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Liquid crystalline solutions of cellulose in phosphoric acid

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Abstract

It was found that anhydrous phosphoric acid is an excellent direct solvent for cellulose. Dissolution is very fast, and liquid crystalline solutions are formed above a cellulose concentration of 7.5% (w/w) at room temperature; even solutions containing 38% (w/w) cellulose can be prepared. The composition of the solvent is expressed in a P_2O_5 concentration. Anhydrous conditions are obtained above a P_2O_5 concentration of 74% (w/w) (superphosphoric acid). The solutions were characterised by determining the clearing temperature, which was found to increase with decreasing water content in the phosphoric acid solvent and to level off under anhydrous conditions. Cellulose yarns with high moduli and high tenacities were wet spun from the anisotropic solutions. Superphosphoric acid is also capable of dissolving inter aliacellulose acetate, ethyl cellulose and chitin, with formation of anisotropic solutions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose; Liquid crystalline solutions; Yarns

1. Introduction

1.1. Liquid crystalline solutions of cellulose in direct solvents

Commercial cellulose yarns are typically spun from isotropic solutions. Since the development of high performance fibres, such as Twaron®, Kevlar® and Zylon®, it is known, that by using liquid crystalline spinning dopes, improved orientation and mechanical properties are obtained. Two spinning processes from patent literature, of DuPont's O'Brien [1,2] and Michelin's Villaine and Janin [3], respectively, also demonstrate this. In these patent applications, cellulose ester yarns are spun from liquid crystalline solutions and saponified afterwards. Impressive mechanical properties are mentioned.

By using a direct solvent, derivatisation and a post-treatment would be redundant. However, only a few direct solvents for cellulose are known, in which mesophases occur. Lists of mesophases of solutions of cellulose and its derivatives have been given by Gray and Gilbert [4–6]. Direct solvents for cellulose with mesophase formation, that have been mentioned there, are a mixture of *N*-methylmorpholine *N*-oxide and water, a mixture of trifluoroacetic acid and dichloromethane, dimethyl acetamide/lithiumchloride and ammonia/ammonium thiocyanate. Miyamoto and co-workers [7,8] describe the formation of an anisotropic solution of underivatised cellulose in a specific mixture of sulphuric acid (SA), polyphosphoric acid (PPA) and water. No reports are given on high tenacity yarns, spun from any of these solutions.

We have found that liquid crystalline solutions can be formed when cellulose is dissolved in phosphoric acid [9,10]. From British and Russian patents [11–13] isotropic solutions of cellulose in phosphoric acid were known. Also Turbak [14] mentioned phosphoric acid as an interesting solvent for cellulose. However, it was believed that for an anisotropic phase to appear in phosphoric acid either derivatisation (both Kamide et al. [15,16] and Villaine and Janin [17] describe the formation of anisotropic solutions of cellulose derivatives in phosphoric acid), or the use of a cosolvent was necessary as demonstrated by Miyamoto and co-workers [7,8].

The dissolving power of phosphoric acid is very strong, with dissolution occurring within a few minutes. In the viscose process (the commercial process for the preparation of textile and industrial yarns), the residence time of the cellulose in the plant is 1–2 days due to the long ripening, which is a combination of depolymerisation and redistribution of substituents. The short dissolution time in phosphoric acid constitutes a very important advantage in production processes.

For comparison with cellulose also some solutions of

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other polysaccharides, viz. cellulose acetate, ethyl cellulose, and chitin have been prepared. Cellulose acetate is described in a preceding paper [18]. Polymers with a chiral carbon-atom are in principle capable of forming cholesteric (or chiral nematic) phases. The typical optical effects accompanying such phases were observed in one solution.

1.2. Dissolution of cellulose in phosphoric acid

In a preceding paper [18], it was shown that cellulose acetate can be dissolved in phosphoric acid and that anisotropic solutions are formed over a wide range of degrees of substitution. Even cellulose acetate with a DS as low as 0.23 could be dissolved, resulting in an anisotropic solution. The clearing temperature hardly changed upon varying the degree of substitution, provided that the number density of monomeric units remained unaltered. However, the influence of the water content in the solvent was rather large. Addition of 1% (w/w) water caused a decrease in clearing temperature of approximately 7°C. On the strength of both phenomena, it seems likely that phosphoric acid will be capable of dissolving cellulose and forming an anisotropic solution, if only the acid were free of water. The reason why anisotropic solutions of cellulose in phosphoric acid have never been found before probably lies in the handling of phosphoric acid, viz. the problem is that anhydrous orthophosphoric acid is a solid with a melting point of 42°C. If cellulose is to be dissolved in it, it has to be done at elevated temperature. Under these conditions rapid degradation occurs. Moreover, there is always still about 1–2% (w/w) water in the acid and in the process of melting the orthophosphoric acid, dimerisation occurs with formation of water. The presence of this water might account for the limited solubility of cellulose. Additional water is introduced by the cellulose, which contains approximately 5% (w/w) equilibrium moisture. Prior drying of the polymer might solve the problem, but such a treatment will affect the accessibility of the solvent to the material.

