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Scattering function of non-substituted cellulose dissolved in N-methylmorpholine-N-oxide-monohydrate

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SUMMARY: The solution state of non-substituted cellulose dissolved in the monohydrate of N-methylmorpholine-N-oxide was investigated by static light scattering measurements. Molecular masses of the cellulose of several millions g/mol were observed. The overall particle scattering function can be separated into two individually scattering contributions. Two models could explain such a behaviour. First, the results reflect a bimodal distribution of the dissolved polymer consisting of large and small aggregates. The second attempt at an explanation is based on the model of a fringed micelle. The light scattering on different parts of the micelles, the core and the fringes causes the discussed scattering function. The angular dependence of the scattering intensity is simulated by superposition of particle scattering functions and parameter fit.

Introduction

Static light scattering from dilute polymer solutions is the most important method for the absolute determination of the weight-average molecular mass M_w. Moreover, light scattering measurements provide also some other data on the polymers involved, e.g., on the thermodynamic interaction between the polymer and the solvent (the second virial coefficient, A_2), or on the dimension of polymer chains in solution (z-average radius of gyration, $\langle R^2\rangle_z^{1/2} = R_G$). It is possible to obtain some information on the particle shape from the angular dependence of light scattering from large particles, the particle scattering function (form factor) $P(q)$.

Cellulose is one of the most important natural polymers. The investigation of its solution properties has not been treated in sufficient details. A reason for this is the highly ordered structure of native cellulose. Neither the dissolution process nor an often used activation process may disintegrate completely the ordered domains. A characteristic pattern of cellulose solutions seems to be the existence of aggregates of still ordered cellulose molecules.

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The aim of our work is the application of the static light scattering measurement on the determination of shape and size of the aggregates of non-substituted cellulose in the solvent N-methylmorpholine-N-oxide-monohydrate. For this purpose we measure the angular dependence of light scattering at different concentrations of solution and discuss the form factor *P(q)* of a non-interacting system (concentration → 0). For some time, mathematical expressions have been available for the particle scattering functions of different types of macromolecules. Comparing the measured and calculated *P(q)* it seems to be possible, in principle at least, to get useful information on the cellulose molecules in solution.

Experimental

Materials

The cellulose material used in this work was a coniferous sulphate pulp, Buckeye V60, with a degree of polymerisation (DP) of 535. The DP was estimated by intrinsic viscosity measurements in cuoxam [1]. By SEC/MALLS measurements (eluent dimethyl-acetamide/LiCl) we could determine the polydispersity $M_w/M_n < 3$. Merck supplied the reagent grade N-methylmorpholine-N-oxide-monohydrate (NMMNO). Because of its melting point (72 - 73°C) measurements must be done at a higher temperature. The refractive index at 80°C is $n_o = 1.4638$ and was determined with a digital refractometer RX-5000 (ATAGO).

Preparation of cellulose solutions

One of the methods used in the clarification of solutions is their filtration.

About 15 g of molten NMMNO was filtered through a heated sintered glass filter (pore size 1.6 µm) at 90°C. The calculated amount of cellulose sample (concentration range from 0.002 g/cm^3 to 0.03 g/cm^3) was added to the molten solvent under nitrogen and stirred with a magnetic stirrer. The required time for dissolution (4 to 30 hr) depends on the activation procedure.[1)] The cellulose solutions were filtered through a heated glass filter of 16 µm pore size into dust-free ampoules which were repeated washed with condensing acetone, for details see also [2]. Using a glass filter of 5 µm pore size do not change the results. Filtration through filters with smaller pore size was not successful. At stronger filtration conditions the solution could not flow through the pores (high viscosity of the solvent).

[1)] Cellulose was activated by two different procedures: 10 g of cellulose were dispersed in 500 cm^3 deionized water overnight, then filtered and pressed out; cellulose was immersed in liquid ammonia for a few minutes, the ammonia was removed by a steam explosion process [3].

