7638 *Macromolecules* **1997,** *30,* 7638−7640

# Chain Conformation of Cellulose in a Coordinating Solvent

**O. Hanemann and M. Ballauff***

*Polymer-Institut, Universität Karlsruhe, Kaiserstrasse 12, 76128 Karlsruhe, Germany*

*Received July 1, 1997*

**Introduction.** For a long time it has been known that cellulose can be dissolved in a solution of $Cu(OH)_2$ in aqueous ammonia.[1] Solutions of cellulose in this solvent, termed Cuoxam ($[Cu^{II}(NH_3)_4](OH)_2$; "Schweizer's reagent"), have been the subject of two recent studies using static and dynamic light scattering as well as viscosimetry.[2,3] On the basis of previous studies of suitable model compounds,[4] the coordination of cellulose by aqueous $[Cu^{II}(NH_3)_4](OH)_2$ could be studied in detail.[2] A result of particular interest was the finding that the cellulose molecules exhibit a high stiffness in this coordinating agent. The persistence length $l_p$ as determined by static light scattering was found to be 12.8 nm and explained by hydrogen bonds between the $C_6$ OH group and the $C_2$ OH group of the adjacent glucose unit.[3]

Here we wish to study the chain conformation of cellulose in a new coordinating solvent termed Pd-en. This reagent is formed by alkaline aqueous solutions of $Pd^{2+}$ and ethylenediamine. The resulting complex $[(en)Pd^{II}(OH)_2]$ was shown to form well-defined polyolato complexes with low molecular weight carbohydrates that could be studied in detail by single-crystal analysis.[5,6] Figure 1 displays the structure of the coordinated repeating unit of cellulose, which has been derived from these studies.[5,6] In particular, the analysis of the model compounds suggests a strong hydrogen bonding between adjacent repeating units, which should lead to a considerable stiffening of the chains.

The analysis of the chain conformation of cellulose coordinated by Pd-en can be done by conventional methods: Cellulose in aqueous Pd-en forms slightly yellow solutions that can be studied easily by light scattering. Furthermore, the complex $[(en)Pd^{II}(OH)_2]$ is diamagnetic and thus can be studied by NMR.[6] As opposed to solutions of cellulose in Cuoxam, oxidative degradation presents no problem.

Another advantage is given by the fact that the exchange of ligands at the palladium ions is much slower than in case of Cuoxam. Hence, Pd-en solutions of cellulose can be diluted without the formation of a great number of different complexes, as is the case for solutions in Cuoxam.[2] The chain stiffness detected by light scattering therefore can directly be related to a single well-defined complex of $[(en)Pd^{II}(OH)_2]$ and the repeating units of the cellulose.

**Experimental Section.** Measurements have been performed using three samples: a pulp cellulose termed Z630 (Buckey V68) and two samples of linters termed L800 and L1100 (Temming). All samples were used as received.

$PdCl_2$ was obtained from the Degussa Co. Ethylenediamine (Fluka) and $CuSO_4 \cdot 5H_2O$ (Fluka) were analytical grade and used without further purification. Solutions of the cellulose samples in Cu-en were prepared according to ref 7 under an atmosphere of argon at a temperature of 5 °C. Dilution was effected shortly before the measurements by a stock solution of Cu-en.

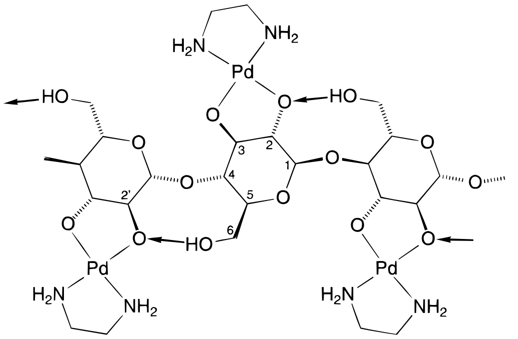

**Figure 1.** Structure of the repeating unit of the coordinated cellulose chains (cf. also refs 5 and 6).

Solutions of cellulose in Pd-en were prepared as follows:[8] An aqueous 0.25 M solution of the complex $[(en)Pd(OH)_2]$ was obtained by reacting $[(en)PdCl_2]$ with $Ag_2O$ with stirring under an atmosphere of Ar. After stirring for 1 h, the yellow solution was filtered off and used immediately. To this solution was added cellulose, and the mixture was kept at 0 °C until full dissolution had taken place. The time needed to obtain a homogeneous solution depended on the molecular weight of the cellulose sample; the highest molecular weight needed ca. 2 weeks. Dilution was effected by adding 0.05 M aqueous NaOH with stirring and ultrasonification for 30 min.

