1

Introduction on Polymer Optical Fibers and Amplifiers and a motivation for using densely crosslinked polymer materials

1) Polymer Optical Fibers

1.1 General background

For current communication and computer systems there is a need for high-volume data transfer. Copper wires cannot satisfy this need because of low transmission speed and small signal bandwidth (information-carrying capacity). Information transmission by using optical cables, which transport pulses of light instead of electricity, increases bandwidth with a factor 1,000.\(^1\) Compared to telephone cable it is even a factor up to 10,000. Moreover, signal attenuation is considerably lower for optical systems and thus transmission distance can be much larger without the need for signal boosting. Furthermore, optical cables do not have the problem of electromagnetic interference, which gives, for instance, the problem of cross-talk in copper telephone cables.

Light can be transmitted through transparent media by means of total internal reflection, which is possible in a core-cladding configuration. The cladding must have a lower refractive index than the core.

Silicate glass is the most transparent material known and optical glass fibers with extremely low attenuation of light transmission and high bandwidth have been developed in the past decades. These optical glass fibers have been used for long-distance telecommunications. The basic configuration of an optical fiber and some important characteristics are shown in Figure 1.1.
Figure 1.1  Depiction of an optical fiber.

Figure 1.1 shows a step-index optical fiber, which means that the refractive index is constant along the fiber core cross-section and immediately changes (step-wise) to the refractive index of the cladding. An other possibility is a graded-index fiber, for which the refractive index gradually changes from a high value in the center toward a lower value at the perimeter of the core.

Light rays propagate via discrete paths through a fiber. Each distinct path is called a mode and corresponds to a certain angle of incidence. Consequently, different modes take different times to travel along the fiber. The total number of light modes which can be coupled in is defined by the numerical aperture (NA). The NA is limited by the refractive index difference between cladding and core. The NA is thereby directly related to the angle of acceptance and the latter is given by the formula:
\[ NA = (n_1^2 - n_2^2)^{1/2} = n_0 \sin \left( \frac{\theta_a}{2} \right) \]  

\( n_0 \) = refractive index outer medium (usually air, \( n = 1 \))  
\( n_1 \) = refractive index of the core  
\( n_2 \) = refractive index of the cladding  

The larger the difference in refractive index, the higher is the number of modes which can be guided through the fiber. In a step-index fiber, the number of possible modes \( N_m \) of wavelength \( \lambda \) is related to NA and the fiber diameter \( d \) following Equation 2.

\[ N_m = 0.5 \left( \frac{\pi d NA}{\lambda} \right)^2 \]  

In the situation that only one mode is available for the light rays, the fiber is called single-mode. Single-mode fibers are prepared by reducing the core diameter to dimensions well below the wavelength of the light used. Larger cores can accept more light modes and these fibers are, therefore, called multi-mode. 

The information-carrying capacity of optical fibers is largely determined by the level of signal dispersion and the refractive index profile along the core cross-section. Clearly, the initial modulation of light determines the starting pulse width and the pulse frequency and thus directly the bandwidth of the total system. However, most important for the bandwidth is the level of signal dispersion in the optical fiber. Through signal dispersion, pulses of light start to interfere (overlap of pulses), meaning that information will be lost and the bandwidth will thereby be reduced. The bandwidth is given in bits·km/s or in Hz·km. Signal dispersion is caused by modal, material and waveguide dispersion. Modal dispersion is the dominant factor and is caused by the different path lengths traveled by light modes with different angles of incidence (see also Figure 1.1). The fastest mode is the zero-order mode travelling straight through the centre of the fiber core. In single-mode fibers only the zero-order mode is accepted.
and such fibers have the highest bandwidth (100 GHz⋅km) possible. However, such fibers have extremely small core diameters. The bandwidth of step-index multi-mode fibers is about 10 MHz⋅km. To increase the transmission rate, graded-index fibers with low signal dispersion have been developed. Such fibers can have bandwidths of more than 2 GHz⋅km, still possessing large core diameters (0.5 – 1.0 mm). In graded-index fibers the light spirals through the fiber core. Light travels faster in lower refractive index material. Light modes with a high angle of acceptance have to travel longer distances, but spend most of the time in lower refractive index material, thereby going faster. For light modes with a smaller angle of acceptance the opposite is true. The overall effect is a reduced pulse broadening with respect to step-index fibers.

Glass optical fibers have small core diameters ranging from a few micrometers for single-mode up to 100 – 125 micrometers for multi-mode fibers. Such small core diameters are necessary due to the brittleness of glass. Only with small core diameters do these fibers have some flexibility at room temperature. To protect such a weak core material, several extra layers are necessary, making fiber production costly. The major drawback of such small core diameters, however, is in the coupling of fibers. Minute core-to-core shifts quickly result in high coupling losses. Although this is well-understood, connector design is difficult and costly. A further disadvantage of glass optical fibers is their low numerical aperture (NA ≈ 0.16), which complicates coupling even more. The difficult and costly coupling process is the reason that glass optical fibers are not used for local area networks or computer networks, for which lots of connections have to be realized.

Recently there has been considerable interest in the development of polymer optical fibers (POFs). The ductility of polymers is an important advantage and confers on POFs easy processing, easy handling, low costs and large core diameter. POFs have an extended applicability, e.g. in computer networks, local area networks, datalinks, optical sensors, lighting, etc. The large core diameter, up to 1 mm or more, enables high efficiencies of fiber coupling. Furthermore, because polymers have low densities they are light-weight. Transmission of light occurs with wavelengths from the visible
Introduction

Part of the spectrum (550 - 850 nm), because of the presence of low-loss windows in this particular region. Disadvantages of current POFs are high optical losses and low thermal resistance. Transmission loss is, besides bandwidth, the most important parameter determining the usefulness of an optical fiber. It is expressed in decibels (dB) and measured by using a cut-off method. The attenuation of a fiber is then defined as the logarithm of the ratio between output intensities of the two different fiber lengths and normalized over the length of the fiber cut-off (Equation 3):

\[
\text{Attenuation } (\alpha) = \frac{10}{L} \log \left( \frac{I_2}{I_1} \right)
\]

(3)

\(L\) is the length of fiber cut-off, \(I_2\) is the outgoing light intensity after cutting off a length \(L\) and \(I_1\) the outgoing intensity before cutting.

