New Receiver Optics
for
Wireless Communication with IR-technique

Master Thesis
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Abstract

The aim of this thesis is to investigate the possibility to use a fluorescent receiver to improve performance for IR-links. I have performed an inventory of polymers and dyes suitable for applications in the near infrared region. I then combined polymers and dyes and performed tests on the constructed materials. A spectral broadening have been observed for the dyes in polymeric environment. The fluorescent sheets that I constructed had very low quantum efficiency and were therefore very hard (in some cases impossible) to investigate with the methods used.

I have also investigated different shapes to concentrate light using a lightguide. Here it is desired to minimize leakage and light stocking effects.

The intended application cannot be realized without further development of appropriate materials.
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Appendix 2, Absorption measurements.
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Appendix 5, Quantum yield measurements.
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1. The idea behind the project

The idea behind this project is to design a new kind of receiver for infrared communication using the phenomena of fluorescence.

The aim of this thesis is to investigate the possibility to use a fluorescent receiver to improve performance for IR-links. The investigation has been theoretical as well as practical. The work should mainly be directed towards the application; diffuse IR-links.

The range using IR-technique for wireless communication is often limited by the signal levels at the receivers.

- In cases with low signal levels superposed on background radiation the incoming signal must exceed the NEP (Noise Equivalent Power) of the detector and the noise in the amplifier. Besides this the capacitance of the detector increases and makes it more difficult to receive high-frequency signals.

If the link must rely on diffuse light with no specific direction. The possibility to use optical arrangements to increase the irradiance on, and the signal levels from, the detector is limited.

- In cases where the operation is limited by the background level of DC-light sources (e.g. light bulbs and the sun) the coverage can be improved by increasing the signal levels. This can be done by increasing the detector area. One could say that the shot noise is roughly proportional to one over the square root of the detector area.

- In cases where the operation is limited by the background level of interfering light sources (e.g. HF-driven light tubes) the radial coverage can not be further improved by increasing the detector area. Here spatial filtering, higher frequency of the carrier wave (>500 kHz) and two-color techniques can be helpful.

Studying the two statements above it is possible to conclude that an IR-link with high carrier frequency and large detector area would be a nice solution in many different environments.

The idea of a fluorescent light guide in the receiver is to collect as much light as possible and to concentrate it to a detector area of reasonable size as presented in figure 1.1. The combination fluorescence and light guidance can theoretically give substantial light concentration. Something that is impossible with conventional optics in systems with large acceptance angles.

Fig. 1.1 Combination of fluorescent area and a detector. Guiding the fluorescent to a small detector.
An overview on the basic theory behind the project is given in chapter 2. I discuss the fluorescence phenomena, the principle for capturing the light and different aspects on the light guidance. In chapter 3 I concentrate on infrared dyes. What requirements are wanted for the application and what different dyes are available from manufacturers. I treat the subject of frequency shifts due to changes in dye environment and motivate my choice of dyes used for testing. The next chapter (chapter 4) treats the subject of polymers. First my requirement and then concentrating on the infrared absorption in polymer materials. Due to the problem occurring with infrared absorption in polymers alternative design solutions are discussed in chapter 5.

The mixing of polymers and dyes is treated in chapter 6 both in theory and in practice. The properties of my constructed fluorescent polymeric materials used for tests are given in this chapter. In the following chapter 7 I present the measurement performance for all the tests I performed; verification of fluorescence, absorption, emission and excitation measurements and measurements of the quantum yield. In chapter 8 the results of my measurements can be studied and the conclusions made from the different results are presented in chapter 9.

In chapter 10 I present calculations made on capturing the light and also give an orientation on my evaluations of the shape of the receiver. The different results from mainly chapter 8 and 10 are combined in chapter 11 where I calculate the total efficiency of the thought receiver and discuss improvements needed.

A summary of the thesis can be studied in chapter 12.
2. Basic theory

This chapter aims to give a brief orientation on the fluorescence phenomena and the principles of capturing and guiding light.

2.1 Fluorescence

There are different kinds of atomic transitions that can give fluorescence. Fluorescence involves certain types of light emission. An atom or a molecule has several discrete energy levels (quantised). To visualize this the energy levels can be drawn in a simple diagram as done in figure 2.1. Transitions can take place between these levels and the atom/molecule is then able to absorb or induce emission of light. When an atom/molecule has been excited it will try to return to its ground state (relaxation). The relaxation can be radiative (inducing light emission) or non-radiative (absorbed energy transferred to heat). If the relaxation involves energy levels between ground state and excited level and induce light the process is called either fluorescence or phosphorescence. Phosphorescence involves so called triplet states and forbidden transitions and therefore has a longer lifetime then fluorescence.

![Energy level diagram](image)

**Fig 2.1 Schematic drawing over energy levels for an atom.**

Using the relation $E=hf$ combined with $v=c/\lambda$ we can describe the relation between energy and wavelength as $E=hf/\lambda$ or $\lambda=hf/E$. The energy level diagram can now be transferred to a wavelength spectra as done in figure 2.2 for the energy levels in figure 2.1.

![Absorption and emission spectra](image)

**Fig 2.2 absorption and emission spectra relating to energy levels in figure 2.1.**
The quantised levels can be divided in several levels very close in energy and it is then more correct to speak of energy bands (figure 2.3). It is then possible that the excited molecule first relax non-radiatively to the bottom of the band and then undergoes a transition from there to a lower level. This transition can be either radiating or non radiating.

![Energy Bands Diagram](image)

**Fig 2.3** Schematic drawing of energy levels / energy bands for a molecule.

This will cause broadening of the corresponding wavelength spectra. Besides absorption spectra it is also possible to define excitation spectra. The excitation spectra consists of the absorption that causes radiative emission (e.g. light). This often corresponds directly to the absorption but not always. Thought absorption, excitation and emission spectra corresponding to figure 2.3 can be studied in figure 2.4.

![Absorption, Excitation and Emission Spectra](image)

**Fig 2.4** Absorption, excitation and emission spectra relating to energy levels in figure 2.3.

The absorption (or excitation) and the emission spectra is often combined in one spectra as in figure 2.5.

![Normalized Absorption and Emission Spectra](image)

**Fig 2.5** Absorption and emission spectra combined in same figure.
In a non-resonant process the emitted fluorescent light always has lower energy than the absorbed and is thereby pushed into a longer wavelength region ($\lambda \propto 1/E$). This wavelength transformation can cause problems when it comes to designing NIR-receivers for communication. It is important not to exceed the wavelength sensitivity range for the detector.

2.2 Capturing the light

When a fluorescent material is struck by incoming radiation, energy can be absorbed. The absorbed energy is re-emitted partly as light at the same or longer wavelength. The re-emission is for amorphous solids directed isometrically in space, which makes it possible for us to capture light inside a material with higher refracting index than its surroundings.

