Experimental report

06/09/2022

Proposal: **9-13-985** **Council:** 10/2020

Title: Partially deuterated cellulose derivatives for neutron contrast matching experiments

Research area: Physics

This proposal is a new proposal

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Samples: $C_8H_{16}O_8Na$

Instrument	Requested days	Allocated days	From	To
D11	2	1	17/06/2021	18/06/2021

Abstract:

Cellulose derivatives are an important class of biopolymers, with an estimated production in excess of 10^6 ton/year. While neutron scattering techniques (e.g. SANS or spin echo) are a great tool to understand polymer conformation and dynamics, their application to cellulose polymers remains limited due to the lack of availability of deuterated cellulose. In this proposal, we outline a method to obtain partially deuterated cellulose derivatives. Our approach does not require the deuteration of the cellulose backbone, which is a costly and difficult step and instead relies on introducing HD contrast via acetylation with acetic anhydride. The purpose of the proposal is to demonstrate the feasibility of the proposed method. If successful, this would open up the use of neutron contrast matching techniques to cellulose derivatives and other polysaccharides.

Report on experiment 9-13-985

INTRODUCTION, BACKGROUND & PROPOSAL AIMS

Cellulose based polymers are used in many industrial applications, for example as flow modifiers in food products, cosmetics or oil-drilling fluids, as complexing agents for drug delivery. Compared to common synthetic polymers, which are usually derived from fossil fuels, cellulose derivatives are synthesised from renewable or waste resources. The economic importance of cellulose-based polymers is expected to increase rapidly in the next decades, with bio-polymer production tripling from 2011 to 2020. Of the various available starting products from the earth's biomass, cellulose appears to be the most promising candidate to replace synthetic polymers. For applications requiring solubility in water (e.g. as rheology modifiers), cellulose ethers are at present the most important class of cellulose derivatives.

A current limitation in the study of the behaviour of cellulose derivatives is the lack of availability of deuterated cellulose derivatives. This means that contrast matching experiments, which are widely used to obtain conformational information in the study of synthetic polymers cannot be easily performed. Deuteration of cellulose or other polysaccharides is possible but costly as it typically involves growing plants or bacteria in deuterated media, which is expensive and time consuming. The aim of this proposal is to sidestep this problem by producing partially deuterated cellulose derivatives where the H/D content is not added at the backbone but instead through the substituent groups. With the 1 day of beamtime we sought to obtain preliminary results that would establish the feasibility of the method, with the plan to then submit a follow up proposal for more beamtime if the method could be shown to be feasible.

The scheme shown in Figure 1 outlines the synthesis route to obtain partially deuterated cellulose derivatives. For this proposal, the starting polysaccharide was hydroxypropyl cellulose (HPC). The synthesis steps were carried out using hydrogenated and 99.9% deuterated acetic anhydride. The products are refered to as H-AcHPC and D-AcHPC throughout.

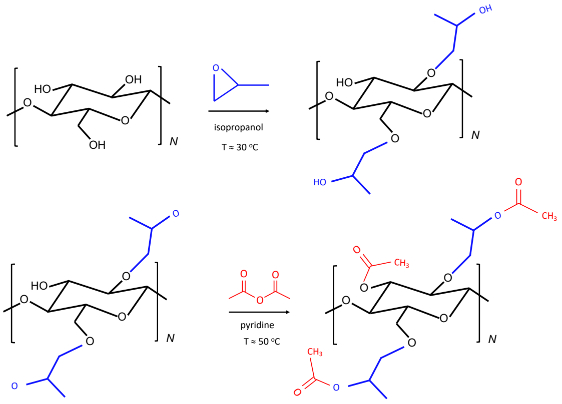

Figure 1: *Reaction scheme for production of partially deuterated cellulose derivatives. First step, shown on the top panel refers to the production of hydroxypropyl cellulose (HPC), which is a commercially available derivative. The bottom panel shows the acetylation step, which was carried out by us using either hydrogenated or deuterated acetic anhydride. This step introduces H/D content on a polymer that is otherwise chemically identical.*

The results obtained in this proposal, discussed in more detail in the next section, showed that the acetylation of the chains lead to two unexpected effects. First, the mass per unit length of polymer (M_L), measured by SANS by analysing the high-q region of the scattering pattern, displayed unrealistically high values. No clear interpretation of this unusual result could be made at this point. However it appears plausible that interchain aggregation and or chain collapse can lead to these results. A further complication is introduced by the fact by the fact that the observed solubilities of the polymers (Ac-HPC) were found to be dependent on the degree of H-content in the solvent (mixtures of CH3OH/CD3OD at different ratios). No clear interpretation could be drawn from these observations. For our future work we plan to move to less polar solvents such as H/D-pyridine, where effects related to deuteration can be expected to be smaller in magnitude.