For a polymer to be transparent it has to be fully amorphous. Polymers which meet this requirement and are applied for POFs are, for instance, poly(methyl methacrylate) (PMMA), poly(styrene) (PS), poly(carbonate) (PC) and poly(siloxane) rubber. Worldwide, research and development have been predominantly focused on PMMA. Transmission losses of commercial PMMA-based POFs are typically 100 - 200 dB/km (100 dB/km means a transmission distance of 200 m if one assumes a technical detection limit of 1% of the initial light intensity). Attenuation of the signal in POFs is caused by various mechanisms. The different contributions to the total loss mechanism can be divided into intrinsic and extrinsic losses. The individual contributions are tabulated in Table 1.

Intrinsic losses are related to the molecular structure of the plastic core material, while the extrinsic losses can be minimized by purification and optimization of the processing. Intrinsic absorption losses are caused by the higher harmonics of molecular vibrations in the IR-region and electronic transitions in the UV-region. In addition to these intrinsic absorption phenomena, which are determined by the medium material itself, absorption by contaminants, such as transition metals and organic impurities can
play a role. They are classified as extrinsic absorptions, in the sense that they are not a property of the polymer, but depend mainly on manufacturing conditions (purification).

Table 1. The individual contributions to the total loss mechanism of polymer optical fibers.

<table>
<thead>
<tr>
<th>Intrinsic losses</th>
<th>Extrinsic losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>scattering</td>
</tr>
<tr>
<td>scattering</td>
<td>absorption</td>
</tr>
<tr>
<td>higher harmonics of C-H vibrations (also O-H and N-H),</td>
<td>Rayleigh scattering</td>
</tr>
<tr>
<td>Electronic transitions (π-π*, σ-n)</td>
<td>organic contaminants</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Scattering losses include Rayleigh scattering, which is caused by small (~ 0.1 \( \lambda \)) irregularities in the medium, such as fluctuations in density and composition and by anisotropy of polarizability. This form of scattering is intrinsic for a certain polymer and is mainly important in the UV-region of the spectrum, because it is inversely proportional to the fourth power of the wavelength of the scattered radiation (Equation 4). It has been shown that Rayleigh scattering is predominantly caused by fluctuations in density.\(^3\) Equation 4 gives the intensity of light scattering due to fluctuations in density and anisotropy of polarizability (\( \tau_d \)):
From materials point of view, a low refractive index and small compressibility favor reduction of scattering due to density fluctuations. The Cabannes factor corrects for the molecular anisotropy. To illustrate the latter, PS has a Cabannes factor of 2.7, that for PMMA is 1.1. This is ascribed to the planar conformation of the benzene ring while, on the contrary, the methyl group of MMA is sp³-hybridized and is thereby 3-dimensionally structured. Furthermore, the optical polymer may contain orientational birefringence due to processing. This is called quasi-extrinsic scattering and is wavelength-dependent, as well. Although, it is difficult to quantify the contribution to scattering its wavelength-dependency can be described as $\tau = A\lambda^n$, with $n$ somewhere between zero and four, similar to Equation 4.3

Extrinsic, wavelength-independent scattering can be caused by structural imperfections of wavelength dimensions or bigger, e.g. dust particles, microvoids and cracks.

In the UV-region of the spectrum, the losses are due to both electronic absorption, for which mainly aromatic and unsaturated groups and to a lesser extent carbonyl groups are responsible, and Rayleigh scattering. In the near-IR region large loss peaks are caused by vibrational absorptions, mostly from C-H bonds. This accounts for the fact that most POFs have low-loss windows in the visible region of the spectrum, between about 600 – 700 nm.
Chapter 1

The low-loss windows of POFs are normally very narrow, and occur in a range where Rayleigh scattering is still considerable. It would be favorable to substitute the C-H bonds in the polymer (responsible for the large IR-absorption) by C-F or C-D bonds. The higher reduced masses of these groups should cause the fundamental vibrational absorption to shift further into the IR direction, thus expanding the low-loss window. Indeed, work that has been done using deuterated and fluorinated materials has proven the validity of this principle.3,4,5

By optimization of the manufacturing process and replacement of the hydrogen atoms of the C-H bonds by deuterium or fluorine atoms, the losses can be reduced to as low as 10 dB/km. So far, these 'special' POFs are not for real practical purposes, because of the high costs. Very recently, new developments in this field yielded new superior POFs based on cyclic perfluorinated polymers. A theoretical consideration by Koike and coworkers showed a theoretical loss limit of only 0.3 dB/km in the near-IR at 1.3 µm.6 Still, these materials, for instance poly(perfluoroethylene-co-buteryl vinyl ether) and poly(perfluoroethylene-co-trifluorodioxol) (Figure 1.2), have a negative property. They have a large compressibility due to a large molecular volume. Developing amorphous perfluorinated polymers with lower compressibility would lower the loss limit even further. The losses come close to those of glass and replacement of optical glass fibers even for long transmission distances is no longer a utopia. For comparison: glass fibers have losses of 0.15 dB/km at 1.55 µm. Of course, the costs of such polymer materials need to be reduced.