First study what happens when light strikes a non-fluorescent compared to a fluorescent material. The light is refracted in the surfaces according to Fresnel’s formula ($n_l \sin \theta_i = n_t \sin \theta_t$). If light is incident on a denser medium (as in our case) the light is refracted towards the normal of the surface. When the light leaves the denser medium it is refracted from the normal according to the same formula. If the incident angle in the later case is greater than a certain value (the critical angle) total internal reflection occurs and the light will then stay inside the denser medium.

![Fig 2.6 Principle of capturing of light inside a denser media.](image)

By using a fluorescent medium it is possible to capture light as visualized in figure 2.6. How is it then possible to guide it to a spot, for example a detector?

2.3 Aspects on the shape of the receiver

By shaping a fluorescent medium in a suitable way it is possible to collect light and guide it to a spot for detection. Designing the shape of the receiver the area of use should be considered. In my case an important demand is that the receiver should be sensitive over a wide angle. To increase the light levels striking the receiver it is possible to use surrounding mirrors as in figure 2.7 but the mirrors are not allowed to obstruct any incoming light (consider $\theta$).
Other very important factors is the capture and guiding efficiency. One wishes to guide as much light as possible to the detector. Several factors must be considered and will be discussed in the following chapter. Besides this the receiver must also be easy to handle and possible to construct.

2.4 What will have impact on the efficiency

2.4.1 Geometric efficiency

The receiver must be formed so that the leakage of light is minimized. Edge surfaces should be kept as planar as possible with smooth curving to minimize the leakage. The end surfaces not directed to the detector could be provided with reflective material to avoid losses. See figure 2.8.

2.4.2 Conversion efficiency

The fluorescent substance in the receiver should be chosen so that the conversion between absorbed and emitted light (the quantum yield) is as high as possible. This to maximize the capture of the light and avoid absorption losses.

2.4.3 Absorption

Non-radiant. The non-radiant absorption gives rise to pure losses. As low absorption as possible is to prefer on all wavelengths but those for the incoming signal. For the wavelengths of the incoming signal one wishes that the absorbed light gives rise to as much emitted fluorescence light as possible (high quantum efficiency). As earlier mentioned the emitted fluorescence light often
has longer wavelengths than the absorbed signal and it is therefore ideal if the absorption and emission spectra’s overlap as little as possible and has steep flanks.

Secondary fluorescence. Since there in practice always exists an overlap between the absorption and emission spectra secondary fluorescence will occur. Light already captured in the receiver can cause a new fluorescent process and thereafter leak out of the receiver as illustrated in fig 2.9.

Fig 2.9 Secondary fluorescence can give loss of light.

The time the signal spend in the receiver can be prolonged by the same effect, as illustrated in figure 2.10.

Fig 2.10 Repeated secondary fluorescence can increase the time it takes for the signal to reach the detector.

2.4.4 Summary

We have four main factors that will have impact on the efficiency:

- Geometric efficiency.
- Conversion efficiency.
- Non-radiant absorption
- Secondary fluorescence

These factors will affect each other but can mainly be optimized one by one.
3. Infrared dyes

This chapter gives an orientation on infrared dyes. I discuss the requirements for thought application and perform an inventory over available dyes. Frequency shifts in the dyes due to use of different solvents is also discussed.

3.1 Dye requirements

Excitation spectrum with high excitation somewhere in the region around 875 nm. (It is possible to find fast light diodes for communication at other wavelengths as well.) Since I was not sure of how large frequency shift that would occur after combining the dye with a polymer it was hard to know exactly what I was looking for (see later chapters). I would like to have a steep flank against longer wavelengths, interference with shorter wavelengths are quite easy to avoid using absorption filters.

The only requirement for the emission spectra is that the light is emitted mainly below 1050 nm so that cheap and fast photo diodes are available. An ideal spectra can be studied in figure 3.1.

![Ideal dye spectra for my application (after being combined with polymer).](image)

Fig 3.1 Ideal dye spectra for my application (after being combined with polymer).

Other important factors concerning the dye are:

- Decay rate (\(\gamma\) or \(\tau\)) for the emission.
- If they are poisonous.
- Quantum yield (exc. to em.)
- Possible solvents, is it possible to bind them to plastic?

The decay must be fast enough for communication at a speed of 1Mbit/sec. There will be other effects slowing down the speed of the receiver but initially the speed is set by the fluorescence lifetime.

The resulting device must not be dangerous to handle.

The initial effect on total quantum efficiency will be determined by the conversion effect of the dye. It is very important that it is as high as possible.

Since the idea of the application is to combine the dye with a polymer material it must be possible to do so.
3.2 Dye inventory

I have contacted a wide variety of dye manufacturers around the world. I have been looking for dyes with an excitation peak somewhere in the region 830 to 950 nm with steep flanks towards longer wavelengths. The offering of near infrared dyes is unfortunately rather small. Most dye producers has no dyes for the infrared region what so ever. Exciton and Lambdachrome offers some laser dyes with absorption peaks around 830. I also located a Japanese manufacturer that offers a rather wide variety of dyes for the NIR-region.

Interesting dyes:

- IR-132, no longer manufactured.
- IR-140, L-C and Exciton.
- IR-143, Exciton.
- IR-144, L-C and Exciton.
- NK-124, Nippon Kankoh-Shikiso kenkyousho
- NK-1162, Nippon Kankoh-Shikiso kenkyousho

Spectra and other information from the manufacturers concerning the dyes can be studied in appendix 1. One of the most interesting dyes from my point of view (e.g. IR-132) is unfortunately no longer manufactured. For the dyes in the IR-series I also found indications that their absorption spectra don’t correspond to their excitation spectra. The excitation seems to be shifted towards shorter wavelengths. For IR-140 the absorption peak in Methanol was measured to 800 nm and the excitation peak to 712 nm.

3.3 Frequency shift of the dye

The excitation and emission spectra’s will be shifted due to effects from the solvent. The total frequency shift results from different interactions. The effects are very hard to predict and I have chosen to work with "trial and error". It is however of interest to make a short review of the different effects. The spectra of many fluorophores, especially the ones with polar substituents on the aromatic rings, are sensitive to the (both chemical and physical properties) properties of the solvents. There are both general and specific effects where the specific exceeds the general. For examples of what will cause the different kind of effects see table 3.1.

<table>
<thead>
<tr>
<th>General</th>
<th>Specific</th>
</tr>
</thead>
<tbody>
<tr>
<td>refractive index</td>
<td>chemical interaction</td>
</tr>
<tr>
<td>dielectric constant</td>
<td>H-bonding etc.</td>
</tr>
</tbody>
</table>

Table 3.1 Examples of properties in solvent causing general and specific effects on the fluorophore.