Static laser-light-scattering measurements

Light scattering was measured with a SLS-2 goniometer (SLS Systemtechnik, Germany) using He-Ne laser ($\lambda_0 = 632.6$ nm), in the angular range 30 –145° (in steps of 5°) and at 80°C. Dibutylphthalate was filtered and then used as immersion liquid in the apparatus. All measured data were corrected in respect to self-absorption of the slightly brown coloured solutions (Eq. 1).

$$\left(\frac{Kc}{R_\theta}\right)_{corr} = Kc\left(\frac{R_{\theta,c}}{T_c} - \frac{R_{\theta,solvent}}{T_{solvent}}\right)^{-1} \qquad (1)$$

The transmission of solution T_c and solvent $T_{solvent}$, respectively, was measured with a UV-spectrometer (Shimadzu UV-2101PC) at 632.8 nm.

For the evaluation of light scattering data, the knowledge of the refractive index increment $\partial n/\partial c$ of the polymer in a given solvent at a chosen temperature and wavelength is required. For the sample V60 $\partial n/\partial c = (0.061 \pm 0.007)$ cm³/g was measured at 632.8 nm and at 80°C with a DR-1 differential refractometer (SLS Systemtechnik, Germany). For comparison, in (Ref. 4) the refractive index increment was estimated to be $\partial n/\partial c = 0.0687$ cm³/g.

Results and Discussion

The processing of light scattering data by Zimm's method and related methods is well established. A relationship for evaluation of static light scattering data from dilute polymer solutions is given by

$$\frac{Kc}{R_\theta} = \frac{1}{M_w P(q)} + A_2 c \qquad (2)$$

In this equation, R_θ is the normalised scattering intensity (Rayleigh ratio) at the scattering angle θ, c is the concentration, K is the optical constant, $P(q)$ is the particle scattering factor, and q is the magnitude of the scattering vector that is related to the scattering angle by:

$$q = (4\pi n_o / \lambda_o)\sin\theta/2 \qquad (3)$$

An evaluation of our light scattering data by Zimm's method was impossible (high molecular mass of the scattering particles). Because of that we took the Guinier-Zimm plot in which $ln(Kc/R_\theta)$ is plotted against $(q^2 + kc)$, where k is an arbitrary constant (Figure 1). This method should be used if a polymer solution contains molecules with very high molecular mass, globular structures, or particles of different sizes. As well the Guinier-Zimm plot should be recommended for compact structures.

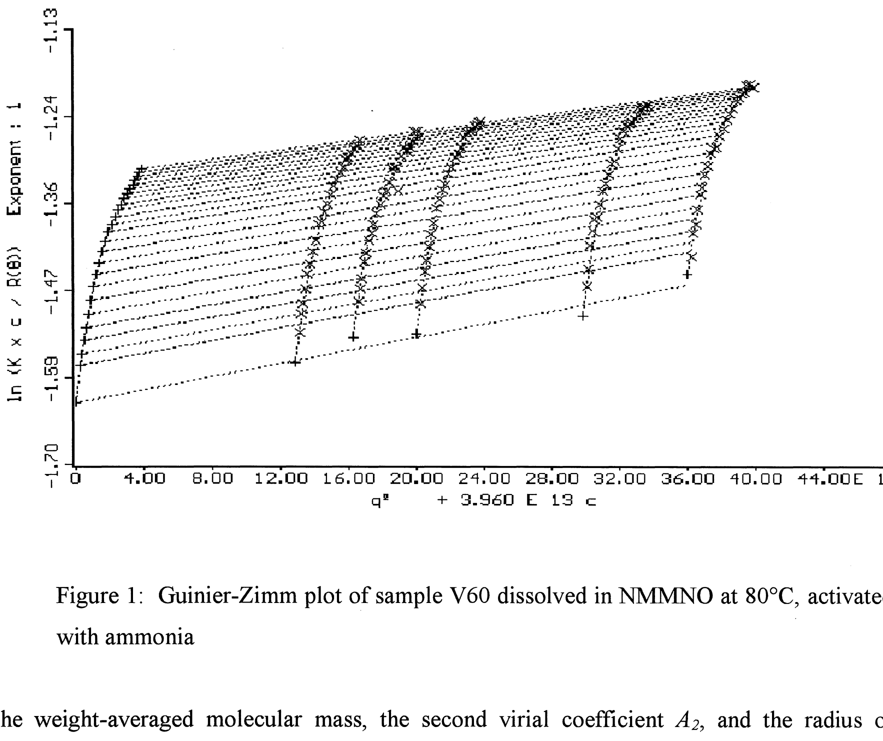

Figure 1: Guinier-Zimm plot of sample V60 dissolved in NMMNO at 80°C, activated with ammonia

