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

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2000

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Citation for published version (APA):

Flipsen, T. A. C. (2000). *Design, synthesis and properties of new materials based on densely crosslinked polymers for polymer optical fiber and amplifier applications*. s.n.

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Fabrication and characterization of Polymer Optical Fibers based on a polycarbosiloxane network core material

ABSTRACT

A multi-mode step-index polymer optical fiber has been developed based on a highly crosslinked polycarbosiloxane as core material and a fluorinated polyolefin (poly(fluoroethylene-*co*-fluoropropylene) - FEP) cladding layer. The combination offered a system with a high thermal stability both optically and dimensionally up to at least 200°C. The polymer optical fiber was produced by injection of a poly(phenylmethylvinylhydro)siloxane crosslinkable prepolymer in a FEP-tubing, after which the prepolymer was cured *in situ*. From attenuation measurements losses as low as 0.98 dB/m at 780 nm were found. The refractive indices of the core material and the cladding are 1.48 and 1.30, respectively. The large difference in refractive index results in a high value for the numerical aperture of 0.70. The prepolymer is a single-component, self-crosslinking and conveniently processable system. The combination of a low attenuation and easy processability makes these materials very suitable not only for polymer optical fibers, but for all kinds of optical components.

The main part of this chapter has been published in *Journal of Applied Polymer Science*, **67**, 2223 (1998).

INTRODUCTION

In the search for thermally and dimensionally stable polymer optical fibers (POFs) crosslinked polymers are good candidates for making the core material.^{1 - 3} By crosslinking, the dimensional stability is not limited by a softening point and properties are retained above the T_g . This effect is strongly enhanced for highly crosslinked polymers. The maximum temperature at which the POF can operate is then determined by the thermal stability of the polymer system. As polysiloxanes have a very thermally stable backbone, densely crosslinked networks made thereof are superior candidates, which can fulfill all the requirements.

This chapter describes the application of a new type of densely crosslinked polysiloxanes for polymer optical fibers with high thermal stability. Besides low intrinsic optical losses and a thermally stable backbone, these materials are crosslinked without production of volatile products and without shrinkage, which allows their use for bulk applications such as polymer optical fibers and planar waveguides.^{4,5} In this chapter the focus is on application in polymer optical fibers.

EXPERIMENTAL

Analysis

Glass transition temperatures were measured with a MDSC (Modulated-DSC) 2920 apparatus from TA-Instruments. For these measurements a scan speed of 3 °C/min, an amplitude of 1°C and a period of 60 s were used. The glass transition temperature was defined as the midpoint of the DSC curve. The thermal stability was measured with a Perkin Elmer TGA-7 apparatus operating at a scan speed of 10 °C/min in a nitrogen atmosphere. For the measurement of the polycarbosiloxane polymer networks a ceramic pan was used. The conventionally used platinum cups are easily solubilized by the polymer due to a strong complexation of platinum with residual silicon-vinyl groups of the polymer.

The mechanical properties were determined on cylindrically shaped specimens (diameter: 0.76 mm) with an Instron 4301 tensile tester at room temperature (20°C). The crosshead speed was 10 mm/min and the gauge length 25 mm.

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Measurement of the bulk density was done in absolute ethanol by measuring the exact volume of the specimen (~ 1 g). The values of the density of ethanol and their dependence on temperature were taken from literature.⁶

Atomic Force Microscopy (AFM) on the inner surface of the FEP-tubing was performed with a Topometrix Discoverer AFM. Profile measurements were done with a Sloan DEKTAK 3030ST Surface Texture Analysis System with a needle force of 10 mg.

Contact angle measurements were conducted with a home-built setup. The angle a droplet of ultra-pure water made with the polished surface of the material was determined with a camera. Refractive indices of the prepolymers were determined with an Abbé-refractometer working with the D-emission line of sodium, being 589.3 nm at 20°C . The refractive index of the cured polymers was measured on a film with a Metricon 2010 prism coupler in two directions (n_0 and n_e) at 20°C and at wavelengths of 633, 803 and 1300 nm.

The attenuation of light of the produced POFs was measured via the cut-back method for wavelengths from 600 nm to 1000 nm. The light source was a halogen-tungsten lamp coupled to a grating monochromator. The exit intensity was measured with a silicon-photodiode.