Both problems, i.e. the solid character of the phosphoric acid and the water it contains, can be overcome by considering orthophosphoric acid to form part of the P_2O_5–water system, thereby creating the possibility of working under anhydrous conditions and even providing for a water-binding capacity, to compensate for the water contained by the cellulose. The P_2O_5 concentrations to which orthophosphoric, pyrophosphoric and polyphosphoric acid correspond are 72.4, 79.6 and 84% (w/w), respectively, whereas compositions in between the first and the second concentrations are referred to as superphosphoric acid. The equilibrium distribution of the various phosphoric acids is dependent on the P_2O_5 concentration as is given by Ullmann [19]. It was shown in a preceding paper [18] that the acid is anhydrous above a P_2O_5 concentration of 74% (w/w), which composition can be obtained by the addition of, e.g. polyphosphoric acid to the melt of orthophosphoric acid. The polyphosphoric acid binds the excess of water and it is therefore partially hydrolysed. As we can see from the phase diagram in Ullmann [19], the melting temperature of the acid decreases above a P_2O_5 concentration of 72.4% (w/w); moreover, these systems can be supercooled. Thus, a mixture of orthophosphoric acid and polyphosphoric acid was prepared. It was supercooled and cellulose was added, which appeared to dissolve very quickly with formation of a very viscous, fibre forming, glossy, birefringent solution.

The range in which anisotropic solutions can be formed has been examined. They have been analysed by polarisation microscopy.

2. Experimental

2.1. Raw materials

Orthophosphoric acid (crystallised, 99% (w/w) H_3PO_4) was supplied by La Fonte Electrique SA, Bex Suisse, pyrophosphoric acid (97%, w/w) by Fluka Chemika, polyphosphoric acid (85% (w/w) P_2O_5) by Merck or (84% (w/w) P_2O_5) by Stokvis, and phosphorus pentoxide (min 98%, w/w) by J.T. Baker. Unless mentioned otherwise Viscokraft and Buckeye V65 (both DP 700–750) and V60 (DP 800) were used as cellulose samples. The Buckeye sheets were powdered at International Filler. Furthermore, some samples were hydrolysed to a low DP at the Akzo Nobel laboratory at Obernburg, Germany. Ethyl cellulose (DS = 2.46,DP = 269) was obtained from Janssen Chemica and chitin from Fluka Chimica ($M_w = 400{,}000$).

2.2. Definitions

The presolvent is defined as the acid mixture before the addition of polymer, and the solvent as the composition of the acid mixture after the addition of polymer. The solvent consists of all the phosphoric acid components, including the anhydride and water. Whereas the equilibrium moisture introduced by the cellulose is therefore considered also to be part of the solvent, no equilibrium moisture of the polymer is contained in the presolvent. The given cellulose concentration is based on the dry weight of the polymer. This does not mean that the polymer is dried in advance, but the cellulose concentration is corrected for the amount of water it contains. In most cases, the equilibrium moisture content of the cellulose raw material is 5% (w/w).

2.3. Preparation of the solution

Superphosphoric acid presolvents were prepared in an IKA-Duplex kneader, by mixing two or more of the following components: orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$), polyphosphoric acid ($H_6P_4O_{13}$), phosphorus pentoxide (P_2O_5) and water. The solid components have to be melted completely, either before or after mixing them with the other components, because the presolvent is supercooled and residual crystals might serve as nuclei for crystallisation. Furthermore, some time is needed to arrive at the new equilibrium distribution of the phosphoric acid system. The equilibration speed is low, which is also given by Gmelin [20]. In order quickly to obtain an equilibrium in the solvent, the starting materials should be as close as possible to this state of equilibrium. Therefore, most of the solutions were prepared by using a mixture of orthophosphoric acid and polyphosphoric acid. The components were mixed and heated in the kneader for some time in order to obtain more or less a state of equilibrium. The presolvent was supercooled and cellulose was added. The solutions were highly viscous, glossy, fibre forming and birefringent.

The influence was examined of dissolution temperature, type and strength of the acid, cellulose concentration and molecular weight distribution. The molecular weight distributions of the cellulose samples were recorded by size exclusion chromatography (SEC). To that end, cellulose was dissolved in DMAc/LiCl. In addition, the degree of polymerisation (DP) was determined by means of a viscosity measurements (DP_v) in copper II ethylene diamine (cueen). Furthermore, the dissolution of chitin and ethyl cellulose was studied.

2.4. Determination of the clearing temperature

Upon the cellulose solution being heated, it becomes isotropic. The temperature at which this happens is called the clearing temperature (T_c). Under the polarisation microscope, the anisotropic solution displays a bright and colourful image. Upon heating, the colours start to fade until in the end a dark field appears.