The weight-averaged molecular mass, the second virial coefficient A_2, and the radius of gyration $\langle R^2 \rangle_z^{1/2} = R_G$ were calculated from the slopes and the intercept of the extrapolated $(c \rightarrow 0;\ \theta \rightarrow 0)$ scattering curves (Table 1).

Activation	DP_{cuoxam}	$M_w / 10^6 g\ mol^{-1}$	R_G /nm	$A_2 / 10^{-6} mol\ cm^3\ g^{-1}$	n_w
None (N)	535	55.2	201	2.1	637
Water (W)	510	17.5	171	1.9	211
Ammonia (A)	485	10.7	167	4.0	136

Table 1: Molecular parameters of sample V60 activated by different procedures

As expected the determined molecular mass of the cellulose sample is higher than the value determined by intrinsic viscosity measurement in a cuoxam solution. Assuming, that the cellulose is molecularly dissolved in cuoxam[5], an apparent aggregation number n_w can be calculated ($n_w = M_w/\{162\ DP_{cuoxam}\}$). The activation procedure influences the results of the scattering experiments. The molecular mass of the non-activated sample is higher than that of the activated samples. However, single cellulose molecules are not detectable in NMMNO.

As shown in Figure 1, the angular dependence of the logarithm of the reciprocal scattering intensity at concentration $c \rightarrow 0$ is non-linear. Different effects could cause this:

- the high molecular weight of the scattered particles;
- the cellulose sample has a very broad or a bimodal molecular weight distribution;
- the solution contains at least two species of cellulose particles with different size.

The curvature of the angular dependence of light scattering from cellulose solutions in NMMNO is due to the fact that the polymer does not dissolve molecularly. It follows from the calculated aggregation number that super-molecular particles exist in the solution. They scattered light very intensely at low angles of observation. Due to their large dimensions the intramolecular interference of scattered light decreases the scattering intensity at large angles. For aggregated polymer solution it is well-known that only a small part of the molecules forms aggregates. They have a very high molecular mass, which influences the M_w of the whole sample very strong. For the further discussion of the form-factor it is assumed that the non-linear angular dependence of the scattering intensity is due to particles of different sizes in the solution. If this assumption is valid, the measured overall scattering curve is a superposition of two or more scattering functions. A useful method for the analysis of the overall scattering function is the so-called Guinier factorisation which was described by Gruber and Schurz[6]. The prerequisite is that scattering functions of different particles can be described by the Guinier approximation of globular structures:

$$P(q)^{-1} = e^{\frac{(qR_G)^2}{3}} \qquad (4)$$

Burchard et al.[7] showed that in terms of the soft-sphere model of a regular hyper-branched molecule $P(q)$ follows up to rather large value of $(qR_G)^2$ ($(qR_G)^2 \approx 15$) an exponential decay as represented by Eq. (4). The "soft sphere" consists of a centrosymmetric unit of 3 branches, each of which terminates in another trifunctional branch point (first shell) and so on to successive shells. Assuming that the cellulose particles behave as soft spheres the scattering function of particles with $R_G \leq 130$ nm can be approximated by Eq. (4) over the whole range of scattering angles used in our measurements (for particles with $R_G \leq 210$ nm up to $\theta = 80°$, respectively). The intensity of the scattered light at large angles, $\theta > 90°$, results from the smaller particles. Their scattering function can be approximated by a tangent on the overall scattering curve (at $c \rightarrow 0$) for larger values of the observation angle. The scattering curve of the larger particles is given as the difference between the overall scattering curve and the scattering curve of the smaller particles. The slopes of the tangents and the remaining scattering curves, respectively, give the R_G of both kinds of particles and the intercepts are the products of the concentration of the particles and their molecular mass ($w_i M_{wi}$) concerned. The remaining scattering curve was found as a straight line. From this it can be concluded, that the overall scattering function can be represented as the superposition of only two scattering functions. An explanation for this behaviour could be that the solution contains two kinds of particles with different sizes. The smaller particles (subscript 2) are aggregates too. A calculation of the molecular masses of the larger and smaller aggregates is impossible because the weight fractions w_1 and w_2 are unknown. In opposite to $w_2 M_{w2}$ the activation procedure had no influence on R_{G2}. This is understandable if the shape of particle 2 is independent on activation and w_2 changes, or if w_2 is independent on activation and the shape ($<R^2>$ - M – relation) changes.

