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# New Reactive Polymeric Systems for Use as Waveguide Materials in Integrated Optics

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**Summary:** Cross-linked polymeric materials are used in a wide range of applications. Special compositions are used in micro-system technologies and its utilization is extending to integrated optics. We have been working for several years in the field of polymers for optical applications.

Highly fluorinated polycyanurate systems have been proven as promising waveguide materials in integrated optics. The refractive index can be adjusted reproducibly in a wide range almost continuously. The layer quality was optimized. Low optical losses of less than 0.3 dB/cm@1550nm were obtained and working optical prototypes were developed. The birefringence had been a major problem, but this was solved by adjusting the coefficient of thermal expansion of substrate and film.

We will report in this paper on the polycyanurate ester resins and the new triazine containing polymeric systems.

**Keywords:** integrated optic, optical loss, polycyanurate ester resins; triazine, waveguide

## Introduction

Today, in the age of telecommunications and the internet, the amount of data that is transferred is growing continuously. So called killer-applications like video-on-demand, virtual reality, huge electronic databases, file-sharing and online-games require greater and greater bandwidth. However, it is not only these "fun" applications that require fast data-transfer. The modern information-society has the need for worldwide fast access to e-mail, important files, bank accounts, scientific literature, stock exchanges, product ranges of companies, etc.

To cope with this huge amount of data, optical telecommunications technology is a sufficient tool. Due to its huge bandwidth, with more than 40 Tbps, the glass fiber has almost completely replaced the copper wire for long-range data transmission. The potential of the glass fiber is

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such that all telephone-calls worldwide could conceivably be transferred at once via one single fiber. And the use of the glass fiber now extends more and more to short-distance applications, for example in the automotive or aeronautic fields. Especially for these last two applications the insensitivity of glass fiber to electromagnetic fields, as produced by, for example, cellular phones; and its lower weight in comparison to the copper wire are among the advantages of glass fiber. In about ten years we will likely see an all-optical network with glass fiber connections to every single house or even to every single computer.

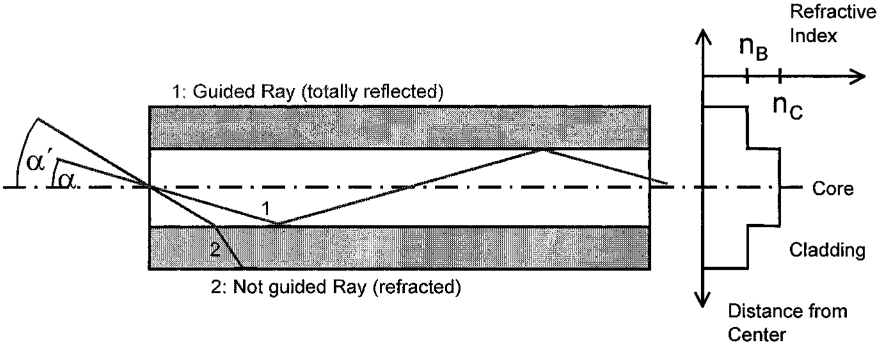


Fig. 1. Waveguiding in the glass fiber or in the waveguide of an optical device. To be guided, the rays must be launched inside of an acceptance angle (1), otherwise the ray is refracted into the cladding.

However, an all-optical network not only consists of glass fibers, but also of a number of different integrated optical devices, such as multiplexers, demultiplexers, thermooptic switches, attenuators, etc. that are needed to run such a high-speed network.

Currently, most optical components are realized by using silica-based optical waveguides, but polymers have many advantages compared with these established silica-based devices. Polymeric materials can provide a significantly higher refractive index-contrast between waveguide core and cladding, which results in smaller devices. Furthermore polymers posses a thermooptic coefficient that is ten times higher than that of silica. Additionally the heat capacity of many polymers is one order of magnitude higher than silica. Hence, a thermooptic switch made from polymer requires a switching power that is only about one percent of that of inorganic switches. Particularly big switching matrices with thousands or more switches can be realized without the well known problem (in microprocessor-technology) of waste heat. Last but not least, polymeric devices can be produced at lower costs, through techniques established in semiconductor production.

