MODELING AND ANALYSIS OF LIGHT-INDUCED PHASE SEPARATION IN LIQUID CRYSTAL-POLYACRYLATE SYSTEMS

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Modeling and analysis
of light-induced phase separation
in liquid crystal-polyacrylate systems

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Abstract

During holographic exposure of monomer and liquid crystal (LC) mixtures, phase separation (PS) can take place. Then, a liquid phase (monomer and LC) and a polymer phase (polymer, monomer and LC) coexist. In order to obtain separated polymer and LC layers using PS, the polymerization rate and the diffusion rate need to be balanced. A phase separation model and a reaction-diffusion model were combined to study this. Subsequently, a Bragg grating prepared from a blend of monomers (67 wt% dipentaerythritolhydroxypentacrylate, 15 wt% N-Vinyl-Pyrrolidone and 18 wt% hexafluoro bisphenol ‘A’ diacrylate) and LCs (E7) was used to verify the model.

Firstly, a model describing the PS behaviour during the formation of Bragg gratings is proposed. The van der Waals interactions, represented by the interaction parameter \( \chi \); 0.5 for infinitely long polymers, were found not to induce PS. However, network elasticity, reflected by an efficiency factor \( 0 < \epsilon < 1 \), did. Decreasing either \( \chi \) or \( \epsilon \) shifted the PS-line to higher monomer conversion. Above a critical LC concentration, a nematic ordered liquid phase was present, in addition to the isotropic liquid phase.

For the holography mix, the conversion at PS was measured with DSC. By fitting the model to the experimental PS-line the value of \( \chi \) was determined to be 0.46, \( \epsilon \) was assumed 1 due to heavy cross-linking of this particular system.

Consequently, a simulation to evaluate the onset of PS in a holography sample (7:3 monomer:LC, 150 nm pitch, 1.7 mW cm\(^{-2}\), 30s exposure at room temperature) resulted in PS starting at 39 nm from the intensity maxima. An accurate method to determine the layer thicknesses experimentally remains to be established. However, increasing the illumination intensity resulted in transparent samples, while a higher initial LC concentration produced completely white scattering films, none of them yielding measurable layers. These two features were predicted by the model; and showed how delicate the balance between polymerization rate and diffusion rate is.

Finally, in order to characterize the efficiency of phase separation in confined layers, the feasibility of using nuclear reaction analysis for the depth profiling of the liquid crystal was investigated. Due to small concentration differences between the layers and the low overall concentration of nitrogen throughout the sample this technique is not suitable for the depth profiling of Bragg gratings.
Phase separation in LC-acrylate systems

Contents

1 Introduction 1

2 Theoretical background 5
  2.1 Bragg gratings ................................................. 5
  2.2 Polymer-LC Bragg gratings ..................................... 5
    2.2.1 Nematic liquid crystals ................................... 5
    2.2.2 Switchable diffraction gratings ........................... 7
    2.2.3 Cholesteric self-stratification .......................... 7
    2.2.4 Holography ................................................. 9
  2.3 Radical chain polymerization ................................ 10
  2.4 Phase separation .............................................. 12
    2.4.1 Isotropic mixing: Flory-Huggins ......................... 12
    2.4.2 Network swelling: Dušek .................................. 15
    2.4.3 Nematic ordering: Maier-Saupe ......................... 16
    2.4.4 Binary nematic mixtures: extension of Maier-Saupe ..... 18
    2.4.5 Conversion-phase diagrams ............................... 19
  2.5 Diffusion ........................................................ 21
    2.5.1 Diffusion law .............................................. 21
    2.5.2 Diffusion coefficients as function of degree of polymerization ........................................ 22

3 Simulation results: phase separation and reaction-propagation 23
  3.1 Formalism ..................................................... 23
  3.2 Procedure ..................................................... 25
    3.2.1 Phase separation line .................................... 25
    3.2.2 Reaction-diffusion ....................................... 26
  3.3 Weight of effects ............................................. 29
    3.3.1 Isotropic mixing ......................................... 29
    3.3.2 Network elasticity ....................................... 30
    3.3.3 Nematic ordering ......................................... 30
## 3.4 Simulation results: phase separation lines

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4.1 Interaction parameter: $\chi$</td>
<td>31</td>
</tr>
<tr>
<td>3.4.2 Network elasticity: $\epsilon$</td>
<td>32</td>
</tr>
<tr>
<td>3.4.3 Nematic ordering</td>
<td>35</td>
</tr>
<tr>
<td>3.4.4 Binary nematic mixture</td>
<td>36</td>
</tr>
</tbody>
</table>

## 3.5 Simulation results: reaction-propagation lines

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5.1 Influence of $\chi$ on diffusion</td>
<td>38</td>
</tr>
<tr>
<td>3.5.2 Network elasticity: $\epsilon$</td>
<td>40</td>
</tr>
<tr>
<td>3.5.3 Nematic ordering</td>
<td>40</td>
</tr>
<tr>
<td>3.5.4 Binary nematic mixture</td>
<td>41</td>
</tr>
</tbody>
</table>

## 3.6 Combination of the models

Page 42

## 4 Experimental methods

### 4.1 Chemicals

Page 45

### 4.2 Holography set up

Page 47

### 4.3 Analysis techniques

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.1 Nuclear reaction analysis</td>
<td>49</td>
</tr>
<tr>
<td>4.3.2 Photo differential scanning calorimetry</td>
<td>51</td>
</tr>
<tr>
<td>4.3.3 Scanning electron microscopy</td>
<td>54</td>
</tr>
</tbody>
</table>

## 5 Comparison model results - experimental results

### 5.1 DSC measurements

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.1 DSC results</td>
<td>55</td>
</tr>
<tr>
<td>5.1.2 Double bond conversion vs. monomer conversion</td>
<td>56</td>
</tr>
</tbody>
</table>

### 5.2 SEM measurements

Page 61

## 6 Conclusions and recommendations

Page 63

## A Nuclear reaction analysis for nitrogen depth profiling: a feasibility study

### A.1 Selection of the reaction

Page 67

### A.2 Experimental set up

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.2.1 Accelerator set up</td>
<td>68</td>
</tr>
<tr>
<td>A.2.2 Detectors</td>
<td>70</td>
</tr>
</tbody>
</table>

### A.3 Samples

Page 71

### A.4 Estimated $\gamma$-yield

Page 71

### A.5 Results and discussion

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.5.1 Gamma detection</td>
<td>72</td>
</tr>
<tr>
<td>A.5.2 Depth profile</td>
<td>73</td>
</tr>
<tr>
<td>A.5.3 Particle detection</td>
<td>74</td>
</tr>
</tbody>
</table>

### A.6 Conclusions

Page 77
Chapter 1

Introduction

Polymer optical components have gained importance in the last few decades. The wide range of optical properties of polymers, and their advantages like the ability to produce flexible, thin film devices on a large scale, have brought them to this position. Optical systems for data transport, display technology, filters and polarizers are widely used nowadays [1]. Combining polymers with liquid crystals (LCs), increases possibilities even further. The LC molecules can be aligned by an external electric field, since LCs are electrically anisotropic. By aligning the molecules to each other, the refractive index of liquid crystals can be tuned. One specific application in e.g. LCD screens, are switchable diffraction gratings. These gratings are comprised of periodic structures (Bragg gratings) consisting of alternating polymer and LC layers.

Bragg gratings are usually prepared by holographic UV-exposure of an isotropic reaction mixture containing different multi-functional acrylates and a non-reactive liquid crystal. A photo-initiator that decomposes into radicals upon illumination and this way starts the chain forming reaction is added. By photo-polymerization, the two-component system monomer-liquid crystal is converted into a three-component system: monomer-polymer-LC. Two phases can exist: the liquid phase containing un-reacted monomer and LC, and the matrix phase containing the polymer network swollen by monomers and liquid crystal molecules.

A position-dependent intensity pattern induces a position-dependent reaction rate, that creates local distortions in the compositional equilibrium causing diffusion of the reactive materials to the high-intensity sites. Non-reactive material is transported to the low-intensity sites. For a certain LC concentration, a 'critical' composition where the two phases can coexist is reached.
Phase separation in LC-acrylate systems

locally and phase separation can take place. The liquid components separate from the polymer, forming droplets inside the polymer matrix, called a polymer-dispersed liquid crystal (PDLC). These droplets contain liquid crystalline material and some unreacted monomer, having a different refractive index than the optically isotropic polymer. In this study, a model describing both the diffusion and the phase separation process in isotropic and liquid crystalline three-component mixtures is proposed. A combination of theories is used to describe the thermodynamic behavior of the reaction mixture upon UV-photo-polymerization.

DSC (differential scanning calorimetry) experiments are performed to determine the monomer conversion at phase separation. These results are compared with the conversion predicted by the model. The layer thicknesses of prepared Bragg gratings are analyzed by SEM (scanning electron microscopy) and compared to the model results.

An alternative way to produce polymer Bragg gratings, cholesteric self-stratification, is discussed. This method makes use of chiral dopants to induce cholesteric alignment in liquid crystals. The LC molecules then lie in helices with a specific periodicity; the cholesteric pitch. By substituting the non-reactive liquid crystal molecules by reactive liquid crystalline monomers, photo-polymerization of such systems is possible. Using a dichroic photo-initiator that aligns in the helices and decomposes when the electric field vector of the incoming light is parallel to its long axis, together with linearly polarized light, a gradient in the polymerization reaction rate can be obtained, causing a local unbalance in the composition. It is expected that this can cause phase separation in the same way as holographic recording. However, an essential difference exists between holography and the cholesteric self-stratification technique. Holographic reaction mixtures consist of a nematic liquid crystal and isotropic monomers. Thus, holographic recording is performed in an isotropic mixture. For cholesteric self-stratification, the starting point is a chiral-nematic system. Therefore both approaches need to be treated significantly differently.

At first, the onset of phase separation is investigated. During polymerization of the monomer-LC mixture, the system is in a three-component phase: monomer-polymer-LC. Phase separation is the process where a liquid phase, containing only liquid components (monomer and LC), emerges from the three-component phase. Droplets containing monomer and LC are formed inside the swollen polymer network.

Two phases can coexist when a system is in thermodynamical equilibrium, expressed as a minimum in Gibbs free energy. In this work, three effects are
assumed to contribute independently to the free energy of a system: isotropic mixing, network elasticity and nematic ordering of the liquid crystalline compounds. Starting point is the Flory-Huggins lattice theory [2] for isotropic mixing, which takes into account the relative sizes of the molecules and the van der Waals interactions between different species. The van der Waals interaction is reflected by the Flory-Huggins interaction parameter \( \chi \), a measure for the change in energy of a system upon mixing. Variations in that parameter and the effect on phase separation are studied.

Network elasticity is also expected to affect phase separation considerably, especially in cross-linking polymerization (as in the multifunctional acrylate system under study in this thesis) a densely cross-linked network is formed that will enhance phase separation. The standard expression for an elastic contribution to the free energy has been used [3]. The number of elastically active network chains and the polymer concentration are included in this expression. An efficiency factor is added to account for deviations induced by elastically ineffective chains. The influence on the phase separation of more or less elastic networks is investigated.

Liquid crystalline molecules add an extra energy term due to nematic ordering. These molecules tend to align along a preferred axis, giving an interaction energy. The theory of Maier-Saupe [4] for nematic ordering is adopted for the holographic technique. Its extension to binary nematic mixtures [5] is adopted to describe the behavior of the liquid crystalline components in nematic mixtures for cholesteric self-stratification. It utilizes a temperature-dependent intermolecular interaction that depends on the order parameter, and a nematic partition function that reflects the number of possible states of the system. Since the LC component can be in 2 states, the isotropic state and the nematic state, the liquid phase can be in two states, nematic or isotropic.

Secondly, the diffusion process was investigated. The driving force for diffusion is a gradient in chemical potential, the free energy per molecule. This gives the opportunity to again study the influence of isotropic mixing, network elasticity and nematic ordering. Combination of the phase separation model and the reaction-diffusion simulation will give an indication of the position in depth where the phase separation takes place first (in time). This is an indication for the final layer thickness of the Bragg grating.

Bragg gratings made from the cholesteric self-stratification technique have not yet been obtained experimentally, therefore the modeling results for
cholesteric systems are used to formulate a recommendation for the starting composition, the temperature and the UV-curing intensity to use in future experiments.

Finally, a feasibility study to use nuclear reaction analysis for the quantification of the liquid crystal concentration in depth of the Bragg grating was carried out. Phase separation induces an oscillating depth profile in the liquid crystal concentration. Nitrogen is specific for the liquid crystal molecules, and can thus be used as a label for the LC in the polymer-LC system.

Resonant reactions have a very narrow energy range where they are likely to occur, and are therefore suitable to do depth profiling of specific elements. The $^{15}N(p, \alpha\gamma)^{12}C$ reaction at 897 keV, has a resonance width of 1.7 keV. By tuning the projectile (proton) beam energy, the depth in the sample where the reaction takes place can be tuned. Reaction products of the selected reaction are a gamma photon of 4.43 MeV and an alpha particle. A Si$_3$N$_4$ test sample was used to investigate the efficiency and depth resolution with which the $\alpha$ particles and $\gamma$ photons can be detected. Particle detection is more efficient than gamma detection, which favors particle detection. With the results of these experiments, an estimate is given for the expected yield from a polymer Bragg grating.
Chapter 2

Theoretical background

2.1 Bragg gratings

Diffraction gratings selectively reflect light of a wavelength proportional to the periodicity of the structure. This well-known effect is called Bragg reflection. A mismatch in refractive indices between subsequent layers causes such a grating to reflect. The wavelength of maximum intensity in interference obeys the Wulf-Bragg condition for diffraction:

\[ \lambda_{\text{max}} = 2 \bar{n} d \sin \xi \]  

(2.1)

where \( \bar{n} \) is the average index of refraction of the materials in the layer, \( d \) the layer thickness and \( \xi \) the angle between the incident beam and the plane of the grating. The efficiency of a Bragg grating depends on the contrast in refractive index between subsequent layers and the number of layers in the grating.

A technique to produce polymer-dispersed liquid crystal Bragg gratings is polymerization-induced phase separation (PIPS). In this section the theory behind two approaches to accomplish phase separation between polymer and liquid crystals is presented.

2.2 Polymer-LC Bragg gratings

2.2.1 Nematic liquid crystals

Organic materials with rod-like (calamitic) molecules often show an intermediate state between an isotropic liquid and a crystal. This meso-state, the liquid crystalline state, exhibits rheological properties of a fluid and crystalline properties of a solid. The crystalline effects are caused by the alignment of
the molecules along a preferred direction, represented by the director $\vec{n}$.

In this study nematic liquid crystals are used. Nematic liquid crystals are orientationally ordered, but no long-range positional order is observed. The calamitic molecules tend to align parallel to each other's long axis, pointing roughly in the same direction (fig. 2.1).

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{nematic_phase.png}
\caption{Nematic phase.}
\end{figure}

To quantify the ordering of the molecules, an order parameter $s$ is defined as follows:

$$s = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$  \hfill (2.2)

where $\theta$ is the angle between the director and the long axis of each molecule.