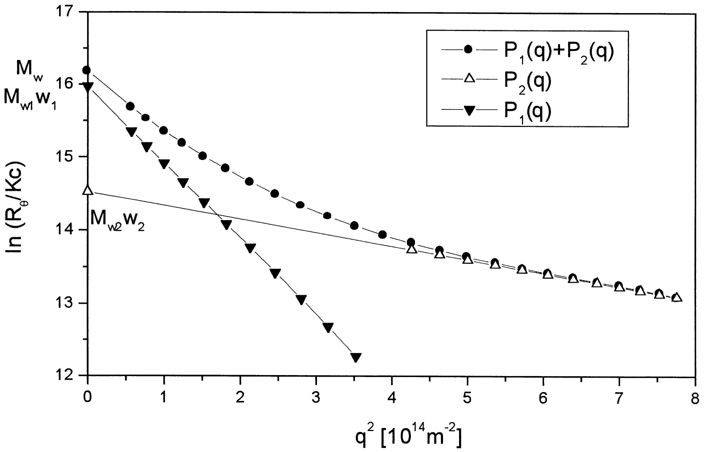

Figure 2: Factorisation of the scattering curve of sample V60 activated with ammonia

Activation	$w_1M_{w1}/10^6$g mol^{-1}	R_{G1} /nm	w_1n_{w1}	$w_2M_{w2}/10^6$ g mol^{-1}	R_{G2} /nm	w_2n_{w2}
None (N)	60	232	694	8.0	72	92
Water (W)	14.4	191	175	3.7	75	45
Ammonia (A)	8.6	175	109	2.0	74	25

Table 2: Results of factorisation of the scattering function (sample V 60)

Frequently in literature authors tried to extract information on the particle shape from a comparison of experimental scattering functions with *P(q)* calculated for different particle shapes. The comparison was performed graphically, often in co-ordinates $P(q)\ u^2$ against u, the so-called Kratky plot, where $u = qR_G$. From a better or poorer fit with one of the theoretical curves, the particle shape was estimated. According to (Ref. 8) three major restrictive pre-requisites exist for a successful interpretation of *P(q)* in terms of particle shape:

- High molecular mass, large part of *P(q)* is measurable;
- The polymer must be strictly mono-disperse in molecular mass, shape and size;
- Accurate experimental data, high scattering intensities of the solutions related to the solvent.

The experimental results are expressed as the ratio Kc/R_θ. In order to estimate the particle scattering function *P(q)* the ratios are calculated in the following term:

$$P(q) = \frac{1}{M_w \left(\frac{Kc}{R_\theta} \right)_{c=0}} \qquad (5)$$

Figure 3 shows calculated particle scattering functions for different shapes of the macromolecules. To get an idea on the shape of the cellulose in NMMNO, we compare the measured *P(q)* with the particle scattering function of mono-disperse coils, hard spheres, soft spheres and homogeneous branched macromolecules (for mathematically formulation and details of the different types of *P(q)* see (Ref. 9)). The differences between the calculated particle scattering functions are significant at high values of u, $u > 2$. Each of the particle scattering function shows a typical asymptotic behaviour, which is a useful tool to distinguish between different particle shapes.