UV-Visible spectra were recorded on a SLM Aminco 3000 Array spectrometer. The measurements were done on the pure prepolymers (no dilution with solvent) in cells with an optical path length of 1 cm.

Materials

Vinylmethyldiethoxysilane and methyldiethoxysilane were synthesized from vinylmethyldichlorosilane (purchased from Acros Chimica) and methyldichlorosilane (purchased from ABCR), respectively. The procedure employed has been described in chapter 3 of this thesis and in a publication.^{4,5} Phenyltriethoxysilane and dimethyldiethoxysilane were obtained from Acros Chimica. All four monomers were carefully distilled twice via spinning band distillation (plate number = 20). The catalyst was a platinum 1,3-divinyltetramethyldisiloxane complex with 3 - 3.5 wt % of platinum in vinyl-terminated polydimethylsiloxane. The catalyst system, purchased from ABCR, was dissolved in 1,3-divinyltetramethyldisiloxane (ABCR) to give a 0.1 wt % platinum concentration. Absolute ethanol (pro analysis) was obtained from Acros Chimica and was used as received. Toluene was distilled freshly from sodium and benzophenone, prior to use. FlorisilTM magnesium silicate, 30 - 60 mesh and pH = 8.5 was obtained from Fluka AG.

FEP-tubing was purchased from Polyfluor Holland with an inner diameter of 0.95 mm and an outer diameter of 1.6 mm.

Synthesis of the poly(phenylmethylvinylhydro)siloxane prepolymer

The basic synthesis of the particular prepolymers has been described in chapter 3 of this thesis and an earlier paper.^{4,5} More or less a similar procedure has been employed, but with some adjustments as reported below.

A round-bottomed flask was charged with 8.0 g (0.033 mol, 25 mol %) of phenyltriethoxysilane, 6.9 g (0.047 mol, 35 mol %) of dimethyldiethoxysilane, 4.3 g (0.027 mol, 20 mol %) of vinylmethyldiethoxysilane, 3.6 g (0.027 mol, 20 mol %) of methyldiethoxysilane and 100 wt %, based on the total weight of the monomers, of absolute ethanol. To the cooled homogeneous solution 34.1 g (150 wt %, based on the total weight of the monomers) of a 20% aqueous hydrochloric acid solution were added dropwise at such a rate that the temperature of the reaction mixture did not exceed 10°C. After the addition was complete, the still homogeneous reaction mixture was stirred for 1 h at room temperature. The mixture was combined with 50 mL of toluene and stirred for 3 h at 60 - 70°C. Hereafter, the toluene layer was separated and washed with an aqueous saturated sodium bicarbonate solution followed by washing with demineralized water until the pH was neutral. The remaining water left from the washing procedure was azeotroped off at 130 - 140°C for 2 - 3 h. The reaction mixture was filtered over a Florisil™ column and toluene was removed *in vacuo* by means of a rotary evaporator. The product was combined with 50 mL of methanol and stirred for 1 h, after which the mixture was filtered through a 0.2 µm Teflon membrane filter. The methanol was removed *in vacuo* by means of a rotary evaporator. Finally the solvent-free polymer was filtered through a 0.2 µm Teflon membrane filter. The polymer was kept under reduced pressure at room temperature for at least 48 h to remove traces of toluene and possibly, low molecular weight volatile oligomeric components. The yield was approximately 85% of a very clear and transparent poly(phenylmethylvinylhydro)siloxane with a found average composition (¹H-NMR) of [PhSiO_{3/2}]_{0.24}[Me₂SiO]_{0.38}[ViMeSiO]_{0.21}[HMeSiO]_{0.18}

Fabrication of polymer optical fibers

The FEP-tubing was thoroughly cleaned before use by ultrasonic rinsing with 20% HNO₃ for 30 min. Thereafter the tubing was flushed several times with demineralized water, filtered (0.2 μm) ethanol and finally with filtered (0.2 μm) pentane. After each flushing step, the tube was dried with pure nitrogen gas. The tube was dried at 80°C *in vacuo* for at least 24 h.

The polymer optical fibres were fabricated by injecting a poly(phenylmethylvinylhydro)siloxane prepolymer, with an average composition of [PhSiO_{3/2}]_{0.24}[Me₂SiO]_{0.38}[ViMeSiO]_{0.21}[HMeSiO]_{0.18}, into a FEP-tube. The prepolymer was filtered over a 0.2 μm Teflon membrane filter and deaerated ultrasonically, prior to injection. The curing of the prepolymer was accomplished *in situ* with 1 ppm of platinum-catalyst (Karstedt) at 150°C for 24 h, producing a step-index polymer optical fiber.