It is possible to make a short summary of different dynamic processes and what they can effect. Different processes as:

- Collision with quencers.
- Rotation and transition diffusion.
- Formation of complexes.
- Reorientation of the environment.
Give rise to:
- Fluorescence anisotropies.
- Decrease in quantum yields.
- Effects on fluorescence lifetimes.
- Changes in excitation and emission spectra.

If the solvent molecules have dipole moment, they reorient around the excited state dipole and thereby effect its energy. The table 3.2ii below shows the different interactions between solvent-solute and their spectral shifts.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NP</th>
<th>NP</th>
<th>P</th>
<th>P</th>
<th>P</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in solute dipole</td>
<td>None</td>
<td>None</td>
<td>Decrease</td>
<td>Increase</td>
<td>Decrease</td>
<td>Increase</td>
</tr>
<tr>
<td>Type interaction</td>
<td>Polarization</td>
<td>Polarization</td>
<td>Polarization, dipole-polarization</td>
<td>Polarization, dipole-dipole, packing</td>
<td>Polarization, dipole-dipole, packing</td>
<td></td>
</tr>
<tr>
<td>Predicted shift</td>
<td>Red</td>
<td>Red</td>
<td>Either direction</td>
<td>Red</td>
<td>Blue</td>
<td>Red</td>
</tr>
</tbody>
</table>

NP = Non Polar  P = Polar
Table 3.2 Interactions between solvent and solute and their resulting shifts.

In my case I suspected a blue-shift due to the use of a non (or at least less) polar solvent instead of a polar as in the data from manufacturers and a red-shift due to the increase of refractive index in the solvent.

I base the prediction of the blue-shift on data for IR-140 and IR-143 from Exciton (table 3.3 below) combined with the polarity of the different solvents (table 3.4 below).

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Ethanol</th>
<th>Methanol</th>
<th>EG/PC 1/1</th>
<th>EG/DMSO3/1</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR-140 ($\lambda_{abs}$)</td>
<td>776</td>
<td>810</td>
<td>823</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR-143 ($\lambda_{abs}$)</td>
<td>838</td>
<td>855</td>
<td>863</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EG=Ethylene Glycol PC=Propylene Carbonate DMSO=Dimethyl Sulfoxide
Table 3.3 Absorption peak data for the dyes, IR-140 and IR-143.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA (in solution)</td>
<td>1.3 - 1.45 debye</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.694 debye</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.703 debye</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>2.315 debye</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide</td>
<td>3.964 debye</td>
</tr>
</tbody>
</table>

No data for Propylene Carbonate available.
Table 3.4 Polarity for different solvents.
The use of a more polar solvents gives an increase of the red-shift. Using a non (or less) polar solvent would therefore give a blue shift compared to the data given for lets say dye dissolved in DMSO which is the most common among the spectra I have received from manufactures.

Non-polar effects will add to this shift. The most significant effect is a red-shift due to changes in the environments index of refraction. There are some formulas derived to calculate shift in absorption frequency, the simplest one describing shift due to polarization effects is the formula:

$$\Delta v = -1.07 \times 10^{-14} \frac{1}{v} \left( \frac{f}{a^3} \right) \left( n^2-(n_2-1)/(2n^2+1) \right), \text{ Note that } \Delta \lambda = -\lambda^2 \cdot \Delta v$$

where $v$ is the frequency of solute transition (in inverse centimeters), $f$ is the oscillator strength of solute transition, $a$ is the radius of the spherical cavity and $n$ is the index of refraction of the solvent. The spherical cavity is an approximation of the "empty space" between the molecules in the solvent where the solute molecules can reside.

Since the solute-solvent polar effects generally dominates over non-polar effects I suspected the resulting shift to be a blue-shift.

3.4 Dye choice (strategy)

I have earlier mentioned that I chose to work according to the "trial and error" principle. I therefore performed testing on some different dyes.

IR-140 The dye is manufactured by Exciton and supplied by Martinsson Elektronik.

IR-143 The dye is manufactured by Exciton and supplied by Martinsson Elektronik.

NK-124 The dye is manufactured and supplied by Nippon Kankoh-Shikiso Kenkyuusho Co. ,Ltd.

Information about these dyes can be studied in appendix 1. Their excitation peaks are located below 875 nm for IR-140 and IR-143 and above for NK-124 (all dissolved in DMSO).
4. Polymers

This chapter gives an orientation on polymers. I discuss the requirements for thought application. Infrared absorption in polymers and other problems that can occur are discussed.

4.1 Polymer requirement

For my application I need to find a material that:
• has low absorption in the NIR region (850-1100 nm).
• is possible and easy to dope with rather big organic compounds.
• is easy to model into a suitable form.
A polymer like PMMA (PolyMethylMetAcrylate) would be ideal if it was not for the high IR absorption (only about 20% transmission over a 30 cm rod for 900 nm). Polymeric design may however offer a way to avoid the high IR-absorption that is characteristic for polymers.

4.2 Infrared absorption in polymers

All organic polymers absorb in the infrared region. This is of great importance when it comes to dope the polymers with infrared absorbing dyes. It is necessary to find a polymer that will not affect the light guidance in such way that the intended application will be impossible. The absorption spectra for polymers is available through manufacturers and the subject can be studied elsewhere in works concerning it.

Typical loss factors are shown in the table 4.1. A way of affecting the absorption through polymeric design is to avoid the absorption due to C-H and O-H bonds.

<table>
<thead>
<tr>
<th>Intrinsic</th>
<th>Absorption</th>
<th>C-H overtone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Electronic transition</td>
</tr>
<tr>
<td></td>
<td>Scattering</td>
<td>Raleigh scattering</td>
</tr>
<tr>
<td>Extrinsic</td>
<td>Absorption</td>
<td>Transition metals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic contaminates</td>
</tr>
<tr>
<td></td>
<td>Scattering</td>
<td>Dust and microvoids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fluctuation in diameter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Boundary imperfections</td>
</tr>
</tbody>
</table>

Table 4.1 Loss factors in polymers.

The fundamental frequency, \( v_f \), of the C-H bond is proportional to the inverse square root of the reduced mass, \( \mu \).

\[
v_f = (1/2\pi) * \sqrt{K/\mu}
\]

\( K \) is the restoring force constant.
Thus the wavelength is proportional to the square root of reduced mass, \( \lambda \propto \sqrt{\mu} \) (where \( \mu \) is the reduced mass). The basic strategy to reduce this absorption is to substitute the hydrogen with heavier atoms, deuterium (D), fluorine (F) or chlorine (Cl) to induce a shift of the
absorbency towards longer wavelengths. Deuterated polymers must be specially synthesized and are very expensive there are however fluoridated polymers commercially available.

\[
\begin{align*}
C-H & \quad O-H & \quad C=O \\
-D & \quad -D & \quad C=O \\
-F & \quad -F & \quad C-C \\
-Cl & \quad -Cl & \quad C=C
\end{align*}
\]

Fig. 4.1 C-H and O-H groups should be avoided to improve the NIR-transmission.