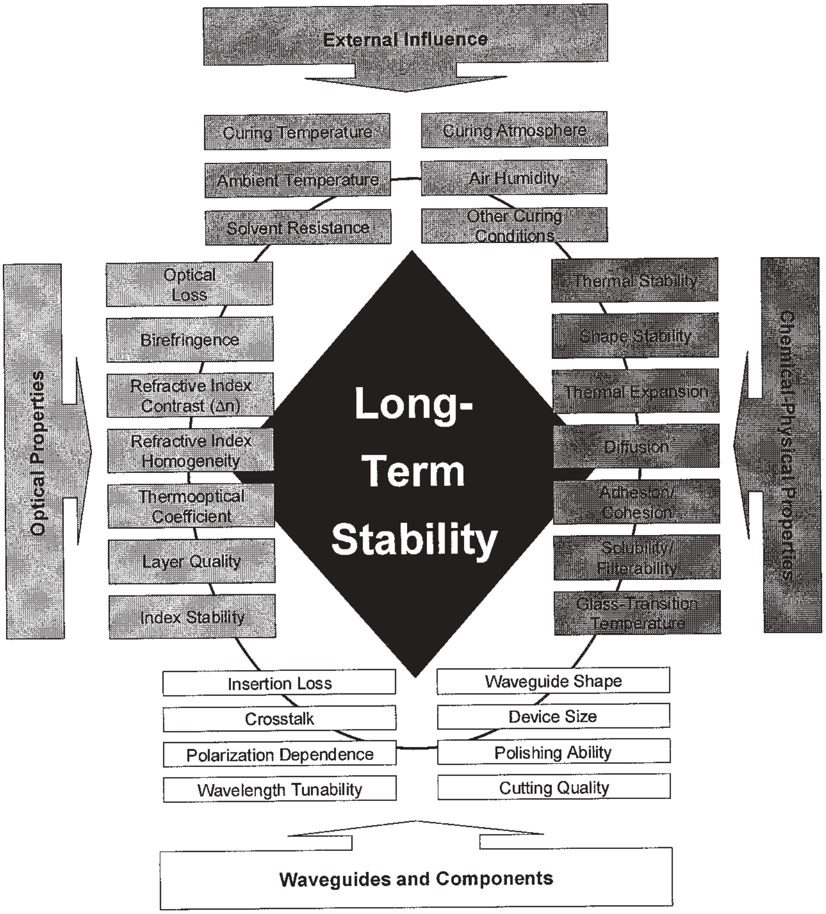


Fig. 2. Requirements on polymers for use as waveguide materials, external influence and device properties.

The dimensions of these waveguides are in the range of the light guiding core of the glass-fiber, about 5-7 μm. The surrounding cladding material must show a slightly lower (about 0.01) index of refraction, to allow waveguiding by total internal reflection at the interface between both media, as shown in Figure 1.

## Demands on Polymers for Use in Integrated Optics

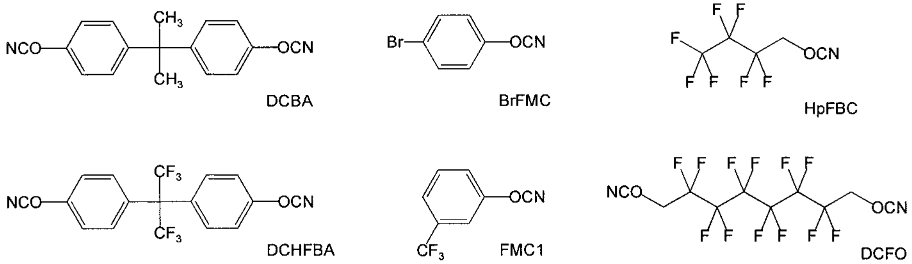
In order to be used as a waveguiding material, the polymers used in integrated optics must meet a number of different demands, as shown in Figure 2. The optical loss must be very low, which is hindered by the fact that -NH, -OH, and weaker C-H groups absorb in the region around 1.55 μm, the wavelength of choice for optical data transfer. Thus, the content of these groups in the polymer needs to be kept very low. The refractive index and the index contrast must be adjustable in a reproducible way, as the design of the devices is determined delicately by these parameters. The birefringence of the waveguiding materials must also be very low, to ensure an error free data-transfer. Good adhesion of the different polymer layers to each other and to the substrate is necessary. Finally, the thermal, mechanical and optical stability must be guaranteed for several years, along with the other properties mentioned in Figure 2, as they all influence device performance. Also, external parameters must be taken into account.

