Deuterated Polyethylene Glycol Oligomers

now available at JCNS

Polyethylene glycol (PEG) is one of the most widely used polymers. There is a large number of procedures to synthesize PEG and PEG containing materials in the hydrogenous version but also deuterium labelled. The situation is different for oligomeric PEG, having a molecular weight range of about 200 to 1,000 g/mol. These compounds play an important role in pharmaceutical and cosmetic products, in functional fluids like lubricants or in polymer products. In fundamental research oligomeric PEGs are used as building blocks in synthetic chemistry, as solvent but also in many biological applications. Oligomeric PEG is produced industrially in large quantities. So far, procedures for its synthesis in small quantities using ordinary lab equipment do not exist. Consequently, deuterated PEG oligomers are not available.

At the deuteration lab at JCNS we have established a procedure which now allows the synthesis of these compounds in the lab scale. The process is based on the oligomerization of commercially available deuterated ethylene oxide (d-EO) using deuterated and partially potassium metalated ethylene glycol as initiator (see Figure 1). The reaction can be carried out in a steel reactor at a moderately elevated pressure in the batch mode.

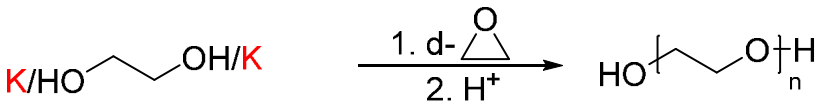

Figure1. Synthesis of deuterium labelled PEG oligomers using partially potassium metalated ethylene glycol-d_4 and ethyleneoxide-d_4 as educts.

The key step of this process is the design of an initiator, which solubilizes in organic solvents. Usually, the transformation of a diol like ethylene glycol to its alkali alcoholate yields highly insoluble products already at low metalation degrees. The same holds for KOH, which is used in industrial high temperature processes for PEG production. This leads to an inhomogeneous initiation process in the ethoxylation step and a broad MW distribution of the product. For this reason, only about 4% of the OH-groups in d-ethylene glycol were replaced by OK-groups with the help of potassium metal and solubilized in 1,4-dioxane. The reaction with d-EO occurred at 100 °C. This procedure was used to synthesize a series of d-PEGs in the molecular weight range between 200 and 600 g/mol. A SEC trace of the product d-PEG 400 is shown exemplary in Figure 2 together with its commercial equivalent. In this case the deuterated variant shows even a slightly narrower MW distribution than the commercial material.

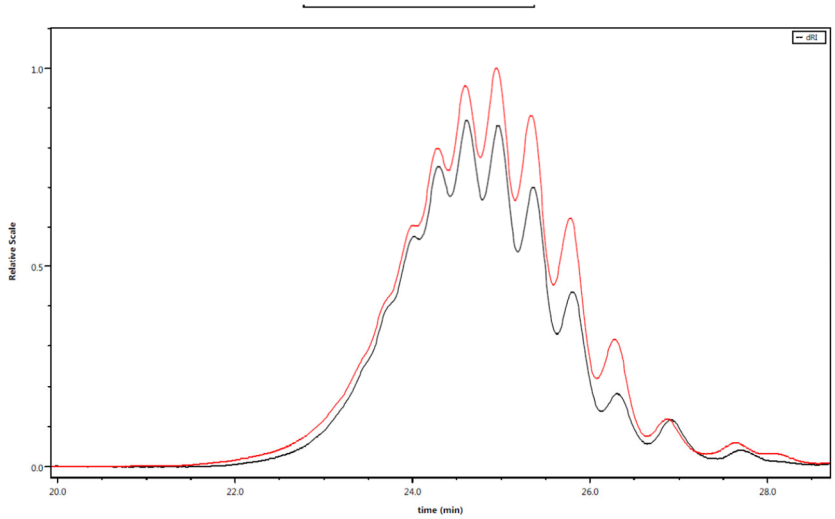

Figure 2. SEC traces of deuterated PEG 400 (black) and the commercial hydrogenous equivalent (red).

As a result of the normal work-up procedure the hydroxyl groups exist in the OH-version. With the help of D_2O, they can be converted to OD. In Figure 3 the ^{2}H-NMR spectrum of deuterated PEG 400 is shown. In pyridine as solvent the OD-end groups appear at 6.0 ppm, the methylene units next to the OD-functionalities are located at 3.85ppm and all residual methylene groups at 3.5 ppm. Using mixtures of h-EO and d-EO, partially deuterated PEGs are accessible. This can be useful for example if a lower scattering length density of the PEG is needed for contrast matching with D_2O.

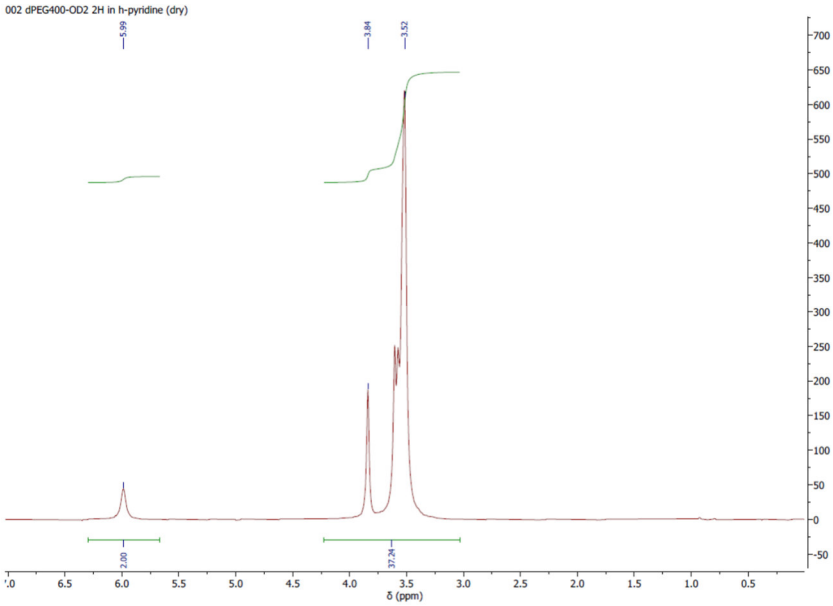

Figure 3. ^{2}H-NMR spectrum of deuterated PEG 400 in dry h-pyridine.