RESULTS AND DATA ANALYSIS

Figure 1 shows representative scattering patterns for H-AcHPC in deuterated methanol (corresponding to full contrast conditions) for various polymer concentrations. Low concentration samples are measured in 5mm cells and intermediate and high concentration samples were measured in 2mm or 1mm cells to optimised acquisition times. Methanol was chosen as a solvent due to high purity and availability in nearly complete deuterated form. Water could not be used as the addition of acetyl groups to the HPC makes it insoluble in aqueous media. We found that the H-AcHPC displays lower solubility in deuterated methanol than in hydrogenated methanol. The reason for this remains unclear to us at this point and further work is

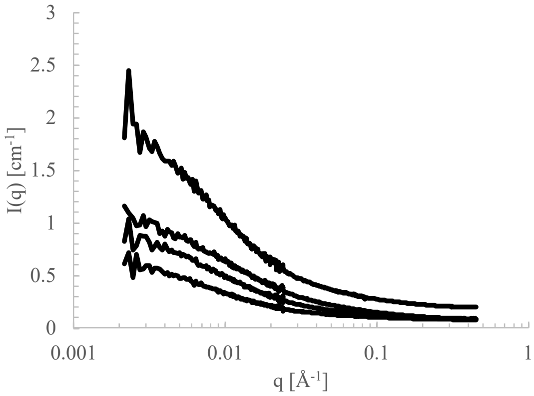

Figure 2: *Scattering profiles for H-AcHPC at different concentrations in MeOD (full contrast conditions).*

needed to elucidate this phenomenon. As will be seen below, the marginal solubility of H-AcHPC in MeOD poses problems in the analysis of the data.

In order to evaluate the data and determine contrast matching conditions it is first necessary to carry out a precise background subtraction. Attempts at calculating the background from the isotopic composition were unsuccessful, with calculated values always yielding background values which were too low. Therefore, we fit the high q data to the following expression:

$$I(q) = Kc\pi/(qb)e^{-q\hat{}2d\_C\hat{}2/4} + Bck \qquad (1)$$

where b is the monomer size and K is a constant which depends on the SLD difference, *c* is the polymer concentration in units of moles per unit volume, and d_C is the chain's cross-sectional diameter. Bck is the background contribution, which arises primarily from incoherent scattering. The cross-sectional diameter d_C was fixed to 10Å, in line with the values obtained in other studies for cellulose derivatives. This value is also close to a calculation of d based on bond lengths for the cellulose polymer.

An example of a fit to Eq. 1 is shown in Figure 3, where equation 1 is seen to provide a good description of experimental data in the high-q region. The samples measured in 5mm cells were found to display values of b (monomer length) identical to those of the samples measured in 2mm or 1mm but the background terms was found to be systematically higher for the 5 mm cells. We do not have an explanation for this unusual feature.[1]

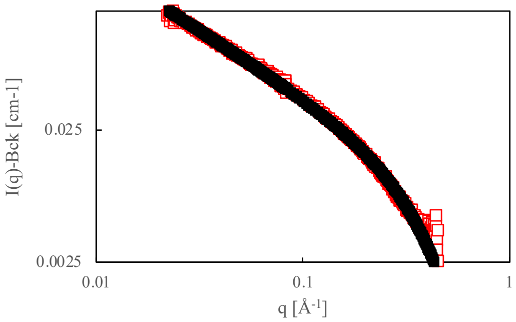

Figure 3: *Example fit of Eq. 1 (black line) to experimental data (red squares). The intensity is shown is after subtracting the background term.*

Figure 4 shows fits to Equation 1 in the Holzer representation (qI vs q), where the height of the low-q plateau is proportional to the mass per unit length of the polymer chain. Based on these fits, the values obtained for the monomer length were found to be b ≈ 1nm, independent of polymer concentration. This is approximately double the value expected from bond length calculations and also from previous experiments on other cellulose derivatives such as NaCMC. Possible sources of error such as moisture content in the polymer powder or misestimation of the monomer molar mass and/or contrast are judged to be less than 10%. Other sources of error such as errors in the calibration are of similar magnitude. Therefore, we the very large value of b ≈ 1nm cannot be attributed to experimental error. Extrapolating the inverse reduced intensity (c/I) to zero concentration did not alter the obtained mass per unit length values. Since the fitted value of b is clearly unphysical because the cellulose chain cannot be stretched to twice it's contour length, we conclude that the most likely explanation is that the term concentration term in equation 1 must take a value of roughly half it's nominal one. This could occur, if for example, a large fraction of the chains are aggregated and contribute to the high-q end of the spectra with a smaller weight than expected for fully dispersed chains. This interpretation is consistent with the observed marginal solubility of the H-AcHPC in deuterated methanol. With regards to the determination of the h-d contrast matching point, because samples in d-solvent were measured primarily in 5mm cells (to minimise acquisition times) and samples in h-rich solvents were measured in 1mm cells (to minimise multiple scattering), no reliable estimate of the contrast matching point could be obtained.

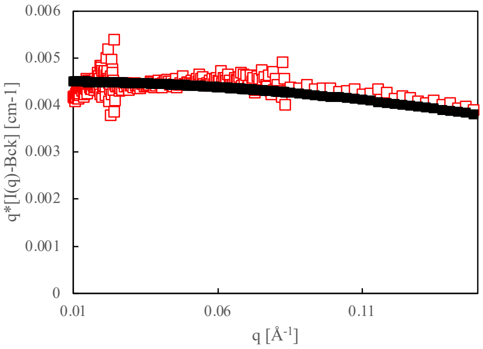

Figure 4: *Same data as in figure 3 in Holzer plot representation. The value of the low-q plateau is proportional to the mass per unit length of the polymer.*

CONCLUSION

For the Ac-HPC/Methanol system the technique proposed in the introduction is not suitable because of the difference in solubility and conformation of Ac-HPC in hydrogenated and deuterated methanol. Therefore, for future experiments we will try less polar solvents, where we expect H/D labelling to have a smaller influence on the solution thermodynamics.

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[1] Note that the reduction protocol by Brûlet, A., Lairez, D., Lapp, A. and Cotton, J.P., 2007. Improvement of data treatment in small-angle neutron scattering. Journal of Applied Crystallography, 40(1), pp.165-177.was employed, which takes into account the angular dependence of the transmission.