## Polycyanurate Ester Resins

Polycyanurate ester resins are a lesser known class of high-performance-polymers, developed in the late 1960s as base materials for printed circuit boards. They show high thermal and mechanical stability and good adhesion properties on various surfaces. They are used as encapsulants and adhesives, in flame stable composites, in laminates, as friction materials, in lightweight construction, in automotive engineering, and in the aircraft industry.[1]

Scheme 1 shows some basic cyanate monomers, from which we synthesized several polycyanurate copolymers used as waveguide materials.

The two dicyanates DCBA and DCHFBA were purchased from Lonza AG, Switzerland, and used without further purification. The other mono- and difunctional cyanates were synthesized using the cyanogen-bromide method as reported by Martin and Bauer.[2]



Scheme 1. Some basic cyanate monomers.

The basic reaction used to obtain polycyanurates from the corresponding monomers is the cyclotrimerisation of aromatic or fluoroaliphatic cyanate esters, as shown in the reaction scheme in Figure 3.

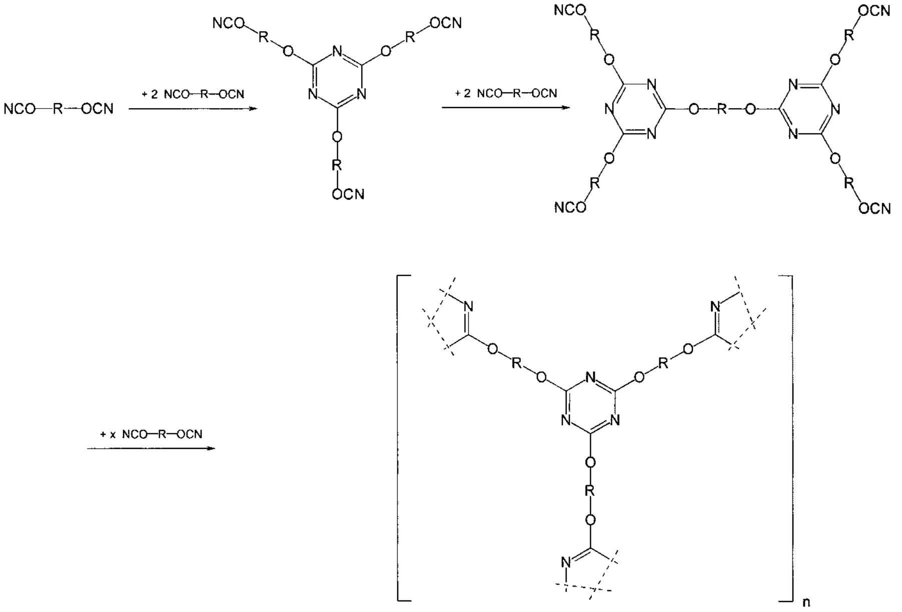


Fig. 3. Polycyclotrimerisation and network formation.

A difunctional cyanate molecule reacts with two other cyanate molecules and forms a triazine. This triazine has three free reactive groups left; therefore it can react with further monomers and forms the pentamer, the heptamer and higher oligomers, until finally a highly branched three-dimensional network is built. At sufficiently high temperatures and appropriate reaction times an almost complete transformation of the cyanate-groups can be obtained.