Due to the anisotropic character of the LC phase, its properties are anisotropic as well. The refractive index of nematic liquid crystals is anisotropic, noticeable as birefringence. Light polarized parallel to the director has a different index of refraction (extraordinary refractive index $n_e$) than light polarized perpendicular to the director (ordinary refractive index: $n_o$). The birefringence is then:

$$\Delta n = n_e - n_o$$  \hfill (2.3)

For a completely isotropic state, the average refractive index is:

$$\bar{n} = \sqrt{\frac{2n_e^2 + n_o^2}{3}}$$  \hfill (2.4)

The dielectric properties of the nematic liquid crystal is coupled to the refractive indices as:

$$\varepsilon_{\parallel} = n_e^2$$  \hfill (2.5)
$$\varepsilon_{\perp} = n_o^2$$  \hfill (2.6)

Dielectric anisotropy is specified as:

$$\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$$  \hfill (2.7)

In an electric field, the director turns to align the largest of the dielectric constants with the field direction. This way, the direction of the nematic molecules can be changed by applying an external electric field.
2.2.2 Switchable diffraction gratings

Using the anisotropic properties of LC molecules, a periodic structure of alternating liquid crystal and polymer layers can act as a switchable Bragg grating (Figure 2.2). When the refractive index of the polymer is matched with \( n_e \) of the LC, and an electrical field is applied in the grating direction as in Figure 2.2 right, the Bragg grating will appear transparent to light. This is called the ON state of the switchable Bragg grating. Without electrical field the LC molecules are oriented randomly, with an average refractive index that differs from that of the polymer (Figure 2.2 left). The OFF state reflects incident light, with the reflection wavelength and efficiency depending on the grating periodicity and the refractive index contrast.

The layered structure described above can be obtained by using the phase separation that occurs upon polymerization of a mixture of non-reactive liquid crystal and reactive monomers. This phase separation can be induced by starting the polymerization reaction at specific depths. In the ideal case perfectly separated layers are formed. However, in a more realistic case LC droplets are formed in a polymer matrix, in a layer-like structure. In the following sections (2.2.3 and 2.2.4) two methods to achieve this: cholesteric self-stratification and holographic recording, will be discussed.

2.2.3 Cholesteric self-stratification

The incorporation of a chiral dopant in a nematic host induces a macroscopic helical twist distortion in the bulk of the sample. Molecules then
lie in a quasi-nematic layer-like structure, also called a cholesteric or chiral-nematic phase, with the director of the layers twisted around a helical axis perpendicular to $\vec{n}$. The spatial period of such a helix is called helical pitch $p$ (Fig. 2.3). For a cholesteric mixture between glass plates on which an planar orientation layer is applied, the helical axes will be perpendicular to the glass plates. Due to its birefringence, the cholesteric LC will reflect light of a specific wavelength and handedness, depending on the pitch and the handedness of the helices. The cholesteric reflects light of the same handedness as its own. The other handedness is transmitted by the film. It acts as an ordinary diffraction grating. The lattice constant $d$ then equals half a pitch.

![Figure 2.3: Cholesteric liquid crystal.](image)

Substituting some of the non-reactive liquid crystal with reactive LC monomers makes polymerization possible. A switchable Bragg grating with the periodicity of the cholesteric will be formed if:

1. the polymer phase separates from the non-reactive nematic LC
2. polymerization occurs at every half pitch

Condition 1 is the subject of this thesis, and will be elaborated extensively in the following chapters. Condition 2 can be fulfilled by using linearly polarized light and a dichroic photo-initiator. A molecule of the latter aligns in the helix and is excited with a maximum efficiency by light polarized parallel to its director. Reaction is started at every half pitch and un-reacted monomers diffuse to the reactive sites. Thus, at every half pitch a polymer layer is formed. The nematic LC will phase separate from the polymer and will be located between the polymer layers, giving the required refractive structure for a switchable reflection filter.
2.2.4 Holography

Holography is a widely known technique for recording and reproducing an image of an object through the use of interference effects. In the context of this project it is applied for the recording of periodic structures in isotropic LC-polyacrylate mixtures. Using the fact that photo-polymerization, or rather the initiator activation is intensity-dependent, the interference pattern will induce a distribution in the reaction initiation as a function of depth. Subsequently phase separation takes place and leads to a periodic, layered structure of - ideally - alternating LC and polymer layers. Note that the polymerization reaction is started throughout the whole sample. However, the reaction rate varies with depth due to the intensity gradient, and this is essentially what causes the phase separation.

In a typical set-up designed to make a Bragg interference filter, a coherent laser beam is split up by a beam splitter and directed such that a two-beam interference pattern is present in the sample holder region. The interference can then be expressed as:

\[ I(x) = (I_1 + I_2) \left( 1 + V \cos \frac{2\pi x}{\Gamma} \right) \]  \hspace{1cm} (2.8)

with \( V \) the fringe constant,

\[ V = \frac{2\sqrt{I_1 I_2} \cos \theta}{(I_1 + I_2)} \]  \hspace{1cm} (2.9)

and \( \Gamma \) the periodicity, determined by Bragg's law:

\[ \Gamma = \frac{\lambda_L}{2\pi \sin \theta} \]  \hspace{1cm} (2.10)

where \( \bar{n} \) is the average refractive index of the H-PDLC material, \( \lambda_L \) the wavelength of the writing beam and \( \theta \) the half angle between the 2 beams in the sample.

Experimentally, the two interfering beams usually do not have an equal intensity, which causes an additional offset in the light intensity. This means that polymer will be present in the LC layers as well.
2.3 Radical chain polymerization

In this study, the polymerization mechanism used is radical chain polymerization. The steady state kinetics of polymerization can be divided into three stages: initiation, propagation and termination. In the initiation step, the initiator decomposes into radicals that subsequently attack a monomer unit (M) to form a chain carrier (RM*)[6].

\[
\text{initiator} \rightarrow^{k_d} 2R^* \quad (2.11)
\]
\[
R^* + M \rightarrow^{k_i} RM^* \quad (2.12)
\]

where \(k_d\) is the rate of decomposition and \(k_i\) is the initiation rate. When a reaction is photo-initiated the initiation rate \(v_{ip}\) depends on the intensity of the light absorbed [6].

\[
v_{ip} = 2\phi \epsilon I[M] \quad (2.13)
\]

with \(\phi\) the quantum yield, \(\epsilon\) the extinction coefficient, \([M]\) the monomer concentration and \(I\) the local light intensity. The factor 2 is introduced because two potentially effective radicals are produced in the initiator decomposition.

Propagation is the growth of the macromolecular chain by a kinetic chain mechanism:

\[
RM_n^* + M \rightarrow^{k_p} RM_{n+1}^* \quad (2.14)
\]

The propagation rate \(k_p\) is assumed to be the same for each step, so that:

\[
v_p = k_p[M][RM_n^*] \quad (2.15)
\]

\([RM_n^*]\) is the concentration of growing chain ends, which is usually low at any particular time. The rate of disappearance of monomers reflects the conversion of monomer into polymer, so \(v_p\) is the rate of polymerization.

In principle, termination takes place when the kinetic chain is brought to a halt by one of following processes:

- interaction of two active chain ends
- reaction of an active chain end with an initiator radical
- termination by transfer of the active center to another molecule which may be solvent, initiator or monomer
- interaction with impurities or inhibitors
The dominant effect is the reaction between active chain ends. It can be expressed as:

\[ v_t = 2k_t[RM_n^*][RM_n^*] \]  

(2.16)

From equations 2.13 and 2.16, an expression for the concentration of growing chain ends \([RM_n^*]\) can be deduced. The reaction reaches a steady state where radical formation is exactly counterbalanced by the rate of destruction (termination):

\[ v_{ip} = v_t \]  

(2.17)

During the reaction this gives for the concentration \([RM_n^*]\):

\[ [RM_n^*] = \sqrt{\frac{\phi c I[M]}{k_t}} \]  

(2.18)

For photo-polymerization the overall rate of polymerization (which equals the propagation rate) becomes then:

\[ v_p = k_p \sqrt{\frac{\phi c I[M]}{k_t}}^{3/2} \]  

(2.19)

Acrylate monomers are molecules that can hold one or more reactive acrylate groups. Acrylate groups contain a double bond between the two carbon atoms (C=C) that is subjected for the radical chain reaction. For a monoa crylate, having only one reactive group, the reaction rate is equal to the rate at which those double bonds react. An acrylate monomer is converted as soon as one acrylate group has reacted and fixed the monomer to the polymer chain. This implies that monomer conversion equals double bond conversion.

When a monomer contains more acrylate groups, cross-linking can take place, which is the formation of a network, linking one polymer chain to another. For cross-linking monomers, there is no longer a simple correlation between the double bond conversion and the polymerization rate (monomer conversion rate). Only at the initial stages of polymerization a linear relationship exists between double bond conversion and monomer conversion. At later stages where hardly any free monomers are left, most reactions involve pendant double bonds, i.e. unreacted C=C bonds on a monomer that is already converted.
2.4 Phase separation

Before polymerization starts, a liquid two-component phase exists with monomers and LC molecules. During polymerization, the two-component system monomer-LC is transformed into a three-component system: monomer-polymer-LC. However when the reaction has proceeded to a certain monomer conversion, the polymer network can no longer hold the liquid components and phase separation takes place.

Two phases can be distinguished: the matrix phase (phase I) and the liquid phase (phase II). The matrix phase is a three-component phase, containing polymer, monomer and liquid crystal. The liquid phase is a two-component phase, containing monomer and liquid crystal, which is also present before any reaction takes place. The subject of this section is to describe the phase behavior of this system.

Upon polymerization, the ratio of polymer-monomer-LC is changed locally. Assuming that each reaction step induces only a local disturbance of the thermodynamic equilibrium, a thermodynamic treatment of phase separation is legitimate.

Coexistence of two phases in a system is characterized by the equality of the intensive variables (variables that are not dependent on the size of the system) in both phases. Consequently, the chemical potential \( \mu \) of all components in both phases must be equal:

\[
\mu_{I}^{I} = \mu_{I}^{II},
\]

(2.20)

The chemical potential of a component is the derivative of the Gibbs free energy (G) of the system to the number of molecules of that component.

\[
\mu_{i} = \left( \frac{\partial G}{\partial n_{i}} \right)_{T,n_{j}(j\neq i)}
\]

(2.21)

The next sections give an overview of the thermodynamic models that describe the contributions of isotropic mixing (Flory-Huggins), network elasticity (Dušek) and nematic ordering (Maier-Saupe) to the Gibbs free energy. An important assumption is made: these three effects contribute independently to the free energy of the system.

2.4.1 Isotropic mixing: Flory-Huggins

The isotropic mixing of polymers, monomers and solvents is described by the Flory-Huggins lattice model [2]. The fundamental thermodynamic equation
to describe a mixing process relates the Gibbs free energy function $G$ to the enthalpy $H$ and the entropy $S$:

$$G = H - TS$$ (2.22)

Mixtures will be homogeneous, well-mixed, when the Gibbs free energy of mixing is negative:

$$\Delta G^M \leq 0$$ (2.23)

In order to understand the thermodynamics, a connection between the macroscopic behavior and the behavior on molecular level of the mixture needs to be established. Statistical mechanics provides this connection, in terms of the Boltzmann relation. This relation links the entropy to the total number of distinguishable microscopic states $\Omega$.

$$S = k_B \ln \Omega(n, V, E)$$ (2.24)

with $k_B =$ Boltzmann’s constant. Consider an ideal mixture of two components, species 1 and 2, with respectively $n_1$ and $n_2$ molecules in the mixture, ordered in a lattice of size $n_1 + n_2$. Since all molecules have the same size, every molecule occupies one unit cell in the lattice. The number of possible configurations is:

$$(n_1 + n_2)!$$ (2.25)

Since two molecules of the same species are indistinguishable, the total number of distinguishable states of the system becomes:

$$\frac{(n_1 + n_2)!}{n_1!n_2!}$$ (2.26)

Using Stirling’s approximation ($\ln n! = n \ln n - n$, for large $n$) this yields for the entropy:

$$S = -k_B(n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2})$$ (2.27)

In the three-component system monomer-polymer-LC, the components are large and unequal in size. Therefore they can occupy different numbers of unit cells in the lattice. This necessitates the conversion of number of molecules into volume fractions. Name $n_{lc}$, $n_m$, $n_p$ the number of LC, monomer and polymer molecules with respectively $N_{lc}$, $N_m$, $N_p$ unit cells occupied per molecule. The volume fraction of a species $i$ in the mixture is then: $\frac{n_iN_i}{n_pN_p + n_mN_m + n_{lc}N_{lc}}$.

Extending equation 2.27 to a three-component system of large molecules:

$$S^M = -k_B[n_m \ln \phi_m + n_{lc} \ln \phi_{lc} + n_p \ln \phi_p]$$ (2.28)
Phase separation in LC-acrylate systems

So far, this derivation has been carried out assuming no heat or energy exchange upon mixing, which is an unrealistic situation. From regular solution theory, an expression can be obtained for $\Delta H^M$. The energy change is assumed to originate from the exchange of contacts between monomer-monomer, LC-LC and polymer-polymer with monomer-LC, polymer-LC and monomer-polymer contacts. For two components, i and j, this can be represented by:

$$(i - i) + (j - j) \rightarrow 2(i - j) \quad (2.29)$$

where the formation of an i-j contact requires breaking of i-i and j-j contacts. The change in energy can be expressed as an interchange energy $\Delta \epsilon_{ij}$ per contact, given by:

$$\Delta U^M = \Delta \epsilon_{ij} = \epsilon_{ij} - \frac{1}{2}(\epsilon_{ii} + \epsilon_{jj}) \quad (2.30)$$

Here $\epsilon_{ii}$ and $\epsilon_{jj}$ are the contact energies for each species. Consequently, if the total volume remains constant upon mixing, the energy of mixing $\Delta U^M$ can be replaced by $\Delta H^M$. When q new contacts are formed in the solution, the enthalpy of mixing becomes:

$$\Delta H^M = q\Delta \epsilon_{ij} \quad (2.31)$$

The number of contacts can be estimated from the lattice model by assuming that the probability of having a lattice cell occupied by a molecule of a certain species is simply the volume fraction of that species, $\phi_i$. Thus, every molecule is surrounded by $\phi_i N_i z$ molecules of species i, with z the lattice coordination number. For $n_j$ molecules:

$$\Delta H^M = n_j \phi_i N_i z \Delta \epsilon_{ji} \quad (2.32)$$

From the definition of $\phi_j$, $N_i n_j \phi_i = n_i \phi_j$, which is the "van Laar" expression derived for regular solutions. To eliminate z, a dimensionless parameter $\chi_i$ is introduced. It is defined as:

$$k_B T \chi_{ij} = z \Delta \epsilon_{ij} \quad (2.33)$$

The final expression for the enthalpy becomes:

$$\Delta H^M = k_B T \chi_{ij} n_i \phi_j \quad (2.34)$$

Having calculated the entropy and enthalpy contributions to mixing, these can now be combined to give the expression for the free energy of mixing,
Phase separation in LC-acrylate systems

\[ \Delta G^M = \Delta H^M - T \Delta S^M. \]

For the monomer-polymer-LC system the Gibbs free energy of mixing is:

\[ \Delta G^M = k_B T \left[ n_m \ln \phi_m + n_{lc} \ln \phi_{lc} + n_p \ln \phi_p + \sum_{i<j} \chi_{ij} n_i \phi_j \right] \tag{2.35} \]