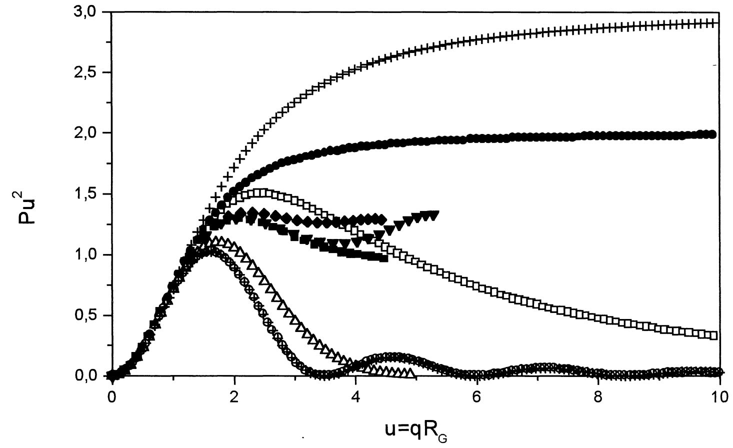

Figure 3: Kratky plot of the calculated and measured *P(θ)*

P(θ) u^2 versus *u* with $u = qR_G$ (R_G determined from the initial slope of the scattering function)

calculated: +: poly-disperse coil; ●: mono-disperse coil; □: homogeneous branched; Δ: soft sphere ⊕: hard sphere;

measured: ◆: V60 (W); ■: V60 (A); ▼: V60 (N)

In our experiments the measured *P(q)* cannot be described by one of the theoretical functions. They show a maximum like globular and branched particles and at sample V60 (N) a slight upward curvature at higher values of *u*. (The slight upward curvature may be caused by reflection on the cuvette, which can be observed at high values of the scattering angle. For data calculation in Fig. 3 we used only scattering intensities measured at $\theta < 135°$)

We try to fit the measured scattering function by a superposition of two particle scattering functions:

$$M_w P(q) = w_1 M_{w1} P_1 + w_2 M_{w2} P_2 \qquad (6a)$$

$$P(q) = a P_1 + (1-a) P_2 \qquad (6b)$$

where a is the weighted fraction of the large particles (subscript 1), $a = w_1 M_{w1}/M_w$.

In our opinion it seems to be plausible to approach the particle scattering function of a soft sphere (soft-sphere model of a regular hyper-branched molecule) for the large particles.

For the simulation of the overall scattering function we use the following combinations:

- Soft sphere – soft sphere

$$P(u)=a\cdot\exp\left(-\frac{1}{3}u^2\right)+(1-a)\cdot\exp\left(-\frac{1}{3}u^2\left(\frac{R_2}{R_1}\right)^2\right) \qquad (7a)$$

- Soft sphere – homogeneous branched[2)]

$$P(u)=a\cdot\exp\left(-\frac{1}{3}u^2\right)+(1-a)\cdot\left(1+\frac{1}{6}u^2\left(\frac{R_2}{R_1}\right)^2\right)^{-2} \qquad (7b)$$

- Soft sphere – linear poly-disperse chain

$$P(u)=a\cdot\exp\left(-\frac{1}{3}u^2\right)+(1-a)\cdot\left(1+\frac{1}{3}u^2\left(\frac{R_2}{R_1}\right)^2\right)^{-1} \qquad (7c)$$

The variable u is given by the product of q and R_G of the whole polymer in the solution (obtained from the Guinier-Zimm plot) or by the product of q and the radius of gyration of the high molecular component R_1 (R_{G1} obtained from the Guinier factorisation). The Eqs. (7) are valid for the last assumption. In this case the fit parameters are a and R_2, otherwise a, R_1 and R_2. Table 3 lists the results of the fit procedure.