The substitution H with F will also affect the chemical resistance in the polymer and make it stiffer. In many applications this is desirable but not when the polymer should be as easy to dissolve and dope as possible. To obtain higher IR-transmission and also keep the dopeability it is possible to use a polymer which consists of both normal H-monomer and fluoridated monomers.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{CH}_3 & \quad \text{O} \\
\text{C}=\text{O}
\end{align*}
\]

Fig. 4.2 Different monomers can be combined to reach desired polymer properties.

\[
\begin{align*}
\text{O} & \quad \text{CF}_3 \\
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}
\]

Fig. 4.3 HFDA-HFDAM-33 commercially available polymer from DuPont\textsuperscript{vii}.

4.3 Dopeability for polymers

The possibility to dope polymers with dyes varies. PMMA is very easy to dissolve in for example chloroform then stir in the dye and dry as a film. Fluoridated polymers are less easier soluble but there are commercially available polymers partly fluoridated that is possible to dissolve and mix with dye. It is important that not too much dye is mixed in because then the dye will crystallize and the desired function of the plastic film will not be obtained. For the same reason it is important not to break down the structure of the dye during the mixing process.
4.4 Polymer choice (strategy)

I choose to work with PMMA to make the mixing process as easy as possible. I used thin samples in my testing so I was able to neglect loss in the polymer. This makes it possible to calculate the improvement I would receive using a polymer with higher transmission. I will also try to perform tests using a polymer with higher IR-transmission that is, HFDA-HFDAM-33 a commercially available polymer from DuPont\textsuperscript{1}.

4.5 Mixing procedure

PMMA

1. Dissolve dye in chloroform.
2. Dissolve PMMA in chloroform.
3. Mix the two solutions.
5. Pour the PMMA/dye/chloroform solution in the bowl.
6. Evaporate.
7. Tap out the dye/polymer plate.
8. Cut the plate with sharp knife to desired shape.

More sure to do this in a well evaporated area.

More about mixing polymers and dyes in a later chapter (Mixing polymer and dye).

\textsuperscript{1} Supplied by Ms Weigand from DuPont, Germany.
5. **Alternative design solutions**

Due to the high IR-absorption in many polymers it is interesting to try to find alternative solutions for the receiver. Perhaps it would be possible to use a thin fluorescent substrate on some kind of light guide or make use of a fluent light guide. Different solutions are possible and I only intend to give a brief orientation of them here.

### 5.1 Combination of polymer film and glass guide.

It would perhaps be possible to attach a thin plastic film over a formed glass based light guide as illustrated in figure 5.1.

![Figure 5.1](image1.png)

*Fig 5.1 Thin polymer substrate on edge of glass waveguide.*

If one matches the refractive index between the polymer sheet and the glass there will be no reflection in the border region. Most of the light transport would now be in a material with quite low IR-absorption. There are several factors to consider when deciding the thickness of the film and of the light guide, for example:

- It is to prefer to have as much as possible of the transport in the glass. E.g. thin polymer sheet and rather thick light guide.
- It is necessary to catch almost all IR-light in the device. E.g. thick enough polymer sheet (doped as high as possible).
- It is necessary not to destroy the time resolution between the pulses. E.g. thin enough light guide because of pulse broadening due to difference between modes and other effects.

It is possible to consider an alternative design of this idea as in figure 5.2.

![Figure 5.2](image2.png)

*Fig 5.2 Thin polymer substrate inside glass waveguide.*

The same factors needs to be considered for this design. Though the polymer sheet would be more protected in this case.
5.2 Use of fluent light guides

Another possibility is to dissolve the IR-fluorescent dye in a fluid and use the solution in a fluid light guide as in figure 5.3. The use of fluent light guides would however be very impractical.

5.3 IR-dye doped in glass

It could be interesting to try to dope another material than a polymeric one, for instance glass as suggested in figure 5.4. (This could be further investigated ....)

Maybe it would be possible to use some kind of glass fiber material.
6. Mixing polymer and dye

In this chapter I describe the mixing between polymer and dye. Proper fractions are calculated and the practical method used is described. The properties of the samples used in my tests are given in this chapter.

6.1 In theory

The mixing fractions of polymer and dye must be adjusted so that almost all incoming signal radiation will be absorbed. Problem with crystallization of the dye can occur if the dye fraction is too high. The polymer/dye sheets were produced in Petri bowls of two different types described in figure 6.1.

![Diagram of two Petri bowls with different diameters](image)

Fig 6.1 The two different types of Petri bowls used.

I wish to produce sheets with a thickness of about 1 mm. The needed amount polymer can be calculated.

$$\rho_{PMMA} = 1.18 \times 10^3 \text{kg/m}^3$$

1. $$V = \pi \times (0.04)^2 \times 10^{-3} \approx 5.027 \times 10^{-6} \text{ m}^3$$
   $$m = V \times \rho_{PMMA} \approx 5.931 \text{ gram}$$

2. For one section
   $$V = \frac{1}{4} \pi \times (0.05)^2 \times 10^{-3} \approx 1.9635 \times 10^{-6} \text{ m}^3$$
   $$m = V \times \rho_{PMMA} \approx 2.317 \text{ gram}$$

Let's say that 98% absorption is desired over a path of 1 mm.

$$\varepsilon_{average} \approx 1 \times 10^5 \text{ L/(mole*cm)}$$
(approximated from information received from manufacturers.)

$$I = I_0 \times e^{-\varepsilon \times \lambda}$$

$$[\varepsilon] = \text{L/(mole*cm)} \quad [\lambda] = \text{mole/L}$$

$$0.02 = e^{-1 \times 10^5 \times \lambda}$$

$$\lambda = -\ln 0.02 / 1 \times 10^4 \approx 3.912 \times 10^{-4} \text{ mole/L}$$
1. \( V \approx 5.027 \times 10^{-6} \text{ m}^3 \)
   Amount dye \( \approx 1.966 \times 10^{-6} \text{ mole} \)

2. For one section
   \( V \approx 1.9635 \times 10^{-6} \text{ m}^3 \)
   Amount dye \( \approx 7.681 \times 10^{-7} \text{ mole} \)

The calculations are combined with the molar weight of the dyes to give the amount dye in gram needed for desired absorbency (see table 6.1).