Use was made of a Leitz-orthoplan-pol and a Jenaval polarisation microscope (magnification 100×). Approximately, 100 mg of the solution were introduced between two slides. The sample was transferred to a Mettler FP 82 hot stage, in which it was heated at a heating rate of 5°C/min. When the image had turned from coloured to almost black, the temperature was recorded. This temperature is taken to be the clearing temperature T_c. Solutions with a high clearing temperature were assessed quickly. And in order to prevent degradation in a second run on a fresh sample, the starting temperature was chosen approximately 20°C below the clearing temperature, after which the normal heating procedure was started.

2.5. Preparation of yarns

Orthophosphoric acid and polyphosphoric acid were mixed in a thermostated vessel at a ratio such that the presolvent had a P_2O_5 concentration of approximately 74% (w/w). During mixing, the temperature was kept above 42°C in order to melt the phosphoric acid crystals and equilibrate the mixture. Powdered cellulose containing approximately 5% (w/w) equilibrium moisture and the solvent were thoroughly mixed in a ZSK 30 twin screw extruder. The DP of the raw material, as determined by a viscosity measurement in a copper II ethylene diamine/water mixture was approximately 800. The solution containing 19% (w/w) of dry polymer was filtered, heated and extruded through an assembly of spinnerets jointly containing 1500 capillaries of 65 μm diameter. The filaments passed through an air gap, in which they were subjected to drawing and went through a falling jet coagulation bath containing acetone. The acid was further removed from the yarn by washing with water in jet washers to achieve a phosphorus level of 0.43% (w/w), part of which appeared to be bonded to the cellulose. The yarns were neutralised with a 2% (w/w) Na_2CO_3 solution, washed to a sodium content of 0.53% (w/w), finished, and dried on heated godets at a speed of 100 m/min.

The mechanical properties of the new fibres, coded B, are compared with the following cellulose fibres: a textile yarn Enka® Viscose, Cordenka® 660 and 700 tire yarns, a high modulus Cordenka® EHM yarn, which are all prepared according to the viscose process. A more detailed structural and mechanical analysis will be given in a separate paper by Northolt [21].

Tensile measurements were performed with the Zwick 1445 Tensile Tester at 21°C and 65% R.H. Test lengths of 25 and 100 mm with a strain rate of 10%/min were applied. The filament linear density was determined with a vibroscope.

3. Results and discussion

3.1. Influence of composition and temperature of the (pre)solvent

Equilibration of the phosphoric acid system is slow. The speed depends on inter alia temperature, acid strength and composition of the starting materials. By Raman spectroscopy it was demonstrated that hydrolysis had insufficiently progressed after one night at room temperature when equal masses of polyphosphoric acid and water were mixed. From ^{31}P-NMR measurements, it was found that when orthophosphoric and polyphosphoric acid were used for the preparation of superphosphoric acid, the state of equilibrium was reached in 50 min at a temperature of 40°C. By adding 2% (w/w) water to superphosphoric acid, it took several hours before a new state of equilibrium was reached.

Gmelin [20] indicates that upon the acid being diluted from approximately 84 to 54% (w/w) P_2O_5 complete hydrolysis is obtained after 90 and 22 min at 50 and 70°C, respectively.

Mostly a combination of orthophosphoric acid and polyphosphoric acid was used, this system being close to the state of equilibrium, and the mixture was kept sufficiently long at elevated temperature. However, also other combinations were used, as demonstrated in Table 1. In all cases, the material was kept at elevated temperature for some time to melt the crystals and for the phosphoric acid system to be equilibrated to some extent.

For all the solvents good solubility was reached, which

Table 1
Influence of type of acid on clearing temperature of solutions containing 11.4% (w/w) cellulose

Wt parts acid	P_2O_5 in solvent (%, w/w)	T_c (°C)
80.6 H_3PO_4/19.4 PPA	73	49
88.0 PPA/12.0 H_2O	74	43
92.7 $H_4P_2O_7$/7.3 H_2O	74	43
74.8 P_2O_5/25.2 H_2O	73	48

resulted in obtaining glossy, fibre forming, anisotropic solutions. The clearing temperatures of these solutions did not vary widely. For the solutions containing 11.4% (w/w) cellulose, the clearing temperature is approximately 45°C. Very good solubility is obtained at approximately 73–74% (w/w) P_2O_5 in the solvent, equivalent to H_3PO_4 concentrations slightly over 100% (w/w). From these experiments, it follows that the solvent can be defined by a P_2O_5 concentration, irrespective of the starting materials, provided that the state of equilibrium is reached. By Kamide and co-workers [7,8,15,16], when dissolving cellulose (derivatives), orthophosphoric, pyrophosphoric and polyphosphoric acid have been considered as separate substances, even when used in the dilute form.