Cellulose tricarbanilates (CTC) were synthesized according to Saake et al.[9] using a 35-fold excess of phenyl isocyanate. Molecular weights were determined by viscosimetry[10] using solutions of CTC in dioxane at 25 °C. The respective Mark−Houwink relation was taken from Sutter and Burchard.[11]

Intrinsic viscosities were determined using an Ubbelohde-viscosimeter (Schott, I) modified to exclude oxygen and $CO_2$. Light scattering intensities were recorded with a SOFICA-P6D-42000 apparatus equipped with a laser (633 nm). All solutions were filtered through a hydrophilic filter (Gelman Science, nominal pore size 450 nm).

The refractive index increment ($dn/dc$) (0.182 mL/g) was determined with a Brice-Phoenix differential refractometer at two different wavelengths and extrapolated to 633 nm. Gel permeation chromatography (GPC) was done on 5 $\mu$m columns using tetrahydrofuran as solvent at a flow rate of 1 mL/min. Detection was done with a UV/vis detector (254 nm; Spectra-Physics).

**Results and Discussion.** In the course of the present investigation we have used three sample of cellulose. All samples have been characterized first with regard to molecular weight and molecular weight distribution. The degree of polymerization was determined by viscosimetry in Cu-en. The degrees of polymerization have been derived using the Mark−Houwink relation supplied by ref 10; the respective results are gathered in the second column of Table 1. To corroborate these results, all cellulose samples have been converted into tricarbanilates (CTC) following the procedure of Saake et al.[9] The cellulose tricarbanilates have been analyzed by viscosimetry in dioxane to yield the molecular weights given in Table 1.

Furthermore, the CTCs could be used to measure the breadth of the molecular weight distributions (mwds). Thus, solutions of the CTCs have been analyzed by gel

---

* To whom all correspondence should be addressed. E-mail: matthias.ballauff@chemie.uni-karlsruhe.de.

S0024-9297(97)00970-4 CCC: $14.00

**Table 1. Characterization and Persistence Length of the Cellulose Samples**

| | $P_{\mathrm{w,Cuen}}{}^{a}$ | $P_{\mathrm{w,CTC}}{}^{b}$ | $M_{\mathrm{w}}/M_{\mathrm{n}}{}^{c}$ | $[\eta]^{d}$ | $M_{\mathrm{w}}{}^{e}$/g/Mol | $\langle s^2\rangle_z{}^{1/2}$/nm$^{e}$ | $P_{\mathrm{w,Pden}}{}^{e}$ | $l_{\mathrm{p}}$/nm$^{e}$ |
|---|---|---|---|---|---|---|---|---|
| Z630 | 522 | 525 | 4.7 | 184 | 176 000 | 39 | 543 | 9.6 |
| L800 | 1048 | 1011 | 2.6 | 285 | 298 000 | 49 | 919 | 9.6 |
| L1100 | 1187 | 1044 | 3.1 | 301 | 291 000 | 50 | 897 | 9.8 |

[a] Determined by viscosimetry in Cu-en using the Mark–Houwink relation of ref 10. [b] Determined by viscosimetry of the cellulose tricarbanilates (CTC) in dioxane.[11] [c] Determined by analysis of the CTCs by GPC. [d] In cm$^3$/g; determined at 25 °C in Pd-en. [e] Determined by light scattering in Pd-en.

