Design, synthesis and properties of new materials based on densely crosslinked polymers for polymer optical fiber and amplifier applications
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Summary

Telecommunication rules today’s society more and more and it’s impossible to imagine life today without it. The amount of information circulating grows every day, the intensive use of internet being a good example. As information transfer is increasing, there is a need for high-volume data transfer systems with high transmission speeds. Nowadays, electrical pulses through copper wires are mostly used as the carrier of information. However, if light is used instead of electricity, the amount of signals (information) that can potentially be sent per second without interference of individual signals, increases by a factor $10^6$. The use of light instead of electricity not only has a large impact on telecommunication, if applied in computers their operating speed would increase by a factor $10^6$. However, at the moment, the limit is not set by the capacity of the carrier, but by the way either electricity or light is modulated. For long-distance transfer of light signals, special optical glass cables have been developed. Simply depicted, an optical cable consists of a very transparent core and a transparent covering layer (the cladding), which must have a lower refractive index than that of the core material. If a cable is fabricated in such a configuration, light will stay inside the core by the physical principle of internal reflection and can be transported over a certain distance. Glass is superior in transparency but not in mechanical properties compared to polymers. Glass is brittle and as a consequence the core of the glass optical cables needs to be very thin in order to have some flexibility without the problem of fracture. The diameter is usually in the order of 0.1 mm for so-called multi-mode fibers. The small diameter makes coupling of fibers difficult and time-consuming. For local-area fiber networks in particular, huge numbers of couplings are necessary. Therefore, the use of optical glass fibers is a very expensive option for those applications.

As polymers are far more ductile than glass, larger core diameters up to 1 mm or more are feasible without losing flexibility. However, polymers do suffer from a lower transparency. This means that their application is limited to local-area networks. Transparent polymers applied as polymer optical fibers are poly(methyl methacrylate) (PMMA), polystyrene and polycarbonate. PMMA is the most transparent bulk material
known at this moment and is most widely used. A drawback of PMMA is its low glass transition temperature ($T_g$). PMMA cannot be used above temperatures of 80 °C, at which softening and a consequential loss of properties sets in. This limits its applicability tremendously. Higher-$T_g$ materials, such as polycarbonate are applicable, but they suffer from high intrinsic optical losses, resulting in low transmission distances. A broader discussion about the use of polymers for optical cables and the state of the art is given in the first half of chapter 1.

In connection with the limitations described above, the aim of our research has been: 1) to develop new materials which are highly transparent and have high heat distortion temperatures, 2) to fabricate heat-stable polymer optical fibers from them, and 3) to develop polymer optical fibers capable of amplifying light.

*Densely crosslinked polymers* were thought to be capable of satisfying the requirements. Such materials are amorphous, have high $T_g$’s or at least maintain their optical properties above the softening temperature. Moreover, they are intrinsically highly transparent as they have low compressibilities, resulting in very little (Rayleigh) scattering. Two types of materials were found to be of interest: poly(isocyanurate)s and poly(carbosiloxane)s. For these materials no side-products are formed during the crosslinking reaction, which is a prerequisite for fabricating polymer optical fibers.

**Chapter 2** describes the work performed on poly(isocyanurate)s. Isocyanurates are formed by the trimerization of isocyanates. If one starts with a diisocyanate, a dense three-dimensional polymer network is obtained. Polytrimerization usauly does not occur without a catalyst. Efforts have been made to find catalysts that show good activity, are highly selective and result in highly transparent materials. A major problem encountered was yellowing of the materials upon polymerization at high temperatures. This indicated that yellowing may also develop during high-temperature use, which is undesirable. The selectivity and conversion is found to be very important in making highly transparent poly(isocyanurate)s. Upon testing several monomers, hexamethylenediisocyanate (HDI) was found to be the best candidate. A superior transparent material has been made from this monomer using a neodymium catalyst.
The catalyst, being a bimetallic crown ether complex, was developed for light-amplifying purposes. Details about the synthesis and structure can be found in Appendix A.

As a second alternative, densely crosslinked poly(carbosiloxane)s have been developed (chapter 3). Basically, the development started with applying sol–gel chemistry. Sol–gel chemistry is used as a low-temperature synthetic route for making glass. However, the route also has options to organically modify the glass structure providing polymer-like properties such as ductility. To prepare the densely crosslinked poly(carbosiloxane)s, hydrosilylation was employed as the crosslinking reaction. Materials development resulted in novel self-crosslinkable, one-component systems. Those materials were developed for the first time and were found to be very suitable for polymer optical fibers. As the materials were new, a thorough investigation of their properties was necessary.

Chapter 4 covers the structure–property relations of the poly(carbosiloxane)s. The densely crosslinked materials showed ideal rubber-elastic behavior in the rubbery state. The mechanical properties were dependent on the chemical composition, crosslink density and the glass transition temperature. Unfortunately, the glass transition temperatures of the poly(carbosiloxane)s were not very high (around 40 °C). Attempts have been made to raise the value by incorporating bulky groups either as side group or in the polymer backbone. The bulky groups were derived from norbornane. Indeed, an effective increase in $T_g$ was found. Introduction of norbornane as a silicon side group (Figure 1) led to the most effective increase in $T_g$. A major drawback encountered for all norbornane-derivatized polymers was a severe yellowing upon curing. Therefore, these materials were not of interest for polymer optical fibers (see chapter 5).
The final objective was to make polymer optical fibers from the two materials described above. Chapter 6 deals with the fabrication of an optical fiber from polytrimerized HDI (Figure 2). The polytrimerization was allowed to proceed until just before the start of gelation. Subsequently, the polymerizing mixture of moderate viscosity was injected into FEP (fluoroethylene-co-fluoropropylene) tubing. The FEP-tubing has a very low refractive index and acts as the cladding of the fiber.

