Molecular dynamics in thin glassy films
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In this Chapter, we describe the glass-formers we have used in our experiments and their bulk properties. We also explain how we make uniform thin films and characterise their quality.

Among all families of materials presenting a glass transition we can mention: amorphous polymers, network materials (oxides), alcohols, molten salts, orientationally disordered crystalline materials and other complex liquids. In this thesis we have studied materials (Fig 2.1) that belong to the polyalcohols family. These materials are characterised by the presence of hydroxy functional groups that are known to create H-bonded networks. Our compounds carry elongated stiff side-groups that can give rise to a liquid crystalline behaviour.

2.1 Hydrogen-bonded glass-formers

In the plot of the relaxation time versus $T_g/T$, as originally done by Angell [9, 84], alcohols [85] and polyalcohols [86] are found to occupy the intermediate region between
 Hydrogen-bonded glass-formers in thin films

<table>
<thead>
<tr>
<th>Glass former</th>
<th>$T_g$ (K)</th>
<th>$m(T_g)$</th>
<th>$\beta(T_g)$</th>
<th>$\beta_{pred}=(250-m)/320$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>375</td>
<td>139</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Poly(propylene glycol)</td>
<td>197</td>
<td>117</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>274</td>
<td>93</td>
<td>0.50</td>
<td>0.49</td>
</tr>
<tr>
<td>1,2,6-Hexanetriol</td>
<td>202</td>
<td>74</td>
<td>0.60</td>
<td>0.55</td>
</tr>
<tr>
<td>Salol</td>
<td>218</td>
<td>73</td>
<td>0.60</td>
<td>0.55</td>
</tr>
<tr>
<td>1,3-Butanediol</td>
<td>173</td>
<td>65</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>Glycerol</td>
<td>190</td>
<td>53</td>
<td>0.65</td>
<td>0.62</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>167</td>
<td>52</td>
<td>0.61</td>
<td>0.62</td>
</tr>
<tr>
<td>$n$-Propanol</td>
<td>109</td>
<td>40</td>
<td>1.00</td>
<td>0.66</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1500</td>
<td>20</td>
<td>0.70</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 2.1: Glass transition temperature $T_g$, fragility $m(T_g)$, stretch exponent $\beta(T_g)$ and exponent predicted by Eq. 1.10, for various H-bonded materials compared to the fragile polystyrene and strong silica. The measurements were performed with different techniques (see [9] and references therein).

strong and fragile extremes. In Tab. 2.1 a few H-bonded glass-formers are listed by descending fragility, compared to two extreme soft and strong materials that are polystyrene and SiO$_2$. Monohydric alcohols tend to be stronger than polyalcohols, whose fragility is closer to that of polymeric materials.

One peculiar feature of hydrogen-bonded glass-formers is the fact that, for many of these materials, the observed relaxation processes (in particular measured by dielectric spectroscopy) exhibit time dependences closer to a single exponential that what is expected from their fragility [9]. In other words, their stretch exponent $\beta$ appearing in the KWW law (Eq. 1.9) is closer to 1 than predicted by the law generally valid in glasses (Eq. 1.7). Especially monohydric alcohols exhibit strictly Debye-like relaxations (see propanol in Tab. 2.1). The general $m(\beta)$ law becomes more valid as the number of OH groups per molecule increases, in particular for polymers.

2.2 Glass-formers with mesogenic side-groups

Glass-formers with mesogenic side-groups combine the dynamic features of glasses with the optical properties of fluid liquid crystals, making them interesting for
2.3 Our materials

Electro-optical and optoelectronic applications. The first low-molecular-weight liquid crystalline glass-formers discovered in the '70s [87, 88] suffered from having low glass transition temperatures [89, 90], often below ambient temperature. Many of them presented morphological instabilities with a tendency to recrystallise upon thermal cycling between the glass phase and the isotropic liquid. Only recently [91, 92, 93] new substances have been discovered with \( T_g \) high enough to make them suitable for example as optical memories or retardation layers in liquid crystal devices. One usual synthetic way consists in attaching elongated mesogenic pendant groups to a rigid core through flexible spacers. In general, the glass forming ability is due to mutual volume exclusion effect between the rigid core and the flexible elongate mesogenic group, avoiding crystallisation. In our material [91] the glass formation is mainly due the ability of hydrogen-bonded network formation. When these materials are cooled down from the isotropic phase, they show first one or several liquid crystalline phases before the glass transition occurs, freezing in the structure of the last liquid crystalline phase.