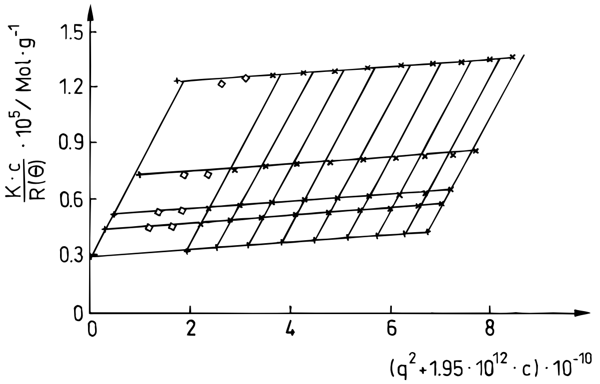

**Figure 2.** Zimm-plot of the coordinated cellulose sample L1100 (cf. Table 1).

permeation chromatography (GPC) calibrated by polystyrene samples. Universal calibration was achieved using the Mark–Houwink relation of ref 12. The resulting nonuniformities as expressed by the ratio of the weight-average- to the number-average molecular weight are gathered in Table 1. The nonuniformity $M_{\mathrm{w}}/M_{\mathrm{n}}$ is considerably higher than the value 2 expected for a most probable distribution. A similar breadth of the mwd has been found by Evans[13] as well as by Saake et al.[9] for samples of comparable source and pretreatment. They are afflicted by possible losses of low molecular weight material during workup and will therefore present lower bounds of $M_{\mathrm{w}}/M_{\mathrm{n}}$.

As mentioned above, Pd-en has a number of distinct advantages as solvent for cellulose. A point of particular importance is the stability of these solutions against oxidative degradation. While degradation presents a serious problem with Cuoxam, solutions of cellulose in Pd-en turned out to be stable when in contact with air for several hours. Possible degradation can be monitored easily by measuring the intrinsic viscosity $[\eta]$ after certain intervals. Experiments using Cuoxam as solvent demonstrated a strong decrease of $[\eta]$ within 1 h unless the handling and the measurements are done with strict exclusion of oxygen. The intrinsic viscosity measured in Pd-en-solutions remained unchanged under these conditions. Table 1 collects the values of $[\eta]$ measured at 25 °C.

The slightly yellow color of the Pd-en solutions imposes no problems in the course of a light scattering experiment conducted at 633 nm wavelength. A careful check by measuring the UV–vis spectra of these solutions showed indeed that there is no adsorption at this wavelength. Also, the refractive increment (d*n*/d*c*) could be determined for these solutions. Figure 2 displays the Zimm plot resulting from sample L1100.

Given the molecular weight $M_{\mathrm{o}}$ of the fully coordinated repeating unit (324.4), the $M_{\mathrm{w}}$ thus obtained (cf. column 6 of Table 1) may now serve to check the extent of reaction along the cellulose molecule. Table 1 displays the $P_{\mathrm{w,Pden}}$ values that result from the $M_{\mathrm{w}}$ and $M_{\mathrm{o}}$. The $P_{\mathrm{w,Pden}}$ values thus obtained from viscosimetry are slightly smaller than the $P_{\mathrm{w,CTC}}$ taken from light scattering of the CTC derivatives, although this difference is within experimental uncertainty. From this comparison it is safe to conclude that practically all repeating units are coordinated.

The radii of gyration obtained from light scattering can be used together with the polydispersities to calculate the persistence length $l_{\mathrm{p}}$ of the coordinated cellulose chains. The theory of the wormlike chain by Benoit and Doty[14] may be used to derive a relation between the weight-average contour length $L_{\mathrm{w}}$ of monodisperse chains and $l_{\mathrm{p}}$. Schmidt[15] has extended this theory to include nonuniform samples exhibiting a Schulz–Zimm distribution, which yields

$$\langle s^2\rangle_z = \frac{(m+2)l_p}{3y} - l_p{}^2 + \frac{2yl_p{}^3}{m+1} - \frac{2l_p{}^4}{m(m+1)}\left(y^2 - \frac{y^{m+2}}{\left(y+\frac{1}{l_p}\right)^m}\right) \tag{1}$$

where $m = (M_{\mathrm{w}}/M_{\mathrm{n}} - 1)^{-1}$ and $y = (m + 1)/L_{\mathrm{w}}$. The last column of Table 1 gives the resulting persistence length calculated for each sample. Good agreement is seen for all molecular weights under consideration here despite the fact that the samples used herein exhibit molecular weight distributions differing considerably in width. Cellulose in aqueous Pd-en has thus been characterized as a wormlike chain with a persistence length comprising more than 20 repeating units. On the other hand, the measured persistence length is considerably less than the values obtained from covalently substituted cellulose chains as, e.g., CTC ($l_{\mathrm{p}}$ = 17 nm[16]).