RESULTS AND DISCUSSION

Synthesis of the prepolymers and the polymer networks

The synthesized prepolymers are based on four different types of monomers, viz. phenyltriethoxysilane, dimethyldiethoxysilane, vinylmethyldiethoxysilane and methyldiethoxysilane. For the nomenclature of the polymer the same monomer sequence has been used resulting in poly(phenylmethylvinylhydro)siloxane. Before synthesis the monomers were distilled twice via a spinning band distillation with a plate number of 20, to obtain a maximum purity.

The prepolymers were produced via co-hydrolysis and condensation reactions.^{4,5} The trifunctional monomer, phenyltriethoxysilane (PTES), was used to introduce branching of the polymer backbone. The branching points will turn into network junctions after the curing reaction has been accomplished. Because they are present in a large amount before the curing step, the polymer system will show only a minute or even a negligible degree of shrinkage. This is a very important issue because the prepolymer is injected into a tubing and for a good contact with the wall of the tubing shrinkage of the core as a consequence of the curing reaction may not occur. If the contact is not adequate, this undoubtedly forms a source of scattering. Generally, shrinkage is a large problem when applying polymer networks, however.

Chapter 7

The prepolymers are highly soluble in common organic solvents and gelation during the synthesis was prevented by cyclization reactions. These cyclization reactions are well known for siloxane polymerization. It was found that the ring structures have a molecular structure similar to that of the non-ring structures and are able to crosslink as well.^{4,5} The incorporation of ring-like structures is favorable for the thermal stability of the cured polymer.⁷

A final step during working up is fractionation of the prepolymer. In this step methanol is used to separate the major low molecular weight part from the minor high molecular weight part. This provides a very clear prepolymer. Namely, the higher molecular weight part tends to phase separate from the lower molecular weight part, which can result in a slightly turbid prepolymer. The number-average molecular weight of the prepolymer under investigation (poly(phenylmethylvinylhydro)siloxane, 25/35/20/20 mol %), is typically 1200 g/mol, resulting in a moderate viscosity.^{4,5}

For the synthesis, a solvent like THF or ethanol is used to homogenize the reaction mixture. If such a solvent is not used, and the hydrochloric acid is added to the pure monomer system, then after a short while a phase separation occurs. It is obvious that the higher molecular weight molecules become less soluble in the monomer/water mixture and will phase separate. These molecules become less available for the catalyst system and cannot grow easily and homogeneously to higher molecular weights. If, on the other hand, a solvent is used which is able to solubilize both the monomer/water/hydrochloric acid phase and the polymer phase formed, polymerization can take place more homogeneously in the complete system. This results in a smaller distribution of the molecular weight and above all in a very clear prepolymer. Nonetheless, a fractionation step is applied, but the yield of highly transparent polymer is high.

The polysiloxane prepolymer is a single-component system and has a moderate viscosity, which results in a conveniently processable system. Moreover, this makes a thorough purification of the solvent-free prepolymer (filtering and deaeration), prior to the processing, feasible. The prepolymer possesses both functional groups needed for the curing reaction. Crosslinking occurs intermolecularly via hydrosilylation reactions,

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which is a clean crosslinking reaction without the production of volatiles, if proper conditions are chosen (Figure 1). No problems with volatile crosslinking agents or inhomogeneous mixing of non-volatile crosslinkers arise. If volatilization of crosslinking agents would occur during processing, the crosslinking could become insufficient. The second problem may occur if a high molecular weight polymeric crosslinker is applied. An inhomogeneous mixing can give rise to density fluctuations on a nanometer or micrometer scale with a consequential scattering of light.

