

## **Lab rapport for exercise 2: Rotation diffusion (electrically induced birefringence)**

Introduction: Our objective in this exercise was to measure the transient electrically induced birefringence (TEB) in a macromolecule solution of scleroglucan with different lengths on the excitation pulse and two pulses together to find whether there is a permanent or temporarily dipole. The relaxation time is used to estimate the molecules rotational diffusion coefficient and equivalent axis ratio.

Theory: The alignment of molecules along an axis can be established by placing the molecules in an electric field,  $\vec{E}$ . Rigid macromolecules will align themselves with the field because there will always be induced a dipole momentum in the molecule. In addition, there might be a permanent dipole momentum in the macromolecule.

If the electric field is turned off, the free rotational diffusion will move towards an isotropic distribution. The free rotational diffusions change toward this has a time lapse that is determined by the rotational diffusion coefficient,  $D_R$ . The measuring technique that we used took advantage of the property that a macromolecule solution where the molecules are not isotropically distributed shows optical birefringence. Its purpose was to show the alignment of the molecules, meaning the distribution of the free rotational distribution.

To further elaborate on this part of the theory, an explanation of the terms rotational diffusion and birefringence is needed. The random re-orientation of molecules is an important process for many biophysical probes. Due to the equipartition theorem, larger molecules re-orient more slowly than do smaller objects and, hence, measurements of rotational diffusion constants can give insight into the overall mass and its distribution within an object. A formal definition of rotational diffusion is: a process by which the equilibrium statistical distribution of the overall orientation of molecules or particles is maintained or restored.

The other term was birefringence: crystalline materials can have different refraction-indices associated with different crystallographic orientations. A refractive index describes how light propagates through that medium.

$$n = \frac{c}{v} \quad (1)$$

$n$  = refractive index,  $c$  = speed of light,  $v$  = phase velocity. (1) is the formula for obtaining the refractive index.

Kerr-effect is a change in the refractive index of a material in response to an applied field. In fact, electrically induced birefringence is often referred to as the Kerr-effect. For our exercise it means that when a medium is optically birefringent it means that it has refractive indices  $n_x$  and  $n_y$  that are different for light polarized in the x- and y-direction.

For our discussion and results part we were given a few equations that will most likely be useful there.

$$\frac{I(t)}{I_0} = \frac{\delta^2}{4} \quad (2), \text{ where } I(t) \text{ is the intensity after a certain time, } \delta = \text{phase and } I_0 = \text{where the intensity of the coming in on the polarizer.}$$

Birefringence  $\Delta n$  has a time lapse dependant by  $D_R$ .

$$\Delta n = \Delta n_0 e^{-6D_R t} \quad (3)$$

Where  $n_0$  is equal to  $\Delta n$  at  $t = 0$ .

From this we can derive the decay time. And from the decay time,  $\tau$ , the diffusion coefficient can easily be determined.

$$\tau = 1/(12D_R) \quad (4)$$

When the  $D_R$  is determined we can calculate the friction coefficient,  $f_R$  from the Einstein relation.

$$D_R f_R = kT \quad (5)$$

This again gives the relative rotation friction coefficient,  $F'_R = \frac{f_R}{f_0}$  for spheres.

That leads to

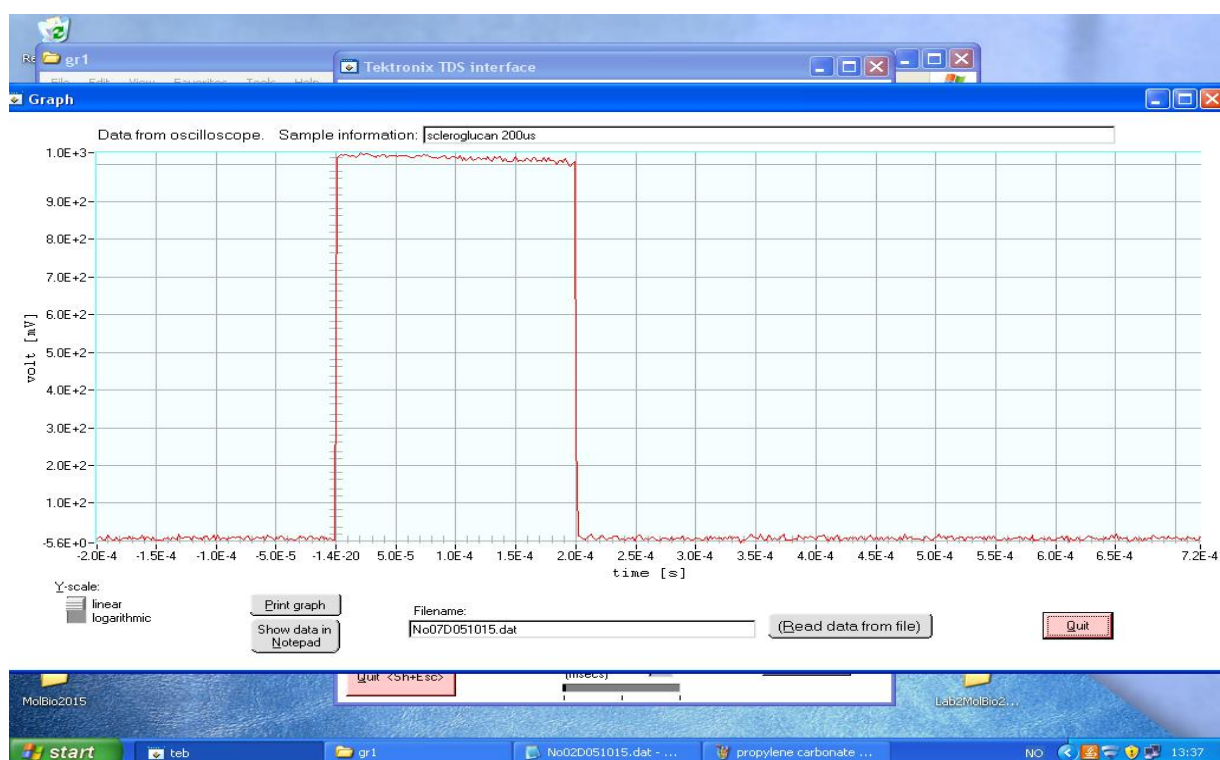
$$f_o = 8 * \pi * n * R^3 \quad (6)$$

The equivalent sphere radius R is established from the molecule weight and the density of the molecule. If we assume that the molecule is rigid and has the shape of an ellipse, we can determine its axis ratio.