The resulting optical fiber had an optical attenuation, the most important property of an optical fiber, of 1.58 dB/m at 615 nm. The material was very tough and had a $T_g$ of 140 °C. The polymer optical fiber can thus be applied at temperatures of at least 140 °C, but higher temperatures are not a problem due to the dense three-dimensional structure.

Figure 2:  Trimerization of hexamethylenediisocyanate (HDI) to a three-dimensional poly(isocyanurate) network.
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Chapter 7 describes the fabrication of an optical fiber from a poly(carbosiloxane) made from a poly(phenylmethylvinylhydro-siloxane) prepolymer with an average composition of \([\text{PhSiO}_{3/2}]_{0.24}[\text{Me}_2\text{SiO}]_{0.38}[\text{ViMeSiO}]_{0.21}[\text{HMeSiO}]_{0.18}\) (see Figure 3). Upon curing in situ in a FEP-tubing at 150 °C for 24 hours a polymer optical fiber was produced. The attenuation of light was found to be 0.98 dB/m, meaning that transmission of light is possible over at least 20 m. The material possessed extremely good thermal stability. The optical fiber could be applied at temperatures up to 200 °C.

![Chemical structure](image)

**Figure 3:** The formation of a polymer network by intermolecular hydrosilylation crosslinking reactions.

As already mentioned, a major drawback of using polymers is their high transmission losses relative to glass. To overcome this shortcoming of polymer optical fibers and thus to increase the transmission span, amplification of light is necessary. This can be achieved by doping the core material with a material capable of luminescing at the signal beam wavelength. By a stimulated emission process the weakened optical signal is regenerated in strength. This concept has been applied successfully in glass optical fibers. In polymer optical fibers, it has only been demonstrated using organic dye molecules (fluorophores). However, inorganic
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Fluorophores, represented by bivalent and trivalent lanthanide ions are of much more interest. Our research has been aimed at developing a polymer optical fiber amplifier based on trivalent lanthanide ions, because 1) they have a high optical damage threshold; 2) their photophysical properties are insensitive to the local environment; 3) they possess sharp, well defined, fluorescent bands; 4) they exhibit large shifts between the absorption and fluorescence wavelengths, and 5) their fluorescence wavelength is tunable. However, they do suffer from an insolubility in organic media, an extremely low absorption capacity (the fluorescent f-f transitions are forbidden) and a severe susceptibility to non-radiative energy quenching (ion–ion and environmental vibrational overtones from mainly C-H and O-H bonds). Nevertheless, the lanthanide ions can be applied upon enveloping in an insulating organic sheath. The organic sheath should overcome all the aforementioned problems. This is extensively reviewed in the second half of chapter 1.

Research exploring the aforementioned field is described in chapter 8 of this thesis. Crown ethers, $\beta$-diketonates and polybipyridines have been investigated as an insulating sheath. Crown ethers did not enhance the luminescence intensity as they are not capable of absorbing energy and transferring it intramolecularly to the enveloped metal ion. The bipyridine complexes were very laborious to prepare and without alkyl-substituents were poorly soluble in organic polymer media. $\beta$-diketonates, on the other hand, were relatively simple to prepare, were versatile in substituents, showed good complexation with lanthanide ions and showed highly efficient energy transfer.

Three diketonate molecules were chelated to one single lanthanide (III) ion. To complete the coordination sphere, synergic molecules were added. As a result, empty coordination sites will not be available for strongly energy-quenching water molecules. Trioctylphosphine oxide (TOPO) is such a synergic agent, which besides completing the insulating sheath also adds to the solubility due to the large alkyl chains.

To enlarge the overall absorption capacity the diketonate moiety has been substituted by 2-($t$-butylyphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (abbreviated as PBD). PBD is a well-known laser dye with a high extinction coefficient. It absorbs high amounts of energy that can be transferred efficiently to the chelated lanthanide
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The synergic agent may also be phenanthroline or bathophenanthroline, which both enormously add to the energy-harvesting capacity of the complex and thereby enhance the intensity of fluorescence of the complex.

Figure 4: Europium chelate with a PBD-substituted β-diketonate and trioctylphosphine oxide as synergic ligand.

An europium-doped active polymer optical fiber has been made by dissolving 1 wt.% of Eu(PBD)$_3$(TOPO)$_2$ complex (Figure 4) in trimerizing HDI. The fiber showed strong red luminescence (613 nm) upon side-pumping with 354 nm UV-light (see the picture on the cover of this thesis). The lifetime of fluorescence was 0.66 ms, which is high. This result revealed the importance of using a densely crosslinked polymer matrix. Unfortunately, the number density of europium (III) was too low to measure amplification of light in the active polymer optical fiber. The number density was $10^{18}$ cm$^{-3}$ and should preferably be $10^{20}$ cm$^{-3}$. The solubility needs to be enlarged by alkyl-substitution. Further optimization of the energy-harvesting capacity can help to lower the pump power threshold for light amplification and help to reduce the necessary number density of lanthanide ions. Cascade energy transfer has been demonstrated in the solid state with a 90/10 blend of PBD with Eu(PBD)$_4$. Intermolecular energy transfer was found to co-operate well with intramolecular energy transfer. In conclusion, the energy transfer concept is very well applicable in developing a polymer optical fiber amplifier.