Also GI-POFs based on poly(perfluoroethylene-co-buteryl vinyl ether) (Cytop®) have been manufactured. Because of its lower refractive index and attenuation, the perfluoropolymer shows a much lower material dispersion than PMMA.7 Optimization of the refractive index profile will eventually lead to bandwidths of over 10 GHz-km.8
1.2 Compressibility

As argued above, Rayleigh scattering is mainly caused by density fluctuations intrinsically present in (amorphous) polymers. Refractive index and compressibility are the two factors influencing the intensity of scattering as has been shown by Equation 4. The compressibility ($\beta$) of an amorphous polymer is largely determined by its molecular volume or more specifically by the cross-sectional area, $A$ ($\text{Å}^2$), per polymer chain.\textsuperscript{9,10}

\[
\log (10^5 \beta_{T_{\text{lii}}}) = -0.21 + 0.55 \log A
\]  

(5)

$T_{\text{lii}}$ refers to the liquid-liquid transition temperature and $\beta$ is expressed in bar$^{-1}$. Boyer concluded that $T_{\text{lii}}$ is about $1.2 T_g$ (K).\textsuperscript{9,11} Taino and Koike defined, based on the work of Boyer and Miller, a correlation of the cross-sectional area per polymer chain with $N_e$, the number of chain atoms between physical entanglements.\textsuperscript{9,12}

\[
\log N_e = k_1 + k_2(\log A - 2)
\]  

(6)

The constants $k_1$ and $k_2$ have values of 2.929 and 0.614, respectively. $N_e$ correlates to the molecular weight between entanglements $M_e$ by $N_e = M_e / m$, where $m$ is the molecular weight per chain atom ($m = M_0 / Z$); $M_0$ in turn is the molecular weight of a monomer unit and $Z$ is the number of chain atoms in the monomer unit.
Boyer and Miller suggested a correlation between $M_e$ and the volume of the monomer unit in the chain, $V$ (cm$^3$/mol), of $M_e \propto V^{1.67}$. The molecular volume of the monomeric unit can be calculated from Equation 7.

$$V = \frac{M_0}{\rho} \quad (7)$$

where $\rho$ is the density of the polymer (g/cm$^3$). Taino and Koike$^9$ showed that for thermoplastic amorphous polymers Boyer's relation was more precisely given by:

$$M_e = 18.3 \, V^{1.67} \quad (8)$$

In conclusion, the compressibility is dependent on the cross-sectional area per polymer chain, which in turn is dependent on $M_e$ and molecular volume. Densely crosslinked polymers, characteristically having a low value for the molecular weight between crosslinks $M_e$ (here $M_e$ replaces $M_c$), possess a small cross-sectional area per (network) chain, and therefore, low compressibility.

The isothermal compressibility of polymers increases linearly with temperature $T$ for $T_g < T < T_{ll}$ and hereafter for $T > T_{ll}$ again linearly, but with a smaller slope. For amorphous thermoplastic polymers this relationship has been empirically expressed as:

$$\left( \frac{1}{\beta_{T_{ll}}} \right) \frac{d\beta}{dT} = 4.8 \times 10^{-3} \, K^{-1} \quad \text{for } T_g < T < T_{ll} \quad (9)$$

$T_{ll}$ is believed to be a transition from a liquid state with a fixed structure to a true liquid state. Above $T_{ll}$ entire macromolecules are able to move (macro-brownian motion). Below $T_{ll}$ movement is limited to micro-brownian motion (rotational and vibrational motions of chains).$^{11}$ The molecular structure of network polymers, particularly densely crosslinked, is fully fixed and one cannot speak anymore about a liquid-liquid
transition. The compressibility-temperature dependency is, therefore, expected to be extremely small in value for densely crosslinked polymer materials. A large molecular volume results in a large compressibility, but in a lower refractive index. Clearly these two physical properties are effectively working against each other in relation to scattering loss. Because of very low compressibilities, densely crosslinked polymers have small Rayleigh scattering intensities.

1.3 Thermal resistance of POFs
One drawback not mentioned in detail is the low thermal resistance regarding optical properties for most thermoplastic polymers. Examples of application of POFs at high temperature are found in the automobile and aerospace industry. A thermal resistance of at least 120 – 140°C and sometimes even higher is necessary for such applications. The thermal resistance is related to the inherent polymer structure (e.g. backbone structure, glass transition temperature, physical and chemical crosslinking). The POFs available today are produced from thermoplastic core polymers like poly(methyl methacrylate) (PMMA), poly(styrene) (PS) and poly(carbonate) (PC), which have glass transition temperatures of 100, 90 and 150°C, respectively. Close to the $T_g$ and at higher temperatures, softening of these materials occurs, with a consequential loss of properties, among which the optical properties.

Although poly(carbonate) is often used for its high $T_g$, it has the disadvantage of high intrinsic losses. Moreover, it is severely sensitive to environmental stress cracking, which introduces an extra difficulty in the processing. Furthermore, poly(carbonate) has an insufficient intrinsic thermo-optical stability as it is sensitive to oxidative decomposition at high temperatures.

The intrinsic thermal stability of a crosslinked polymer is considerably higher than that of an uncrosslinked polymer. Polymer networks are dimensionally stable above $T_g$, though this is related to the crosslink density, which will possess a certain threshold value. For satisfactory crosslinked polymers the optical properties can be retained
above $T_g$ in the 'rubbery' state. Such is certainly the case for densely crosslinked polymers ($M_c \leq 1000$ g/mol).

### 1.4 Current status of high-temperature-stable POFs (HT-POFs)

Continuously, improvements of graded-index profiles and improvement of the thermal resistance related to optical properties are hot topics in worldwide POF research. Furthermore, for GI-POFs based on polymers with low softening points, the instability of the refractive index profile with temperature is a serious problem. So far, GI-POFs can only be used at low temperatures.