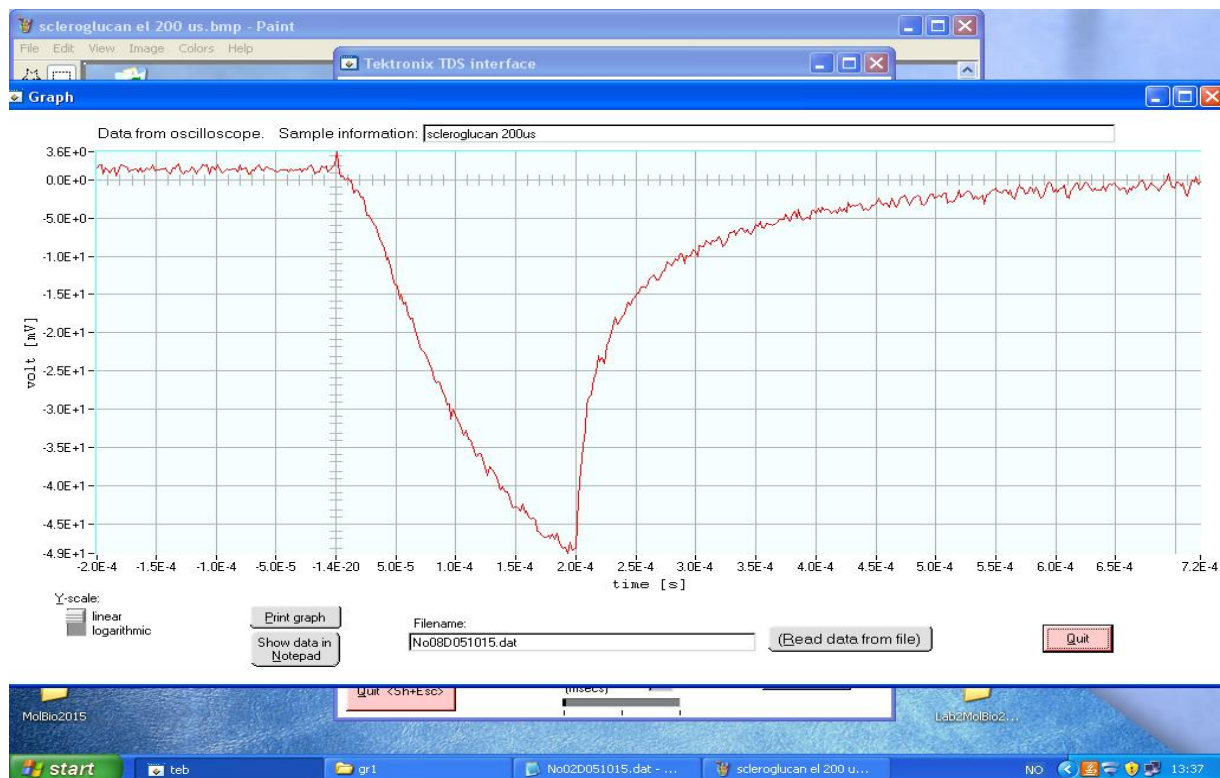
Method and apparatus: The equipment used in this experiment was an Argon-laser. The wavelength of a laser is dependent on the components used to create the laser, so a purely Argon laser gives wavelengths between 530nm and 450nm. Other tools used were scleroglucane, propylene carbonate, oscilloscope, computer, syringe, Kerr-cell, pulse generator, polarisator. A figure of the setup can be found in the walkthrough of the laboratory exercise and is therefore not necessary in this text.

With regard to the actual method, it largely consisted of inserting a sample (of for example propylene carbonate) into the cuvette, that was later placed in the Kerr-cell. The laser is shot through the Kerr-cell and then the analyzer, before it goes through a PM-rod to an oscilloscope that is connected to a computer. We get up several graphs that we are supposed to analyse to achieve our required targets.