<table>
<thead>
<tr>
<th>Dye</th>
<th>molar weight</th>
<th>d=80 mm</th>
<th>d=100 mm (1 sect.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR-140</td>
<td>779.19</td>
<td>1.53 mg</td>
<td>0.60 mg</td>
</tr>
<tr>
<td>IR-143</td>
<td>810.42</td>
<td>1.59 mg</td>
<td>0.62 mg</td>
</tr>
<tr>
<td>NK-124</td>
<td>532.47</td>
<td>1.05 mg</td>
<td>0.41 mg</td>
</tr>
<tr>
<td>Rhod. 6G (for test)</td>
<td>479.02</td>
<td>0.94 mg</td>
<td>0.37 mg</td>
</tr>
</tbody>
</table>

Table 6.1 Amount dye in grams needed for desired absorbency.

Note that these values are calculated for a value of \( \varepsilon = 1 \times 10^5 \text{ L/(mole*cm)} \) and that the amount dye needed is proportional to \( 1/\varepsilon \). It is therefore easy to predict the changes in dye needed when \( \varepsilon \) varies.

If I dissolve 25 mg of each dye in Chloroform until I reach a total volume of 250 ml my solutions would contain 0.1 mg/ml. The amounts of the different substances for proper mixing according to calculations are given in table 6.2 (the dyes being dissolved as above).

<table>
<thead>
<tr>
<th>Bowl</th>
<th>PMMA (g)</th>
<th>IR-140 (ml)</th>
<th>IR-143 (ml)</th>
<th>NK-124 (ml)</th>
<th>Rhod. 6G (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d=60 mm</td>
<td>3.336 g</td>
<td>15.3 ml</td>
<td>15.9 ml</td>
<td>10.5 ml</td>
<td>9.4 ml</td>
</tr>
<tr>
<td>d=100 mm (one section)</td>
<td>2.317 g</td>
<td>6.0 ml</td>
<td>6.2 ml</td>
<td>4.1 ml</td>
<td>3.7 ml</td>
</tr>
</tbody>
</table>

Table 6.2 Amount PMMA (in gram) and dye solution (in ml) needed for desired absorbency.

The mixing and evaporation was initially performed with Rhodamine 6 G to see if any problems (for example with crystallization of the dye) would occur. No problem with crystallization was observed. A lot of other difficulties unfortunately occurred; problems to dissolve the PMMA pellets, long evaporation time to for the chloroform, among other.

6.2 In practice

6.2.1 PMMA

Through my calculations I have a rough idea about the quantities needed in the mixing procedure. My intention is only to test the principle and for that purpose the fluorescent plastic sheets don’t need to be of the highest quality. I used a Rhodamine 6G solution and tried different methods to find a working procedure sufficient for my needs.

There were a lot of problems to dissolve the polymer. Also, it was hard to avoid voids inside the polymer/dye-sheets. Because of the problem with dissolving the polymer it was impossible to control the exact amount of polymer and thereby also the dye concentration in the sheets.
I chose to simply dissolve PMMA in chloroform and add a certain amount of dye solution to each sample. Then I evaporated the mixtures without interfering with the process. To approximate the fraction dye in the resulting plastic sheets I kept track of how many moles dye that was used in each sample. I then weighed the resulting polymer sheet to approximate the volume of the sample. Since I knew the amount of added dye I could combine these two pieces of data to calculate the dye concentration. The concentration needed for ultimate functionality will have to be further investigated.

The dye solutions were prepared containing 1 mmole/L. These solutions were pipetted into the samples.

The samples I used to work with have the following properties.

<table>
<thead>
<tr>
<th>DYE</th>
<th>IR-140 (low conc.)</th>
<th>IR-140 (high conc.)</th>
<th>IR-143 (low conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (g)</td>
<td>4.79</td>
<td>4.63</td>
<td>4.81</td>
</tr>
<tr>
<td>Volume (m³)</td>
<td>4.06*10⁻⁶</td>
<td>3.92*10⁻⁶</td>
<td>4.08*10⁻⁶</td>
</tr>
<tr>
<td>Amount dye (μmole)</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Conc. dye (μmole/ g)</td>
<td>0.209</td>
<td>0.648</td>
<td>0.208</td>
</tr>
<tr>
<td>Conc. dye (mole/ m³)</td>
<td>0.246</td>
<td>0.765</td>
<td>0.245</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DYE</th>
<th>IR-143 (high conc.)</th>
<th>NK-124</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (g)</td>
<td>4.18</td>
<td>3.28</td>
</tr>
<tr>
<td>Volume</td>
<td>3.54*10⁻⁶</td>
<td>2.78*10⁻⁶</td>
</tr>
<tr>
<td>Amount dye (mmole)</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Conc. dye (μmole/ g)</td>
<td>0.718</td>
<td>0.304</td>
</tr>
<tr>
<td>Conc. dye (mole/ m³)</td>
<td>0.847</td>
<td>0.360</td>
</tr>
</tbody>
</table>

Table 6.3 Properties for the samples used in testing.

6.2.2 Pyralin

I also prepared samples with dye doped inside pyralin (a fluoridated polymer from DuPont). Dye dissolved in chloroform was mixed with fluent polymer. I let the samples evaporate for about 8 hours in room temperature. The samples was thereafter baked in a hot oven at 90 degrees Celsius for 60 minutes.

Unfortunately the samples etched so hard to the glass that they were almost impossible to separate from the Petri bowls.
7. Measurements

A lot of different measurements were performed on my polymer/dye samples. In this chapter I describe the different types of measurements made and the methods used to perform the tests.

7.1 Rhodamine 6G

Initially measurements were performed on polymers doped with Rhodamine 6G. Rhodamine 6G fluoresces in the visible wavelength region so it was easy to view the light beams.

7.1.1 Sample fluorescence

I first used an Ar+ laser to ascertain that the samples were fluorescing. A sample was put in the beam and it was possible to see that the green light from the laser was converted to longer wavelengths as the sample gave an yellow impression. This gave an positive identification that fluorescence was present in the sample.

7.1.2 Absorption spectra

Absorption spectra was measured using a "white light" xenon-lamp combined with a spectrograph. The experimental setup was calibrated from 556 to 1200 nm. This is not the most interesting region when performing measurements on Rhodamine 6G samples but the setup was not originally set up for this experiment. The experimental setup can be studied in figure 7.4 in the chapter 7.2.2, infrared dyes (absorption spectra). The spectra can be studied in appendix 2.

7.1.3 Emission spectra

To study the emission spectra I used an Ar+ laser combined with a monochromator as described in figure 7.1.

\[\text{Ar+ laser (514 nm)} \rightarrow \text{monochromator (Oriel)} \rightarrow \text{detector (Hamamtsu)}\]

Fig. 7.1 Equipment used to get emission spectra from Rhodamine samples.