The chemical potentials are the derivatives of the free energy, shown here for the three components: the monomer (2.36), the LC (2.37) and the polymer (2.38)

\[ \frac{\mu_m^M}{k_B T} = \frac{1}{k_B T} \left( \frac{\partial G^M}{\partial n_m} \right) = \ln \phi_m + \left. \left( 1 - \phi_m \right) - \phi_{lc} \left( \frac{N_m}{N_{lc}} \right) - \phi_p \left( \frac{N_m}{N_p} \right) \right) \tag{2.36} \]

\[ + \chi_{m-nc} \phi_{nc} (\phi_{lc} + \phi_p) N_m \]

\[ - \chi_{m-nc} \phi_{nc} \phi_p N_m \]

\[ \frac{\mu_{lc}^M}{k_B T} = \frac{1}{k_B T} \left( \frac{\partial G^M}{\partial n_{lc}} \right) = \ln \phi_{lc} + \left. \left. \left. \left( 1 - \phi_{lc} \right) - \phi_m \left( \frac{N_{lc}}{N_m} \right) - \phi_p \left( \frac{N_{lc}}{N_p} \right) \right) \right) \tag{2.37} \]

\[ + \chi_{m-nc} \phi_{nc} + \chi_{p-nc} \phi_p \left( \phi_m + \phi_p \right) N_{lc} \]

\[ - \chi_{m-nc} \phi_{nc} \phi_p N_{lc} \]

\[ \frac{\mu_p^M}{k_B T} = \frac{1}{k_B T} \left( \frac{\partial G^M}{\partial n_p} \right) = \ln \phi_p + \left. \left. \left. \left( 1 - \phi_p \right) - \phi_{lc} \left( \frac{N_p}{N_{lc}} \right) - \phi_m \left( \frac{N_p}{N_m} \right) \right) \right) \tag{2.38} \]

\[ + \chi_{p-nc} \phi_{nc} + \chi_{m-nc} \phi_m \left( \phi_{lc} + \phi_m \right) N_p \]

\[ - \chi_{m-nc} \phi_{nc} \phi_m N_p \]

2.4.2 Network swelling: Dušek

Solvent molecules can diffuse into a cross-linked polymer network, causing swelling of the network. The elasticity of the network chains aims to resist this, giving an extra energy to the system. Dušek provides an expression for the contribution of the network deformation by swelling to the Gibbs free energy [7]:

\[ \frac{\Delta G^{el}}{n_p k_B T} = \nu e \left[ \frac{3}{2} A \Phi^2 \Phi^{-2/3} \left( \phi_p^{-2/3} - 1 \right) + B \ln \phi_p \right] \tag{2.39} \]

\( \nu_e \) is the number of elastically active network chains. For networks with a Gaussian chain length distribution, \( \nu_e \) is related to the network chain length \( (m_c) \) between cross-links: \( \nu_e / n_p = \phi_p / m_c \). Further, \( \Phi_p \) is defined as the polymer volume fraction during cross-linking. The network is assumed to remain homogeneous upon the formation of each new cross-link. Therefore \( \Phi_p \) is equal to \( \phi_p \) after the first cross-link is formed, up to the point of phase
Phase separation in LC-acrylate systems

16

separation, before cross-linking $\Phi_p$ is zero. A and B are:

$$A = 1 \quad B = 2/f$$

(2.40)

where $f$ is the functionality (=number of reactive groups) of the monomers.

From eq. 2.39 the elastic contribution to the chemical potentials can be found:

$$\frac{\Delta \mu_m^e}{k_B T} = \frac{\Delta \mu_{ic}^e}{k_B T} = \frac{1}{m_c} \left[ A \left( \frac{\Phi_p}{\Phi_p^c} \right)^{2/3} - B \right] \phi_p$$

(2.41)

2.4.3 Nematic ordering: Maier-Saupe

Below the nematic to isotropic transition temperature, a liquid crystal component prefers to be nematically ordered. This ordering also gives a contribution to the Gibbs free energy. Maier and Saupe developed a mean-field theory for this nematic ordering contribution.

Assuming each molecule has a well defined long axis with polar angles $\phi$ and $\theta$, the distribution function $f(\phi, \theta)$ can be defined. The next step is to introduce a convenient thermodynamic potential, which will be minimum in the equilibrium state. It is convenient to use the free enthalpy ($G$) per molecule (or chemical potential).

$$G^n(p, T) = k_B T \int f \log(4\pi f) d(\cos \theta) d\theta d\phi + G_1(p, T, S)$$

(2.42)

The decrease in entropy due to the anisotropic angular distribution is described by the integral. The logarithm originates from the Gibbs entropy formula:

$$S = -k_B \sum_\nu P_\nu \ln P_\nu$$

(2.43)

where $P_\nu$ is the probability for the system to be in a state $\nu$. In this particular case, this probability is related to the distribution function $f$.

$G_1$ describes the effects of intermolecular interactions, and is assumed to be quadratic in the order parameter $s$:

$$G_1 = -\frac{1}{2} U(p, T) s^2$$

(2.44)

Minimizing $G$ with respect to all variations of $f$ that satisfy the constraint

$$\int f d(\cos \theta) d\theta d\phi = 1$$

(2.45)

gives this form of the distribution function is:

$$f(\theta) = \frac{1}{Z} \exp \left( \frac{-u(\theta)}{k_B T} \right)$$

(2.46)
u(θ) is the energy associated with one particular orientation of a molecule to the director:

\[
\frac{u(\theta)}{k_B T} = -\frac{1}{2} m (3 \cos^2 \theta - 1)
\]

(2.47)

with m a mean-field parameter, expressing the strength of the mean field. Z is the nematic partition function, the total number of possible states of the system:

\[
Z = \int \exp \left( -\frac{u(\theta)}{k_B T} \right) d(\cos \theta)
\]

(2.48)

The intermolecular interactions are described by:

\[
G_1 = -\frac{1}{2} \nu \phi \nu_s^2
\]

(2.49)

where s is the order parameter

\[
s = \frac{1}{2} (3 < \cos^2 \theta > -1)
\]

(2.50)

\[
< \cos^2 \theta > = \int \cos^2 \theta f(\theta) d(\cos \theta)
\]

(2.51)

and \( \nu \) a quadrupole interaction parameter defined as:

\[
\nu = 4.54 \frac{T_{ni}}{T}
\]

(2.52)

with \( T_{ni} \) the nematic to isotropic transition temperature of the liquid crystal. The orientational order parameter s may be evaluated based on the free energy minimization approach by taking the derivative of equation 2.42

\[
-\frac{d \ln Z}{ds} + s \frac{dm}{ds} + m - \phi \nu s = 0
\]

(2.53)

The first two terms cancel out each other, which gives:

\[
m = \phi \nu s
\]

(2.54)

Note that the order parameter is defined as a function of the distribution function f, which in turn depends on the mean field parameter m. Therefore s can be expressed as a function of m. De Gennes [4], proposes the following relationship:

\[
s(m) = c_1 m + c_2 m^2 + c_3 m^3 + c_4 m^4
\]

(2.55)

with

\[
c_1 = 0.1983 \quad c_3 = -0.01653
\]

(2.56)

\[
c_2 = 0.03768 \quad c_4 = 0.001458
\]

(2.57)
For a given set of temperature and composition, substitution of 2.54 in 2.55 yields a solution for $s$. Graphically the possible solutions for $s$ can be seen as the intersections of 2.55, a sigmoidal curve, and 2.54, a straight line with slope $(\frac{1}{\phi_{lc}})$. When the slope is greater than a critical value (determined by the tangent point, $s_c \approx 0.44$, $m_c \approx 2.00$), there is no intersection except $s = 0$, implying that the system is in the isotropic state. In a mixture of an isotropic monomer and a nematic liquid crystal, the critical composition $\phi_{ni}$ to have a nematic phase in the mixture can be calculated from the critical order parameter $s_c$.

$$\phi_{ni} = \frac{T}{T_{ni}} \quad T \leq T_{ni}$$  \hspace{2cm} (2.58)

A more convenient form of 2.42 is:

$$\frac{G^n}{k_B T} = \frac{\phi_{lc}}{N_{lc}} \left[ -\ln Z + \frac{1}{2} \nu \phi_{lc} s^2 \right]$$  \hspace{2cm} (2.59)

The chemical potentials contribution from the Maier-Saupe theory are the derivatives of 2.59:

$$\frac{\mu^n_{lc}}{k_B T} = \frac{1}{k_B T} \left( \frac{\partial G^n}{\partial \phi_{lc}} \right) = -\ln Z + \frac{1}{2} \nu \phi_{lc}^2 s^2$$  \hspace{2cm} (2.60)

$$\frac{\mu^n_m}{k_B T} = \frac{1}{k_B T} \left( \frac{\partial G^n}{\partial \phi_m} \right) = \frac{1}{2} N_m \nu \phi_{lc}^2 s^2$$  \hspace{2cm} (2.61)

**2.4.4 Binary nematic mixtures: extension of Maier-Saupe**

In the previous chapter the free energy contribution of the nematic phase of a single nematic component (LC) in an otherwise isotropic mixture was

![Graphical presentation of the self-consistent solution for the order parameters][1]

**Figure 2.4:** Graphical presentation of the self-consistent solution for the order parameters [8].
discussed. For the mixing of two liquid crystalline compounds, as will be the case in the samples for cholesteric self-stratification, an extension of the Maier-Saupe nematic free energy theory is necessary. Following the theoretical scheme of Brochard et al [9], the free energy density of a binary nematic mixtures may be described as [5]:

\[
\frac{G^n}{nk_B T} = -\frac{\phi_1}{N_1} \ln Z_1 - \frac{\phi_2}{N_2} \ln Z_2 - \frac{1}{2} \nu_{11}s_1^2 \phi_1^2 - \frac{1}{2} \nu_{22}s_2^2 \phi_2^2 - \nu_{12}s_1s_2 \phi_1 \phi_2
\]  

(2.62)

(2.63)

Where \(\nu_{11}\) and \(\nu_{22}\) are the nematic interaction parameters of the pure components, whereas \(\nu_{12}\) represents the cross-interaction between dissimilar molecules. The orientational order parameters \(s_1\) and \(s_2\) are calculated with the method described in section 2.4.3 and shown in Figure 2.4. Previously the nematic interaction parameters was shown to be inversely proportional to temperature:

\[
T_n = 4.54 - \frac{1}{T_n} - 4.54 - \frac{1}{T_n^2}
\]  

(2.64)

From equation 2.63 it follows that \(G\) only can be calculated when \(\nu_{12}\) is known. However, the exact relation of \(\nu_{12}\) to \(\nu_{11}\) and \(\nu_{22}\) is not known. It is proposed by Chiu and Kyu [5] that \(\nu_{12} = \nu_{21}\) and is proportional to the square root of the product of \(\nu_{11}\) and \(\nu_{22}\):

\[
c = \frac{\nu_{12}}{\sqrt{\nu_{11}\nu_{22}}}
\]  

(2.65)

where \(c\) is the proportionality constant characterizing the relative strength of the cross-interaction. This yields for the chemical potentials of both components due to their nematic character:

\[
\frac{\mu_1}{kT} = \frac{1}{2}N_1\nu_{11}s_1^2 \phi_1^2 + \frac{1}{2}N_1\nu_{22}s_2^2 \phi_2^2 + N_1\nu_{12}s_1s_2 \phi_1 \phi_2 - N_1 \ln Z_1
\]  

(2.66)

\[
\frac{\mu_2}{kT} = \frac{1}{2}N_2\nu_{11}s_1^2 \phi_1^2 + \frac{1}{2}N_2\nu_{22}s_2^2 \phi_2^2 + N_2\nu_{12}s_1s_2 \phi_1 \phi_2 - N_2 \ln Z_2
\]  

(2.67)

### 2.4.5 Conversion-phase diagrams

To have a graphical representation of phase separation due to polymerization in a monomer-LC mixture, the concept of ternary conversion-phase diagrams, introduced by Boots [10] is adopted. It combines the thermodynamics of the three-component system (monomer-polymer-solvent) with the conversion of monomer molecules into polymer.
The following relation holds between the conversion $\alpha$ and the overall volume fractions:

\begin{align*}
\phi_m &= (1 - \alpha)(1 - \phi_{lc}) \\
\phi_p &= \alpha(1 - \phi_{lc})
\end{align*}

(2.68)  
(2.69)

Phase separation of the three-component system into the two phases, matrix phase (phase I) and liquid phase (phase II) as described in section 2.4 is under study here. Together with the condition that the sum of all volume fractions equals one in both phases:

\begin{align*}
\phi_p^I + \phi_m^I + \phi_{lc}^I &= 1 \\
\phi_m^I + \phi_{lc}^I &= 1
\end{align*}

(2.70)  
(2.71)

and the requirement of equality of chemical potentials in both phases for having coexistent phases,

\begin{align*}
\mu_m^I &= \mu_m^{II} \\
\mu_{lc}^I &= \mu_{lc}^{II}
\end{align*}

(2.72)  
(2.73)

all equations needed to find all possible combinations of $\phi_p^I$, $\phi_m^I$, $\phi_{lc}^I$ and $\phi_{lc}^{II}$ for which 2 phases can coexist are available.

Figure 2.5 shows an example of a conversion-phase diagram. The line CD will be called the phase separation line. Points to the left of this line refer to a one phase system (phase I); points to the right of the line refer to a two-phase system (phase I and II). Hence, CD is comprised of the points with the lowest conversion that satisfy the conditions 2.72 and 2.73.

Figure 2.5: Conversion-phase diagram.

Polymerization takes place on a horizontal line of constant LC-concentration in the diagram, called polymerization line. At some point X in the diagram,
Phase separation in LC-acrylate systems

Phase separation takes place and phase II emerges, containing only monomer and LC. From the fact that at the moment of phase separation the volume of phase II is infinitesimal, the composition of phase I at that point is equal to the overall composition before phase separation. For a certain liquid crystal volume fraction, the conversion at which the phase separation takes place and the composition of the second phase can be determined as follows. Equations 2.68 and 2.69 give \( \phi_p^I \) and \( \phi_m^I \) as a function of the conversion \( \alpha \). From 2.71, \( \phi_m^{II} \) is given as a function of \( \phi_{lc}^{II} \). This leaves 2 variables, \( \phi_{lc}^{II} \) and \( \alpha \), which can be obtained by solving 2.72 and 2.73.

The conversion-phase diagram visualizes how the phase separation behavior depends on the initial composition of the reaction mixture. The procedure to solve 2.72 and 2.73 as described here cannot be carried out by analytical methods. A numerical solution to this set of equations is proposed in chapter 3.

It is important to realize the difference between a conversion-phase diagram and a phase diagram. In a phase diagram, the size and structure of the molecules of each component are invariable, each point represents a certain ratio of the component. During polymerization however, this is not necessarily the case. The polymer increases in weight, and also changes in molecular structure and molecular size distribution. Therefore at each point in the diagram, the composition of the system as well as the polymer itself are different.

2.5 Diffusion

2.5.1 Diffusion law

Photo-polymerization with an non-uniform intensity induces local distortions in concentration that induce a transport of material, diffusion. Fick's first law for steady-state diffusion states that the flux is proportional to the concentration gradient [11]:

\[
J = -D \frac{dc}{dx}
\]

(2.74)

where \( J \) is the diffusion flux in \( \text{m}^{-2}\text{s}^{-1} \), \( D \) the diffusion coefficient in \( \text{m}^2\text{s}^{-1} \) and \( c \) the concentration in particles \( \text{m}^{-3} \).