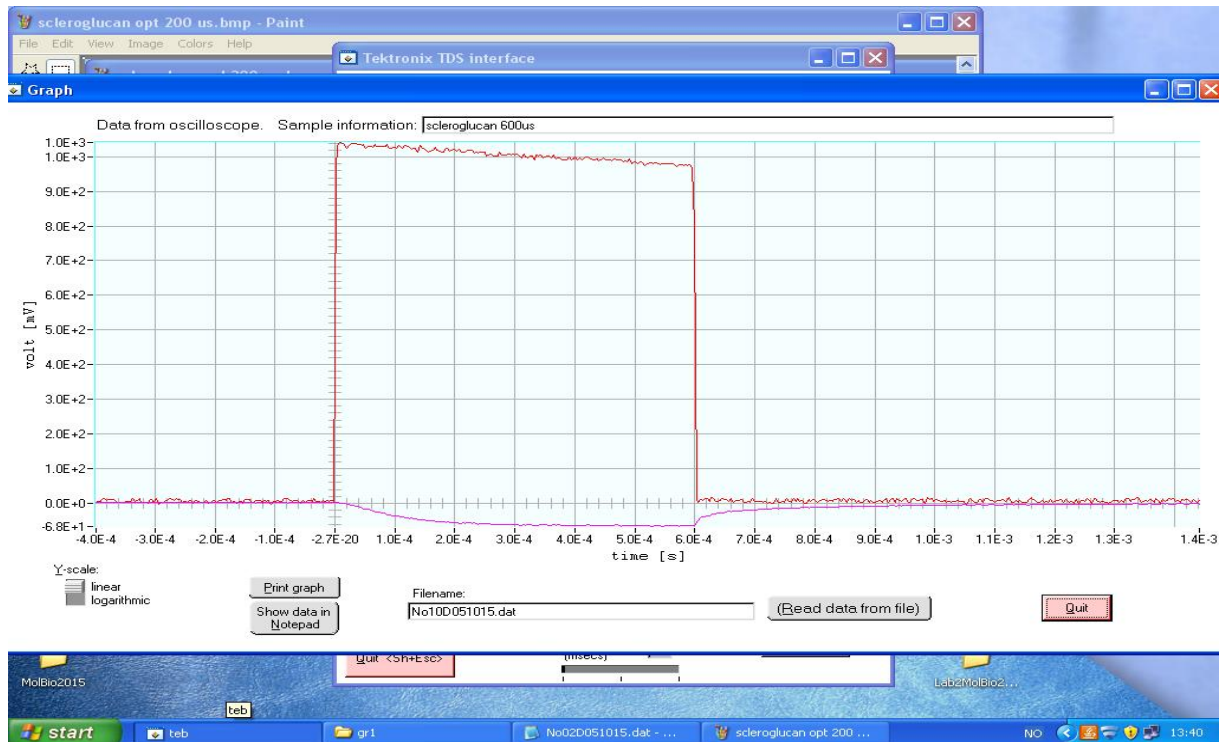
## Result and discussion:



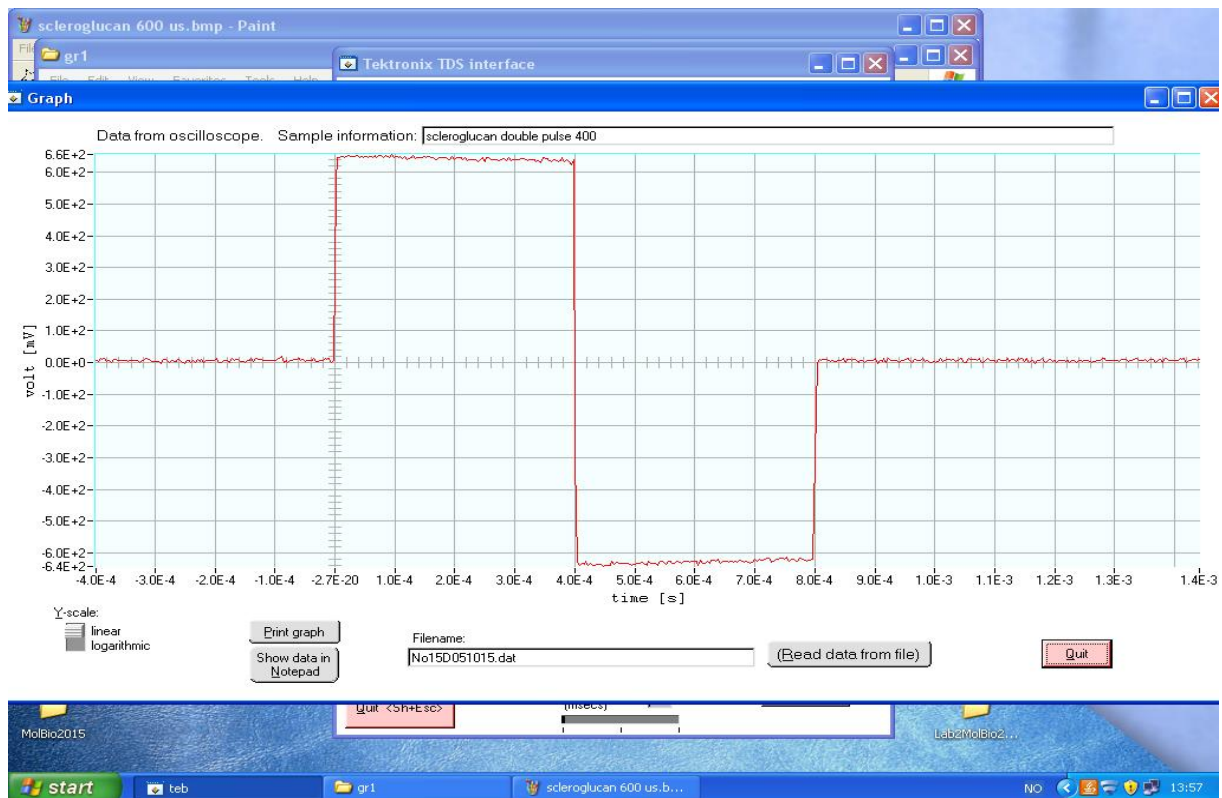
This was the first graph we acquired, it's purely the electric pulse with a pulse length of 200us.