Curing took place under the influence of 1 ppm platinum catalyst for 24 h at 150 °C. The relatively slow curing process can be accelerated by adding more catalyst. This introduces a dramatic increase of the optical losses, however.⁸

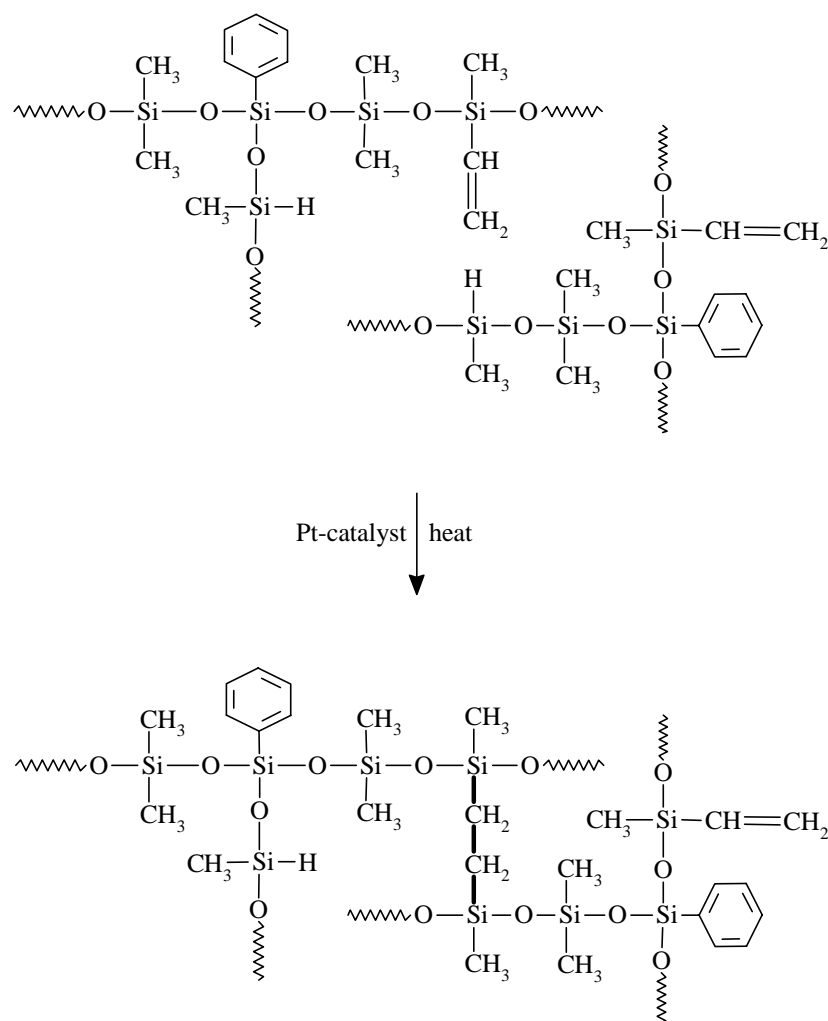


Figure 1. *The formation of a polymer network by intermolecular hydrosilylation crosslinking reactions.*

Properties of the core material and the polymer optical fiber manufactured thereof

The glass transition temperature of the densely crosslinked system was determined to be 14°C. This is not a high value when it is compared to the more conventional polymers, but due to the dense network structure this system is dimensionally stable above its T_g and the optical properties are retained. That the system is very densely crosslinked is reflected in the value of the molecular weight between crosslinks, M_c , which was found to be 300 g/mol.^{9,10} The mechanical properties were measured at room temperature (20°C) and showed a stress at break of 16 MPa, an elasticity modulus of 350 MPa, and an elongation at break of 22%. The polycarbosiloxane core is surrounded by a very tough FEP-sheathing (tubing). The mechanical properties of the tube were 120 MPa in tensile strength and an elasticity modulus of 1.7 GPa. The strain at break was 500%. The combination of these mechanical properties results in a very tough material (a toughness of 440 MPa). In combination, therefore, the core and the cladding materials produce a strong and tough polymer optical fiber. To do so, a good contact of the core with the cladding is important. In case of a good contact the very tough thermoplastic lining can dissipate energy from the core material, which results in a mechanically stable fiber. Strong contact can be based on two contributions, a chemical bond type interaction (covalent or physical, i.e. Van der Waals interactions) and a mechanical interaction by anchorage at a rough surface. In synergism they add to the total adhesive interaction. The inner surface of the FEP-tubing is very smooth as has been demonstrated by atomic force microscopy (AFM) and profilometry. From an AFM topography image (Figure 2) an average roughness of 11.2 nm was calculated. The maximum change in height was 200 nm, which was also found in the profile measurements. Because of such a smoothness, adhesion is predominantly based on a chemical interaction. A prerequisite for a good contact is, above all, a good wetting of the inner surface of the tubing by the prepolymer. The fluorinated tubing material has a low surface tension (contact angle with water is 107°).¹¹ For a good wetting the contact angles of both substrate (cladding) and polymer

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(core) need to be in the same range. Polysiloxanes are known to have low surface tensions. From contact angle measurements an angle of 103° was found for the crosslinked material, which is very close to the value of FEP.