Equation	Activation	a	R_1/nm	R_2/nm
(7a)	None	0.899	232 *)	65
	Water	0.895	224	48
	Ammonia	0.903	200	59
(7b)	None	0.897	232 *)	71
	Water	0.901	191 *)	42
	Ammonia	0.895	175 *)	55
(7c)	None	0.894	232 *)	78
	Water	0.895	191 *)	44
	Ammonia	0.899	175 *)	59

Table 3: Results of the form factor analysis according Eqs. (7)

*) R_1 was taken from the Guinier factorisation (Figure 2, Table 2)

[2)] starbranched molecule, functionality f >>1, M_W/M_n of the branches = 2

The calculated values of R_2 are independent on the chosen particle scattering function. The *u*-region is too small to distinguish between different particle scattering functions.

Figure 4 shows the measured and calculated scattering functions of the non-activated sample V60. The correspondence between the fitted and measured curve is rather good and confirms our suggestion.

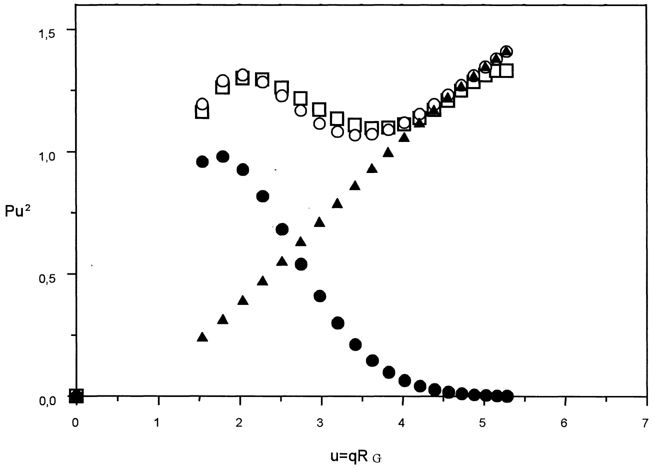

Figure 4: Superposition of particle scattering functions according to Eq. (7c)
□: *P(q)*, measured; ○: *P(q)*, calculated; ●: $P_1(q)$; ▲: $P_2(q)$

As shown in this paper, the angular dependence of light scattering yields important information on the size and shape of the scattering particles. To sum up the results of the light scattering experiments and the discussion of the scattering functions, we propose a model for the structure of the cellulose dissolved in NMMNO. The measured overall scattering function can be assumed as superposition of at least two different particle scattering functions. Two different models could explain this. On the one hand, the solution could contain cellulose particles of different size (and shape), that means a broad size-distribution of the cellulose aggregates exists. On the other hand, the cellulose could form a wide-extended super-molecular structure. The scattering function is determined by the shape and size of the whole particle at small values of q and by a part of this particle at high values of q. The whole particle consist of regions of different density comparable with the core and the fringes of a fringed micelle. However, a decision between these two models based only on static light scattering measurements is impossible.

To obtain additional information concerning particle dimension or dimension distribution the properties of the system studied have to be investigated with other methods. In the case of cellulose dissolved in NMMNO the quasielastic light scattering seems to be a helpful method. The experiments do not show a two-particle system [2]. This is a further reason why we propose a model for the cellulose dissolved in NMMNO which is based on the model of the fringed micelle (Figure 5). The shape of the whole micelle or the core of the micelle show the scattering function of a globular or hyper-branched structure. The shape of the fringes is unknown and cannot elucidate, because the measurable range of qR_G is too small.

To summarise, one can say that the described model for the supermolecular structure of non-substituted cellulose dissolved in N-methylmorpholine-N-oxide-monohydrate is a proposal, which is not a contradiction to the measurements. Nevertheless the model of fringed micelle must be quantified by calculation of the corresponding form factor.

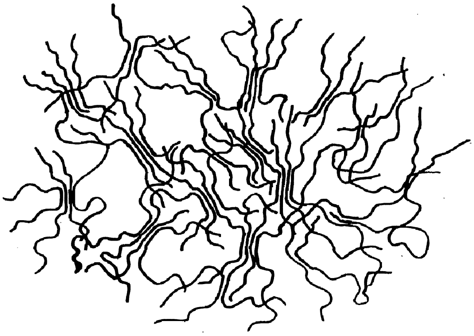

Figure 5: Model for the dissolved cellulose in NMMNO

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