The range in which good solubility and anisotropy was found was rather narrow, performance being optimal between 72 and 76% (w/w) P_2O_5 in the solvent. However, this range can be widened by the addition of, e.g. water shortly before, together with or after the supply of the cellulose, advantage being taken of the slow kinetics of the phosphoric acid system.

Solutions with a lower P_2O_5 content were prepared by using a presolvent of 74.4% (w/w) P_2O_5, adding cellulose and subsequently supplying water drop by drop. In the solution, the cellulose concentration was 17.1% (w/w). The clearing temperature as a function of the P_2O_5 concentration in the solvent is shown in Fig. 1. Prior to precipitation, a large amount of water may be added to the solution. The effect of the P_2O_5 concentration in the solvent is very pronounced below approximately 73% (w/w). Above that level, no influence of the P_2O_5 concentration is found. This can be explained by the amount of water in the solvent, which is also indicated in Fig. 1 and which is based on the equilibrium data. As was the case for cellulose acetate, the influence of traces of water is enormous. And as we can see from Fig. 1, the effect of water on the clearing temperature of the cellulose solutions even exactly equals that in the case of the cellulose acetate solutions. In the graph, an equivalent cellulose concentration is used as defined in a previous paper [18].

The enhanced solvent quality at higher P_2O_5 concentrations is not due to the presence of the stronger pyrophosphoric acid, but to the absence of water, since the clearing temperature levels off above a P_2O_5 concentration in the solvent of 73% (w/w). Though the amount of water seems to be small, expressed in molar quantities the water content is rather large. The molar ratio of water and glucose units is 2 and 4 at a P_2O_5 concentration of 68 and 65% (w/w), respectively. The detrimental effect of water on solutions of cellulose acetate was already recognised [18], the clearing temperature being plotted against this molar ratio.

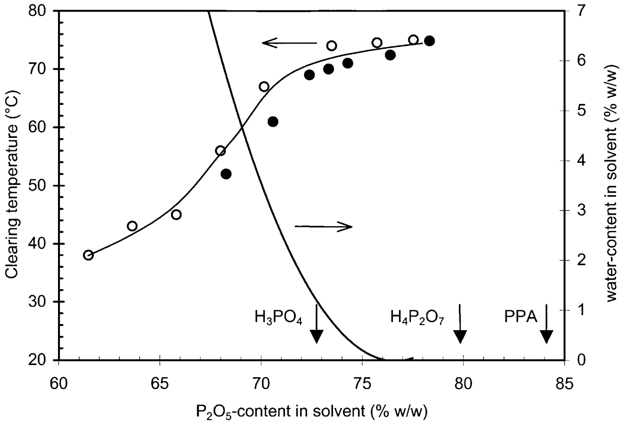

Fig. 1. Influence of P_2O_5 content in solvent on clearing temperature for solutions of cellulose (solid circles) and cellulose acetate with a DS of 2.74 (open circles). The solutions had an equivalent cellulose concentration of 17.1% (w/w). Also indicated is the amount of water in the solvent based on equilibrium data.

Fig. 2 displays the influence of the dissolution temperature on the dissolution time. The dissolution time is here defined as the time needed to form glossy, fibre forming, birefringent solutions, the dissolution time being strongly dependent on the solvent temperature. Also the type of kneader has an influence on the dissolution time. It was found, that a twin screw extruder providing for a residence time of only 2 or 3 min can be used for the dissolution process. This is described in our patent application [9]. These dissolution times are very short as compared with the time needed in the preparation of isotropic solutions of

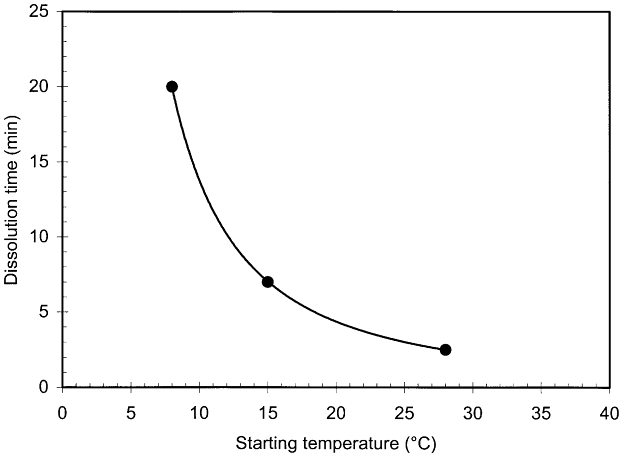

Fig. 2. Dissolution time in an IKA kneader, defined as the time in which a birefringent, fibre forming, glossy substance is obtained, as a function of starting temperature when 17.1% (w/w) cellulose is dissolved in a presolvent of 74.4% (w/w) P_2O_5.

cellulose in phosphoric acid as demonstrated in various patent applications [11–13]. Mention is made of dissolution times of hours and even days. The commercial viscose process also requires very long dissolution and reaction times. The residence time of the cellulose from raw material to yarn in a viscose plant is between 24 and 48 h. The short dissolution times of the present system will have a very favourable effect on the economy of the phosphoric acid process.