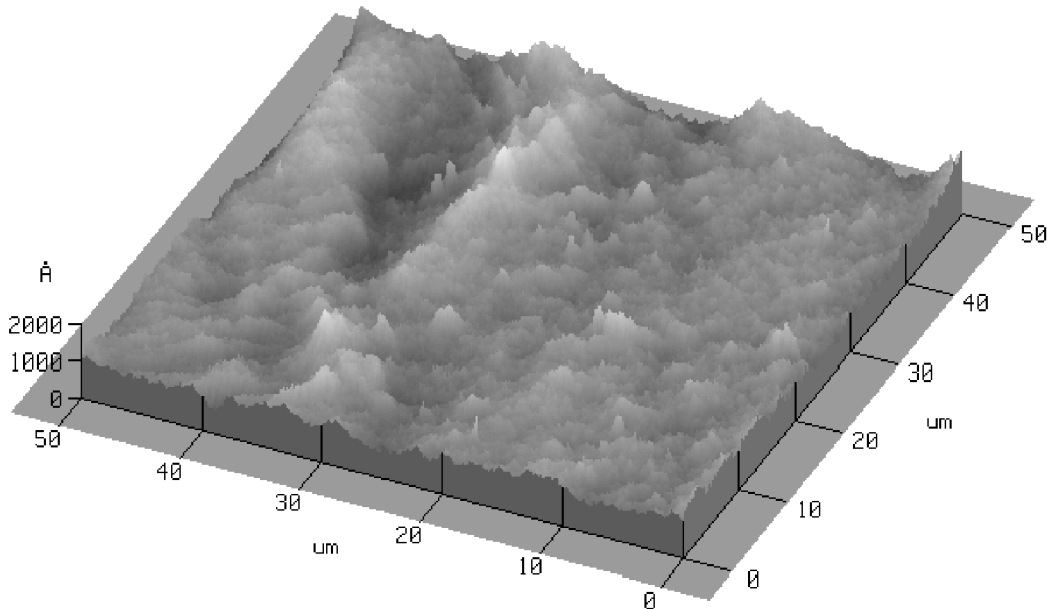


Figure 2. An AFM topography image of the inner surface of the FEP tube used.

Generally, crosslinking leads to a shrinkage of the polymer. Especially in the case of highly crosslinked polymers this can be a severe problem. In a confined volume like a tube this means a decrease of the diameter of the core and thereby the contact with the cladding is lost. The curing of the poly(phenylmethylvinylhydro)siloxane prepolymer was found not to be accompanied by any measurable extent of shrinkage. This resulted in a nicely fabricated optical fiber without any signs of release of the core from the cladding. A picture of the cross-section of the optical fiber in (Figure 3) indicates a good contact of the core and cladding. A good contact is not only important for good mechanical stability, but for low optical losses as well. The roughness of the

cladding layer is significantly smaller than the wavelength of the propagating light and does not contribute strongly to the total loss mechanism.



Figure 3. A picture of the cross-section of the polymer optical fiber. The surface has not been polished. The actual size is 0.95 mm for the core and 1.6 mm for the outer diameter of the fiber.

The refractive index of the prepolymer was found to be 1.464 (at 589.3 nm), which is rather high for polysiloxane-based systems. The presence of the phenyl groups, which possess a high degree of polarizability, are responsible for this high value. Upon curing a refractive index of 1.483 at 633 nm is reached. Due to the crosslinking a densification of the polymer system takes place accompanied with a rise in refractive index. As has been shown above, the densification did not give rise to a measurable extent of shrinkage in diameter of the core, however. In the table the refractive indices are listed for 3 different wavelengths. The refractive index was measured on a planar film in two directions, parallel to the plane (n_0) and perpendicular to the plane (n_e). The table shows that in both directions exactly the same refractive indices are found. This indicates that the material is entirely isotropic in terms of light refraction and thus does

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not show any signs of birefringence. From the table one can also see the wavelength dependence of the refractive index. For higher wavelengths a lower refraction of light is caused by the material, because of a smaller interaction between the light and the material. For the optical fiber similar conclusions can be drawn. Upon injection of the prepolymer into the tubing an orientation of the polymer in the direction of the fiber axis might occur. However, because curing is a relatively slow process here, there is enough time for the polymer system to relax to an unperturbed, non-birefringent state, before gelation constrains the conformation. This is an advantage over the high- T_g thermoplastic polymers, for which often an orientation of polymer chains in the direction of the fiber axis, i.e. extrusion direction, leads to birefringence. Scattering of light because of birefringence is an important extrinsic loss factor of such polymer systems.

