g., for the preparation of highly oriented fibers. Of course, from an environmental perspective phosphoric acid is preferred to trifluoro acetic acid.

![Graph showing clearing temperature of cellulose triacetate (CTA) solutions in phosphoric acid (solid circles) and trifluoroacetic acid (open circles) both determined by means of polarization microscopy.](image)

**Figure 2.9:** Comparison between clearing temperature of cellulose triacetate (CTA) solutions in phosphoric acid (solid circles) and trifluoroacetic acid (open circles) both determined by means of polarization microscopy.
2.3.3 Discussion

It was demonstrated that whereas the water content in solutions of cellulose in phosphoric acid plays a major role in the formation of a liquid crystalline phase, the degree of acetylation is of minor importance. This is rather surprising in that in the formation of mesophases of cellulose the stress has always been on the role of derivatization. As formulated by Gray strongly acidic or polar solvents, however, promote the formation of such phases, reducing the importance of the nature and the amount of substituents\(^3\). The latter statement has been confirmed in the present work. As a matter of fact, the degree of substitution is of lesser significance considering the number density of chains in the solution. To that end an equivalent cellulose concentration has been defined.

We can compare the experimental results with theories on the subject. Consider a chain with a Kuhn length \(L_k\) and a diameter \(d\). Both in the Flory and in the Onsager approach the critical volume fraction \(\phi^*\) is inversely proportional to the axial ratio \(x = \frac{L}{d}\)\(^\text{32,34}\):

\[
\phi^* \propto \frac{1}{x}
\]  

(2.2)

Suppose that the Kuhn-length and thus the chain flexibility is unaffected by the substitution, then the critical volume fraction scales with the molecular weight of the monomeric unit of the cellulose acetate \((M_{\text{mon}})\) as:

\[
\phi^* \propto \frac{d}{L_k} \propto M_{\text{mon}}^{\frac{1}{2}}
\]  

(2.3)

The critical equivalent cellulose concentration \((c^*_{\text{cell, eq}})\) relates to the critical volume fraction as:

\[
c^*_{\text{cell, eq}} = c^*_{\text{CA}} \times \frac{162}{M_{\text{mon}}} = \phi^* \frac{\rho_{\text{pol}}}{\rho_{\text{sol}}} \times \frac{162}{M_{\text{mon}}}
\]  

(2.4)

Assuming constant densities of the polymer \(\rho_{\text{pol}}\) and of the solution \(\rho_{\text{sol}}\) the critical equivalent cellulose concentration scales with the molecular weight of the monomer as:

\[
c^*_{\text{cell, eq}} \propto M_{\text{mon}}^{-\frac{1}{2}}
\]  

(2.5)
To give an example: in accordance with this rough estimate the ratio of the critical equivalent cellulose concentrations at a DS of 0.23 and of 2.74 is 1.3. Therefore, in this approach the effect of substitution on the critical equivalent cellulose concentration is not very pronounced. In the experiments, however, an even smaller difference was found; but the Kuhn length will probably be affected by substitution, and solvation effects will also play a role.

Another line of theories is based on mean-field theories. In that approach the so-called coupling constant determinative of the orienting potential is related to the anisotropy of the polarizability. Therefore, it is remarkable that whereas the clearing temperature hardly depends on the degree of substitution, the birefringence, which is related to this anisotropy of the polarizability, is strongly influenced. Later on, the theory turned into a phenomenological one, the original meaning of the coupling constant in the Maier-Saupe theory being abandoned.

Furthermore, water is the critical component in the formation of a liquid crystalline phase in that it has a detrimental effect. Possibly, this is due to the fact that cellulose acetate competes with water for the interaction with phosphoric acid. Thus, the solvent quality is decreased causing a less extended chain.

2.4 Conclusions
It was already known that cellulose acetate can be dissolved in phosphoric acid. But in the present paper we have studied the influence of substituent and solvent separately. It is demonstrated that cellulose acetate can be dissolved in phosphoric acid with widely varying acid concentrations. Water appears to have a detrimental effect on the anisotropy of the solution.

The influence of the degree of substitution has been studied on cellulose acetate samples with varying degrees of acetylation. We have succeeded in preparing cellulose acetate samples in a wide range of degrees of substitution by partial saponification. Good solubility in superphosphoric acid was observed over the entire range, which is remarkable in itself; for in other solvents the solubility strongly depends on the degree of substitution: in organic solvents solubility only occurs in very narrow ranges of the DS.

It was demonstrated that the best way of studying the influence of the degree of substitution is to consider a number density of polymer chains. To that end an equivalent cellulose concentration was defined, which is the cellulose concentration having the same molar amount of glucose units as the cellulose acetate solution. When a constant molar quantity of cellulose acetate was dissolved the clearing temperature varied only slightly with the degree of substitution.
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