In the search for high-temperature-stable POFs most emphasis is given on using poly(carbonate)s for the fibre core. Because of its high $T_g$ and excellent mechanical properties it is a good candidate. Mitsubishi Rayon developed an optical cable with a PC core and a cladding of Teflon® AF.\(^{13}\) They reported a minimum loss of 1 dB/m at 770 nm, which is sufficient for use in automotive applications. The exact molecular basis of the polycarbonate is not reported. In view of the relatively high losses it is expected to be based on bisphenol-A.

Arton™, a cyclo-olefin (polynorbornene) developed by Japan Synthetic Rubber Co. Ltd. has a glass transition temperature of 170°C and shows excellent thermo-optical behavior.\(^{14,15}\) Minimum loss measured using the cut-back method was reported to be 1.2 dB/m at 660 nm. Fluorinated poly(norbornene)s have been applied as cladding material by Hoechst AG.\(^{16}\)

Toray Industries developed a poly(methyl methacrylate-co-isopropylmaleimide) copolymer possessing a $T_g$-value of 135°C (Figure 1.3).\(^{17}\) Losses as low as 0.25 dB/m have been reported.

Acome, in France, uses the same strategy and prepared terpolymers from methyl methacrylate, styrene and cyclohexylmaleimide.\(^{18}\) The thermoplastic polymer has a $T_g$ of 177°C. No optical measurements have been reported, so far.

Other copolymers of MMA with bornyl, menthyl, fenchyl and adamantyl methacrylate have been developed to increase the $T_g$-value.\(^{3,19}\) However, these materials are very brittle at room temperature.
Introduction

![Molecular structure of poly(methyl methacrylate-co-isopropylmaleimide) copolymer. T_g-value is 135°C.](image)

Figure 1.3. Molecular structure of poly(methyl methacrylate-co-isopropylmaleimide) copolymer. $T_g$-value is 135°C.

Some examples of the application of crosslinked materials for POF cores have been found. Hitachi Wire applied crosslinked (meth)acrylates. A heat resistance temperature of 170°C is given and a transmission loss of 1.5 dB/m.\textsuperscript{13} UV-curable mixtures of methyl methacrylate, 2-ethylhexyl acrylate and poly(ethylene)glycol 200 diacrylate have been inserted in a heat-shrinkable FEP-tubing. After crosslinking, the polymer network had a $T_g$ of -34°C when 70% 2-ethylhexyl acrylate was incorporated. No loss measurements were reported.\textsuperscript{20} Poly(siloxane) core POFs have been developed by Bridgestone Corporation based on a methylphenylsiloxane elastomer and hydrosilylation curing (attenuation of 0.45 dB/m at 770 nm)\textsuperscript{21} and by Shin-Etsu Chemical Co. who have prepared POFs with cores based on hydrosilylation-curable organopolysiloxane prepolymers (attenuation 0.8 dB/m at 660 nm).\textsuperscript{22} In a German patent, the manufacturing of optical components from poly(cyanurate)s (Figure 1.4), has been described. Losses of 10 dB/m and 100 dB/m at 1.3 and 1.55 µm, respectively, have been reported.\textsuperscript{23}
Chapter 1

\[ \begin{align*}
\text{Figure 1.4.} & \quad \text{Poly(cyanurate) prepared by trimerization of a hexafluoropropyl bisphenol A-based dicyanate. Such densely crosslinked materials have been applied for optical components.}^{23}
\end{align*} \]

1.5 Strategy and outline of this thesis concerning passive HT-POFs

The research strategy has been grounded on developing POFs with cores prepared from densely crosslinked polymer networks. Amorphous fluorinated thermoplastics, having low refractive indices and possessing high thermal stability are cladding materials of first choice. Application of a densely crosslinked thermoset core providing thermo-optical and thermo-dimensional stability combined with a fluorinated thermoplastic cladding providing thermal stability, environmental protection and mechanical ductility, covers the desirable polymer properties for HT-POFs. Densely crosslinked polymers not only possess higher thermal resistance and better dimensional stability, but also have the advantages of a theoretically lower attenuation
Introduction

compared to their thermoplastic counterparts. The latter is a consequence of a lower compressibility and thereby less Rayleigh scattering.

Densely crosslinked polymers are commonly prepared from polyesters, epoxides and polyurethanes.24,25 Introducing cyclic structures will further improve the thermal stability of such polymer systems as has been applied in polyurethane chemistry by introducing isocyanurate rings. These rings are formed by trimerization of isocyanates. A densely crosslinked system entirely consisting of isocyanurate rings is a promising candidate for a POF possessing high thermal-optical and thermo-dimensional stability. Moreover, unlike polyurethanes, N-H bonds are absent and, therefore, these materials posses intrinsically low optical losses in the visible spectral region. Work done on this field is described in chapters 2 and 6.

Parallel to this work ample research has been performed on densely crosslinked poly(siloxane) networks. Poly(siloxane)s are composed of silicon-oxygen bonds, similar to glass. As glass possesses superior optical properties, densely crosslinked poly(siloxane)s, prepared via a sol-gel route, are promising materials for high temperature stable POFs. Combining the ductility of polymers, transparency of glass and it’s high thermal stability, all desirable properties are brought together. The work explored in this direction is described in chapters 3, 4, 5 and 7.