Table 1. *Refractive indices at three different wavelengths and in two directions (parallel, n_o , and perpendicular, n_e , to the plane) for the cured poly(phenylmethyl-vinylhydro)siloxane with 25 mol % phenyltriethoxysilane (PTES) incorporated.*

wavelength (nm)	n_o^{20}	n_e^{20}
prepolymer (589.3)	1.464	
633	1.483	1.483
830	1.475	1.475
1300	1.472	1.472

The refractive index of the prepolymer is given for 589.3 nm, measured parallel to the plane. The measurements were performed at 20°C.

Figure 4 shows a typical attenuation spectrum of an optical fiber based on poly(phenylmethylvinylhydro)siloxane polymer with 25 mol % of PTES. The lowest attenuation is experienced in a window at 780 nm and amounts to 0.98 dB/m. The spectrum shows the higher harmonics of the fundamental C-H stretching vibrations and bending vibrations, the combination of which results in doublet absorption peaks

in the visible part of the spectrum. The number of C-H bonds present can be calculated with Equation 1.

$$N = \rho n_{\text{C-H}} / M_{\text{ru}} \quad (1)$$

N = number of C-H bonds in mol/cm³

ρ = density of the bulk in g/cm³

$n_{\text{C-H}}$ = number of C-H bonds per repeat unit

M_{ru} = molecular weight of a single repeat unit

For the polycarbosiloxane under investigation, the density was found to be 1.145 g/cm³, which results in an intrinsic number of C-H bonds of 0.068. The value for PMMA is 0.095, which is significantly higher. PMMA is extensively used as optical fiber core material, and is known as the (protonated) material with the lowest optical losses in the visible. In the near infrared (1000 - 1500 nm) PMMA has very high intrinsic losses due to the C-H overtone absorptions, however. The polycarbosiloxanes, on the contrary, have a dramatically lower number of C-H bonds in the backbone structure and are therefore very promising materials for use in the near infrared region. The losses in the near infrared have not been measured so far, but losses far below 10 dB/m at 1000 nm indicate good optical transparency in this part of the spectrum. With this advantage these materials may become very suitable for planar waveguiding (short optical path lengths) of near infrared light. As the conventional optical glass fibers, which are widely used for telecommunications, operate at 1300 and 1550 nm, low-loss and high-NA planar waveguides based on polymers would offer prospects of a more wide-spread, easy and low-costs application of optical fibers for local area networks.