3.2. Influence of cellulose concentration

The influence of the concentration of cellulose, dissolved in a presolvent of 74.4% (w/w) P_2O_5, on the clearing temperature is demonstrated in Fig. 3. Anisotropy is already observed above a concentration of 7.5% (w/w) at room temperature. This demonstrates that phosphoric acid is a very powerful solvent, for anisotropy is observed at much lower concentrations than in the other direct solvents mentioned in the introduction. The higher end of the curve shows the strength of the solvent. Solutions up to 38% (w/w) cellulose were prepared. This indicates that under anhydrous conditions phosphoric acid is an excellent solvent for cellulose. At high cellulose concentrations, the slope can be seen to flatten out, which can probably be attributed to degradation, as occurring above a temperature of 60°C.

In the graph, a comparison is being made with poly (*para*-phenylene terephthalamide) (PPTA) and poly {2,6-diimidazo[4,5-b:4′,5′-e]pyridinylene-1,4-(2,5-dihydroxy)-phenylene} (PIPD or 'M5', a new rigid rod yarn). Data of these systems were taken from Picken [22] and Lammers [23], respectively. At room temperature, cellulose and PPTA display liquid crystallinity at equal weight fractions. As the concentration increases, the increase in clearing temperature is much higher for PPTA than it is for cellulose.

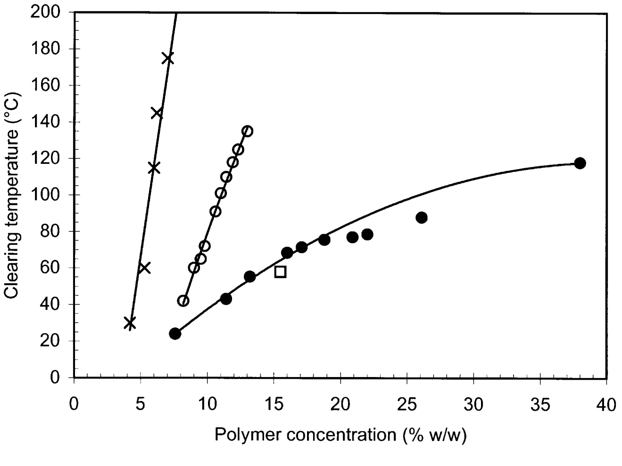

Fig. 3. Clearing temperature as a function of polymer concentration for cellulose in a presolvent of 74.4% (w/w) P_2O_5 (solid circles) versus solutions of PPTA in sulphuric acid (open circles), and solutions of PIPD in polyphosphoric acid (crosses) after Picken [22] and Lammers [23], respectively. The clearing temperature of a solution of chitin with an equivalent cellulose concentration of 15.5% (w/w) is also indicated (open square).

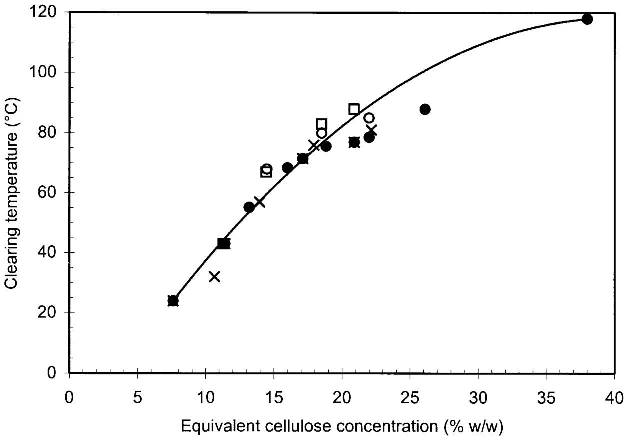

Fig. 4. Clearing temperature as a function of equivalent cellulose concentration for solutions of cellulose (solid circles), and cellulose acetate with a DS of 0.23 (crosses), DS of 0.77 (open circles) and a DS of 2.74 (squares).

In Fig. 4, the data on cellulose were added to the graph of the cellulose acetate grades from the preceding paper [18]. The line for cellulose practically coincides with those for the cellulose acetates if the equivalent cellulose concentration is used.

3.3. Influence of molecular weight distribution

The molecular weight distributions of the various cellulose samples are shown in Fig. 5. The DP values are listed in Table 2. The clearing temperature of these solutions containing 15% (w/w) cellulose in a presolvent of 74.4% (w/w) P_2O_5 is displayed in Fig. 6 as a function of the DP_w. A notable influence is found of the DP_w on the clearing temperature. However, considering that the contour length by far exceeds the persistence and even the Kuhn length, it is strange that there should be a dependence on the DP_w in this range at all. Ciferri [24] states that the persistence length of cellulose based systems are in the order of 100–200 Å.