2.3 Our materials

The two glass-formers used in this thesis (Fig. 2.1) were originally synthesised and patented by Akzo-Nobel [91] that provided the first batches of both materials. Later a second batch was synthesised by W. Jager and P. Kouwer in the Polymer Materials and Engineering group at the University of Delft. The two compounds are made of a sulfonic core and four identical branches, each of them supporting one hydroxy group. The difference between the two glass-formers comes from the end-group attached at position 4' on the biphenyl groups. A hydrogen substituent leads to the simple glass forming material [A] = \( \text{C}_7\text{H}_{68}\text{N}_{2}\text{O}_{10}\text{S} \) (Mw=1153.42 Da, \( T_g = 78/85 \) °C, for the \( T_g \) determination method see Sec. 2.3.1). With a cyano substituent in position 4' we obtain, for the pendant group, the well-known cyanobiphenyl mesogenic group widely used in liquid crystal science [94]. With this substituent, one gets the material [B] = \( \text{C}_7\text{H}_{64}\text{N}_{6}\text{O}_{10}\text{S} \) (Mw=1253.46 Da) that exhibits a nematic liquid crystalline phase (with the mesogenic groups parallel in average to each other). The compound has a nematic-isotropic transition \( T_{ni} = 137 \) °C and a glass transition \( T_g = 106/110 \) °C. However, we have never observed any birefringence in our films, even when they were thick enough for birefringence to be detected by polarisation microscopy. We have no indications that a possible mesogenic character of the molecules plays any role in our experiments.
We have studied on both compounds the effect of confinement on the glass transition (Chap. 3). With compound [B] that carries non-linearly polarisable groups (cyanobiphenyl groups), we have also performed dynamic second-harmonic generation measurements to study the reorientation dynamics under confinement (Chap. 6). The advantage of these low-molecular-weight glass-formers is their relative simplicity.

The more widely used polymers have the disadvantage of having dynamics involving more complicated relaxation processes that are often hard to distinguish in narrow temperature ranges. In thin films, the confinement of polymer chains often complicates the dynamic behaviour. Moreover, small molecules can be obtained with a higher chemical purity and without molecular weight or composition distribution. The small size of our molecules has however the disadvantage that the

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**Figure 2.1:** *Chemical structures of the compounds used in this thesis.*
2.3 Our materials

![DSC scan for compound B](image)

Figure 2.2: DSC scan for compound [B]. 1 and 3 are respectively the first and second heating run and 2 is the intermediate cooling run.

**characteristic lengths in the system should be smaller than in polymeric systems. As a consequence, confinement effects will appear at smaller film thicknesses.**

### 2.3.1 Bulk characterisation

Our materials have been characterised by DSC, NMR and UV-visible. The chemical-physical characterisation was performed to localise the bulk glass transition temperature and to evaluate the purity of the samples. The two samples presented good solubility in aromatic ethers, esters and phenols. On the other hand poor solubility was encountered in linear alcohols and hydrocarbons.

**Differential scanning calorimetry (DSC)**

The glass phase transition and the nematic-isotropic transition (for compound [B]) were determined by DSC by use of a Perkin Elmer differential calorimeter. Samples were measured over the temperature range from -34 to 200 °C using heating-cooling rates of 20 Kmin$^{-1}$. DSC thermographs (Fig. 2.2) present two main features during heating: an increment of specific heat at the glass transition and a peak for the

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1We thank S.J. Picken, W. Jager and P. Kouwer of the Polymer Materials and Engineering group at the University of Technology of Delft, for providing DSC and NMR characterisation. NMR analyses were performed by J.A.J. Geenevasen at UvA
Figure 2.3: *UV-visible absorbance spectra for compound [A] (circles) and [B] (squares) in chloroform solution*

Nematic-isotropic transition. The reported values for $T_g$ are the onset and endpoint of the isobaric heat capacity jump and $T_n$ is the temperature at the heat flow peak maximum evaluated on the second heating run (3 in Fig. 2.2).

**UV-visible spectroscopy**

Fig. 2.3 shows the UV-visible absorbance spectra over the wavelength range 250-400 nm for the two compounds considered. Aromatic rings typically absorb in the UV region of the spectrum. For compound [B] we observe a shift of the peak to longer wavelengths due to the electronegative CN functional group. The peak is centered around $\lambda_{max}=293$ nm. Note that the 266 nm frequency used in our second-harmonic generation experiments in Chap. 5 and Chap. 6, falls on a shoulder of the peak. We can then deduce that the generated second-harmonic frequency will undergo a small internal absorption in the material.