During the formation of PDLCs, the concentration within the diffusion volume changes in time. Then Fick's second law for non-steady state diffusion
Phase separation in LC-acrylate systems

applies.

\[ \frac{dc}{dt} = \frac{d}{dx}\left( D \frac{dc}{dx} \right) \]  
(2.75)

A concentration gradient manifests itself in a gradient of the chemical potential. The theory described in former sections gives an expression for the local chemical potential. So the driving force for diffusion is a gradient in the chemical potential. The flux of particles is then given by [12]:

\[ J = -\frac{Dc \, d\mu}{kT \, dx} \]  
(2.76)

The general diffusion equation then becomes:

\[ \frac{dc}{dt} = \frac{d}{dx}\left( \frac{Dc \, d\mu}{kT \, dx} \right) \]  
(2.77)

2.5.2 Diffusion coefficients as function of degree of polymerization

The diffusion coefficient \( D \) as defined in Fick's Law 2.76 is a constant, independent of the composition and morphology of the sample. Obviously during polymerization the mobility of the molecules is decreasing due to the formation of the polymer network. Therefore \( D \) has to be a function of \( \phi_p \). From free volume theory [11] the following expression for \( D \) can be obtained:

\[ \left( \ln \frac{D(\phi_m)}{D_p} \right)^{-1} = K_1 \left( \frac{1}{\phi_m} + K_2 \right) \]  
(2.78)

Where \( \phi_m \) is the monomer volume fraction, \( D_p \) is the monomer diffusion coefficient in the pure polymer, and \( K_1 \) and \( K_2 \) are positive constants described in the free volume theory.
Chapter 3
Simulation results: phase separation and reaction-propagation

3.1 Formalism

The expressions of the chemical potentials for monomer and liquid crystalline molecules are the governing equations for both phase separation and reaction-diffusion. Isotropic mixing, network elasticity and nematic ordering contribute independently to the Gibbs free energy. This implies that the chemical potentials due to these three effects add up independently to the total chemical potential of both compounds.

\[
\mu_{\text{total}}^m = \mu_m^M + \mu_m^{el} + \mu_m^n \tag{3.1}
\]

\[
\mu_{\text{total}}^{lc} = \mu_{lc}^M + \mu_{lc}^{el} + \mu_{lc}^n \tag{3.2}
\]

However, in their current condition the expressions for the chemical potentials are not suitable to be used in a numerical model. In the coming paragraphs, the three terms will be discussed separately and expressions will be derived that can be exploited in a simulation program.

Expressions for \(\mu_m^M\) and \(\mu_{lc}^M\) were derived in section 2.4.1. Since polymer and monomers are comprised of the same building blocks, the interaction parameter \(\chi_{m-p}\) between monomer and polymer is assumed zero. In addition, the sizes of the monomer and liquid crystal molecules in the system under study are presumed to be comparable. Consequently, it is assumed that \(N_{lc} = N_m = 1\). When the assumption is adopted that the polymer chains are infinitely long, \(N_p = \infty\). The formulation of the chemical poten-
tials for monomers and liquid crystals are simplified considerably:

\[
\frac{\Delta \mu^M_m}{k_B T} = \ln \phi_m + \phi_p + \chi_{m-\text{lc}} \phi_{\text{lc}}(\phi_{\text{lc}} + \phi_p)N_m - \chi_{p-\text{lc}} \phi_{\text{lc}} \phi_p N_m
\]

(3.3)

\[
\frac{\Delta \mu^M_{\text{lc}}}{k_B T} = \ln \phi_{\text{lc}} + \phi_p + (\chi_{m-\text{lc}} \phi_m + \chi_{p-\text{lc}} \phi_p)(\phi_m + \phi_p)N_{\text{lc}}
\]

(3.4)

If cross-linking polymerization is started in a monomer-solvent solution, phase separation may occur either before or after gelation. In the latter situation an infinite network is present almost from the start of the reaction and phase separation can be induced by the increasing elasticity of the swollen network during polymerization. For the system under study in this thesis, cross-linking is virtually instantaneous. So in this case, network elasticity has to be taken into account.

Network elasticity is described in section 2.4.2. Before expression 2.41 can be used, an estimation for the inverse network chain length needs to be established. Since the average functionality of the monomer blend used is 3.8, the mean-field estimate for \( m_c \) valid for tetrafunctional (\( f = 4 \)) monomers from [10] can be used.

\[
m_c^{-1} = \frac{x^2}{\alpha} = \frac{2 - \alpha - 2\sqrt{1 - \alpha}}{\alpha}
\]

(3.5)

Here \( \alpha \) is the monomer conversion (\( = \frac{\text{np}}{m_{\text{m}, \text{start}}} \)), \( x \) the conversion of reactive groups - which makes \( x^2 \) the probability that a unit is cross-linked, and \( x^2/\alpha \) the fraction cross-links within the reacted units.

An overall efficiency factor \( \epsilon < 1 \) is added to the elastic terms to account for the fraction of elastically ineffective network chains. Since cross-linking is instantaneous upon polymerization for the holographic system, \( \Phi_p \) equals \( \phi_p \) at all times. This gives for the chemical potentials, with \( x^2/\alpha \) as in 3.5:

\[
\frac{\Delta \mu^M_m}{k_B T} = \frac{\Delta \mu^M_{\text{lc}}}{k_B T} = \epsilon \left( \frac{x^2}{\alpha} \right) \frac{\phi_p}{2}
\]

(3.6)

For the description of the nematic ordering one has to discriminate between the holographic and the self-stratification approach. Holographic recording
Phase separation in LC-acrylate systems

concerns one liquid crystalline component in an otherwise isotropic mixture. The regular Maier-Saupe theory can be applied (2.4.3);

\[
\frac{\mu_{lc}^n}{k_B T} = -\ln Z + \frac{1}{2} \nu \phi_{lc}^2 s^2
\]  
(3.7)

\[
\frac{\mu_m^n}{k_B T} = \frac{1}{2 N_{lc}} \nu \phi_{lc}^2 s^2
\]  
(3.8)

Self-stratification is carried out starting in the cholesteric phase, containing a non-reactive liquid crystal and a liquid crystalline monomer. Then the extended theory for nematic ordering in binary nematic mixtures described in section 2.4.4 has to be utilized:

\[
\frac{\mu_{lc}^n}{k_T} = \frac{1}{2} \nu_{mm} s_m^2 \phi_m^2 + \nu_{lc} s_{lc} \phi_{lc}^2 + \nu_{mlc} s_m s_{lc} \phi_m \phi_{lc} - \ln Z_m
\]  
(3.9)

\[
\frac{\mu_m^n}{k_T} = \frac{1}{2} \nu_{mm} s_m^2 \phi_m^2 + \nu_{lc} s_{lc} \phi_{lc}^2 + \nu_{mlc} s_m s_{lc} \phi_m \phi_{lc} - \ln Z_{lc}
\]  
(3.10)

3.2 Procedure

3.2.1 Phase separation line

In section 2.4.5, an analytical method for determining the points in a phase diagram where two phases can coexist was proposed. However, the set of governing equations for phase separation is not analytically solvable. Therefore, a numerical method is suggested here. The main idea is to calculate the total chemical potential for all possible compositions of phase I and phase II, and then compare those results with each other, giving the composition of both phases at phase separation.

Phase I consists of polymer, monomer and liquid crystal, which gives three volume fractions to vary. But the sum \( \phi_p^I + \phi_m^I + \phi_{lc}^I = 1 \), which cancels out one parameter. Two parameters need to be varied to obtain all possible compositions of the three-component phase. The liquid crystal volume fraction and the conversion were selected arbitrarily to do this. For phase II, the same line of reasoning leaves one variable volume fraction, \( \phi_{lc}^{II} \).

For every possible combination of \( \phi_{lc}^I, \alpha \) and \( \phi_{lc}^{II} \), the chemical potentials of monomer and liquid crystal in both phases (\( \mu_{lc}^I, \mu_{lc}^{II}, \mu_m^I \) and \( \mu_m^{II} \)) are calculated separately. The condition for phase separation, \( \mu_l^I = \mu^{II}_l \) is then verified. The combinations of \( \phi_p^I, \phi_m^I \) and \( \phi_{lc}^I \) that satisfy the conditions \( \mu_l^I = \mu_{lc}^I \) and \( \mu_m^I = \mu_{lc}^{II} \) are the points in the conversion-phase diagram where the two
phases can coexist. The composition of phase I at phase separation is equal to the overall composition of the system, since at the moment of phase separation, the volume of phase II is infinitely small.

A summary of the procedure is depicted in Figure 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Phase I</th>
<th>Phase II</th>
</tr>
</thead>
<tbody>
<tr>
<td>choose:</td>
<td>$\phi_{lc}^I \alpha$</td>
<td>$\phi_{lc}^{II}$</td>
</tr>
<tr>
<td>derive:</td>
<td>$\phi_p^I \phi_m^I$</td>
<td>$\phi_m^{II}$</td>
</tr>
<tr>
<td>calculate:</td>
<td>$\mu_m^{total,I}$</td>
<td>$\mu_m^{total,II}$</td>
</tr>
<tr>
<td></td>
<td>$\mu_{lc}^{total,I}$</td>
<td>$\mu_{lc}^{total,II}$</td>
</tr>
<tr>
<td>check:</td>
<td>$\mu_m^{total,I} = \mu_m^{total,II}$</td>
<td>$\mu_{lc}^{total,I} = \mu_{lc}^{total,II}$</td>
</tr>
<tr>
<td>at PS:</td>
<td>$\phi_{lc}^I \phi_m^I \phi_p^I$</td>
<td>$\phi_{lc}^{II} \phi_m^{II}$</td>
</tr>
</tbody>
</table>

Figure 3.1: Schematic representation of the procedure to calculate the phase separation line.

3.2.2 Reaction-diffusion

The reaction-diffusion model developed by Christian Leewis [11] simulates the diffusion behavior of two reactive monomers with different reactivity in samples prepared by mask illumination.

A step in the reaction is assumed to give only a small distortion of the equilibrium, which justifies a thermodynamic treatment. The mask illumination pattern is divided into discrete steps. In each reaction step, a small volume of polymer is formed, depending on the intensity and the monomer concentration in the segment. This causes an inequality in the chemical potential between segments. Chemical potential gradients are the driving force for diffusion. The discretized diffusion equation gives the change in concentration due to diffusion between segments. After this diffusion step, new volume fractions per segment are obtained. Hereafter, a new reaction step can be performed.

Although this is already a very comprehensive model, holographic exposure of mixtures containing both reactive and non-reactive components as investigated in this thesis, demand for some subtle modifications.
Firstly, the chemical potentials are adapted to the system of interest. Isotropic mixing, network elasticity and nematic ordering are incorporated in the chemical potentials used in the diffusion equation. Diffusion due to surface tension is omitted, since the samples prepared do not hold open surfaces.

Secondly, the illumination pattern is changed from a step illumination to the \( \sin^2 \) intensity distribution of a holographic interference pattern (equation 2.8). The pattern is divided into discrete steps, between which diffusion can take place due to a difference in chemical potential. The intensity gradient causes a gradient in the reaction rate, that in turn induces chemical potential differences.

The diffusion behavior will be plotted in two different ways. Concentration as a function of depth will be used to visualize the in-depth profile of all volume fractions, conversion-phase diagrams will be used to visualize the diffusion behavior of the components in a sample during ongoing polymerization. At every depth, the composition is calculated by the simulation program. This composition represents one point in a conversion-phase diagram. Plotting all compositions of one specific depth in time gives a line in the diagram. This line will henceforth be called the reaction-propagation line.

For a typical holography sample with starting composition of 70 wt% monomer and 30 wt% liquid crystal, the depth profile of volume fractions after an illumination time of 30s with a maximum intensity of 1.7 mW/cm\(^2\), pitch of 150 nm, is shown in graph 3.2.

For two specific points in depth, at maximum intensity and at minimum intensity, an example reaction-propagation line is plotted in a ternary conversion-phase diagram (Figure 3.3). If no diffusion would occur, the lines would be horizontal, like normal polymerization lines. Due to the faster depletion of monomers at the point of high intensity the reaction-propagation line bends slightly downward due to diffusion of monomer to the reactive sites, which gives a higher concentration of polymer at the higher intensity side. The low intensity point shows more diffusion, the diffusion coefficient decreases less due to less rapid polymer formation because polymer is formed less rapidly there. This gives monomers and LC molecules more time to diffuse, so a larger materials transport takes place.

The diagram in Figure 3.3 represents an idealized situation, and is therefore only meant to illustrate the reaction-diffusion behavior of a holographic mixture.
Figure 3.2: Depth distribution of monomer, polymer and LC volume fractions in a typical holography sample. Illumination time is 30 seconds, pitch is 150 nm.

Figure 3.3: High and low intensity reaction-propagation lines of a typical holography sample.
3.3 Weight of effects

To evaluate the relative importance of the different terms in the expression of the chemical potential, the following situation is considered. Assume a theoretical sample that contains two phases with composition \( \phi_{1c} = 0.3, \phi_{m} = 0.35, \phi_{p} = 0.35 \) and \( \phi_{1m}^{II} = 0.3, \phi_{m}^{II} = 0.70 \). The polymer chains are assumed to be infinitely long, monomer and LC molecules are of the same size \( (N_{m} = N_{lc} = 1) \). With these assumptions, an estimate of the influence of variations in the different parameters on the numerical values of the chemical potentials has been studied.

3.3.1 Isotropic mixing

With the assumption that \( \chi_{m-p} = 0 \) and \( \chi_{p-lc} = \chi_{m-lc} = 0.5 \) the terms in the expression for the chemical potentials become:

\[
\frac{\mu_{m}^{M}}{kBT} = \ln \phi_{m} + \phi_{p} + \chi_{m-lc}\phi_{ic}(\phi_{ic} + \phi_{p}) - \chi_{p-lc}\phi_{ic}\phi_{p} \tag{3.11}
\]

\[
\frac{\mu_{lc}^{M}}{kBT} = \ln \phi_{lc} + \phi_{p} + (\chi_{m-lc}\phi_{m} + \chi_{p-lc}\phi_{p})(\phi_{m} + \phi_{p}) \tag{3.12}
\]

Approximate values for the terms in 3.11 and 3.12 for phase I and II with a composition as described in the previous paragraph are shown in Table 3.1:

<table>
<thead>
<tr>
<th></th>
<th>phase I</th>
<th>phase II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln \phi_{ic} )</td>
<td>-1.204</td>
<td>-1.204</td>
</tr>
<tr>
<td>( \ln \phi_{m}  )</td>
<td>-1.049</td>
<td>-0.350</td>
</tr>
<tr>
<td>( \chi )-terms ( \mu_{lc} )</td>
<td>0.245</td>
<td>0.245</td>
</tr>
<tr>
<td>( \chi )-terms ( \mu_{m} )</td>
<td>0.045</td>
<td>0.045</td>
</tr>
</tbody>
</table>

The logarithmic term changes with composition, while the interaction terms keeps the same value, no matter what the composition is. The latter is caused by the assumption that \( \chi_{p-lc} = \chi_{m-lc} = 0.5 \). Now the question is whether phase I and II can coexist as a consequence of isotropic mixing alone. The answer is: no. For one component e.g. the liquid crystal, the chemical potential in the two phases can become equal (see Table 3.1 rows 1 and 3), i.e. when \( \phi_{1c}^{II} = e^{\phi_{ic}} \phi_{1c}^{I} \). Let \( \phi_{1c}^{I} = 0.3, \phi_{m}^{I} = 0.35 \) and \( \phi_{p}^{I} = 0.35 \), as in the example case. Then \( \phi_{1c}^{II} = 0.43 \) satisfies this condition. However, the chemical potential of the other component will never be equal in the two phases. The
difference $\mu_{m}^I - \mu_{m}^{II}$ for this example is -0.14. No phase separation will be predicted by considering solely isotropic mixing.

Yet, an inequality of the interaction parameters between LC-monomer and LC-polymer does create an additional difference in the chemical potential. Even though this is a very small difference - in the order of $\mu_{i}^I - \mu_{i}^{II} = 0.01$ for $\chi_{m-Bc} - \chi_{p-Bc} = 0.1$ - it will give a small range of compositions in which two phases can coexist, which will be elaborated further in section 3.4.1. Nevertheless, this effect is so small that it will be neglected in the remainder of this chapter.

### 3.3.2 Network elasticity

The presence of the polymer network in phase I necessitates the addition of a network elasticity term to the chemical potential for that phase. For the theoretical sample, its magnitude is 0.0395, and it is linearly dependent on the polymer volume fraction (equation 3.6). Since no network is present in the second phase, the network elasticity term for phase II is 0. This induces a larger difference between the chemical potentials of the different phases, giving rise to a stronger driving force for phase separation. With decreasing polymer volume fraction of phase I, the isotropic term increases, which compensates for the change in chemical potential due to network elasticity. Since this effect is a factor of 4 larger than the difference in interaction parameters will ever create, a possibility for coexistence of the two phases is expected in a large range of volume fractions.