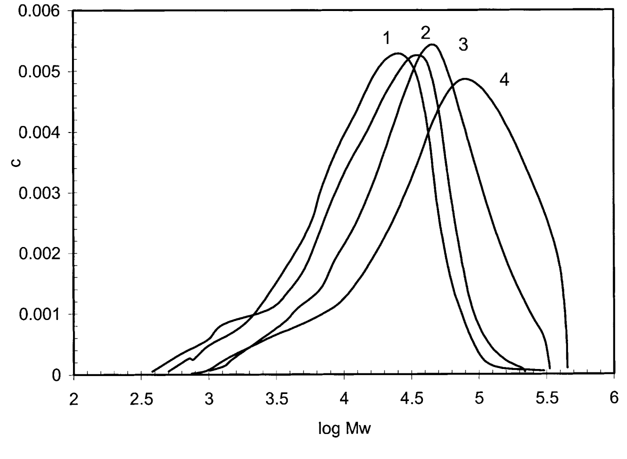

Fig. 5. Molecular weight distribution of the cellulose samples 1–4 listed in Table 2.

Table 2
DP of the cellulose samples: DP_w (by SEC) and DP_v (by viscosimetry in copper II ethylene diamine), the fraction with a contour length smaller than 300 Å, and clearing temperature T_c of the solutions containing 15% (w/w) cellulose in a presolvent of 74.4% (w/w) P_2O_5

Sample[a]	DP_w	DP_v	Fraction < 300 Å	T_c (°C)
1	160	200	0.22	44
2	198	235	0.19	48
3	367	400	0.09	58
4	740	675	0.07	65

[a] The samples 2 and 4 were supplied by Buckeye (P and G 7483 and V65, respectively), the samples 1 and 3 were hydrolysed V65 samples, supplied by Akzo Nobel Central Research Obernburg.

The Kuhn length will be 200–400 Å then, corresponding to a DP of 40–80. Ambrosino and Sixou [25] found for acetoxypropyl cellulose and hydroxypropyl cellulose in the melt that after a steep rise the clearing temperature as a function of DP levelled off. The contour length at the change of slope was considered to be of the order of the persistence length. It might be realistic to regard the low molecular weight fraction merely as a diluent, which does not contribute to the anisotropy of the solution. As a first approximation, the fraction with a contour length smaller than 300 Å is taken to be a disturbing factor. In Fig. 6, this low molecular weight fraction is shown together with the clearing temperature. The larger the fraction is of low molecular weight material in the solution, the lower the clearing temperature. Optimum results will be obtained upon lowering this fraction, which is not necessarily attended with an increase in DP_w. This is of course a very rough approximation; for also the low molecular weight fraction consumes a certain amount of solvent, although the use of this fraction makes the influence of the molecular weight distribution more apparent than the average value, as expressed in the DP_w. Another cause for the dependence of the clearing temperature on the DP_w might be that the relaxation times increases with increasing DP_w, which might slow down the pace at which the phase transition is achieved.

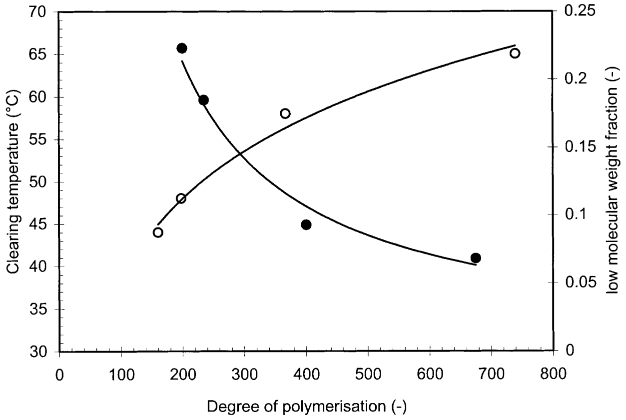

Fig. 6. Low molecular weight fraction (contour length smaller than 300 Å, solid circles) and clearing temperature (open circles) as a function of the DP_w.

3.4. Comparison with theory

The clearing temperature is only moderately influenced by the cellulose concentration. Analogously to the description of Picken [22], the clearing temperature being expressed in K and the concentration in % (w/w), the data in Fig. 3 can be fitted by:

$$T_c = 208c^{0.17} \tag{3.1}$$

Conversely, it can be stated that the critical concentration is strongly affected by temperature. For simplicity, the difference between mass and volume fractions is omitted. Both in the Onsager [26] and Flory [27] approach the critical volume fraction merely depends on the axial ratio of the rigid element, determined by the persistence length or the Kuhn length. For high axial ratios the critical volume fraction ϕ' in both approaches is inversely proportional to the axial ratio x:

$$\phi' \propto \frac{1}{x} \tag{3.2}$$

Taking the persistence length or the Kuhn length to be temperature dependent can incorporate temperature effects. However, the dependence of this characteristic length on the temperature would be unrealistically high then, viz. it would scale with T^{-6}. Since the Onsager approach is a virial treatment, temperature effects can also be incorporated in one of the virial coefficients. In the lattice treatment too, the so-called soft interactions, mostly attractive forces between the molecules were incorporated. According to Ciferri [28], the thermal effect, introduced by these soft interactions is rather small, and insufficiently accounts for the large temperature effect on the critical volume fraction.