During the period of research we have been confronted with an incredible growth of worldwide research activities in the field of polymer optical fibers. Japan and the USA are in this field undoubtedly ahead of the rest of the world. Within Europe, France and Germany try to follow Japan and the USA as close as possible. Fortunately, our concept was quite exceptional and is believed to really contribute to the existing knowledge in this internationally important field of activity.
2) Polymer Optical Fiber Amplifiers

2.1 General background

POFs are inherently ridden with a significant loss of optical energy through diverse mechanisms, as has been explained in the previous section. The interest in using polymers for optical telecommunication applications has resulted in an increasing need for optical signal amplifying systems as such applications demand long transmission distances. To lengthen the transmission span of polymer optical fibers one has to compensate the loss of energy by coupling the fibers to an amplifying medium (Figure 2.1). Such an amplifying medium contains a material capable of luminescing at the signal beam wavelength. The luminescent material needs to be pumped by a laser beam, which excites the molecules to a higher energy level, thus generating a population inversion of electronic states. A beam travelling through the amplifying medium will stimulate the emission of light which is of the same wavelength and phase. In a polymer optical fiber amplifier (POFA), emission is stimulated by the attenuated signal, and thus the signal is regenerated in strength. Like in the case of a laser, it is important to maintain population inversion, since net emission of radiation only takes place if the upper state is more densely populated than the lower one.\textsuperscript{26}

To overcome the problem in optical glass fibers, luminescent rare earth (lanthanide)-doped optical glass fiber amplifiers have been developed.\textsuperscript{27,28,29} Optical glass fibers have their lowest loss in the near-infrared region. Neodymium and praseodymium are therefore useful lanthanides as they have emission bands around 1.30 $\mu$m, erbium is very useful with an emission band at around 1.55 $\mu$m. New developments in improving the transparency of glass resulted in a low-loss window at 1.55 $\mu$m (third telecommunication window), for which erbium-doped fiber amplifiers (EDFA) have been developed. However, the disadvantage of a glass matrix for optical amplifiers is the fact that the attainable doping levels are low; for silica glasses as low as ca 0.1 mole percent.\textsuperscript{30} At higher doping levels, clustering of the rare earth ions, causing
Introduction

Figure 2.1. Polymer optical fiber amplifier configuration.

quenching of the luminescence, is a major problem. As a consequence, long lengths of fiber are necessary to reach sufficient levels of gain. This has led to the investigation of the possibilities of using fluoride glasses, which can be doped to concentrations of up to a few mole percent. On the contrary, polymer matrices can be doped to much higher concentrations than silica glasses, provided that suitable lanthanide complexes are used. This allows the production of compact, low-cost lanthanide-based fiber amplifiers. Beside the lanthanide complexes, another group made up of strongly fluorescent organic dyes form suitable candidates for optical amplifier materials. It would be a tremendous gain if an erbium-doped polymer fiber amplifier (EDPFA) could be made compatible with the 1.55 μm wavelength used in optical glass fiber telecommunication technology. However, polymers face the problem of strong quenching of luminescence due to high-energy vibrational modes of mainly C-H bonds. Amplification of light in the third telecommunication window by EDPFA is a development for the future. For such a development fully fluorinated polymers may be
good host matrices and hence rare earths have to be made compatible with these. The 'heavy' fluorine atoms are responsible for shifting the vibrational modes to lower energy and thereby for reducing the quenching of luminescence in the visible and especially in the near-infrared spectral region.

The recent explosion of POF developments and applications in spite of their inherently high absorption losses emphasizes the importance of research on lanthanide or organic dye doped polymer amplifiers.

No commercially feasible POFA systems have been reported yet, but some work has been done. Sharma et. al. reported optical gain in a europium hexafluoroacetyl acetonate-doped (up to 2 wt.%) poly(lauryl methacrylate) 1.5 cm short fiber (fiber diameter of 0.180 mm). However, this is the only report, so far, describing POFA action with rare earths. Koike and co-workers produced a rhodamine B-doped poly(methyl methacrylate) graded-index POFA with high gain efficiency (up to 22 dB).

Any fluorescent dye (fluorophore), either organic or inorganic, must meet certain requirements to ascertain considerable amplification and make it useful for POFA. Koike and co-workers identify five:

- The fluorophore must have a reasonable quantum yield of fluorescence in the chosen bulk, because this characteristic is intimately related to the probability of stimulated emission.
- The fluorophore must have high photochemical stability, because the majority of POFA configurations require that the dye is capable of undergoing multiple excitation cycles for continued operation.
- Minimal overlap between the fluorophore fluorescence and its absorption spectrum, because amplification phenomena rarely occur within the region of overlap due to self absorption by the fluorophore.
- The fluorophore must absorb the radiation of the pump source and must maintain the population inversion required for stimulated emission.
- Adequate solubility and thermal stability of the fluorophore in the chosen bulk.
As stated above, organic as well as rare earth fluorophores may be suitable for producing a POFA. However, there are several reasons for choosing rare earth-doped polymers for amplifier purposes instead of organic dye-doped polymers. These are the following:

- Traditional organic fluorophores, although quite efficient, suffer from a low optical damage threshold, whereas the more photochemically stable rare earth fluorophores show much better durability.
- The photophysical properties of organic fluorophores are highly dependent upon the local environment of the surrounding medium. In the case of rare earth fluorophores, however, these properties are essentially invariant with the nature of the host material.
- Rare earth fluorophores possess sharply defined fluorescence bands and large Stokes shifts (excitation wavelengths are 150 - 300 nm separated from the principal fluorescence wavelengths).
- Rare earth fluorophores have long-living fluorescent excited states (in the order of msec).
- The different rare earths (lanthanides) give a broad spectrum of emission bands and are therefore useful for a tuning on the desired wavelength, which has to be amplified.