### 3.3.3 Nematic ordering

For a liquid crystal content higher than the critical $\phi_{ni} = \frac{f}{n_i}$ - typically around 0.9 for e.g. E7, a commercial mixture of LC molecules - the nematic ordering of the liquid crystal adds an extra term in the expression for the monomer and liquid crystal chemical potential. The nematic term for the monomer is in the order of 0.4, for the liquid crystal around 0.05. Again, this is different for the two phases, so nematic ordering will influence the position of the phase separation line in the conversion-phase diagram. Since the nematic ordering only plays a role in a certain range of LC volume fractions, and the fact that network elasticity also induces phase separation, rises the idea that not a single phase separation line in one conversion-phase diagram exists, but several.
3.4 Simulation results: phase separation lines

In the previous section the procedure to obtain phase separation lines and the way to interpret them was explained. In this section variations and importance of the interaction parameter, the network efficiency and nematic ordering on the possible occurrence of a phase separation line are investigated.

3.4.1 Interaction parameter: $\chi$

The interaction parameter between two components denotes the gain in energy upon mixing of these components. Therefore, when the $\chi$ of one component (i) with a certain component (j) is larger than the $\chi$ of that component (i) with another component (k), the j-k mixing is the more stable one. This means that in a system containing components i,j and k the contact between i and k is energetically more favorable than the contact between j and k. Consequently, different $\chi$'s between the components in a system could be the driving force for phase separation.

Since polymer and monomers consist of the same building blocks, the interaction parameter $\chi_{m-p}$ was assumed to be zero. However, the interactions between monomer-LC and polymer-LC do have a non-zero $\chi$. Several models exist that describe the behavior of $\chi$, as a function of composition and temperature [13]. These will not be discussed in detail here. A commonly used value for the interaction parameter between polymers and solvents (here monomers and LCs) is 0.5, the critical value for infinitely long chains [14].

It is suspected that an LC has a weaker interaction (larger $\chi$) with a polymer than with a monomer i.e. the LC gives preference to be near monomers. Therefore it was evaluated whether a phase separation line can be found on the basis of this difference in interactions. Since the difference in interaction parameters is expected to be very small, due to the similarity in size and functional groups of the monomers and the polymer-units, values of $\chi_{p-lc} = 0.55$ and $\chi_{m-lc} = 0.45$ were chosen. The resulting phase separation line is shown in Fig. 3.4. A phase separation line is observed, although in a very narrow volume fraction region with a high liquid crystal content.

Consequently, to simplify the interpretation of the conversion-phase diagrams, it is proposed that $\chi_{m-lc} = \chi_{p-lc} = \chi$. Chemical potentials are then further simplified to:
\[ \frac{\Delta \mu^M_m}{k_B T} = \ln \phi_m + \phi_p + \chi \phi^2 \]  
\[ \frac{\Delta \mu^M_{lc}}{k_B T} = \ln \phi_{lc} + \phi_p + \chi (\phi_m + \phi_p)^2 \]  

Note that with this assumption, no phase separation is expected based on only the isotropic mixing described by Flory-Huggins.

Figure 3.4: Phase separation line, considering only isotropic mixing. Interaction parameters are $\chi_{p-lc} = 0.55$ and $\chi_{m-lc} = 0.45$.

3.4.2 Network elasticity: $\epsilon$

In the expression for the chemical potential due to a cross-linked network, an efficiency factor $\epsilon$ was introduced. This section gives an overview of the effects of an elastic network on phase separation. More substantially, variations of $\epsilon$ and $\chi$ are studied.

For a $\chi = 0.5$, the term for a heavily cross-linked network ($\epsilon=1$) is added to the Gibbs free energy. This results in the phase separation line shown in Figure 3.5. As can be seen in the graph, a lower limit for the LC content exists, that will be called solubility limit. The physical meaning of this limit is that upon full polymerization of a system with an LC content below this limit, the LC will remain dissolved in the polymer network. Decreasing the
Network strength (as e.g. is the case for mono- or di-acrylates) gives the phase separation line in 3.6. The line for $\epsilon = 1$ is also shown in this diagram. A less elastic network adds less driving force for the phase separation, intuitively it squeezes out the liquid component less hard. The solubility limit increases, a higher LC content is needed to obtain phase separation.

To what extent the strength of the intermolecular interactions influences phase separation that is induced by network elasticity, is examined next. Phase separation lines for $\chi = 0.3$, $\chi = 0.5$ and $\chi = 0.7$ are plotted in figure 3.7.

When there is more interaction between LC-monomer and LC-polymer, the interaction parameter $\chi$ is lower and the phase separation line shifts upward. This signifies that for the same LC content, phase separation occurs at a higher conversion. For a higher value of $\chi$, phase separation occurs earlier. This is plausible, since a stronger interaction is energetically more favorable. Accordingly, the system will remain in the well-mixed three-component phase up to a higher monomer conversion.

For a realistic holography experiment using multi-functional acrylates and LCs, the values for $\chi$ and $\epsilon$ can be assumed to be 0.5 and 1.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{phase_separation_line}
\caption{Phase separation line, considering isotropic mixing ($\chi = 0.5$) and an elastic network ($\epsilon = 1$).}
\end{figure}
Figure 3.6: Shift of the phase separation line due to network efficiency factor ($\chi = 0.5$).

Figure 3.7: Shift of the phase separation line due to the interaction parameter $\chi$ ($\xi = 1$).
3.4.3 Nematic ordering

Below the nematic to isotropic transition temperature, a liquid crystal is in the ordered nematic phase. As from a certain LC concentration in an otherwise isotropic mixture, the LC will be nematically ordered. When the contribution to nematic ordering is added to the Gibbs free energy, an isolated area is found in the phase separation diagram (Fig. 3.8). A new, ordered phase appears.

![Phase separation diagram](image)

*Figure 3.8:* Phase separation lines, calculated with contributions to the chemical potential including isotropic mixing (Flory-Huggins), elastic network and nematic ordering. Area A: phase I, area B: both phase I and II in the isotropic state and area C: phase I and II, II in the nematic state.

Examine the compositions in the three separated areas of the diagram, it is found that the lower area (A) is the same phase I as before, consisting of polymer, monomer and liquid crystal. Area B is a two-phase area, containing phase I and phase II (monomer and LC), with the LC in phase II in the isotropic phase. In area C another liquid phase, phase III, is apparent, which contains only monomer and LC like phase II. However, the difference is that the LC volume fraction is high enough for the LC molecules to be in the nematic phase. The intersection of the phase separation line with the monomer-LC axis gives the critical composition for the LC to be in the nematic phase: $\phi_{ni}$. 
3.4.4 Binary nematic mixture

The phase separation line for a cholesteric mixture is calculated with the combination of isotropic mixing, network elasticity and the extended Maier-Saupe theory for binary nematic mixtures. Once more, it has to be pointed out that cholesteric self-stratification experiments are carried out with the mixture in the nematic state. Therefore the experiment temperature is chosen above the crystalline transition temperature and below the nematic to isotropic transition temperature of both the LC monomers and the non-reactive LCs. The resulting phase separation line is shown in Figure 3.9.

![Figure 3.9: Conversion phase diagram of a binary nematic system, experiment temperature is in the nematic phase below $T_{ni}(LC)$ and $T_{ni}(M)$.](image)

However, the shape of this line differs significantly from the phase separation line of a holographic system (e.g. Figure 3.5), which experimentally proved to separate in confined LC-polymer layers upon photo-polymerization. Therefore it is expected that in a cholesteric system at this temperature no layers can be created by phase separation.

However, by dosing the experimental temperature above the $T_{ni}$ of the LC, but below the $T_{ni}$ of the monomer, and still be in the nematic phase (except for high LC concentrations), yield another PS-line. For that case, the phase separation line is given in Figure 3.10. At the low LC concentrations, this line is comparable to the phase separation line of a holographic system.
Phase separation in LC-acrylate systems

3.5 Simulation results: reaction-propagation lines

Reaction-propagation lines describe the local change in composition of monomer and liquid crystal molecules upon polymerization. In a reaction step a certain amount of polymer is formed, which is different in depth of the sample, giving rise to a gradient in the chemical potential. This is the driving force for diffusion. A way to study the influence of isotropic mixing, elasticity and ordering on the diffusion, is to examine the effect on the driving force for diffusion of different polymer volume fractions in 2 subsequent depth intervals.

To study the phase separation behavior along the reaction-propagation line, the terms in the chemical potential corresponding to isotropic mixing, nematic ordering and elastic networks, containing $\phi_p$ and $\phi_m$ need to be considered. These terms are summarized in table 3.2.

Polymer is formed more rapidly at higher light intensity sites, giving a higher polymer volume fraction at those sites. In the columns, towards high or towards low denotes that the driving force for diffusion is towards the high or low light intensity side, so towards the higher or lower polymer volume fraction. For the investigation to the effects of the different parameters this table will be used as a reference.
Table 3.2: Influence of isotropic mixing, network elasticity and nematic ordering on the diffusion of monomers and LCs.

<table>
<thead>
<tr>
<th>Effect</th>
<th>( \phi_p )-dependence</th>
<th>( \phi_m )-dependence</th>
<th>Effect on M</th>
<th>Effect on LC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing</td>
<td>linear</td>
<td>logarithmic</td>
<td>towards high</td>
<td>towards high</td>
</tr>
<tr>
<td>Elasticity</td>
<td>linear</td>
<td>no</td>
<td>towards high</td>
<td>no</td>
</tr>
<tr>
<td>Ordering</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

3.5.1 Influence of \( \chi \) on diffusion

The monomer chemical potential due to isotropic mixing depends linearly on the polymer volume fraction and logarithmic on the monomer volume fraction. The interaction parameter contributes with a quadratic dependence on monomer and polymer fractions, plus 2 terms that are linear in \( \phi_m \) and \( \phi_p \) and a cross term, plus \( \chi \).

\[
\frac{\Delta \mu^M}{k_B T} = \ln \phi_m + \phi_p + \chi (1 + (\phi_m + \phi_p)^2 - 2\phi_p - 2\phi_m - 4\phi_m\phi_p) \tag{3.15}
\]

In the expression for the chemical potential of the monomer, the quadratic and the linear terms cancel out since the increase in polymer is the same as the decrease in monomer. However, a negative cross-term remains. Since \( \phi_m\phi_p \) is maximum 0.25, \( 4\chi\phi_m\phi_p \) can maximum be \( \chi \). The contribution of the chi-terms to the chemical potential of the monomer will therefore always be positive. For the depth interval with a higher polymer volume fraction, the total contribution of \( \chi \) to the chemical potential is the highest. Subsequently, the total \( \mu^M \) will be less negative at the high polymer volume fraction depth interval. This implies that the interaction term will try to impede the diffusion of monomers to the reactive sites. For the liquid crystal, only the quadratic term in \( \phi_m \) and \( \phi_p \) remains.

\[
\frac{\Delta \mu^L}{k_B T} = \ln \phi_m + \phi_p + \chi (\phi_m + \phi_p)^2 \tag{3.16}
\]

Therefore, the van der Waals interactions - represented by \( \chi \) do not play a role in the diffusion of the liquid crystal. Nevertheless, the \( \mu^L \) is lower in the low intensity regions than in the high intensity regions, due to the compositional entropy. It therefore induces diffusion towards the low intensity regions.

The assumption that the interaction between monomer and liquid crystal is the same as the interaction between liquid crystal and polymer, together with the assumption that a monomer-polymer interaction parameter is zero
implies that the contribution of the interaction parameter terms to the chemical potentials is the same for all possible combinations of compositions. Moreover, the contribution of the interaction parameter in the Flory-Huggins chemical potential (equations 2.36 and 2.37) is in the order of 0.05 - 0.2, while the other terms are of size in the order of 1. The effect in the driving force for diffusion due to interactions between subsequent depth intervals is therefore very small.

Therefore hardly any difference can be observed between the diffusion behavior of the model with or without the incorporation of the chi-parameters. In figure 3.11 the difference between the final depth distribution of liquid crystal for chi is zero and chi is 0.5 for an illumination time of 100 seconds is shown.

![Figure 3.11](image_url)

**Figure 3.11:** Difference in LC depth distribution after 100 seconds exposure between $\chi = 0$ (red) and $\chi = 0.5$ (blue). Only isotropic mixing is considered.

Following the reaction-propagation line in a conversion phase diagram is a more dynamical way of visualizing the system during polymerization. The conversion changes as a function of time so the conversion on the M-P axis can be seen as a timescale. The reaction-propagation line at 10% of maximum intensity with and without incorporation of the interaction parameter is shown in Figure 3.12. The red line depicts zero chi, the blue line shows the case of chi is 0.5. The effect of the interaction parameter is indistinguishable.
3.5.2 Network elasticity: $\epsilon$

The network elasticity gives a contribution to the chemical potential, the driving force for diffusion that scales linearly with the polymer volume fraction. Depth-dependent polymerization induces a contrast in polymer volume fraction between subsequent layers. Since the elastic contribution is always positive ($\epsilon$, $x^2/\alpha$ and $\phi_p$ in 3.6 are always positive), the chemical potential of both monomer and liquid crystal will be higher when more polymer is present. Therefore the network elasticity produces a driving force away from the high polymer volume fractions. Both monomer and liquid crystal experience a driving force towards the low intensity regions due to the network elasticity. Note that the diffusion of liquid crystals is therefore enhanced, while the monomer is hindered in its diffusion to the reaction sites.

The difference between no network present and an elastic network present is shown in figure 3.13.

3.5.3 Nematic ordering

The contribution to the chemical potential due to the nematic ordering depends on the monomer and polymer volume fraction via a cross-term that is exactly the same for both monomer and liquid crystal. The nematic partition function does not depend on volume fractions, while the intermolecular
interactions are characterized by a $\phi_{ic}^2$ dependence. Since $\phi_{ic} = 1 - \phi_m - \phi_p$, and the monomer volume fraction decreases with the increase of polymer formed, the quadratic and linear terms cancel out. The cross-term remains.

\[
\frac{1}{2} \nu \phi_{ic}^2 s^2 = \frac{1}{2} \nu (1 - \phi_m - \phi_m)^2 \\
= \frac{1}{2} \nu (1 + (\phi_m + \phi_p)^2 - 2\phi_m - 2\phi_p - 4\phi_m\phi_p)
\]  

Therefore the nematic ordering does not have an effect on the diffusion driven by a chemical potential. However, nematic ordering might nevertheless influence the diffusion in a different way. It is not out of the question that a nematically ordered compound has a slightly lower diffusion coefficient, which might also be anisotropic in nature as a result of the ordering. A quantitative evaluation of this effect is beyond the scope of this thesis.

3.5.4 Binary nematic mixture

The construction of a reaction-propagation line for a binary nematic mixture is more complicated than it seems at first sight. Whereas for holographic samples, the diffusion takes place in an isotropic mixture, in a cholesteric mixture molecules lie in nematically ordered layers. Moreover, the intensity
Phase separation in LC-acrylate systems

42

Figure 3.14: Reaction-propagation line at 10% of maximum intensity, 100 seconds exposure. Red = isotropic mixing and network elasticity, blue = isotropic mixing, network elasticity and nematic ordering. No significant difference is observed.

Gradient is applied perpendicular to the long axis of the molecules, so the diffusion direction of the liquid crystalline molecules is also perpendicular to the long axis. Nematic liquid crystals have a diffusion coefficient that is anisotropic. The diffusion coefficient perpendicular to the long axis can be up to 10 times less than the diffusion coefficient parallel to the long axis [15]. The exact behavior is not known, yet the diffusion coefficient in binary nematics (for cholesteric self-stratification experiments) is estimated to be in the order of $10^{-11}$, a factor 10 lower than the diffusion coefficients of the isotropic components in the initial states of a holography experiment.