**Nuclear magnetic resonance (NMR)**

Proton and carbon nuclear magnetic resonance in CDCl$_3$ and TMS were performed to verify both the correct structure and the purity of the synthesised materials. $^1$H NMR spectra (Fig. 2.4) showed four multiplet in the 3.2-4.6 ppm region as indication
of the resonance of the three different groups of aliphatic hydrogens and the hydroxy hydrogens. At lower magnetic field three groups of multiplets were present in the 6.8-7.7 ppm region as fingerprint of the aromatic hydrogens. Unfortunately the spectra were not clear enough to make a definitive assignment of each peak to a hydrogen position in the molecules. An indication for the quality of the sample was the ratio of the area of the peaks corresponding to aliphatic hydrogens over that corresponding to aromatic hydrogens. The ratio 28/40 for compound [A] and 24/40 for compound [B] is in good agreement with the proportion of the different hydrogens of the molecules displayed in Fig 2.1. $^{13}$C NMR spectra ($\delta=0$-170 ppm) did not give further quantitative information besides localising the carbon resonance for the cyano groups at 118.9 ppm for compound [B].

### 2.4 Thin films

We have studied the behaviour of the above glass-forming materials in the form of thin films. These films were obtained by spin coating from a solution. The thickness and quality of these films were characterised by x-ray reflectivity (see Chap. 3) and atomic force microscopy, as described below.
2.4.1 Spin coating

Spin coating is widely used for the deposition of uniform thin films. A liquid solution of the desired material is deposited on the substrate, which is then brought into rotation around the normal to the surface for a fixed time, with a rapid initial acceleration. The centrifugal force of the spinning induces a radial flow of the solution with most of the solution being ejected off the surface. Subsequently the solvent evaporates leaving a solid-like thin film of the solute on the substrate [95].

The final thickness of the film was first predicted with a simple model developed by Meyerhofer [96] who considered a decoupling of the fluid flow in the first stage of the spinning from the solvent evaporation in a second stage. In the first stage, the system is then simply a Newtonian liquid flowing on a rotating surface [97]. The real situation is more complicated because evaporation takes place already during this first stage. The coupling of the flow and the evaporation makes the modeling rather challenging and it can only be solved numerically. Most of the previous studies [98] were conducted on polymer solutions, but they can also be applied in our case. A scaling law was found for the final film thickness

\[ h_0 \propto \left( \frac{\eta_0}{\rho \omega} \right)^{1/2} x_s, \]

where \( \eta_0 \) and \( \rho \) are the viscosity and density of the solution respectively, \( \omega \) is the spinning speed, and \( x_s \) is the solute mass fraction in the solution. The important parameters are then the spinning speed, and the viscosity and boiling point of the solvent. Experimentally the spinning speed is tuned in a small range, thus it has a small influence on the final thickness as verified by extensive experiments by Hall et al. [99] for thin \( (h_0 > 200 \text{ nm}) \) and ultrathin \( (h_0 < 200 \text{ nm}) \) polymer films. The dependence of the film thickness on the concentration for polymers follows different power laws depending on their molecular weight.

Fig. 2.5 shows the thickness \( h_0 \) we measured on our spin coated films for compounds [A] and [B]. The thickness was varied by changing the concentration of solute in the solution from 1 to 40 mg ml\(^{-1}\) while keeping the rotating speed constant at 2000 rpm for a total spinning time of 30 sec. Both materials fall on the same trend line. For polystyrene films [100] it was noticed that the linear power law of Eq. 2.1 fits the thickness dependence only for the dilute regime while for the semi dilute regime or for high molecular weights, the exponent in the power law is higher than 1. Our data also showed two slightly different regimes. For concentrations \( C > 5 \text{ mg ml}^{-1} \) the least square fit for the data is purely linear, \( h_0 = (29 \pm 1)C \), while for concentrations \( C < 5 \text{ mg ml}^{-1} \) the thickness varies as a power law \( h_0 = (37 \pm 1) \cdot C^{0.85} \). The interpretation of this behaviour goes beyond the scope of this thesis.
The choice of the solvent can be determinant for the quality of the final films. Very volatile solvent tends to yield rough film surfaces. Therefore we avoided using highly volatile solvents and chose to prepare solutions from cyclopentanone (b.p. 130.65 °C, \( \rho = 0.948 \text{g cm}^{-3} \)). The phase diagram for compounds [A] and [B] in cyclopentanone was not known. Both compounds were completely soluble in the range of used concentration. For all spin coated films we observed smooth free interface of the films as spun. This behaviour can be interpreted as the absence of a critical point in the phase diagram, beyond which demixing would occur, or as the freezing-in of the configuration before crossing this critical point during solvent evaporation.