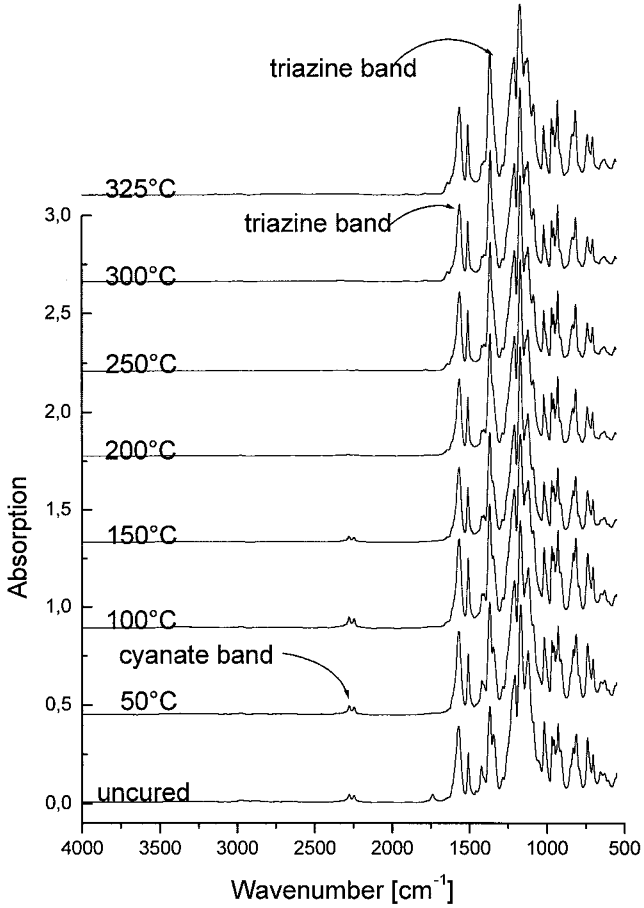


Fig. 4. IR-spectra of the ternary copolymer DCHFBA:DCFO:HpFBC (61,99:6,28:31,74 mole-%). Offline-measurement of thin films on silicone, cured at different temperatures.

This reaction has the great advantage that no by-products, neither gaseous nor liquid, are formed during the reaction. The syntheses of the (pre-)polymers were performed by polymerization of difunctional cyanates in bulk in sealed vials at temperatures between 140 and

190°C. The reaction was stopped rapidly at conversion rates between 40 and 48-% using liquid nitrogen. The prepolymers were dissolved in 2-ethylethoxyacetate and the solutions (45-65 wt.%) were filtered under cleanroon conditions through 0.2 µm PTFE-membrane-filters. Thin films were obtained by spin coating and thermal curing.

The progress of the curing can be examined by the decrease of the cyanate band in the wavenumber region around 2250 $cm^{-1}$ and by the increase of the triazine bands at 1370 and 1558 $cm^{-1}$ (Figure 4).

## Optical Properties

The first step to obtaining a polymeric waveguide material was to adjust the refractive index and find a material pair with a sufficient index-contrast (about 0.010, depending on the design of the integrated optical device and the waveguide dimensions). This can easily achieved with polycyanurates as shown in Figure 5. Almost all monomers can be combined with one another, so the refractive index can be adjusted over a broad range. It can be seen that almost every refractive index between 1.48 and 1.59 can be realized using these materials.

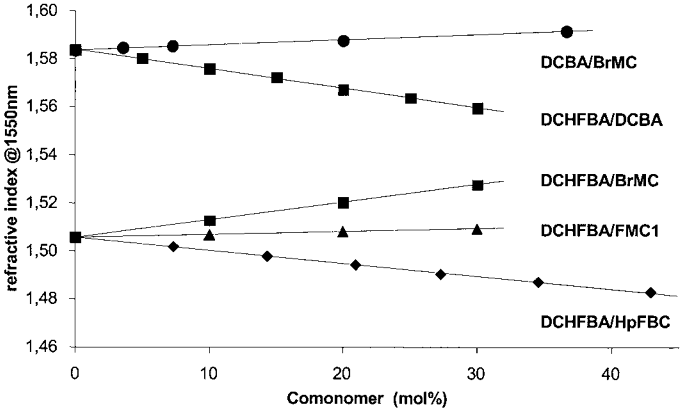


Fig. 5. Refractive index of different copolymers versus comonomer-content.