The sample was excited with 514 nm and I then scanned the monochromator over longer wavelengths to obtain the emission spectra. The spectra was mainly located between 550 and 630 nm with a peak at 580 nm. The spectra can be studied in appendix 3.

7.1.4 Excitation spectra

I measured the excitation spectrum for the PMMA-Rhodamine combination using a quite simple method described in figure 7.2.
I used a filter (Schotts RG 590) to block the exciting wavelengths. The signal detected is caused by fluorescence converting incoming light to longer wavelengths that can pass by the filter. I varied the incoming light between 420 and 570 nm and could thereby detect the shape of the excitation spectra. Compared to spectra taken of Rhodamine 6G in methanol there is no significant wavelength shift for the excitation spectra but a broadening of the spectrum has occurred. The excitation peak is located at 537 nm. The spectra can be studied in appendix 4.

7.1.5 Quantum yield

To get information about the quantum yield I studied different configurations between the monochromator and the filter. The quantum yield in the polymer was determined to be approximately 49%. This value is to be compared with the value 0.9 which is given in literature for Rhodamine 6G in methanol. The measurement results and calculations are given in appendix 5.

7.2 Infrared dyes.

I also performed measurements on my samples of polymer doped with different infrared dyes. The near infrared region is not in the visible wavelength region so it was not possible to see the light beams. This made the alignment and investigations a bit more complicated. As I had indication that absorption and excitation spectra do not match each other for some of the infrared dyes I tried to obtain both absorption and excitation spectra, but there were a lot of problems with this since the fluorescence was quite weak.

7.2.1 Verification of fluorescence in the samples

I first used a diode laser (780 nm), a Schotts RG 850 filter and an IR-viewer to be able to register if fluorescence was present in the samples (see figure 7.3). If I could see the dye/polymer samples much clearer through the filter than non fluorescent objects when illuminated with the laser this indicates that a fluorescent process is present. The fluorescence converts incoming light to longer wavelengths and the light is then able to pass through the low-pass filter.
Fig. 7.3 Principle for verification of IR fluorescence in samples.

<table>
<thead>
<tr>
<th>exciting wavelength</th>
<th>IR-140</th>
<th>IR-143</th>
<th>NK-124</th>
</tr>
</thead>
<tbody>
<tr>
<td>780 nm</td>
<td>fluorescence ver.</td>
<td>fluorescence ver.</td>
<td>fluorescence not ver.</td>
</tr>
</tbody>
</table>

The dye NK-124 showed no fluorescence but it should be kept in mind that the absorption peak for this dye is located much further (924 nm) in the IR-region. The absence of suitable filters in this region calls for a different method to check whether the samples fluoresces.

7.2.2 Absorption spectra

White light source
To obtain absorption spectra I worked with an system with a white light source (a xenon lamp) and a spectrograph as shown in figure 7.4. Due to problems with registering a fluorescence signal I knew that the quantum efficiency was very low and could therefor neglect the contribution of fluorescence light striking the detector.

Fig 7.4 Experimental setup used to obtain absorption spectra using a white light source.
I hereby obtained the collimated transmission \( T_{col} = \exp(\text{abs + sca}) \). The scattering was approximated as wavelength independent and spectra for the absorption profile was constructed by normalizing (dividing) with a measurement without sample present. The spectra obtained can be studied in Appendix 2. Note that the approximation of wavelength independent scattering not is absolutely correct, my samples contains impurities and this will give Raleigh scattering that indeed is very wavelength dependent (inverse proportional to the fourth power of the wavelength). If the result of a measurement performed on a thin PMMA sample without dye is studied one notices that the absorption seems to be stable over the whole wavelength region. Hence the wavelength dependence of the Raleigh scattering can be neglected.

**OPO-system**
I also used a setup were the light source was an OPO-system (Spectra Physics). The OPO (Optical Parametric Oscillator) is a pulsed light source with substantial fluctuations in peak power. The set up for the experiment can be studied in figure 7.5 and 7.6. To avoid damaging optical surfaces the beam was reflected in two glass plates reducing the energy to 0.16% \((0.04 \times 0.04 = 0.0016)\). Then I could control the incoming light on the "black box" (see figure 7.5) using neutral density filters. This was needed to be able to control the signal level on channel 1 and 2 and avoid saturation in the detectors.

![Diagram of OPO system](image)

*Fig. 7.5 Set up for the measurements with the OPO system.*
The transmission could be registered by dividing the signal on detector 1 with the signal on detector 2. The software used was a LabView program by Petter Weibring, LTH. The received data and spectra can be studied in appendix 2.

### 7.2.3 Emission spectra

Diode lasers were used to get initial information about emission spectra, setup can be studied in figure 7.7. The exciting wavelength could be varied by changing the diode. This also gave a brief orientation of the excitation spectra (at least the probable range).

I excited the sample with the diode laser and then scanned the second monochromator manually over longer wavelengths. The signals were very weak and hard to separate from laser light scattered inside the monochromator.

**IR-140**

The spectra was located between 870 and 995 with a peak at 910 nm. The measurement data, shape of the spectra and explanations can be studied in appendix 3.

**IR-143**

The spectra could not be categorized. The measurement data, shape of the spectra and explanations can be studied in appendix 3.

**NK-124**

It was not possible to detect any fluorescence.
7.2.4 Excitation spectra

Unfortunately no absorption filters with sufficient efficiency in the IR-region were available. I tried to adjust the equipment used for Rhodamine measurements using a second monochromator fixed on a wavelength longer then the exciting ones as can be studied in figure 7.8.

![Diagram of equipment used to get excitation spectra from Infrared dye samples.]

Since I now only register fluorescent signal in a limited wavelength area and also look on a much smaller acceptance angle I was not able to get a detectable signal. A method, to increase the signal levels, would be to use a set up with an OPO (Optic Parameter Oscillator) focused on the samples (see figure 7.9).

![Diagram of thought set up for the “black box” for excitation measurements with the OPO system.]

The monochromator should be tuned to the wavelength of the emission peak for the examined sample and the OPO should then be scanned over a region of shorter wavelengths.

Due to the low quantum yield in the samples (which I knew would make the experiment hard to perform) and lack of time these experiments were not performed.
7.2.5 Quantum yield

An approximation of the quantum yield was made by using a laser diode at 790 nm and a RG 850 filter. Different configurations of the sample and filter in front of the detector gave me as for Rhodamine an approximative value of the quantum efficiency for the samples containing IR 140 and IR 143. No value could be obtained for the sample containing NK 124 as no fluorescence could be detected. The calculations can be studied in appendix 5.