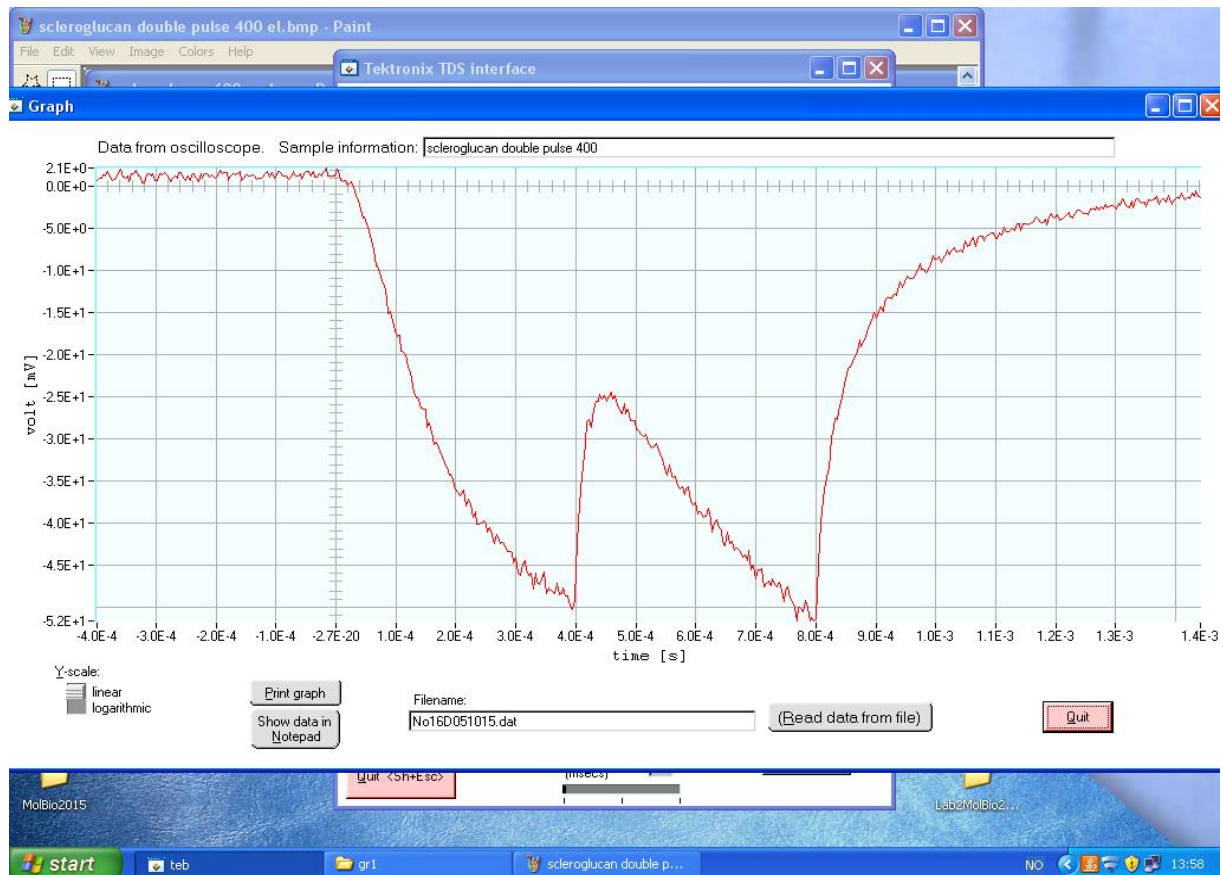
Graph number two, it shows the optical pulse with a pulse length of 200us.



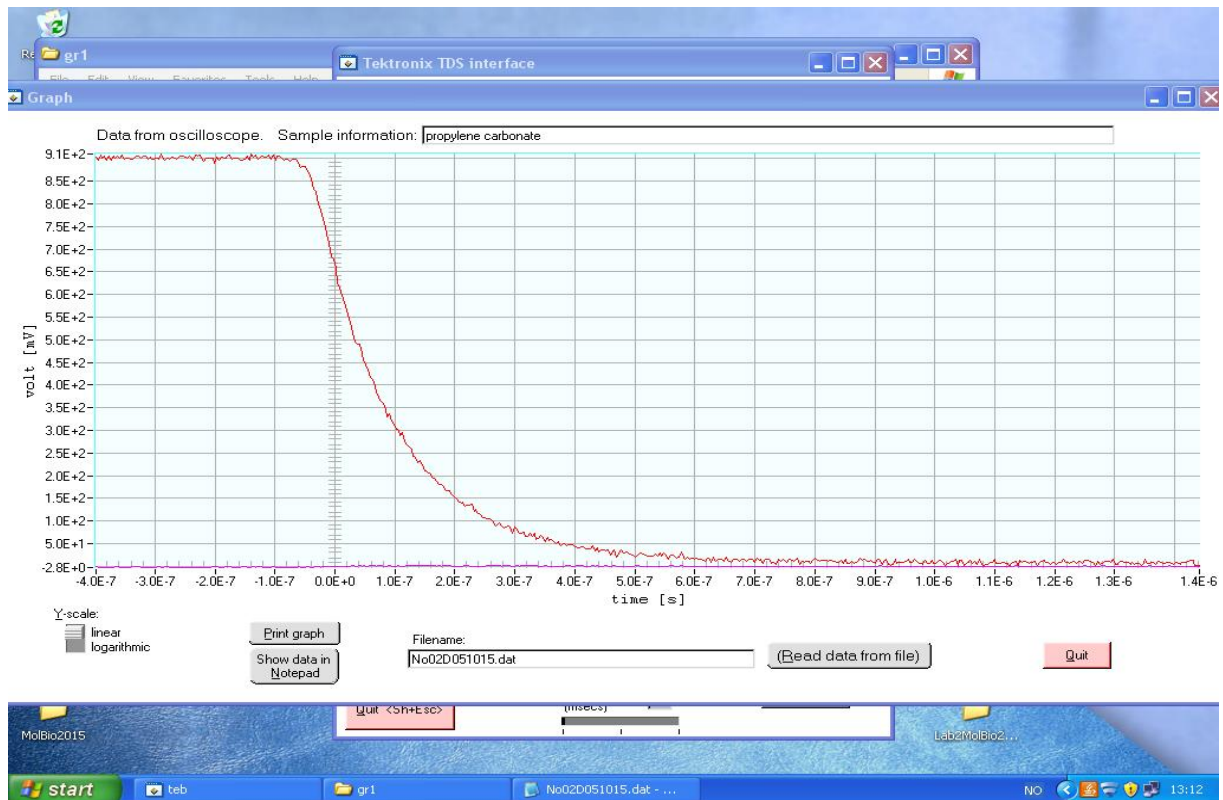
Same material as before, but this time with a laser length of 600us (both optical and electrical)



One of the tasks was to use a double pulse laser on the material to see how it reacts, this is the double pulse for electric with 400us laser length.