In view of their fluorescence characteristics, lanthanide complexes are expected to be promising amplifier materials. It has been shown that they exhibit high fluorescence quantum yields (80% for a Eu$^{3+}$-complex, reported by Halverson)$^{34}$ Moreover, laser behavior of Eu$^{3+}$-complexes in various matrices has been reported.$^{35,36,37}$ This phenomenon is based on the maintenance of a population inversion followed by stimulated emission and is closely related to the phenomena encountered in fiber amplification. It is expected that a compound exhibiting laser behavior may also be a suitable candidate for amplification purposes. The relevant characteristics of lanthanides and their compounds will be discussed in some more detail, below.
Chapter 1

2.2 The lanthanides

The lanthanides form the 4f-series of the periodic table. This means that along this series, the 4f shell of the atom is filled. The valence shell of the atom is made up of the 4f, 5d and 6s electrons present. The differences in energies between these orbitals are small and, therefore, different types of configurations occur among the lanthanides. Usually, this is done in such a way that the relatively stable half-filled (4f^7) and filled (4f^{14}) f-shells are favored. This results in an adopted configuration of [Xe]4f^76s^2 for, for instance, europium (Eu) and [Xe]4f^6 for Eu^{3+}.

Formally, the lanthanide 4f-electrons belong to the valence shell of the atom or ion. However, the 4f-orbitals in the lanthanide series are located relatively close to the nucleus, and hence the 4f-electrons are shielded very effectively by outer electrons (5s^25p^6). This makes them largely unavailable for chemical reactions. In practice, the lanthanide 4f-electrons do not behave as valence electrons, and their presence does not materially alter the chemical behavior of the element. This circumstance is illustrated by the fact that all lanthanides resemble each other closely from a chemical point of view. The presence of any number of shielded 4f-electrons does not essentially effect the noble-gas-like configuration [Xe] that the atom presents to incoming species.

2.3 Photophysical properties of terpositive lanthanide ions

The lanthanide ions Tb^{3+}, Dy^{3+}, Eu^{3+}, Sm^{3+} (terbium, dysprosium, europium and samarium) are known to be very efficient emitters with fluorescence wavelengths in the visible region (roughly 550 - 650 nm), which place them within reach of the low-loss windows of most polymeric materials. Figure 2.2 shows the important energy levels of these terpositive lanthanide ions, together with their main luminescent transitions.

Lanthanides absorb radiation in very sharply defined bands. The intensity of the absorption bands tends to be low, however. These absorption characteristics are caused by the fact that the absorption is due to an electronic transition within the 4f-arrangement (f-f transition). According to the selection rules for atomic spectra, f-f
transitions of free lanthanide ions are forbidden (the LaPorte selection rule). This rule
states that in a centrosymmetric molecule or ion, the only allowed transitions are those
accompanied by a change of parity (ungerade $\leftrightarrow$ gerade).\textsuperscript{26, 42} The f-f transitions do not
involve a change of parity and therefore they are forbidden for a centrosymmetric
configuration as encountered in a free ion. When the symmetry of the ion is removed
by interaction with an asymmetrical external crystal field, the transition becomes more
allowed, however. Such an asymmetric crystal field can be introduced by a mixed
assembly of ligands. However, as has been argued above, the 4f-eletrons, which are
responsible for the absorption, are shielded to the extent that the influence of the
crystal field in splitting the electronic states is low, resulting in narrow absorption
bands and low absorption intensities (low extinction coefficients). The shielding of the
4f-electrons also accounts for the observation that the absorption spectra of the
lanthanide ions are only weakly perturbed upon complexation with a ligand. The effect
is limited to slight displacements of the bands, usually to higher wavelength. Also, the
narrowness of the absorption bands indicates that the electronic transition does not
excite much molecular vibration as it occurs. This again indicates that the responsible
electrons interact only weakly with the ligand, and therefore do not behave as true
valence electrons.
Chapter 1

2.4 Fluorescence

The reason for the interest in Tb$^{3+}$, Dy$^{3+}$, Eu$^{3+}$ or Sm$^{3+}$-complexes for use as amplifying material in POFAs is the very efficient fluorescence of the ions at 545, 573, 613 and 643 nm, respectively.\textsuperscript{41, 42} The ions have to be exited in the UV-region of the spectrum. Their principal absorption wavelengths are at 368, 365, 395, 402 nm, respectively.\textsuperscript{38} Like the UV-absorption, the fluorescence is due to a 4f-4f electronic transition. It has been argued above that the 4f-electrons are shielded to the extent that both bonding interactions with ligands and the crystal field have an extremely limited effect on the 4f electronic transitions. The same holds for the fluorescence; again the fluorescence is hardly affected by the ligands surrounding the cation. This circumstance allows the use

---

Figure 2.2. Energy level diagram of important lanthanides capable of luminescing at wavelengths in the visible spectral region. The spectroscopical terms of the individual levels are shown, as well.
Introduction

of virtually any ligand system without altering the characteristic fluorescence properties. This is an important notion, since a suitable ligand system is needed in order to solve some serious practical problems faced when free lanthanide ions are doped in a polymer matrix and make lanthanide ions useful for application in POFAs. The main problems are:

- Solubility of salt in organic polymer is low, causing easy clustering of the rare earth ions. Clustering is a main mechanism of luminescence quenching.
- Luminescent state is very sensitive to non-radiative decay.
- Absorption intensity is low.

Examination of the requirements for amplifier materials named by Koike and co-workers, will show that these problems will virtually prevent efficient POFA action of simple, purely ionic lanthanide compounds. Therefore, requirements are imposed on the ligand system in order to solve these difficulties. This is discussed in some detail below.