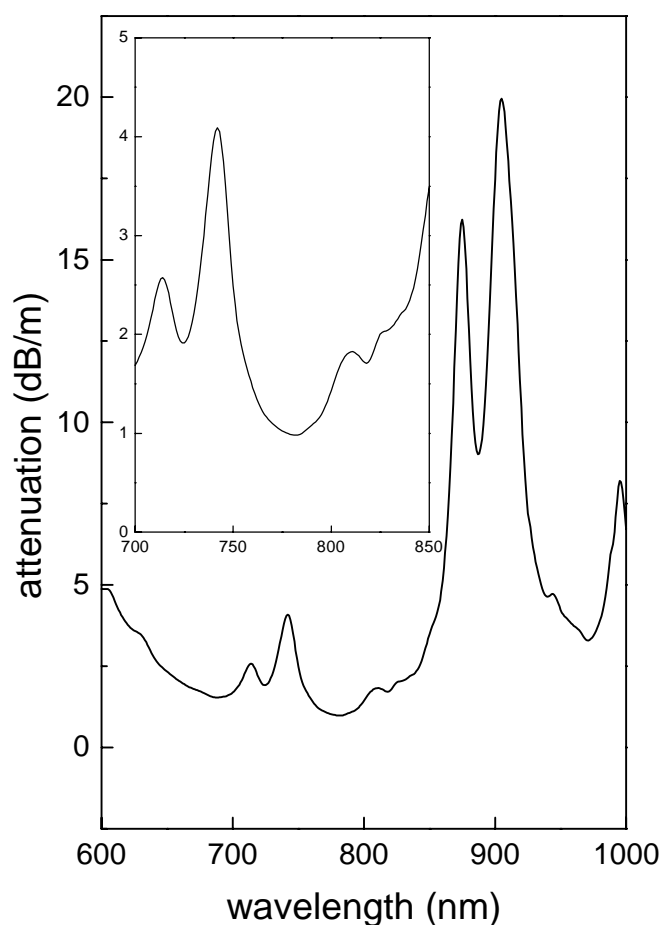


Figure 4. An attenuation spectrum of the polycarbosiloxane-based polymer optical fiber. The optical loss has been determined from 600 to 1000 nm. The lowest loss has been registered at 780 nm being 0.98 dB/m.

Toward lower wavelengths one observes an increase of the absorption by UV-band edge excitations, predominantly caused by the presence of phenyl groups. Surprisingly, replacement of the phenyl groups by cyclohexyl groups resulted not in a decrease of the optical density in the UV. Although the phenyl groups give a strong absorption at 280 nm the peak is very narrow. Introduction of cyclohexyl groups instead of phenyl groups led to a broader peak with a second peak coming up at 350 nm (Figure 5). The only explanation, which can be given for this strange phenomenon is an absorption due to the presence of silicon-vinyl groups and the silicon-hydrogen groups. From UV-Vis measurements a weak absorption is found for the vinylmethyldiethoxysilane

monomer at 270 nm and a strong absorption for the methyldiethoxysilane monomer at 280 nm. Thus apparently, the combination of groups in the prepolymer give rise to new absorptions due to complexation of the particular groups with each other. The ultimate influence in a fiber configuration has not been established. From the UV/Vis spectra one could derive a lower influence of the UV-absorptions of the cyclohexyl-based system onto the attenuation of light if the absorption tail into the visible is considered (Figure 5). A complete conversion of the silicon-vinyl and silicon-hydrogen groups during the crosslinking is expected to lower the contribution of UV-absorptions to the attenuation of light at long optical path lengths.

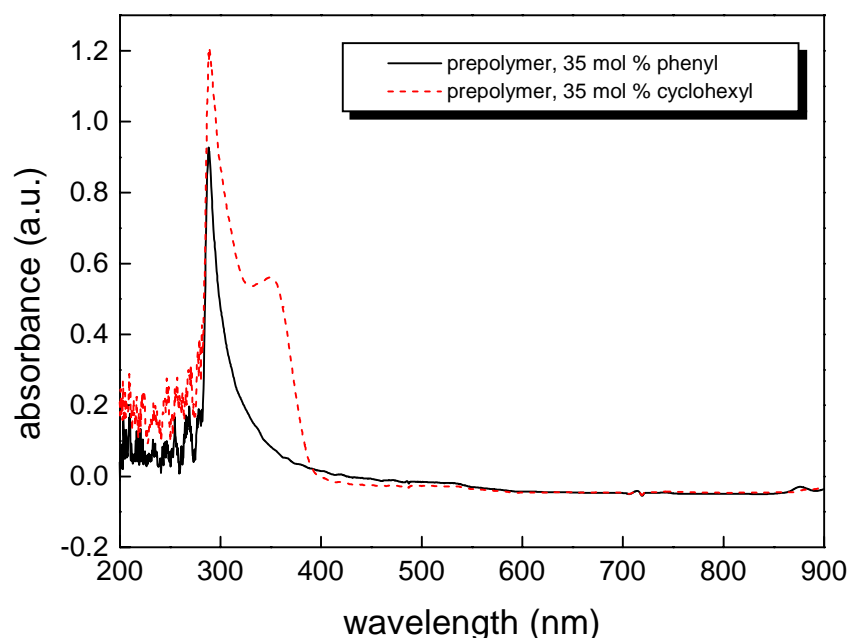


Figure 5. UV-Visible spectra of polycarbosiloxane prepolymers based on phenyltriethoxysilane and on cyclohexyltriethoxysilane. The spectra show the different contributions to the UV-absorptions of the individual polymers.