Another approach is the Maier–Saupe theory [29,30], in which a molecule is oriented in the mean field of its neighbours. Picken [22] incorporated excluded volume terms in the original description. It was derived that the clearing temperature depends on the concentration as

$$T_c = Ac^{2/(1+2n)} \tag{3.3}$$

where n is defined by

$$L_p = k'T^{-n} \tag{3.4}$$

where L_p is the persistence length. For this approach, it follows that for the power n, a value of 5.5 should be used, which is also very high. For aramid solutions, the value of n was found to be 1, and for cellulose derivatives, values ranging from 1.6 to 3.7 were observed by Picken [22] and Ciferri [24], respectively. Ciferri used these values, combined with a lattice or virial treatment, to explain the temperature dependent behaviour of solutions of cellulose derivatives, although he expresses his astonishment about the enormous temperature sensitivity of the persistence length. In the case of cellulose dissolved in superphosphoric acid, the temperature dependence of the critical volume fraction is even higher.

Thus, the source of the pronounced temperature dependent behaviour of the present cellulose solutions is not fully understood yet. Effects of solvatation and polyelectrolyte behaviour might play a role, which is also shown by the influence of water on the clearing temperature. Moreover, the high molecular weight and the high viscosity of the solutions might play a role in the kinetics of the phase transition.

3.5. Cholesteric phases

Solutions of cellulose are in principle capable of forming chiral nematic or cholesteric phases. Some optical effects typical of these phases are described by Zugenmaier [31]. However, under the conditions mentioned above, no optical effects related to a chiral nematic phase were observed. In these cases, the viscosity of these solutions is so high that the characteristic time scale for the pitch to settle is too large. In a degraded sample (a 20% (w/w) cellulose solution was kept at room temperature for some days), the optical effects typical of cholesteric phases were obtained.

3.6. Degradation and derivatisation

During dissolution, there occurs slight degradation, albeit, despite the use of a strong acid, to a rather small extent. During processing to high tenacity yarns, the decrease of the average DP_v is limited, e.g. from 800 to 600.

Due to the presence of dimers in the standard presolvent of 74.4% (w/w) P_2O_5 and more condensed forms at higher P_2O_5 contents, the possibility of the formation of cellulose phosphate is not ruled out. However, derivatisation is not a prerequisite for dissolution, as will be demonstrated below.

The kinetics of the esterification was determined by sampling the solution at various moments, coagulating in acetone and washing in acetone or water and drying. The phosphorus content of the samples was determined by means of ICP-ES. Fig. 2 shows that at 25°C an anisotropic solution was obtained within 3 min. In that time, a DS of 0.007 was found. Hence, 1 glucose-unit of 140 is derivatised, which demonstrates that phosphorylation is not a prerequisite for dissolution and the formation of a liquid crystalline phase. Also liquid crystalline phases were observed at even lower DS values.

Although derivatisation is not essential to the formation of a liquid crystalline phase, conditions can be chosen such that phosphorylation is promoted, which was described by Westerink et al. [32].

3.7. Mechanical properties

Fig. 7 shows the tensile curves of filaments typical of the group of strongest filaments from the bundles for the test length of 100 mm of the fibres prepared by the viscose process and fibre B produced by air gap spinning a liquid crystalline solution of cellulose in phosphoric acid. The values found for the ten strongest filaments out of 50 filaments of fibre B having a test length of 25 mm, with sample standard deviations added in parentheses, are: tenacity $\sigma_b = 1.70$ (0.03) GPa initial modulus $E_i = 44$ (3) GPa elongation at break $\varepsilon_b = 6.5$ (0.3)% and the linear density is 1.43 (0.16) dtex. From the graph, it is apparent that the fibre produced by the present dissolution process has superior mechanical properties over the yarns spun form the conventional viscose process. A more detailed analysis of the structural and mechanical features of the various cellulose yarns will be presented in a separate paper by Northolt et al. [21].