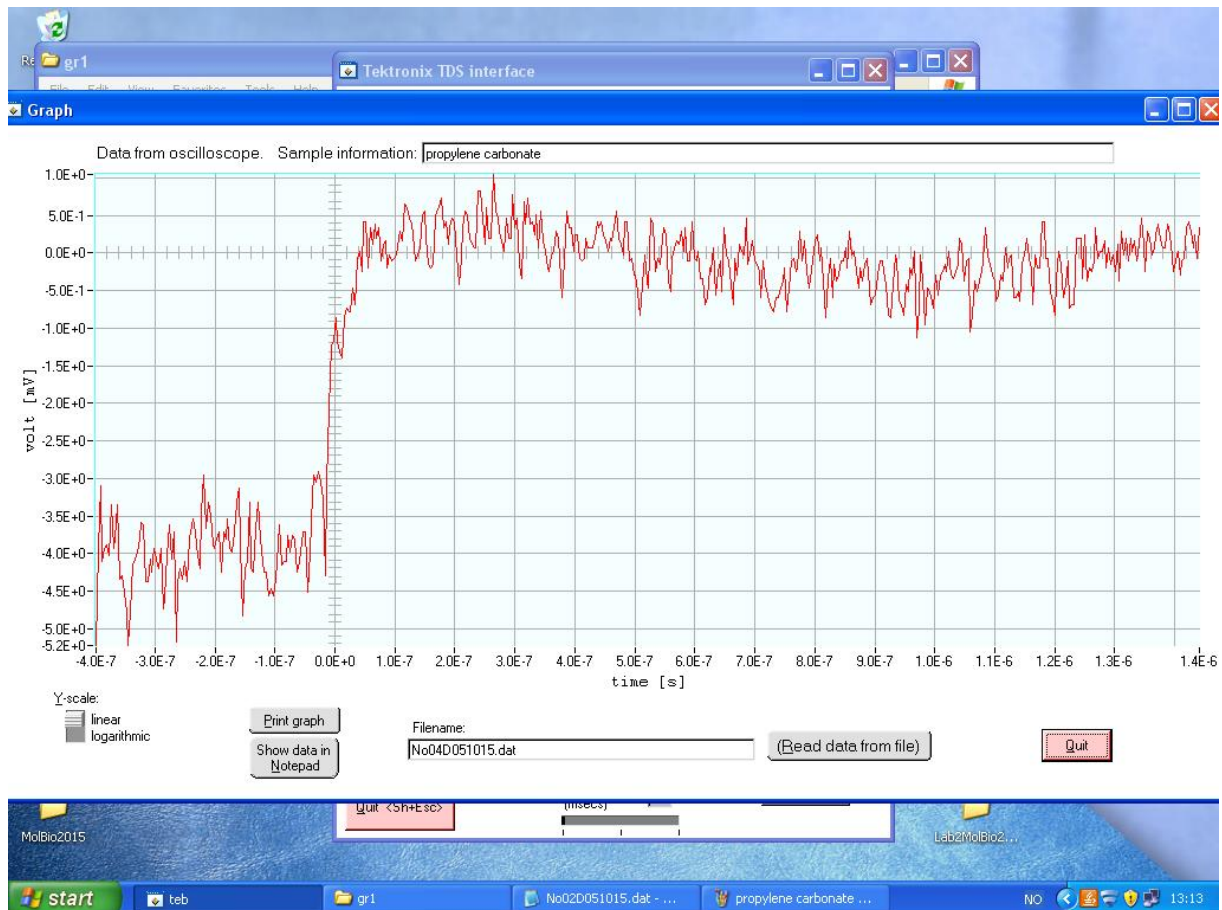


The same as the one graph above, but this is for optical.



We changed material to propylene carbonate in this graph to compare the values, Electric.





The optical values for the new material.

In the discussion part, I will simply respond to the different questions posed to us in the labtext. That should be adequate. But the main findings of this report should be the rotational coefficient, the other coefficients  $f_R$ ,  $f_0$  and  $F'_R$ . The last part was to find the axis ratio, that had to be found graphically.

I will begin with explaining an important term, pulse length. The pulse length is the duration of time the sample is exposed to the pulse. For a given charging pulse length the relaxation time must be significant shorter to ensure maximum charge deposition.

2. In this question, we are supposed to study the different graphs to see if the birefringence is maximally saturated. We will look at the graph with the optical signal and electric pulse together and the one with 200us optical signal alone.

From the optical signal we can see a decrease until 200us. After this we see a upturn up to zero again. So we have a negative voltage that increases while the pulse is on.



For the combined graph, the pulse length is 600us. This indicates the same tendency for the optical signal, while the electric pulse is positive.