*IR-140*
0.81%

*IR-143*
0.69%

*NK-124*
No fluorescence detected in sample.
8. Results of measurements

In this chapter I present the results of my measurements as combined spectra (when possible) together with a value for the quantum efficiency.

8.1 Rhodamine 6G combined with PMMA

Spectra:

Quantum efficiency = 49%
Quantum efficiency = 0.81%
8.3 IR-143 combined with PMMA

Spectra:

Not possible to categorize. Approximation can be studied below.

Quantum efficiency = 0.69%
8.4 NK-124 combined with PMMA

Spectra:

No fluorescence detected.

Quantum efficiency = No fluorescence detected.
9. Conclusions of measurements

Here I present the conclusions I have made from my measurement results.

9.1 Resolvement of the dye’s absorption profile in the samples

All absorption measurements can be studied in appendix 2.

9.1.1 Rhodamine 6G

The absorption profile of the dye seems to be easy to resolve. Since my prime interest was concentrated on infrared dyes I have not made any measurements of absorption in the wavelength region where this dye is primarily used. However the absorption spectra’s edge towards longer wavelengths is easy to resolve as done in absorption measurements with the white light source, appendix 2.

9.1.2 IR-140

The absorption profile of the dye is easy to resolve. The profile is more obvious in the sample named low concentration then in the sample named high concentration. This probably indicates that the sample denoted high concentration in appendix 2 is saturated with the dye which causes the dye to crystallize.

9.1.3 IR-143

The absorption profile of the dye is not very easy to resolve with the equipment used in this work. In the sample named low concentration the profile can be resolved but not in the sample named high concentration. This could be due to some undesired interaction between the polymer and the dye or only be an effect of increasing saturation when preparing the samples causing the dye to crystallize.

9.1.4 NK-124

It is nearly impossible to resolve any absorption profile due to the presence of the dye in the sample. This is probably due to some kind of undesired interaction between the dye and the polymer.

9.2 Spectral shifts in polymer hosts

The conclusions are made by comparing the information received from manufacturers (appendix 1) with information from measurements (mainly appendix 2).

9.2.1 Rhodamine 6G

Since no absorption measurements were made over the interesting wavelength region for this sample my conclusions are based on comparison between absorption profile from manufacturer (app. 1) and excitation measurement (app. 4). I note a red shift of the peak wavelength from 530 to 545 nm. The most significant effect is however a broadening of the spectra. There is no distinct excitation peak in the dye/polymer sample which seems to have a broad and rather flat...
excitation spectra. This broadening could be a result of the use of a denser solvent and also be
influenced by saturation effects in the sample. High concentration of dye in the sample can
cause the different dye molecules to interact with each other causing a broadening of their
energy bands. It is also possible that the absence of a distinct peak is an effect of incoming light
saturating the dye at certain energy levels. The spectral shift is due to a combination of the
effects from the use of a solvent with higher index of refraction (red shift) and the change of
the polarity in the dye environment (blue shift). The absorption spectra from the manufacturer
is made using ethanol as solvent. Since ethanol has low polarity (in comparison to for example
DMSO) the blue shift due to the change in polarity in the dye environment will be dominated
by the red-shift due to change in refractive index.

9.2.2 IR-140

I note a small blue shift of the peak wavelength from 826 to 820 nm however this shift is not
large enough to be ascertained. A more significant effect is as for Rhodamine 6G a broadening
of the spectra. This broadening could be a result of the use of a denser solvent and also be
influenced by saturation effects in the sample as previously discussed in chapter 9.2.1. Probably
is the saturation effect caused by interaction between dye molecules quite important as can be
concluded by comparing the absorption profile for the two different IR-140 samples (low conc.
and high conc.). The spectral shift is due to a combination of the effects from the use of a
solvent with higher refractive index (red shift) and the change of the polarity in the dye
environment (blue shift). The absorption spectra from the manufacturer is made using DMSO
as solvent. Since DMSO has high polarity (in comparison to for example ethanol) the blue shift
due to the change in polarity in the dye environment will be compensated for by the red-shift
due to change in refractive index.

9.2.3 IR-143

I can not note any shift of the peak wavelength. The spectra is quite hard to resolve and the
absorption peak is located in the same region in my measurements and in the information
provided by manufacturers. A significant effect is as for Rhodamine 6G and IR-140 a
broadening of the spectra. This broadening could be a result of the use of a denser solvent and
also be influenced by saturation effects in the sample as discussed in chapter 9.2.1. Probably
the saturation effect is quite important as can be concluded by studying the results for IR-140
but also by comparing the two different IR-143 samples (low conc. and high conc.). The
spectral shift is due to a combination of the effects from the use of a solvent with higher
refractive index (red shift) and the change of the polarity in the dye environment (blue shift).
The absorption spectra from the manufacturer is made using DMSO as solvent. Since DMSO
has high polarity (in comparison to for example ethanol) the blue shift due to the change in
polarity in the dye environment will be compensated for by the red-shift due to change in
refractive index.

9.2.4 NK-124

I can not note any shift of the peak wavelength. The spectra is nearly impossible to resolve but
the absorption profile seems to be located in the same region in my measurements as in the
information provided by manufacturers.
9.3 Fluorescence quenching

The conclusions are made by comparing the information received from manufacturers (appendix 1) with information from measurements (appendix 5).

For all my samples I can note a significant quenching of the fluorescence. This is due to undesired interaction between the dye and the polymer. The quantum yield for Rhodamine dropped from 90% to approximately 49%. For the infrared dyes the quantum yield dropped from approximately 10% to values below 0.9% (for NK-124 no fluorescence whatsoever was detected). To improve the properties of infrared fluorescent polymer sheets more work has to be done on studying the interaction between the dyes and different polymers. This work would need to be concentrated on chemical interaction.
10. Capturing light and evaluating the shape of the receiver

When light propagates inside a media with higher index of refraction than the surroundings it can be trapped inside the denser material. In the following chapter I calculate the probability for capturing light. This probability will change depending on the index of refraction in the media and its surroundings. I then evaluate different shapes of the receiver to try to find a way to guide the light to a detector as efficiently as possible.

10.1 Capturing the light

When light is scattered isotropically, as is the case for many fluorescence processes, the radiation intensity is uniformly distributed over all solid angles. By using Fresnel’s formula, \( n_i \sin \theta_i = n_t \sin \theta_t \), it is possible to calculate the critical angle were total internal reflection occurs. If we study figure 10.1 we can see that total internal reflection occurs if \( \theta_t \) exceeds 90 degrees.

\[
n_i < n_t
\]

![Diagram of light propagating in dense media](image)

Fig. 10.1 Light propagating in dense media.