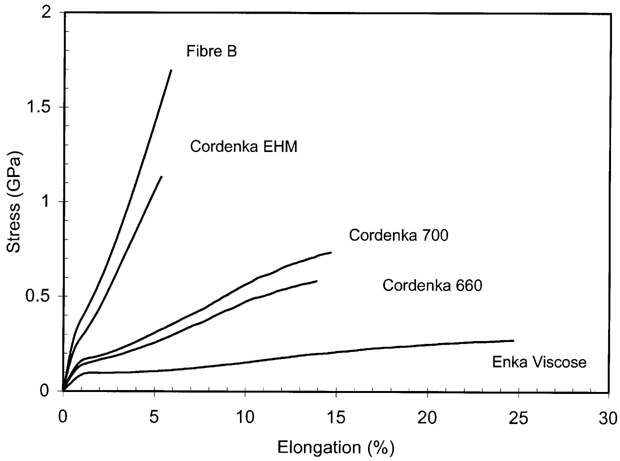

Fig. 7. Filament tensile curves typical of the group of strongest filaments from a bundle for a test length of 100 mm; fibres prepared by the viscose process, and by the new process, presented in this paper (fibre B).

3.8. Cellulose derivatives and other polysaccharides

In the acid mixture used here, with the optimum results being obtained by using a composition of approximately 74% (w/w) P_2O_5, also other polysaccharides can be dissolved. In a preceding paper [18], we have described cellulose acetate, which is soluble over the entire range of degrees of substitution with formation of a liquid crystalline phase.

Ethyl cellulose was dissolved in an amount of 21.4% (w/w), corresponding to an equivalent cellulose concentration of 15% (w/w) (both dry polymer content). Due to the coarseness of the material the dissolution took a relatively long time, and a small amount of material remained undissolved. However, a viscous birefringent solution was obtained. The clearing temperature was found to be 43°C, which is lower than the value for the non-derivatised cellulose, or the cellulose acetate. This lowering can in part be ascribed to the undissolved material; moreover, the molecular weight distribution appeared to be very broad, with a large low molecular weight fraction accounting for a decrease in the clearing temperature.

Chitin was dissolved in an amount of 19.4% (w/w) dry polymer content, which corresponds to an equivalent cellulose concentration of 15.5% (w/w). The clearing temperature was found to be 58°C. This value is added in Fig. 3. The clearing temperature of this chitin solution falls exactly on the line of the clearing temperatures of cellulose, when using the equivalent cellulose concentration.

4. Conclusions

Few solvents are known to be used for the dissolution of underivatised cellulose, and even fewer are those forming anisotropic solutions. The previously found systems mentioned in the introduction hardly seem to be applicable on an industrial scale. We now have found a direct solvent, which is cheap and environmentally friendly. Dissolution occurs very fast, i.e. within a few minutes, rendering the processing into inter alia fibres and films very economical as compared with the conventional viscose process, in which the residence time of cellulose in the plant from sheet to bobbin is 40 h, due to a complicated ripening process. Neither derivatisation nor the use of a cosolvent are needed to obtain liquid crystalline solutions in phosphoric acid.

An increase in clearing temperature was found with phosphorus pentoxide concentration, which levels off above the orthophosphoric acid composition. Upon a further increase in P_2O_5 concentration the solubility decreased. It was found that the best results were obtained when use was made of a solvent having a phosphorus pentoxide concentration, which is just above that of the orthophosphoric acid composition, and which is referred to as superphosphoric acid. Based on the levelling off of the clearing temperature under anhydrous conditions it can be concluded that it is the absence of water and not the presence of the stronger pyrophosphoric acid, which is a prerequisite for optimum solubility and anisotropy.

It was observed that at room temperature the critical concentration for the formation of an anisotropic phase was 7.5% (w/w), which approximately equals the critical concentration for PPTA in sulphuric acid, which indicates that the chain conformation is extremely extended, and thus that this superphosphoric acid is a very good cellulose solvent. The same is also displayed by the high concentrations of cellulose, that can be obtained, viz. at least 38% (w/w), and by the fast dissolution. The critical concentration in superphosphoric acid is much lower than in other direct solvents. Although a strong acid is used as a solvent, degradation of the cellulose is not very strong during processing.

In the present work on non-derivatised cellulose, the same behaviour is observed as for various grades of cellulose acetate a preceding paper, i.e. when the same number density of monomeric units is dissolved the clearing temperature is hardly affected by the degree of substitution.

Cellulose yarns were prepared by air gap spinning the liquid crystalline solutions in phosphoric acid. It was found that high modulus and high tenacity yarns can be prepared following this route. Mechanical properties were by far superior to yarns produced by the conventional viscose process, as will be elucidated in a forthcoming paper.

Superphosphoric acid is also a good solvent for chitin; when equal number densities of monomeric units of chitin and cellulose are dissolved the same clearing temperature is observed.

The high DP of cellulose normally used, viz. approximately 800, prohibits the settling of a pitch in the chiral nematic phases, due to long relaxation times. If strong degradation of the cellulose in the solution is allowed, the intense, viewing angle dependent, colours typical for chiral nematic phases occur.

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