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The numerical aperture (NA) of the step-index polycarbosiloxane-based optical fiber can be calculated using Equation 2.

$$NA = (n_1^2 - n_2^2)^{1/2} \quad (2)$$

n_1 = refractive index of the core

n_2 = refractive index of the cladding

The refractive index of the cladding is 1.30 and that of the core is 1.475 to 1.483 depending on the wavelength. This results in a high value of the NA of 0.70 - 0.71 and corresponds with an angle of acceptance of 90°. The high NA together with a large core diameter enable easy coupling of light into the optical fibres. This results in easy handling and low-costs application of such polymer optical fibers.

The polycarbosiloxane networks are highly thermally stable. Figure 6 shows a thermal gravimetric analysis plot of the polycarbosiloxane network. It is known for polysiloxanes in general, that they have a high thermal stability. Crosslinking improves the thermal stability even further. At 200°C a slight lowering of the mass was observed (~ 1 wt %), which proved to be due to lower molecular weight, uncrosslinked material. As the core is protected by the cladding layer, release of polymer is not possible. So far we have not experienced any influence of this low molecular weight part on the thermal stability of the optical properties.

The cladding material is fully fluorinated and fluorinated polymers are known to be very thermally stable, as well. Therefore, the POF under investigation offers an outstanding thermal stability. The POF can be used at relatively severe thermal conditions, up to 200°C, without losing its optical properties.

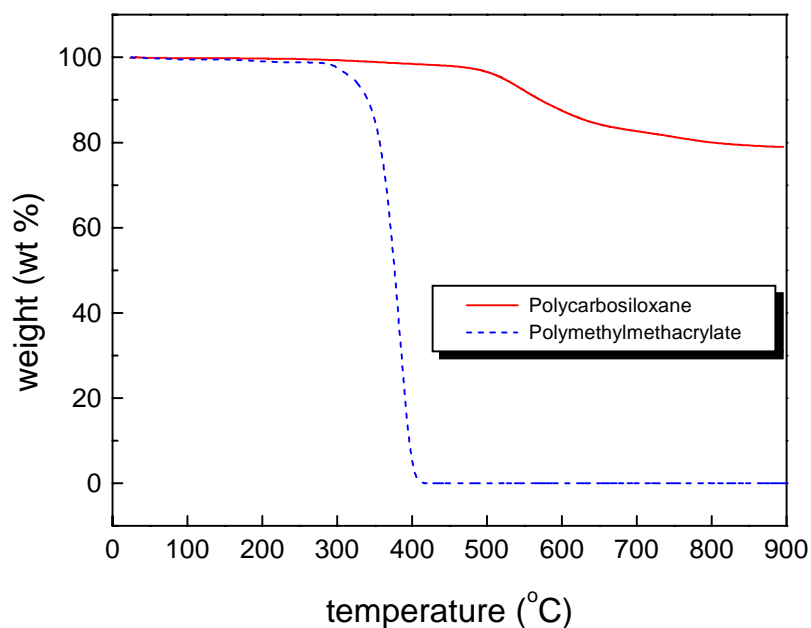


Figure 6. A thermal gravimetric analysis (TGA) plot showing the high thermal stability of the crosslinked polycarbosiloxane. To compare this thermal stability with that of PMMA, conventionally used for polymer optical fibers, a TGA-curve of PMMA is shown as well

CONCLUSIONS

A new thermoset multi-mode step-index polymer optical fiber with a high thermal stability has been presented. The thermoset was produced from a poly(phenylmethylvinylhydro)siloxane prepolymer based on 25 mol % phenyltriethoxysilane (PTES). The prepolymer with moderate viscosity was injected into a FEP-tubing [FEP: poly(fluoroethylene-*co*-fluoropropylene)] and thereafter curing was accomplished at 150°C for 24 h under the influence of 1 ppm platinum catalyst (Karstedt). The combination of a relatively high refractive index core material (1.483) with a low refractive index cladding (1.30) offers a good light guiding polymer optical fiber with a high numerical aperture. Optical losses as low as 0.98 dB/m at 780 nm were registered. As the material is densely crosslinked the dimensions are stabilized over a broad temperature range, at least up to 200°C. Beside polymer optical fibers, the polycarbosiloxanes can be easily applied for planar waveguides. As these

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polymers possess a low intrinsic number of C-H bonds they are also promising for light guiding applications in the near infrared region.

The poly(phenylmethylvinylhydro)siloxane is a single-component, self-crosslinking system that offers easy processing and the crosslinking reaction takes place without production of volatiles.

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