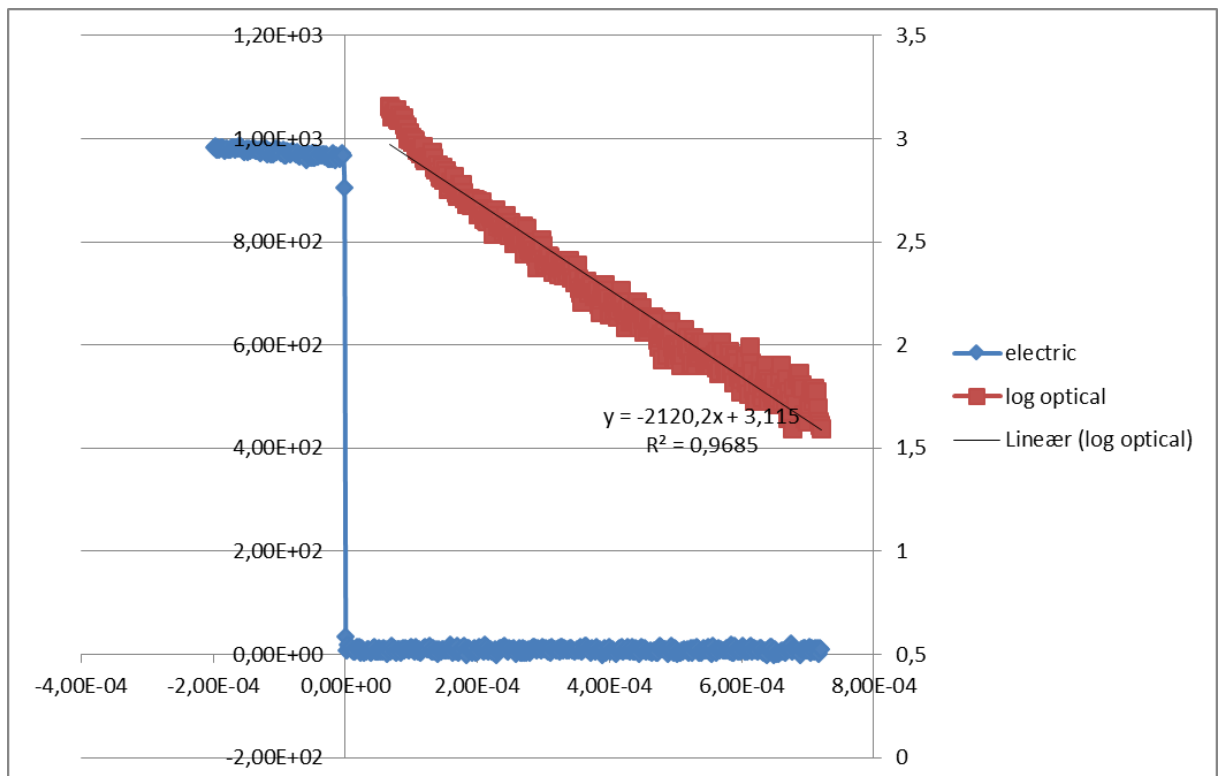
3. The time decay is about  $7.0 \cdot 10^{-4}$  s.

For saturated samples the birefringence is attenuated, meaning decreasing while the pulse goes through the sample, so we can conclude that the birefringence is saturated.

4. No, the relaxation time will not increase as the excitation time increases. This is due to the fact that the sample is saturated. After 200us, the optical signal stops to decrease.
5. First, we have to find the rotational diffusion coefficient. The easiest way to find it, is by using a curve fit of the electric pulse and optical signal. The optical signal represents the intensity as explained in the lab text. Intensity,  $I(t)$ , is the intensity of light we detect after it passed through the sample. We have the this formula for it:

$$\ln I(t) = \ln A_0 - 12D_R t$$

After a curve fitting in excel and consequently a regression of the values, so that we have a function:



We can see from this that we have a graph with  $R^2 = 0.9685$ , so it suffice for our purpose. The function is given by,  $y = -2120.2 \cdot x + 3.115$ . From this we can see that  $\ln A_0 = 3.115$  and  $-12D_R = -2120.2 \cdot x$ .

This again gives that,  $D_R = \frac{2120.2}{12} = 176.67 \text{ s}^{-1}$ . This is the rotation diffusion coefficient. From this we can find  $f_R$ .

$$f_R = \frac{kT}{D_R} = \frac{1.38 * 10^{-23} * 300}{176.67} = 2.3434 * 10^{-23}$$

6. We are going to estimate the relative friction coefficient. The shape is a rigid prolate ellipsoid.

$$F' = \frac{f_R}{f_0}, f_0 = 8\pi * \eta * R^3$$

Spherical volume is given by:

$$V = \frac{4}{3} * \pi * R^3$$

We can also find the volume by density and mass:

$$V = \frac{m}{p} = \frac{3.5 * 10^6}{1.61} = 2173913.043 \frac{\text{cm}^3}{\text{mol}}$$

The volume per molecule then becomes:

$$V_1 = \frac{V}{N_A} = \frac{2173913.043 \frac{\text{cm}^3}{\text{mol}}}{6.022 * 10^{23} \frac{\text{molekyler}}{\text{mol}}}$$

$$V_1 = 3.60995 * 10^{-18} \text{cm}^3$$

We put this answer in the formula for the spherical volume and find the radius of one molecule:

$$3.60995 * 10^{-18} = \frac{4}{3} * \pi * R^3$$

$$R^3 = 8.618 * 10^{-19} \text{cm}^3 = 8.618 * 10^{-25} \text{m}^3$$

*Then we'll get this for the rotation friction coefficient for a sphere*

$$f_0 = 8\pi * 10^{-3} * 8.618 * 10^{-25}$$

$$f_0 = 2.166 * 10^{-26}$$

$$F'_R = \frac{2.3434 * 10^{-23}}{2.166 * 10^{-26}} = 1081.90$$

7. In this assignment we were told to find the axis ratio. I used the MATLAB-coding that we were given to find this. The values that we found were:

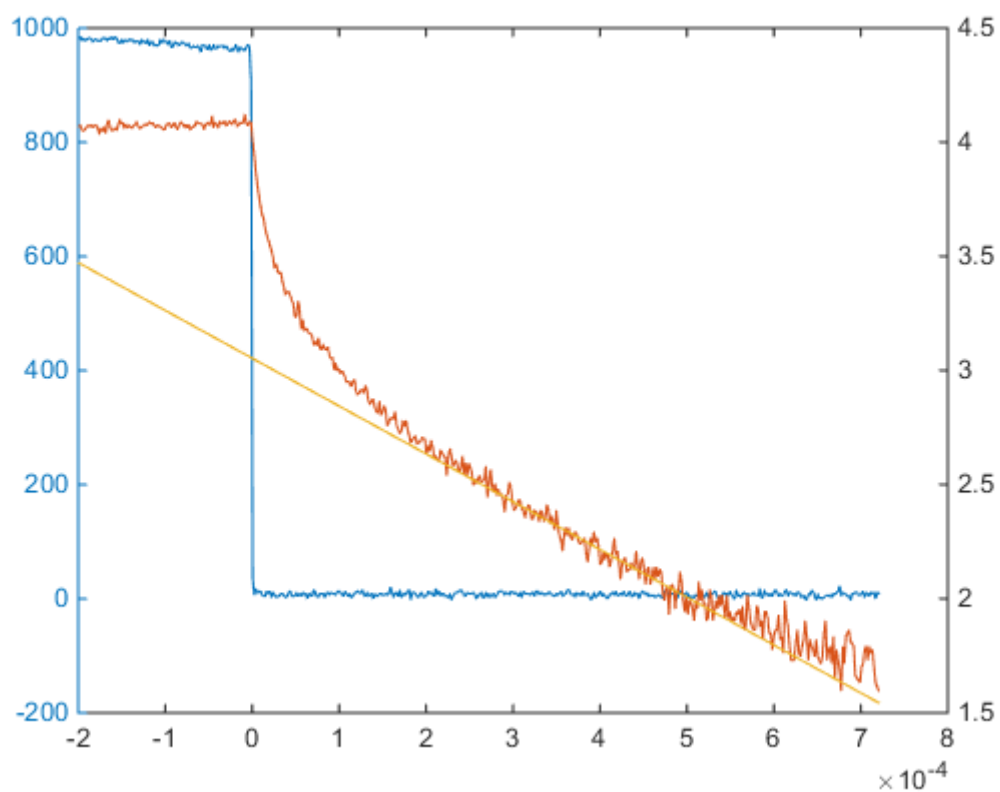
$$D_R = 174.5347$$

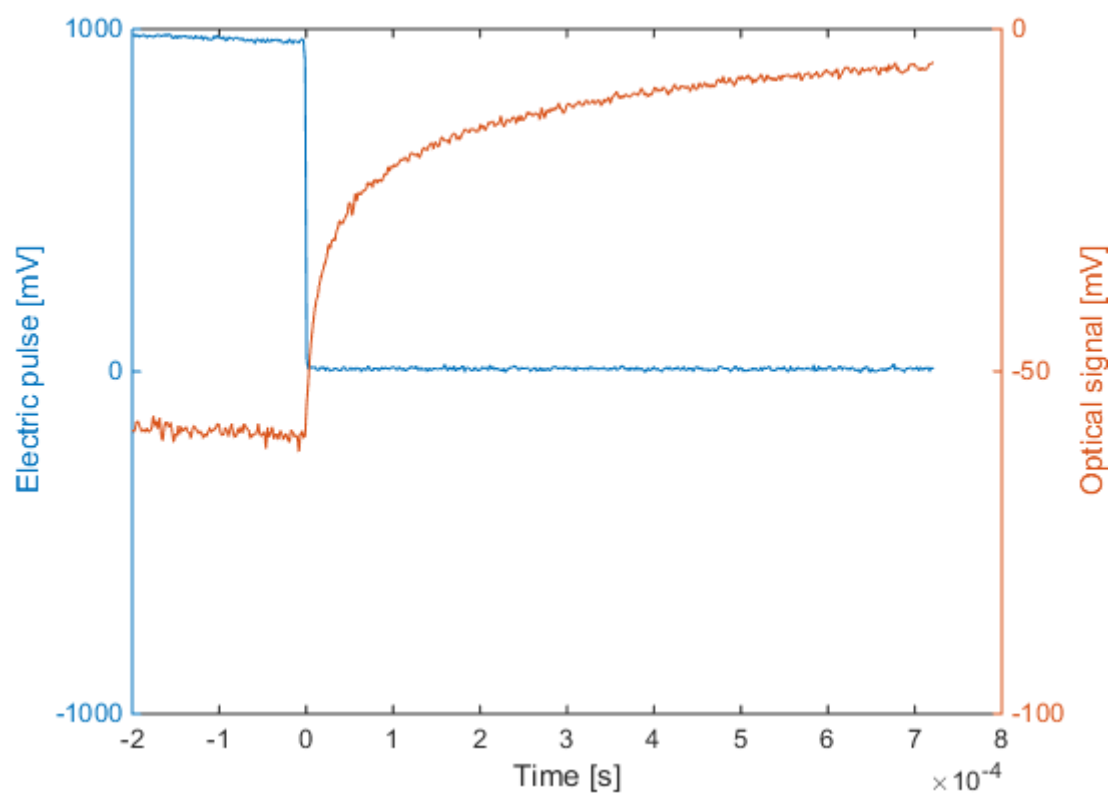
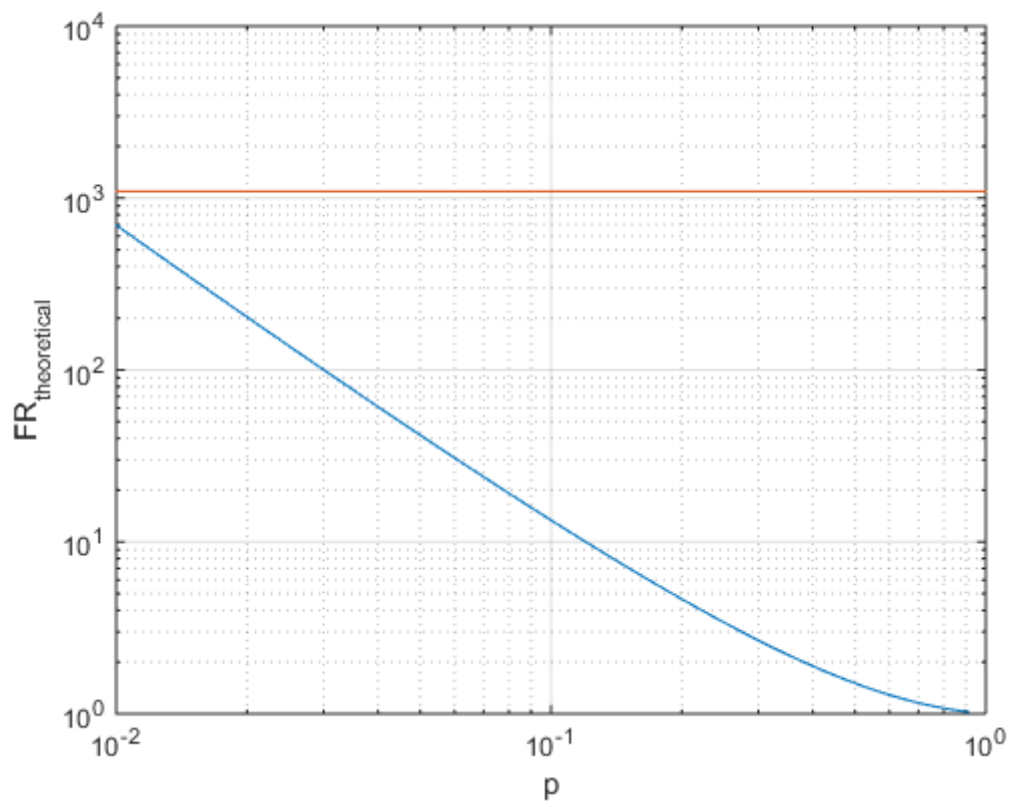
$$f_R = 2.3720 * 10^{-23}$$