The first problem deals with the nature of the lanthanide compound which is both ionic and hygroscopic. The ionic character of the salt prevents it from dissolving in polymer matrices useful for POF applications, while a molecular dispersion of rather high concentration is required for efficient stimulated emission. Clustering of the insoluble lanthanide ions even at low concentrations causes quenching of the fluorescence (by up-conversion and cross relaxation, demonstrated in Figure 2.3). The hygroscopic character of the lanthanide salt makes it impossible to dope the polymer with the lanthanide without introducing co-doping with water, which causes both attenuation and fluorescence quenching. When the lanthanide is enveloped by a number of ligands, the surface of the complex becomes much more organic and solubility is enhanced. Moreover, bulky ligands prevent the ions from clustering and make the compound much less hygroscopic. The latter two of the problems mentioned above and their possible solution will be discussed in the following section.
Chapter 1

Figure 2.3. *Ion-ion de-excitation processes that quench fluorescence in ion clusters.*

2.5 Quenching of lanthanide ion fluorescence and its prevention (encapsulation)
Lanthanide ion fluorescence is extremely sensitive to quenching, especially by water molecules coordinated to the ion. How severe this quenching problem is, was shown by Gallagher.43 He argued that the introduction of a single OH-group into the environment of the terpositive europium cation is sufficient to reduce the lifetime of the excited state from 3.9 to 0.12 ms, thereby decreasing the fluorescence intensity accordingly. Haas and Stein also found the quenching by water to be proportional to the number of water molecules entering the first solvation layer.44 The main quenching mechanism comprises the conversion of excited electronic state energy into vibrational energy of the surroundings and subsequently in heat.45 This non-radiative decay of the excited state is called electronic relaxation. The efficiency of the nonradiative decay is directly related to the matching or mismatching of energy levels between donor and acceptor molecules.46 When the energy levels are well-matched, the energy transfer is fast and quenching is efficient. This is the case for the high-energy -OH vibrational modes.
Introduction

This notion is further developed in the practice of incorporating the ion in an 'insulating sheath'.\(^3^4\) The sheath serves two purposes: firstly, its energy levels do not match with the lanthanide ion excited-state energy levels, and therefore it cannot act as an energy acceptor itself. Suitable compounds are saturated hydrocarbons and fluorinated/chlorinated hydrocarbons. Secondly, the sheath, if made sufficiently bulky, will prevent ion-ion interactions (concentration quenching) and prevents other substances, including quenching agents, from approaching the excited cation. In this way, the cation is shielded from the environment, and the pathway for non-radiative decay is blocked. Figure 2.4 shows practical examples of enveloping a lanthanide ion in an insulating sheath: complexes with crown-ethers,\(^4^7,4^8\) bipyridine cryptates,\(^4^9-5^1\) chelates with diketonates,\(^3^4,5^2-5^4\) hemisperands\(^5^5\) and calix-arenes\(^5^6\). Several articles have been published in which polymeric complexes of rare earth ions are described. Complexes with crown-ether functionalized poly(methyl methacrylate),\(^5^7,5^8\) poly(methacrylic acid),\(^5^9-6^1\) poly(acrylic acid-co-acrylamide)\(^6^2\) and poly(ethylene oxide)\(^6^3\) are examples of those.

2.6 Sensitized fluorescence of lanthanides (process of Energy Transfer)

In order to produce an efficient optical amplifier, it is important that the material used is an efficient emitter of fluorescence radiation. However, the emission of radiation is not the only relevant step in the process. Before emission can take place, the ions need to be electronically excited. The net process involves the following steps:

\[
pump \text{ energy} \rightarrow \text{excited states (population inversion)} \rightarrow \text{emission}\\
\begin{align*}
absorption & \quad \rightarrow \quad \text{stimulated emission} \\
(\eta_1) & \quad \rightarrow \quad (\eta_2) \\
\eta_1 \times \eta_2 &= \eta_{\text{tot}}
\end{align*}
\]

The process of excitation also has a certain efficiency, which can affect the overall efficiency \(\eta_{\text{tot}}\) of an amplifying material. Excitation of the lanthanide cation can be
Chapter 1

achieved by irradiating the ion directly in the absorption bands. As has been described above, the absorption of radiation by lanthanide ions occurs in line-like bands with low intensity. Because of this poor absorption, only a small amount of the pump power is actually converted to lanthanide excited states. The low efficiency of the absorption reduces the total efficiency of the process greatly. This means that a large amount of pump power is wasted. In order to maximize the fluorescence output per unit pump power, a way to maximize the absorption intensity (absorption cross-section) of the lanthanide complex must be found.

A solution to this problem was initiated by the pioneering report of Weissman in 1942. He demonstrated that rare earth chelates, e.g. Eu(III)$\beta$-diketonates exhibit rare earth line emission when irradiated in the chelate absorption band, a phenomenon which is known as sensitized luminescence. The phenomenon has been investigated extensively since, both regarding the mechanism of energy transfer and its occurrence in various systems. The observed behavior of these systems can only be explained by a mechanism of energy transfer from the electronically excited state of the chelate to the chelated lanthanide cation, which in turn undergoes radiative decay. Crosby and Whan concluded that indirect excitation of the rare earths ions occurs through intramolecular energy transfer and that the principal path for this energy is through the lowest triplet state. The pathway through which the energy transfer fluorescence proceeds, as they established it, is presented in Figure 2.5.
Figure 2.4. Examples of chemical ways to encapsulate lanthanide ions. (a) 18-crown-6 complex with nitrate counter ions, (b) mixed-ligand cryptate of bipyridine and ethoxylene (crown-ether) fragments, (c) macrobicyclic ligand system composed of bipyridines, (d) tris(acetyl acetonate) chelate, (e) hemispherand (R = H, alkyl, alkoxyalkyl, etc.), (f) calix[4]arene-based complex (R = chromophore i.e. CH2-naphthalene, CH2-phenanthrene or CH2-triphenylene).
Figure 2.5. Energy scheme illustrating intersystem crossing (ISC) and energy transfer (ET) from ligand to lanthanide ion.