3.6 Combination of the models

The results of the phase separation simulation program and the reaction-diffusion simulation (Figure (Figure 3.15), including all the effects of isotropic mixing, network elasticity and nematic ordering (Figure 3.15) are combined to predict the depth at which phase separation occurs first. This is achieved by going along the reaction-propagation line for all depth intervals until the phase separation line is crossed in a depth interval. The composition and depth at which this crossing takes place first reflects the onset of phase separation.
In the simulation program this procedure is achieved by running the reaction-diffusion program, and checking after each step whether the condition for phase separation (or two coexistent phases) is reached in a particular depth interval. For a standard holography experiment, the pitch is 150 nm, intensity 1.7 mW cm\(^{-2}\), 70:30 composition of monomers:LCs, phase separation starts first at a distance of 39.8 nm from the maximum intensity. In absolute distances this gives an estimated polymer layer thickness of 79.8 nm.

To verify the correctness of the model, 2 properties of a polymer-LC system can be measured. The phase separation line itself, as a result of the phase separation model can be compared with differential scanning calorimetry measurements. DSC measurements provide the conversion at which phase separation takes place for a certain starting composition. Repeating these measurements for different LC concentration therefore gives points on the phase separation line.

Secondly, the relative thicknesses of the polymer and liquid crystal layers can be measured with SEM. These thicknesses are a good indication of the estimations made with the model.
Chapter 4

Experimental methods

A well established technique to prepare Bragg gratings of alternating polymer and LC layers is to make use of an interference pattern from coherent laser beams, i.e. laser holography. Phase separation upon polymerization creates the Bragg layers with the grating periodicity induced by the interference pattern. The phase separation mechanisms have been studied in the previous chapter and the results of the phase separation model will be compared with measurements on holographic Bragg gratings in the next chapter. In this chapter the experimental methods to prepare and analyse polymer Bragg gratings are explained.

4.1 Chemicals

Although the model deals only with one monomer and one liquid crystal component, experimentally, holographic PDLC (h-PDLC) systems have only been realized with multi-component systems. Therefore the model can only be a guide to understand their behavior, by using effective liquid crystal and acrylate properties.

The holographic Bragg gratings were prepared from a mixture of a blend of monomers and the liquid crystal mix E7. The monomer blend consisted of 67 weight percent dipentaerythritolhydroxy pentacrylate (DPHPA, Polyscience Inc.), 15 weight percent N-Vinyl-Pyrollidone (NVP, Aldrich) and 18 weight percent hexafluoro bisphenol ‘A’ diacrylate (6F-bisA, Polyscience Inc.), see Figure 4.1. Since the monomers have different functionalities, respectively 5, 1 and 2 double bonds, the average functionality was estimated to 3.8 double bonds per molecule with an average molar weight of 448.3 g/mole.

The liquid crystal component was E7 (Merck, Figure 4.2), a blend of a cyanoterphenyl and three cyanobiphenyl molecules. It has a nematic to isotropic
Phase separation in LC-acrylate systems

transition temperature of 58 °C, so at room temperature it is in the nematic state. One wt% of the UV-sensitive photo-initiator Irgacure 369 (IRG369, Ciba, Figure 4.3) was added to the mixture. The standard composition for these holography mixtures contained 30 wt% E7, 69 wt% monomer blend and 1 wt% photo-initiator. Structure formulas and molecular weights of the components are summed up in Table 4.1.

*Figure 4.1*: Molecular structures of 1: dipentaerythritol pentaacrylate (DPHPA), 2: n-vinyl pyrrolidone (NVP) and 3: hexafluoro bisphenol 'A' diacrylate (6F-bisA).

**Table 4.1**: Chemical properties of the H-PDLC compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>Molecular weight [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E7(1)</td>
<td>C_{24}H_{23}N</td>
<td>325.45</td>
</tr>
<tr>
<td>E7(2)</td>
<td>C_{18}H_{19}N</td>
<td>249.35</td>
</tr>
<tr>
<td>E7(3)</td>
<td>C_{31}H_{25}NO</td>
<td>307.43</td>
</tr>
<tr>
<td>E7(4)</td>
<td>C_{20}H_{23}N</td>
<td>277.40</td>
</tr>
<tr>
<td>DPHPA</td>
<td>C_{25}H_{32}O_{12}</td>
<td>524.51</td>
</tr>
<tr>
<td>HF-bisA</td>
<td>C_{21}H_{14}F_{6}O_{4}</td>
<td>444.32</td>
</tr>
<tr>
<td>NVP</td>
<td>C_{6}H_{9}NO</td>
<td>111.14</td>
</tr>
</tbody>
</table>
Phase separation in LC-acrylate systems

4.2 Holography set up

Reflection gratings were recorded with the interference pattern of an Ar laser with a wavelength 351 nm. The experimental set up is presented in Figure 4.4.

A time-controlled shutter (s), placed directly after the UV-laser is used to control the illumination time. The UV-beam is focussed by a focussing stage consisting of a UV-lens (f1) and an aperture (a) followed by another UV-lens (f2). A linear polarizer (p1) is used as a filter to reduce the intensity of the beam. A UV mirror (r1) is used to guide the beam after which it passes a half-wave plate (λ/2) and polarizer (p2) to polarize the laser beam horizontally, in the plane of the sample. Hereafter the beam is guided to the sample surface, on which the beam spot has a diameter of approximately 1.5 cm. The reaction mixture is sandwiched between a Si wafer with ~100-150 nm Ag sputtered on top and a glass slide. The laser beam is focussed on the sample, where the incoming and reflected beam generate the interference pattern, described in equations 2.8 and 2.9. The periodicity of the interference pattern and thus the grating pitch can be controlled by tuning the angle of
incidence of the laser beam with the sample normal, $\theta$. When larger pitches are required, $\theta$ has to be increased. However, there is a limit since the glass plate tends to reflect the light when the angle exceeds $30^\circ$. The laser beam then needs to be coupled into the sample via a prism. The prism is placed on top of the glass plate, with a contact liquid in between for matching the refractive indices. This way the angle $\theta$ in formula 2.10 increases, and thus the pitch increases and reduces the total internal reflection between the prism and the glass plate.

The intensity of the laser beam was set to 1.7 mW cm$_{-2}$, and the illumination time was 30s. After the interference pattern had been written, the samples were flood exposed by 0.3 mW/cm$_{-2}$ Philips "facial lamp" for 20 min in order to fix the grating.

The reflection gratings were analyzed by scanning electron microscopy (SEM), from which the grating pitch was determined. Reflection gratings with pitches between 118 to 145 nm were produced (Figure 4.2).

Figure 4.4: Schematic representation of the laser setup, top view.

Figure 4.5: SEM images of reflection gratings prepared with holographic recording.
4.3 Analysis techniques

4.3.1 Nuclear reaction analysis

A possible way to study the formation of gratings is to measure concentration differences in depth. The feasibility of nuclear reaction analysis is studied in this perspective.

In nuclear reaction analysis (NRA) the presence of an element in a sample is detected through the radiation emitted from a nuclear reaction in the target produced by an irradiating ion beam. If long-lived radioactive nuclei are produced by the irradiation and detected afterwards, the method is called activation analysis; if the radiation is emitted instantaneously, it is termed prompt radiation analysis. The latter is the subject of this section.

For a nuclear reaction induced by ion beam bombardment (see Figure 4.6) the general notation $X(a,b)Y$ is used. Here $X$ is the target nucleus and $a$ is the accelerated projectile. $Y$ is the transformed nucleus and $b$ is the reaction product leaving the sample which can be a $\gamma$, $\alpha$ or neutron. The energy released or Q-value of the reaction is equivalent to the mass difference between reactants and products.

$$Q = (m_X + m_a - m_b - m_Y)c^2 \quad (4.1)$$

The kinetic energy $E_b$ of the emitted particle with mass $m_b$ in the direction $\theta$ of a reaction induced by an incident particle with mass $m_a$ and energy $E_a$ is determined by the conservation of total energy and momentum, and in the

![Figure 4.6: Notation used in resonant reactions.](image)
non-relativistic case is given by: \[ [17] \]

\[
\sqrt{E_b} = A \pm \sqrt{A^2 + B}
\]  

(4.2)

where

\[
A = \frac{\sqrt{M_a M_b E_a}}{M_X + M_Y} \cos \theta
\]

(4.3)

\[
B = \frac{M_Y Q + E_a (M_Y - M_a)}{M_X + M_Y}
\]

(4.4)

Equations 4.2, 4.3 and 4.4 show that \( E_b \) is characteristic of the reaction for a given energy.

The specific nature of the reaction cross section, enables the possibility to detect specific isotopes. Either reaction products or gamma rays resulting from the nuclear reaction are detected. Particle detection can suffer from interference with the detection of scattered particles. Therefore usually reactions are selected with a positive \( Q \) value. The reaction products then generally have a large excess of kinetic energy often even above the energy of the incident ion beam. When gamma rays are detected these interferences are absent and the cross section and detector efficiency determine the sensitivity.

Two different NRA-techniques can be distinguished: due to a sharp peak in the reaction cross section (Fig. 4.7), resonant NRA can be used for depth profiling, whereas with non-resonant NRA this is not possible. For resonant

**Figure 4.7:** Schematic representation of nuclear resonance profiling technique. \(^{15}\text{N}(p,\alpha\gamma)^{12}\text{C} \) reaction at 6.385 MeV, FWHM = 1.8 keV.
Phase separation in LC-acrylate systems

NRA the depth $x$ at which a reaction occurs is:

$$x = \frac{(E_0 - E_{res}) \cos \theta}{\left( \frac{dE}{dx} \right)}$$  \hspace{1cm} (4.5)

The yield from a thin layer of thickness $dx$ is given by:

$$dY_i = N_p \sigma(E) \frac{\epsilon_d}{\cos \theta_1} \frac{N_i}{N} dx$$  \hspace{1cm} (4.6)

$$= N_p \sigma(E) \frac{\epsilon_d}{\cos \theta_1} \frac{N_i}{N} \left( \frac{dE}{dx} \right)^{-1} dE$$  \hspace{1cm} (4.7)

$N_p$ is the number of projectiles, $\sigma(E)$ the total reaction cross section, $\epsilon_d$ the detector efficiency, $N$ the atomic density of the material and $N_i$ is the atomic density of the isotope of interest. $(dE/dx)$ is the stopping in the film under investigation with thickness $dx$. Thus, by changing the projectile energy and choosing a reaction with a narrow resonance, the concentration of a certain isotope can be measured as a function of depth.

The total yield at a specific beam energy is given by:

$$Y_i = \int dY_i = \frac{N_p \epsilon_d}{\cos \theta_1} \frac{N_i}{N} \left( \frac{dE}{dx} \right)^{-1} \int \sigma(E) dE$$  \hspace{1cm} (4.8)

The stopping is assumed to be independent of $E$, and is therefore put outside the last integral. The total reaction cross section as function of energy is needed for absolute quantification. Since this is usually not a known quantity, the integral is measured with a standard of which overall composition and concentration of the isotope under study is known.

Theoretically, reactions with alpha particles as projectile could have a better depth resolution, due to their higher stopping power. But, only few well-isolated resonances exist and are suitable for profiling, and the profiled depth is limited.

Nitrogen is a label for the liquid crystal used in the samples in this study. The reaction $^{15}N(p, \alpha\gamma)^{12}C$ at a projectile energy of 897 keV has a cross section of 800 mbarn and a resonance width of 1.7 keV. This reaction was chosen to investigate the feasibility for the depth profiling of nitrogen in a Bragg grating.

4.3.2 Photo differential scanning calorimetry

Method

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the tem-
Phase separation in LC-acrylate systems

Temperature of a sample and reference (empty sample pan) are measured as a function of time. Both the sample and reference are maintained at the same temperature throughout the experiment. Samples are polymerized in the DSC. Upon polymerization less heat will need to flow to the sample than to the reference to maintain both at the same temperature. Assuming that the heat capacity of the sample remains constant, the heat flow is directly related to the C=C conversion. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of energy released during polymerization.

With DSC it is thus possible to determine the reaction heat flow during photo-polymerization as a function of time, at a constant temperature.

\[
\frac{dH}{dt} = V \Delta H_0 - \frac{d[C = C]}{dt}
\]  

(4.9)

In this way one can determine the exact number of C=C bonds that has been converted until a certain point t in time. Here \( \Delta H_0 \) is the apparent heat per C=C bond (78 kJ/mol for acrylates [18]), and \( V \) the reaction volume. From the area under the DSC curve, the reacted number of C=C bonds can be determined.

\[
A(t) = \int_0^t \frac{dH}{dt'}(t')dt'
\]  

(4.10)

The unreacted double bond concentration \([C=C]\) is given by:

\[
[C = C] = [C = C]_0 - \frac{A}{V \Delta H_0} = [C = C]_0 - \frac{A}{\Delta H_0} \frac{\rho}{m}
\]  

(4.11)

with \([C=C]_0\) the initial double bond concentration, \( \rho \) the density and \( m \) the mass of the sample.

Set-up

Double bond conversions were measured using a Perkin Elmer Photo-DSC 7, under nitrogen atmosphere to prevent oxygen inhibition of the initiation. The samples were photo-polymerized in the DSC with a broadband UV-source with a maximum intensity at a wavelength of 365 nm with shutter control. Since heat transfer has a finite rate, the DSC apparatus has a limited detection speed. If double bond conversion is too fast, the double bond conversion at a certain time will be underestimated. Therefore the reaction rate was lowered by decreasing the light intensity. An intensity of 0.017 mW cm\(^{-2}\) was achieved by using a pinhole and a filter in front of the 0.18 mW cm\(^{-2}\) UV-source.

Photo-initiator concentration was 1 wt% for all DSC samples. Sample and reference pan were kept at constant temperature (isothermal) DSC.
Procedure

The following procedure was used for each DSC experiment. The sample pan was placed in the DSC with UV-source on and shutter closed during 5 minutes to obtain a thermal equilibrium in the DSC.

Then the sample was irradiated for 10 minutes during which the sample polymerized. During the experiment the differential heat flow rate to keep both samples at the same temperature was measured. Upon phase separation, a sample that initially was transparent becomes opaque due to the formation of liquid crystal droplets in the polymer matrix. A microscope with camera was installed to determine the time at which the sample became turbid.

After these 10 minutes, the measurement was continued for another 5 minutes during which the shutter was closed. During these last five minutes, no extra radicals are produced and the reaction has the time to terminate. Another advantage of the closed-shutter measuring time is that the samples have the time to reach equilibrium again, so that the baseline is more stable. The latter is necessary to correctly calculate the total heat transfer during the reaction. When determining the total heat, a time interval is chosen starting when the shutter opens and ending at the equilibrated baseline (see Figure 4.8).

Figure 4.8: Illustration of the importance of the choice of the time interval to determine the total heat flow during a DSC measurement.
4.3.3 Scanning electron microscopy

High-resolution imaging of sample surfaces is carried out with a scanning electron microscope (SEM). It uses high energy electrons ($\sim 50$ keV) in a focused beam to scan across a surface. The monochromatic beam of electrons is generated in an electron gun. Imaging is obtained by detecting backscattered electrons or secondary electrons. The former are produced by the elastic interactions between the sample and the incident electron beam. Secondary electrons are specimen electrons that obtain energy by inelastic collisions with beam electrons. A biased electron detector is used to convert the radiation of interest into an electric signal for manipulation and display.
Chapter 5

Comparison model results - experimental results

5.1 DSC measurements

5.1.1 DSC results

DSC measurements were carried out for different LC-monomer blend ratios at 20°C. The total heat released until phase separation occurred was determined with the procedure described in section 4.3.2. The double bond conversion was calculated from the area of the DSC-curve (equation 4.10).