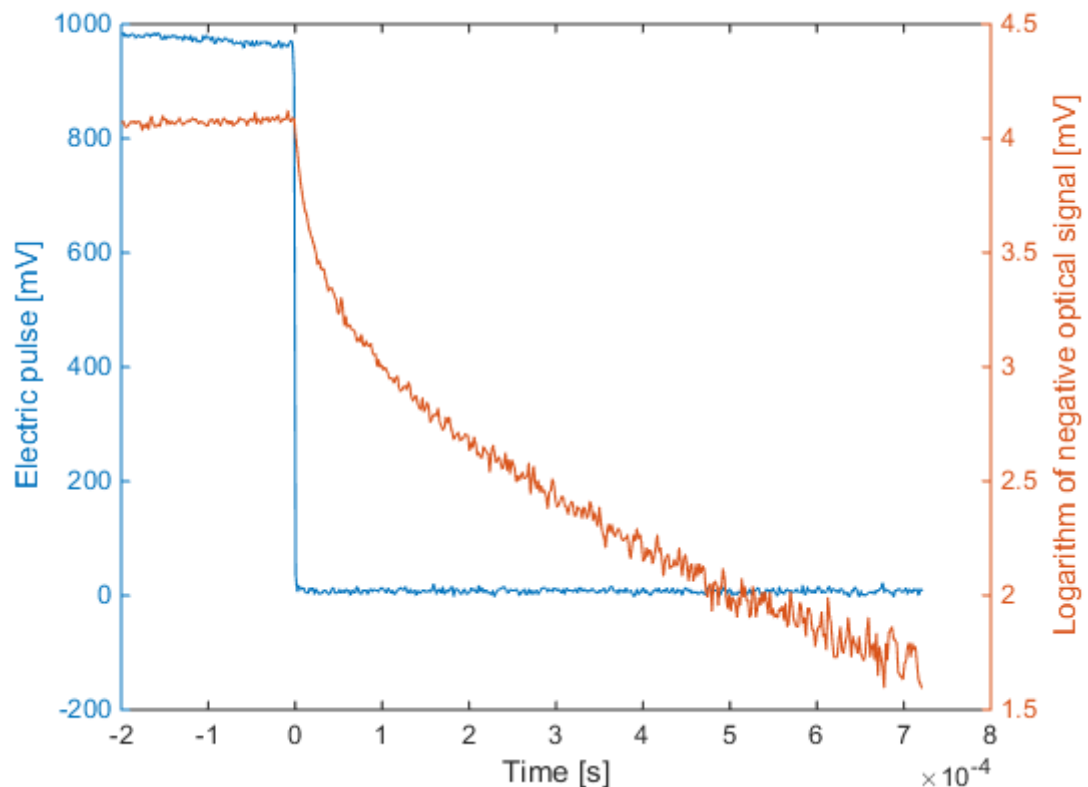
$$f_0 = 2.166 * 10^{-26}$$

$$F'_R = 1095.1$$

These values were based on these graphs that we found with MATLAB:







With regards to the comparison with the graph of the prolate  $< 1$  in the compendium, we can see from the last graph that they are quite similar and therefore our values are most likely to be true.

8. From the studying of the double pulse graph it is clear that there is a permanent dipole rather than a induced dipole.
9. From H we have that the relaxation time for the graph is  $0.2 \cdot 10^{-7}$  s. The decay time of the electric pulse is roughly  $6.0 \cdot 10^{-7}$  s. As we can see they are kind of close, but still different. The difference might of course be due to personal reading error. The relaxation time of the scleroglucane is about  $7.0 \cdot 10^{-4}$ . We can see that the relaxation time of propylene carbonate is considerably less, which was also assumed in the laboratory manual. Propylene carbonate molecules are very small, is the conclusion from assignment 9.

### **Conclusion:**

First of all the most obvious conclusion is that there is a considerable size difference between the two materials that we tested, with regards to the molecules. We can also conclude that with an oscilloscope and a laser, you have the tools to correctly analyse macromolecules and

their electronical properties. The rotational and friction diffusion coefficients are related and are good tools for measuring material properties.