First, the ligand is brought to the excited singlet state $S_1$. As any electronically excited organic molecule, it now has the choice between two relaxation pathways: radiative decay to the ground state $S_0$ (ligand fluorescence) or intersystem crossing to a lower-lying triplet state $T$. Would this second pathway occur in the free, unbound ligand, then the energy would be effectively trapped here; radiative decay to the ground state (ligand phosphorescence) is spin-forbidden and therefore usually slow. The presence of the rare earth ion in the complex, however, provides another possibility, causing the excited ligand molecule to undergo radiationless transition from the excited triplet state to lower-lying excited levels of the chelated ion. In turn, the ion exhibits luminescence by radiative decay, in the case of Eu$^{3+}$ from $^5D_0 \rightarrow ^7F_2$ (613 nm). Whether the energy of the excited-state ion is dissipated radiatively or non-radiatively depends on the spacing of the 4f-levels. Eu$^{3+}$ is one of a small group of lanthanide ions (including Sm$^{3+}$, Tb$^{3+}$ Dy$^{3+}$ and Yb$^{3+}$) where the prime emitting level is fairly isolated, with no close lower-lying levels. In these ions, radiative decay can compete with non-radiative decay. These are the species which can luminesce brightly, provided that non-radiative
Introduction

decay by solvent quenching is minimized. Sensitized luminescence has also been demonstrated for Nd$^{3+}$ and Er$^{3+}$. Due to a larger spacing between the emitting levels and the sensitizing donor states energy transfer is less efficient for these lanthanide ions.\textsuperscript{67}

The process of energy transfer is also referred to as Förster-type, which is said to occur if the acceptor’s spectral absorption overlaps with the spectral emission of the sensitizer (resonance energy transfer).\textsuperscript{68} The efficiency of energy transfer depends on the extent of electric dipole coupling between the sensitizer and acceptor. In organic molecular systems, excitation is accompanied by a transition in electric dipole moment. For energy transfer between organic moieties an overlap of their electric dipole fields is necessary. Calculations showed that this can still be the case if both are separated by distances of up to 100 Å.\textsuperscript{68} In inorganic materials like the lanthanides, excitation is not accompanied by a transition in dipole moment, making such transitions formally not allowed. As discussed above, the latter is not fully true in practice and such transitions become partially allowed, but the transition moments are very small and result in weak electric dipole fields. For combinations of an organic sensitizer and a luminescent lanthanide ion, energy transfer can take place, provided that a suitable combination is taken regarding their energy levels. However, to have an efficient energy transfer, both should be in close proximity or preferably in close contact with each other.\textsuperscript{69}

Through this mechanism of sensitized luminescence, lanthanide chelates and other species can efficiently convert UV-light absorbed by the ligands into visible luminescence of the lanthanide ions. In other words, the ions have been fitted with a very sensitive 'antenna' for picking up UV-radiation. This circumstance also accounts for the interest in these compounds because of their importance in biological applications, e.g. ionic probes.\textsuperscript{70-72}

The sensitizer needs to meet some important requirements to be practically applicable. Firstly, it should possess a high extinction coefficient and undergo an efficient intersystem crossing. It should be noted that in order to have an efficient intersystem crossing, the absorption efficiency may not be too high. A sensitizer with a very high
extinction coefficient corresponds to a ‘very’ allowed $S_0$ to $S_1$ transition. This also means that the probability of the reverse process (stimulated emission and fluorescence) is high, making it less likely that intersystem crossing can occur. Thus, for an efficient energy transfer to a complexed lanthanide ion, the sensitizer extinction coefficient has an optimum. Secondly, the triplet state of the sensitizer should be about 3000 cm$^{-1}$ above the luminescent state of the lanthanide ion in order to transfer energy irreversibly on the timescale of the luminescence (no back-transfer). For Eu$^{3+}$ and Sm$^{3+}$ this means a triplet level $> 18000-20000$ cm$^{-1}$ and for Tb$^{3+}$ and Dy$^{3+}$ 21000-22000 cm$^{-1}$. It should be noted that if a sensitizer can transfer energy to Tb$^{3+}$ and Dy$^{3+}$, it can also do this to Eu$^{3+}$ and Sm$^{3+}$ as a consequence of their luminescent levels being lower in energy. Thirdly, the sensitizer should absorb at the highest possible wavelengths to avoid strong loss of pump power to near-UV absorbing groups of a polymer matrix. Alternatively and most conveniently a non-UV absorbing polymer matrix should be used for optimal circumstances. Such a polymer can be poly(dimethylsiloxane). Densely crosslinked polymers will be most suitable host matrices for fluorescent lanthanide complexes. Through a high degree of crosslinking, the mobility of network chains is severely restricted, which reduces the chance of fluorescence quenching (by C-H bonds of the polymer) by minimizing the number of collisions of the polymer chains with the lanthanide complex. A good protecting sheathing is necessary, still. Concluding, one can state that simply doping a lanthanide ion salt into a polymer matrix will not have the desired effect of yielding a material suitable for amplification of light. A little more work needs to be done. A good way of making the lanthanide cation more compatible with the polymer matrix is incorporating it in a bulky organic ligand sheath. The resulting complex will have a greatly enhanced solubility. At the same time, quenching agents will be unable to reach the excited metal centers through the site isolation. And lastly, the presence of a ligand may enhance the absorption of the complex and through an energy transfer process the fluorescence intensity of the metal may increase significantly. Our current strategy aims at combining these three features into one single ligand. The work carried out in this field is described in chapter 8.
REFERENCES AND NOTES

Chapter 1


Introduction


Chapter 1