![Figure 5.1: Double bond conversion at phase separation for different LC concentrations, UV intensity 0.017 mW cm⁻².](image-url)
From the sample weight and the composition the number of unreacted double bonds present before polymerization was calculated.

The results for the double bond conversion at phase separation are shown in Fig. 5.1. On the x-axis the LC fraction is set out, on the y-axis are the fractions of double bonds converted at phase separation. It is found that in mixtures with a low LC concentration, phase separation takes place at high C=C conversion (25 % for 34 wt% LC). Below 32 wt% liquid crystal, no phase separation is observed. This lower limit for the LC concentration agrees with the solubility limit found in the phase separation simulation, the lowest LC content for which liquid components separate from the matrix phase. It gives a first indication that the model results are plausible.

For high LC concentration phase separation occurs very rapidly after opening the shutter, at a low C=C conversion. Accordingly, the time of phase separation is very hard to image with the microscope, since it happens so fast. Moreover, the limited measurement rate of the DSC further limits the determination of the heat at phase separation for sample with a high LC concentration. Therefore the points measured for the 60-80 wt% LC concentration are questionable.

5.1.2 Double bond conversion vs. monomer conversion

To enable the comparison of model results with DSC measurements, a relationship between the double bond conversion and the monomer conversion needs to be established. A theoretical probability model describing this relationship for mono- and di-acrylates is summarized below.

The double bond conversion is denoted as x, M is the probability that a monomer has not reacted at conversion x. P is the probability for a monomer to be incorporated in the polymer chain at conversion x, which is equivalent to the monomer conversion as defined in section 2.3. For a mono-acrylate, M equals (1-x), P = 1 -(1-x) = x. For a di-acrylate, M = (1-x)² and P = 1 - (1-x)². These expressions are only valid when all double bonds are equally likely to react. In a cross-linking system this is no longer the case.

Therefore, an attempt was made to determine monomer conversion experimentally. The total heat at the end of the measurement was analyzed, to
obtain the total C=C conversion when the polymerization was completed. Results of this are shown in Fig. 5.2.

![Figure 5.2: Double bond conversion after 10 minutes UV-exposure, for different LC concentrations, UV intensity 0.017 mW cm⁻².](image)

It was found that the double bond conversion at the end of the DSC measurement was around 30% for all compositions. The values for the double bond conversion both at phase separation and at the end of the DSC measurement are displayed in Table 5.1

**Table 5.1:** Double bond conversion at phase separation and after 10 minutes exposure.

<table>
<thead>
<tr>
<th>LC content (wt%)</th>
<th>C=C at PS (%)</th>
<th>C=C at end (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (no ps)</td>
<td>0</td>
<td>33.4</td>
</tr>
<tr>
<td>32</td>
<td>28.4</td>
<td>32.7</td>
</tr>
<tr>
<td>34</td>
<td>24.4</td>
<td>31.7</td>
</tr>
<tr>
<td>36</td>
<td>21.2</td>
<td>33.8</td>
</tr>
<tr>
<td>40</td>
<td>14.8</td>
<td>34.9</td>
</tr>
<tr>
<td>50</td>
<td>5.6</td>
<td>31.5</td>
</tr>
<tr>
<td>60</td>
<td>3.3</td>
<td>32.7</td>
</tr>
<tr>
<td>80</td>
<td>2.7</td>
<td>19.3</td>
</tr>
</tbody>
</table>

The non-reacted monomers and the liquid crystals were washed out from the
DSC samples using solvents. Weak solvents: hexane, cyclohexane, cyclohexanone and methanol were used to prevent damage to the polymer. Samples were immersed in the solvents for 30 minutes up to 2 hours. Afterwards the solvent was evaporated by heating the sample to 70°C on a hot plate. A micro-scale balance was used for weighing the samples before and after washing.

The amount of monomer present before the washing can be calculated from the initial weight before washing. Dividing the weight of the polymer after the washing procedure by the initial weight gives the monomer conversion ($\alpha$), assuming that the residue after washing only consists of polymer. The monomer conversions obtained by this method are shown in Table 5.2.

<table>
<thead>
<tr>
<th>LC content (wt%)</th>
<th>monomer conversion (%)</th>
<th>C=C conversion (%)</th>
<th>C=C per monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>93.5</td>
<td>34.3</td>
<td>1.4</td>
</tr>
<tr>
<td>30</td>
<td>90.8</td>
<td>35.5</td>
<td>1.5</td>
</tr>
<tr>
<td>40</td>
<td>79.7</td>
<td>32.2</td>
<td>1.5</td>
</tr>
<tr>
<td>40</td>
<td>97.7</td>
<td>31.3</td>
<td>1.2</td>
</tr>
</tbody>
</table>

It was found that at the end of the DSC measurement on average 1.4 double bond per monomer had reacted. Considering the average functionality of 3.8 double bonds per monomer, less than half of the double bonds per monomer did react. It was expected that this value would be larger, or rather the monomer conversion was expected to be lower.

Two reasons can be found for the high monomer conversion at the end of the DSC measurement. The number of double bonds reacted per monomer has to be considered as a lower limit. If the solvent does not dissolve the monomers and LCs completely, the residue still contains monomers or liquid crystal molecules. Monomers and liquid crystals are trapped in the polymer matrix, leading to an overestimation of the polymer content, which leads in turn to a too high monomer conversion. This overestimation of the monomer conversion gives an underestimation of the average number of double bonds reacted per monomer. Also, since the reaction can continue after the experiment has been stopped, the exact double bond conversion could be slightly higher than the conversion measured with DSC. However this is expected to be a small effect since the samples are brought into air that inhibits further reaction due to its oxygen content.
**Table 5.3:** Calculation of monomer conversion at phase separation, comparison experiment-model.

<table>
<thead>
<tr>
<th>LC content (wt%)</th>
<th>C=C conv. (%)</th>
<th>experimental monomer conversion (%)</th>
<th>PS-model monomer conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>28.36</td>
<td>53.88</td>
<td>89.71</td>
</tr>
<tr>
<td>34</td>
<td>24.37</td>
<td>46.29</td>
<td>87.88</td>
</tr>
<tr>
<td>36</td>
<td>21.15</td>
<td>40.19</td>
<td>87.50</td>
</tr>
<tr>
<td>40</td>
<td>14.76</td>
<td>28.04</td>
<td>81.67</td>
</tr>
<tr>
<td>45</td>
<td>4.86</td>
<td>9.23</td>
<td>63.64</td>
</tr>
<tr>
<td>50</td>
<td>5.60</td>
<td>10.64</td>
<td>40.00</td>
</tr>
<tr>
<td>60</td>
<td>3.34</td>
<td>6.34</td>
<td>60.00</td>
</tr>
<tr>
<td>80</td>
<td>2.71</td>
<td>5.16</td>
<td>30.00</td>
</tr>
</tbody>
</table>

Secondly, for a system that auto-accelerates after gelation, the polymer chains lose their diffusion mobility very rapidly. Consequently they can not terminate, and the pendant (non-reacted) double bonds have a much lower probability to react. After gelation, most monomers react first with one double bond and the pendant double bonds will react much slower.

Taking above discussion into account, the experimentally determined value of 1.4 double bonds reacted per molecule can be considered low. Therefore the monomer conversion was treated as if the monomers were di-acrylates. The expression relating the monomer conversion to the double bond conversion discussed earlier in this chapter was used.

The monomer conversion at phase separation was both determined experimentally by washing out the unreacted monomers and LCs, and predicted by the di-acrylate approximation. The results are listed in Table 5.3: The results for the monomer conversion at phase separation from the model and from the DSC measurements are compared in Figure 5.3:

From the figure it can be seen that the monomer conversion predicted by the phase separation model is much higher than the monomer conversion calculated with the di-acrylate approximation on the experimentally measured double bond conversion from the DSC measurement. Since the real functionality of the monomers is 3.8 double bonds per molecule, the di-acrylate approximation gives an underestimation of the monomer conversion.

The discontinuities at 50 wt% LC for the experimental values and at 60 wt%LC for the model are explained by the transition from a liquid phase
that is isotropic to a liquid phase that is nematic. Since the discontinuity lies at different LC concentrations for the measured and the predicted conversion, and with the knowledge that changes in the interaction parameter and the network efficiency factor shift the phase separation line to other conversions at phase separation, it can be understood that these two parameters could be used to fit the results of the phase separation model with the experimentally determined phase separation line (from the DSC results). The interaction parameter was determined to be 0.46 in this way.

In the region of interest, for the low LC concentrations in Figure 5.3, the relationship between LC concentration and monomer conversion at phase separation is linear for both the experiment and the model. The difference in slope can be explained by the approximation for the relation $C=C$ conversion - monomer conversion. If the functionality of the monomers is higher, the slope of the measured conversion will be steeper.

Therefore, it is concluded that the results of the model are satisfying, but that a more realistic way to convert double bond conversion into monomer conversion needs to be found.
5.2 SEM measurements

To verify whether the predicted depth at which phase separation starts according to the model is in agreement with the experiments, scanning electron microscopy measurements were performed. Cross sections of holographically recorded Bragg gratings were prepared by breaking the samples under liquid nitrogen environment followed by washing out the LCs with methanol. A layer of 10 nm gold was sputtered onto the cross section to prevent charging of the polymer by the electron beam.

When phase separation starts at different depths, e.g. due to a change in the initial composition, light intensity, etc., the relative layer thicknesses of the polymer layer and the LC layer will differ. Therefore, these relative thicknesses can be used to verify the predictions of the model.

Measurements of the periodicity showed that reflection gratings with pitches between 118 to 145 nm were produced. However, the layer thickness is not trivial to determine, especially since the layers formed by holographic exposure were not completely homogeneous, and differed in the order of nanometers.

Instead it was chosen to investigate the layer formation by varying compositions and curing intensities. It was found that increased intensity resulted in optically transparent H-PDLCs, without layers. These are logical results since a higher intensity gives a higher reaction rate, creating less time for diffusion. Therefore, the reaction-propagation line is a straight horizontal line, the same for all depths of the sample and the situation before the recording is frozen in.

Higher liquid crystal content did neither lead to the formation of layers. More liquid crystal means that the reaction-propagation line is shifted upwards in the conversion-phase diagram. Both high and low intensity regions will come to a composition on the phase separation line at some time. Therefore phase separation takes place throughout the whole sample.
Phase separation in LC-acrylate systems
Chapter 6

Conclusions and recommendations

A model describing the phase separation behavior of holography and cholesteric mixtures is proposed, together with an adapted version of Christian Leewis' reaction-diffusion model. Influences of isotropic mixing, network elasticity and nematic ordering, contributing both to phase separation and to diffusion through their contribution to the chemical potential were investigated.

When considering only the isotropic mixing described by Flory-Huggins, neglecting the interaction enthalpy between polymer and monomer, and assuming the other interactions equal, no phase separation is predicted by the model. Introducing a small difference in the intermolecular interactions between monomer-LC and polymer-LC, does lead to phase separation, although this was found to be a very small effect.

However, the elasticity of a densely cross-linked network was found to induce phase separation. An elastic network squeezes out the liquid components, enhancing the phase separation. Investigating the effect of the Flory-Huggins interaction term showed that the strength of this interaction has a significant influence on the phase separation. Weaker interactions, reflected by a higher interaction parameter $\chi$, between LC and the two other components decrease the solubility limit, i.e. the highest concentration of LC for which no phase separation can occur. Increasing the interaction parameter $\chi$ shifts the line downward, which means that for stronger interactions phase separation will take place at a lower conversion. Consequently, the value of the $\chi$ parameter can be obtained by fitting the model with experimental results. For the holography system the value of $\chi$ was determined to be 0.46.
The network efficiency factor, accounting for the elastically inactive chains, was also investigated. Less elastic networks squeeze out the liquid components less hard with the result that the phase separation line is shifted upwards. Consequently, the network efficiency factor can also be used as a fit parameter by comparing the model with experimental results.

Nematic ordering of the liquid crystal in holography mixtures introduces a new state of the liquid phase, in which the liquid crystal is in the nematic ordered phase. For binary nematic systems like the cholesteric self-stratification systems a single phase separation line was found.

By combining the phase separation model and the reaction-diffusion model, the onset of phase separation in a holography sample (70:30 monomer:LC, 150 nm pitch, 1.7 mW cm$^{-2}$, at room temperature, 30s illumination) was estimated on 39 nm from the intensity maxima in the interference pattern.

DSC and SEM measurements were conducted to compare the modeling results with actual conversions at phase separation. The accuracy of the polymer layer thicknesses measured with SEM was low, due to the gradual onset of phase separation in depth which does not provide a clear boundary between the LC layer and the polymer films. However, SEM images showed that when layer formation was predicted by the model, the holographic samples did have a layered structure.

We encountered some difficulties to find a correct relationship between double bond conversion and monomer conversion for a heavily cross-linking system as the holography system is. Gelation is the main cause that monomers loose their mobility to diffuse to reaction sites during the polymerization. Therefore the experimentally measured average number of double bonds reacted per monomer molecule was lower than expected from a cross-linking system. Calculating the monomer conversion from double bond conversion using the di-acrylate model resulted in the underestimation of the monomer conversion. Comparison with results of the model showed that the general trend for the conversions at phase separation of the model agrees with the trend of the measured conversions. However, the phase separation line that was determined experimentally showed a shift with respect to the results from the phase separation model. The interaction parameter and network factor can be used to fit the model to experimental results. Absolute volume fractions however do not agree due to the di-acrylate approximation for the monomer conversion.
Recommendations for future work:

First of all, the relationship between monomer conversion and double bond conversion for the holographic mixture should be established. Experimentally this can be done by washing out the un-reacted monomers and LCs from the polymer (as done in this study). However, since the monomer conversion after extraction was unexpectedly high, it can be supposed that the monomers and LCs were not successfully washed away. This could be checked with FTIR measurements on the residue, since the LCs are marked by the cyano group and the monomers by the un-reacted acrylate group. In the case that monomers and LCs still are present in the polymer, we suggest longer extraction times (e.g. weeks) in the weak solvents mentioned in section 5.1.2, or even stronger solvents, as long as the polymer does not get damaged.

Layered structures have not yet been obtained by cholesteric self-stratification. The phase separation line for a mixture of a nematic liquid crystalline diacrylate and a non-reactive liquid crystal has a shape comparable to the holographic system, for temperatures between \( T_{ni}(LC) \) and \( T_{ni}(M) \). Therefore, it is suggested that molecules with significantly different \( T_{ni}(LC) \) and \( T_{ni}(M) \) are chosen and that experiments are performed at a temperature in between.

Also, a balance between the reaction rate and diffusion rate also needs to be established. Since diffusion for nematic liquid crystals in the direction perpendicular to their long axis, in depth of the sample, is around 10 times slower than diffusion along the long axis. To allow phase separation to create layers in depth, the diffusion has to be increased, either by increasing the diffusion rate or by decreasing the polymerization rate allowing more time for diffusion to the liquid components. The diffusion rate can be increased by elevating the temperature (to just below the clearing temperature), which will enhance the mobility of LC and monomers. A more efficient way to decrease the polymerization rate is by decreasing the intensity of the curing linearly polarized UV-light.