Solutions were spin coated on fused quartz plates (24x15x2 mm). To ensure reproducibility and clean surfaces, the plates were cleaned in a bi-chromate sulfuric acid solution for 24 hours, rinsed in deionised water and dried at 120 °C. Cyclopen-
Figure 2.6: *AFM scan (top) and thickness profile (bottom) of a spin coated film from a cyclopentanone solution of compound [B] (2 mg ml⁻¹) at the edge of a dewetted area.*

tanone solutions were filtered prior to deposition with Fluoropore™ filters (500 nm pore size) from Multipore. Filtering solutions is an essential step to avoid solid particles which would induce macroscopic striation during the spin coating deposition, leading to inhomogeneous film thicknesses.

### 2.4.2 Characterisation by Atomic Force Microscopy (AFM)

To check the quality of the films, we have also performed topographic measurements with an atomic force microscope in tapping mode. AFM measurements were performed with an Explorer™ scanning probe microscope from ThermoMicroscope using a non-contact silicon cantilever with a set point amplitude of 65%. Just after spin-coating, most of the films are perfectly uniform in thickness, with a roughness
2.4 Thin films

Figure 2.7: AFM scans of a thin film (as-spun thickness 94 Å) of compound [B] obtained from a cyclopentanone solution (3 mg ml$^{-1}$), after 5 (left) and 10 (right) hours annealing at 120°C.

...of at most a few nm (peak to peak). Some of the films exhibit dewetted areas that arise from nucleation of a dry spot at a macroscopic defect. The dewetting process generates an accumulation of material on a ridge along the dewetted area as seen on the top image in Fig. 2.6. The film thickness could be measured directly from the height difference between wetted and dewetted points far off the ridge. For the image shown in Fig. 2.6, the spin coated thin film was obtained from cyclopentanone solution of compound [B] with a concentration of 2 mg ml$^{-1}$. From the calibration curve obtained by x-ray reflectivity, we expect a thickness of approximately 67 Å. The bottom image of Fig. 2.6 shows a height profile from the topographic image. The height difference between the left (wetted) and right (dewetted) sides of the ridge is ~6 nm, which is in good agreement with the reflectivity result.

Before performing measurements on our films, they received a well-defined thermal treatment (see Chap. 3 and Chap. 5) including a first heating up of the as-spun films into the liquid phase.

It had already been observed by x-ray reflectivity that films of compound [B] with a thickness between 40 and 100 Å become unstable during the first heating and break up into droplets [101]. This is the so-called dewetting. This dewetting process has been attributed to the restructuring taking place in the film during the first heating of the film after deposition. The film rearranges then from the disequilibrium state left after the quick evaporation of the solvent [101, 102]. This restructuring involves a densification of the interfacial layer with a motion of the molecules towards the interface. This creates regions of reduced density in the material. The resulting density difference destabilises the free interface causing surface modulations. The
mechanism resembles the amplification of thermally activated surface waves that leads to spinodal dewetting in thin films [103].

We have used AFM measurements to confirm the development of the instability and follow it in time. For this we have first annealed the films at 45°C for 5 hours before the temperature was further raised at 0.25 Kmin⁻¹ up to 120°C above $T_g$. The films were then annealed for a certain time at this temperature under dry nitrogen and then quenched at room temperature to solidify the conformation developed during annealing.

In Fig. 2.7 we show the case of a 94 Å thick film (as-spun). It does not show any dewetting after 1 hour of annealing at 120°C, but after 5 hours (left image in Fig. 2.7) dry patches have appeared. After 10 hours (right image in Fig. 2.7) the material is concentrated in ridges in between dewetted areas. It is unclear from these images whether the film has dewetted by the growth of fluctuation of the free surface with a rather larger wavelength, or by nucleation. Thinner films (67 Å as-spun) clearly show surface fluctuations of the free surface with a smaller wavelength (Fig. 2.8).