In this context it is interesting to compare the persistence length found for the coordinated cellulose here with the stiffness determined for typical stiff-chain polymers.[17] Recently, the persistence length of a number of stiff-chain polymers has been investigated thoroughly.[18–22] In the course of these investigations it turned out that polyimides based on *p*-terphenylenediamine and pyromellitic anhydride are characterized by a persistence length of 13 nm.[18] Studies of a polyester, the repeating unit of which incorporates the stiff terphenylene moiety, concluded that here the persistence length is approximately 11 nm.[20,21] Even the poly(*p*-phenylene) chain, which often is considered as the best example of a stiff-chain polymer, exhibits a moderate stiffness only depending on the substituents (13–22 nm).[19,22] The main reason for the rather low stiffness of all these chains seems to be located in the out-of-plane fluctuations of single bonds within the chains.[23–25] The comparison of the stiffness of the coordinated cellulose with these fully aromatic chains thus demonstrates that the coordination leads to a marked stiffening of the chains by the bridging between adjacent repeating units.

**Conclusion.** A novel coordinating solvent for cellulose has been presented. Cellulose forms a kinetically stable well-defined complex with aqueous Pd-en (see Figure 1) that is stable against oxidation. The results obtained here clearly demonstrate that the cellulose chains coordinated by Pd-en exhibit a persistence length of 9.6 nm. The reason for this stiffening of the chains in solution is located in the bridging of the coordinated repeating units (cf. Figure 1) by the hydrogen bonds. A more extended discussion of the complex formation including the analysis of low molecular weight model compounds is under way.[6]

**Acknowledgment.** Financial support by the Bundesministerium für Bildung und Forschung is gratefully acknowledged.

### References and Notes

(1) Schweizer, E. *J. Prakt. Chem.* **1857**, *72*, 109.
(2) Burchard, W.; Habermann, N.; Klüfers, P.; Seger, B.; Wilhelm, U. *Angew. Chem.* **1994**, *106*, 936.
(3) Seger, B.; Burchard, W. *Macromol. Symp.* **1994**, *83*, 291.
(4) Klaasen, M.; Klüfers, P. *Z. Anorg. Allg. Chem.* **1993**, *619*, 661.
(5) Burger, J.; Kettenbach, G.; Klüfers, P. *Macromol. Symp.* **1995**, *99*, 113.
(6) Ahlrichs, R.; Ballauff, M.; Hanemann, O.; Kettenbach, G.; Klüfers, P. *Chem. Eur. J.*, submitted for publication.
(7) Marx, M. *Makromol. Chem.* **1955**, *16*, 157.
(8) Brauer, G. H*andbuch der präparativen anorganischen Chemie*; F. Enke Verlag: Stuttgart, 1981.
(9) Saake, B.; Patt, R.; Puls, J.; Philipp, B. *Papier* **1991**, *45*, 727.
(10) Marx-Figini, M.; Penzel, E. *Makromol. Chem.* **1965**, *87*, 307.
(11) Sutter, W.; Burchard, W. *Makromol. Chem.* **1978**, *179*, 1961.
(12) Evans, R.; Wallis, A. F. A. *J. Appl. Polym. Sci.* **1989**, *37*, 2331.
(13) Evans, R.; Wearne, R. H.; Wallis, A. F. A. *J. Appl. Polym. Sci.* **1989**, *37*, 3291.
(14) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(15) Schmidt, M. *Macromolecules* **1984**, *17*, 553.
(16) Fried, F.; Searby, G. M.; Seurin-Velluti, M. J.; Dayan, S.; Sixou, P. *Polymer* **1982**, *23*, 1755.
(17) Ballauff, M. Structure and Properties of Polymers. *Structure of Liquid Crystalline Polymers*; In Materials Science and Technology; Cahn, R., Haasen, P., Kramer, E., Eds.; Thomas, E. L., Chapter Ed.; VCH: New York, 1993; Vol. 12, Chapter 5.
(18) Schmitz, L.; Ballauff, M. *Polymer* **1995**, *36*, 879.
(19) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Köhler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.
(20) Tiesler, U.; Rehahn, M.; Ballauff, M.; Petekidis, G.; Vlassopoulos, D.; Maret, G.; Kramer, H. *Macromolecules* **1996**, *29*, 6832.
(21) Petekidis, G.; Vlassopoulos, D.; Galda, P.; Rehahn, M.; Ballauff, M. *Macromolecules* **1996**, *29*, 8948.
(22) Galda, P. Ph.D. Thesis, Karlsruhe, 1995.
(23) Jung, B.; Schürmann, B. *Macromolecules* **1989**, *22*, 477.
(24) Jung, B.; Schürmann, B. *Macromolecules* **1992**, *25*, 1003.
(25) Farmer, B. L.; Chapman, B. R.; Dudis, D. S.; Adams, W. W. *Polymer* **1993**, *34*, 1588.

MA970970F