Calculations can be made to decide the critical angle:

\[
n_i \sin \theta_i = n_t \sin \theta_t
\]

\[
\sin \theta_i = (n_t / n_i) \sin \theta_t
\]

\[
\theta_i = \arcsin((n_t / n_i) \sin \theta_t)
\]

set \( \theta_t = \pi / 2 \) (= 90 degrees)

\[
\theta_{\text{critical}} = \arcsin(n_t / n_i) \quad \text{where} \quad n_t < n_i
\]

Using this value we can calculate how much light, undergoing a fluorescence process, that will be captured inside the denser media (see figure 10.2).
Fig. 1.2 Light being isotropically scattered inside dense media.

The solid angle, \( \omega \), is defined as surface area on the unit sphere. The total solid angle is \( \omega = 4\pi \) and a segment is calculated according to \( \omega = 4\pi \sin^2(\alpha/2) \) (see figure 10.3).

Fig. 10.3 Segment of an unit sphere.

We have \( \theta_{\text{critical}} = \arcsin(n_i / n_t) \) and hence a value for this segment will be:

\[
\omega = 4\pi \sin^2\left(\frac{1}{2}\arcsin\left(\frac{n_i}{n_t}\right)\right)
\]

We have a situation as in figure 10.4 with two "escaping segments".

Fig 10.4 Explanation of the two "escape segments"

I chose to compare the value for one segment to half the total solid angle, \( \omega = 2\pi \), and get the fraction light escaping the dense material as:

\[
\text{fraction escaping} = \frac{4\pi \sin^2\left(\frac{1}{2}\arcsin\left(\frac{n_i}{n_t}\right)\right)}{2\pi} = 2 \sin^2\left(\frac{1}{2}\arcsin\left(\frac{n_i}{n_t}\right)\right)
\]
Hence the light being captured inside the dense material will be:

\[
\text{fraction captured} = 1 - 2 \sin^2\left(1/2 \arcsin\left(n_i / n_i\right)\right)
\]

This fraction is depending only on the index of refraction inside and outside the material, \(n_i\) and \(n_e\). We set \(n_e = 1\) (approximation of the index of refraction for air) and calculate the fraction captured for different \(n_i\). The result for different indices of refraction, \(n_i\), is presented in table 10.1.

<table>
<thead>
<tr>
<th>index of refraction</th>
<th>material</th>
<th>fraction captured</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>Pyralin</td>
<td>0.78</td>
</tr>
<tr>
<td>1.56</td>
<td>PMMA</td>
<td>0.77</td>
</tr>
<tr>
<td>1.49</td>
<td></td>
<td>0.74</td>
</tr>
<tr>
<td>1.45</td>
<td></td>
<td>0.72</td>
</tr>
<tr>
<td>1.4</td>
<td></td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 10.1 Fraction of light captured for different indexes of refraction.

### 10.2 Guiding the light to a detector

To model different shapes of the receiver I use a ray-tracing program implemented by Leif Ek at Optronic Consult in Stockholm. The receiver is built up by different geometric areas predefined in the program, it is possible to make aspheric adjustments on the areas which is used to model the taper part.

![Fig. 10.5 Shape of the receiver.](image)

When constructing the receiver model I start with two cylinders, one inside the other to form the body (see figure 10.5 above). The taper part is modeled by two cylindrical cones (with aspheric adjustments) placed inside each other. To avoid light stocking effects in the receiver I keep the cross section area constant or increasing over the taper part. Initial correction polynomials for the aspheric adjustments needed on the two cones that form the taper is calculated using matlab. I evaluated some different shapes and tried to maximize the guiding efficiency. All calculations can be studied in appendix 6.

The highest value for the guiding efficiency I managed to obtain was 25%.
11. Total quantum efficiency

In this chapter I calculate the total efficiency of the thought receiver. I also suggest ways to improve the efficiency through further development.

11.1 Calculation of total quantum efficiency

The total quantum efficiency is calculated by multiplication of the different factors that have impact.

- Absorption of incoming light $\approx 0.93$ (controlled with dye concentration)
- Light capture $\approx 0.7$ (calculated in chapter 10.1)
- Light guidance $\approx 0.25$ (estimated in chapter 10.2)
- Quantum yield $\approx 0.008$ (estimated from measurements, see chapter 7.2.5 and 8.2)

These values gives the total efficiency $\approx 1.3 \times 10^{-3}$. Note that limiting factor is the quantum yield we have total efficiency $\approx 0.16 \times Q_{\text{eff}}$.

It is important to notice that I have not calculated with any absorption or loss through secondary fluorescence. Especially the absorption in the polymer would probably have a rather important impact if not properly considered in the development of fluorescent polymers.

11.2 Suggested improvements

Since the limiting factor is the quantum yield, which has the magnitude of 0.8%, I suggest that any further work should be focused at developing materials that fluoresces in the NIR region with higher quantum yield. For Rhodamine 6G the quantum yield dropped with a factor 2 according to my experiments. A certain decrease in quantum yield must be expected to occur. Anyhow if it is possible to produce plastic materials with IR-dyes whit the same drop factor as for Rhodamine 6G this would give a quantum yield of approximately 5%. The total efficiency of the receiver would then be in the region of 1% which would be acceptable since the effective detector area could be increased more then 100 times.

Receivers for wavelengths around 545 nm could be developed with a much smaller effort using Rhodamine 6G doped in PMMA. The quantum yield achieved in my tests would be sufficient and one also avoids the problem with absorption in the polymer.
**12. Summary**

A device working properly according to the principles of the idea behind this project would be very useful in all infrared communication using diffuse links. However a lot of work remains to be done before such a device is reality.

I have studied fluorescence in polymers doped with different dyes. Both in the visible and the infrared region. I could observe a frequency shift in the dye due to changes in the surrounding polarity and index of refraction. The effect of these to factors compensate each other resulting in a small red shift for the dye that fluoresces in the visible region and no observable shift in the dyes that fluoresces in the infrared region.

I also note a decrease in the quantum yield of the conversion process when the dyes are held in a polymeric surrounding. The decrease is larger for the dyes which fluoresces in the infrared region then for the dye which shows visible fluorescence. This decrease has a very important effect as the efficiency of the receiver device will be directly proportional to the quantum yield in the material. The infrared dyes already in more friendly surroundings shows relatively low quantum yield (≈ 12%) and with the decrease caused by the polymer it drops below 1%. For one of the studied dyes I was not able to detect any fluorescence at all when doped in a polymeric surrounding.

It is also difficult to find a host material for the dye that does not absorb infrared light. There are polymers available with low infrared absorption but they are quite expensive as for now. If a material with a quantum yield of 50% in the fluorescence conversion and with low infrared absorption could be developed it would be possible to construct a receiver device with an efficiency of ≈ 10%. This would be very sufficient indeed as the effective area of the detector could be increased more then 100 times using the method.
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