To verify the formation of layers and the relative layer thicknesses, the depth profile of the liquid crystal and polymer concentration can be studied. Concentration differences in LC between polymer layers and LC layers are expected to be in the order of 40%-60%. Therefore, secondary ion mass spectrometry (SIMS) could be useful to do molecular depth profiling in the Bragg gratings. A feasibility study to use nuclear reaction analysis for this purpose is presented in the appendix.
Phase separation in LC-acrylate systems
Appendix A

Nuclear reaction analysis for nitrogen depth profiling: a feasibility study

In order to characterize the efficiency of phase separation in confined layers, it would be useful to measure the concentration of liquid crystal as function of depth. In a mixture of liquid crystalline monomers and liquid crystals, only the LC component contains N atoms. Thus, by determining the nitrogen concentration depth profile, the distribution of liquid crystal throughout a grating can be investigated. In this section NRA is studied as a possible method to achieve a nitrogen depth profile in a polymer matrix.

A.1 Selection of the reaction

In table A.1 the resonant \( (p,\alpha\gamma) \) reactions of nitrogen with protons within the singletron energy range are shown. \( E_p \) is the proton energy, \( \sigma \) the reaction cross section. \( E_{\gamma} \) is the energy of the gamma photon emitted upon reaction [19].

For depth profiling two characteristics are of importance, the resonance width and the reaction cross section. A narrow resonance will give a thin excited layer, while a high cross section will give a high yield. An interesting candidate for NRA is found in the \( ^{15}N(p,\alpha\gamma)^{12}C \) reaction at 897 keV. Its width of 1.7 keV will give an excited layer in the order of 50 nm thickness. With a \( \sigma \) of 800 mbarn the reaction has a rather high probability. With equations 4.2 and ?? the energy of the emitted alpha particles can be determined. First, the Q-value of the reaction has to be calculated. Writing the reaction as \( ^{15}N(p,\alpha\gamma)^{12}C \), and subtracting the energy of the emitted gamma photon
Table A.1: \((p,\gamma)\) and \((p,\alpha\gamma)\) nitrogen resonances.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E_p) (keV)</th>
<th>(\sigma) (mb) or (S) (eV)</th>
<th>Resonance FWHM (keV)</th>
<th>(E_\gamma) (MeV)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{15}\text{N}(p,\alpha\gamma)^{12}\text{C})</td>
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<td>0.12</td>
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<td>100</td>
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<td>800</td>
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<td>1979</td>
<td>35</td>
<td>23</td>
<td>4.43</td>
<td>100</td>
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</table>

\(Q = (m_{15N} + m_p - m_{^{12}C} - m_\alpha)c^2 - E_\gamma = 1.449\) MeV \hspace{1cm} (A.1)

Then, the alpha energy is:

\(E_\alpha = 420\) keV \hspace{1cm} (A.2)

A.2 Experimental set up

A.2.1 Accelerator set up

The Eindhoven 3.5 MV Singletron accelerator built by High Voltage Engineering Europe (HVEE), depicted in Figure A.1, is used to produce the 900 keV proton beam. An RF oscillating probe current produces a hydrogen or helium plasma in a source at the high voltage terminal of the acceleration tube. Protons are injected into the acceleration tube by the combination
of an extraction voltage and a probe voltage and accelerated by the terminal voltage (TV). The beam then passes an analyzing (or energy-selecting) 90 degrees magnet. A switching magnet enables the operator to select the requested beam line. In the beam line used for these experiments, four quadrupoles, placed just before the vacuum chamber, perform the final focusing. Two sets of slits, the object slit and the aperture slit take care of the object size and the beam current. The last stage is a scanning magnet which allows to scan over the sample with a minimum stepsize of 75 nm. At four positions in the beam line Faraday cups are installed to measure the beam current. The target chamber, shown in Figure A.2 contains the target wheel, that has eight sample positions. The TueDacs software controls the stepper motor for x-y translation and the rotation stage of the target wheel with a respective resolution of 2\(\mu\)m and 0.001 degree. The beam is visualized on a fluorescent ceramic, placed on one of the positions of the target wheel. A cross wire on another position is used to define the origin - or zero-position of the beam. Furthermore, the vacuum chamber contains four detectors. A

![Diagram](image-url)
Si(Li)-detector for PIXE measurements placed at 135 degrees, a passivated implanted planar silicon (PIPS) detectors at 147 and 45 degrees for scattering experiments, are used for the detection of reaction products. An n-type Ge detector is at an angle of 90 degrees, with solid angle times efficiency of about 0.1 msr for the detection of gammas from NRA.

A.2.2 Detectors

Gamma detection

The detector used for the detection of gamma photons is a Canberra GR1520, that is reverse biased with a voltage of 4500 volts. The geometry is a coaxial open end, closed end facing window, with a window diameter of 47.5 mm, length of 43.5 mm and a distance from the window (outside) of 5 mm. Its depletion voltage is -3000 Volts DC. Calibration of the detection system was carried out using $^{137}$Cs and $^{60}$Co reference gamma sources with respective emission lines of 662, 1173 and 1332 keV. In this way a calibration curve for the channel-energy relation was obtained.

Particle detection

Apart from measuring the photons emitted during the reaction also the reaction products, alpha particles in this case, can be detected. For this purpose, either a standard PIPS and or a thin film Si detector placed at 147 degrees with the sample normal were used. The thin film detector has the advantage that scattered protons (800 keV protons deposit 230 keV in the Si layer) can be discriminated very easily since they appear at the low energy side of the spectrum.
For the thin film detector, a high capacity preamplifier of the type Ortec 142C for capacities of more than 400 pF was installed for impedance matching purposes. Since the detector thickness is only 5 µm, applying a positive bias voltage of 10 V is sufficient for a depletion layer thickness equal to the thickness of the detector. A $^{241}$Am$^{244}$Cm alpha-emitter, with alpha energies of 5.443, 5.486, 5.779 and 5.805 MeV was firstly used to test the device, and later for calibration. Alpha particles emitted by this source deposit between 630 and 667 keV in the 5 µm Si, while 420 keV alphas will be completely stopped in the Si layer. These energies are similar, so the AmCm α-source is appropriate to use for calibration.

A standard backscatter detector was also used for detection of α-particles. Energy calibration of the detection system was carried out with a 10 µm thick polycarbonate foil coated with a 100 Ångströms thick nickel layer. Interpretation of these spectra is simpler, since all particles are completely stopped in the detector. Consequently, the energy in the spectrum equals the full energy of the detected particle.

A.3 Samples

A sample with 80 nm Si$_3$N$_4$ deposited by low pressure chemical vapor deposition (LPCVD) on a Si wafer was available in the accelerator lab. A test sample with a thicker layer of Si$_3$N$_4$ was prepared with the help of the experimental plasma physics group at the department of applied physics of the TU/e: by plasma deposition, an 800 nm Si$_3$N$_4$ layer was deposited on a Si wafer. The density of Si$_3$N$_4$ is 3.44 g/cm$^3$, its molar weight is 140.286 g/mole.

In addition, a nitrogen-containing polymer layer of 20 µm on a Si wafer was prepared by doctor blading. The polymer has an approximate density of 1 g/cm$^3$ and an approximate stopping power of 2.8 eV/Ångström.

A.4 Estimated γ-yield

The estimated gamma yield was calculated for the 800 nm Si$_3$N$_4$ layer. The stopping power of Si$_3$N$_4$ for an 897 keV proton is 6.889 eV/Ångström. This implies that the resonance width of 1.7 keV (FWHM) corresponds to a layer thickness of 24.7 nm. The areal density N atoms in such a layer is 1.43 $10^{17}$ atoms/cm$^2$. However, the target isotope of the selected reaction is $^{15}$N, which has a natural abundance of 0.366%. Thus the areal density
of $^{15}\text{N}$ excited by the resonant reaction is $5.234 \times 10^{16}$ atoms/cm$^2$. Gamma rays traveling through matter are attenuated by the sample. Since the detector is placed behind the sample, the transmission of the Si wafer needs to be taken into account. However, for 4.43 MeV gammas the transmission of 2 mm Si is 100%. With an incident beam current of 200 nA ($= 1.25 \times 10^{12}$ protons/second), a solid angle times detector efficiency of 0.1 msr [11] and assuming that the $\gamma$'s are emitted isotropically, the number of detected gamma photons can be calculated with equation 4.7. For measurement with a duration of 15 minutes:

$$Y = 5.234 \times 10^{16} \times 0.8 \times 10^{-24} \times 1.25 \times 10^{12} \times 900 \times 0.1 \times 10^{-3}$$

(A.3)

$$= 471 \text{ counts}$$

(A.4)

A.5 Results and discussion

A.5.1 Gamma detection

The first attempt to detect nitrogen in the 800 nm Si$_3$N$_4$ sample was performed with a proton beam optimized on a terminal voltage of 900 kV. After energy calibration of the Ge-detector, the spectrum shown in Figure A.3 was measured. The low energy peaks result from background radiation, and were also found in the calibration spectra. The peak at 1.77 MeV is a peak from

Figure A.3: Total gamma spectrum from 900 keV protons NRA experiment on 800 nm Si$_3$N$_4$ on Si wafer.
the $^{27}\text{Al}(p, \gamma)^{28}\text{Si}$ reaction in the aluminum sample holder. Enlarging the high-energy side of the spectrum shows the 4430 keV gamma peak from the $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ reaction (Fig.A.4). In 15 minutes, 450 gamma photons were detected, which corresponds to the expected yield (equation A.4). The low detector efficiency at high energies causes the peak to be a continuum from 4400 keV to 4460 keV.

**Figure A.4:** 900 keV proton NRA on 800 nm Si$_3$N$_4$ on Si wafer, 4300-4500 keV gamma energy.

Since polymers on average have a stopping power of 2.5 eV/Ångström for 900 keV protons, the layer that is excited by the proton beam has a thickness of around 70 nm. The areal density of $^{15}\text{N}$ atoms in an excited cyano-polymer layer is then 600 times lower than the $^{15}\text{N}$ density in Si$_3$N$_4$. This low concentration implies that the expected gamma yield from a polymer sample will be 600 times lower than the yield from Si$_3$N$_4$. During a measurement of 1 hour, 3 gamma photons detected can be expected. This is a very low yield, and considering the radiation damage due to the high power density of 288 kW cm$^{-2}$, not a realistic option.

### A.5.2 Depth profile

In order to measure a depth profile of nitrogen, the beam energy needs to be changed in small steps. The procedure for changing the beam energy was as follows: for stability reasons (warming up of the tank) the starting TV was 950 kV. Subsequently, the terminal voltage was lowered to a new level, whereafter the beam current on Faraday cup 4.2 was optimized by adjusting
the 90 degree analyzing magnet, the switching magnet and the magnets in
the microbeam line.

At each depth a measurement with a duration of 50 minutes was performed. The resulting gamma-yield per proton energy is shown in graph A.5. Note that the energy on the x-axis is actually the terminal voltage setting, which is an indication of the actual beam energy. In the present set-up, it is not possible to measure the exact beam energy. On the y-axis the normalized yield

![Graph A.5](https://example.com/graph.png)

**Figure A.5:** Depth profile of 800 nm Si$_3$N$_4$ on Si wafer, obtained with gamma detection from the $^{15}$N($p$, $\alpha\gamma$)$^{12}$C reaction.

is set out. Since the beam current could not be tuned to exactly the same value for each experiment, each yield is normalized with respect to beam current. The error bars represent the error caused by background, which is the square root of the number of counts. This experiment showed that the yield was high enough to detect a concentration gradient in depth of this sample. However, with a more efficient detection method, smaller differences in concentration could be detected.

### A.5.3 Particle detection

Figure A.6 shows the RBS-spectrum of an NRA experiment using 900 keV protons on the 800 nm Si$_3$N$_4$ sample. On the x-axis the energy of the detected particles is set out, on the y-axis the yield. From zero to 900 keV, protons scattered from Si and N are measured. Between 900 keV and 2 MeV,
pile up due to the high beam current appears. Up to 420 keV the alpha particles from the $(p,\alpha\gamma)$ reaction are expected. The background of scattered particles interferes with the detection of the alpha particles originating from the $^{15}N(p,\alpha\gamma)^{12}C$ reaction.

Between 3.4 and 3.7 MeV, particles were detected. Since the energy of these particles is higher than the projectile energy, they cannot be attributed to scattered protons. In the 12 μm cyano-polymer sample, a similar effect was observed. Particles with an energy between 2.7 and 3.7 MeV (Figure A.7) were found.

Since the only common element of the two studied samples is nitrogen, these particles need to originate from a nuclear reaction on nitrogen. The non-resonant $^{15}N(p,\alpha)^{12}C$, which has a high cross section (314 mb) [20] for incident protons of 900 keV. This non-resonant reaction takes place throughout the whole 800 nm thick Si$_3$N$_4$ layer, producing a relatively high yield (estimated 5322 counts). Since 3 MeV alpha particles and 420 keV alphas (down to 0 keV alphas) will deposit the same energy in a thin film detector of 5 μm thick Si, using a thin film detector with inherently a poor energy resolution resulted in continuous spectra in which no peaks can be distinguished.
Figure A.6: RBS spectrum of a 900 keV protons NRA experiment on 800 nm Si₃Ν₄ on Si wafer.

Figure A.7: RBS spectrum of NRA experiment, 900 keV protons on 12 μm CN-polymer on Si wafer.
A.6 Conclusions

NRA was studied for the purpose of nitrogen depth profiling in polymer-LC Bragg gratings. For a test sample of 800 nm Si₃N₄ on Si, gammas produced by the reaction $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ were detected. By increasing the projectile energy, the reaction will occur deeper in the sample. It was shown that a depth profile of nitrogen in the model sample could be measured with this gamma detection.

Particle detection was investigated as a more efficient detection method. Alpha particles of 420 keV have a range of around 800 nm in Si₃N₄. Thus, 800 nm is the the maximum depth that can be profiled using particle detection. This is in contrast with gamma detection, for which the depth has no limit due to their 100% transmission in Si₃N₄ and Si. Leaving the latter out of consideration, another complication was encountered. Interferences of non-resonant $(p,\alpha)$ reactions on nitrogen were observed. Another detection option for the particles would be using a thin film detector, but due to the bad energy resolution and the interferences, this was not a suitable method to detect the alpha particles.

So, nitrogen depth profiling with the $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ is possible for the Si₃N₄ test sample, given that the gammas are detected.

Polymers on average have a stopping power of 2.5 eV/Ångström, three times lower than Si₃N₄, giving an excited layer that is three times as thick, decreasing the depth resolution significantly. This could partially be overcome by tilting the sample with respect to the incident beam, increasing the effective path of the projectiles in the sample. In addition, the nitrogen concentration in E7, the liquid crystal containing the cyano-group, is much lower than in Si₃N₄, where it is higher than 1:2. Taking this into account, a factor 600 less yield can be expected from a polymer sample. With concentration differences between layers of 40-60 %, measurement times would need to be long time (in the order of 4-5 hours per measured depth) to get reasonable statistics. Irradiating for a long time with a power density of 288 kW cm⁻² will result in significant radiation damage to the polymer without cooling. Furthermore, the liquid crystal is a liquid, which will easily evaporate in the high vacuum of the target chamber. A cryogenic stage, and capping of the sample with an evaporation barrier, e.g. polyvinylalcohol, to prevent the latter, would be necessary to overcome these problem.

Another difficulty is to tune the beam energy to measure at the wanted depth. The projectile energy can only estimated roughly with the terminal
voltage value and the setting of the analyzing magnet. Secondly, changing the beam energy is a rather time-consuming occupation. A bias voltage on the sample could be a solution to this.

So, the answer to the question whether N-NRA is a suitable method for nitrogen depth profiling in polymer-LC systems is: no. Considering the small differences in concentration, and the low gamma yield of the liquid crystal, nuclear reaction analysis is not accurate enough to accomplish a depth profile.
Bibliography


Phase separation in LC-acrylate systems


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At the end of this thesis, the moment has come to thank many people. I owe gratitude to so many people that I will probably forget some of them in these acknowledgements.

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