The optical loss of polycyanurate ester resins should be quite low, as an intrinsic property of the polymer is the absence of OH- and NH- groups. Even after the cyclotrimerisation, to form the network, none of these undesireable groups should be present.

The optical loss of different polycyanurate copolymers is shown in Figure 6. The neat DCBA and DCHFBA show a high increase in the loss during crosslinking: The DCBA monomer shows 0.58 dB/cm and DCHFBA 0.48 dB/cm, whereas the fully cured layers show losses around 1.0 dB/cm. The copolymerization with monofunctional cyanates (BrMC, FMC1, HpFBC) results in an amazing reduction of the optical loss with increasing comonomer content down to 0.4 dB/cm. In part this is due to the increasing halogen content of the resulting copolymer, but this effect is only minor, as the binary copolymers consisting of DCHFBA and FMC1 have a constant content of fluorine, and because both DCHFBA and FMC1 have almost identical fluorine contents. The higher contents of monofunctional cyanates result in a decrease of the network density and in a decrease of the glass transition temperature ($T_g$). First results indicate as previously reported,[3] that side reactions (especially the reverse reaction with the formation of the phenol from the cyanates) which cause high optical losses are now inhibited, because the chains are more mobile and the cyclotrimerisation is not hindered by rigid chains.

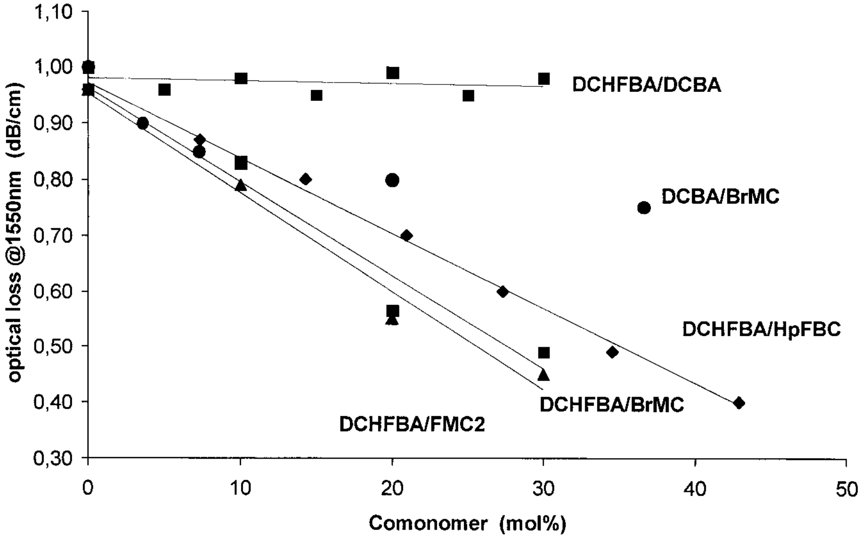


Fig. 6. Optical loss of different copolymers versus comonomer-content.

Further optimization of the copolymers and incorporation of higher fluorine content using the bisfunctional DCFO (Fig. 2) resulted in ternary copolymers with optical losses down to 0.28 dB/cm in the cured layer. Figure 7 shows the optical loss of different copolymers vs. their fluorine content. The increase in the fluorine content also results in a significant decrease of the optical loss. However, it must be considered that the introduction of a higher amount of fluorine into these copolymers is always coupled with a reduction in the network density and $T_g$, as the carrier of high amounts of fluorine are aliphatic monofunctional cyanates (HpFBC) or difunctional aliphatic cyanates (DCFO) with low intrinsic $T_g$.[4]

Optical multiplexers and demultiplexers are especially sensitive to birefringence. Therefore extensive investigations on the reduction of the birefringence of the polycyanurates were done. The birefringence of the polycyanurate layers is a result of the different coefficients of thermal expansion (CTE) between the polymeric layer and the substrate. As previously reported[3, 5, 6] we were able to reduce the birefringence by invention of polymeric substrates and proper adjustment of the substrate-CTE; even negative values were obtained.

As previously reported embedded optical waveguides in good quality could be obtained from the synthesized polycyanurates.[3]

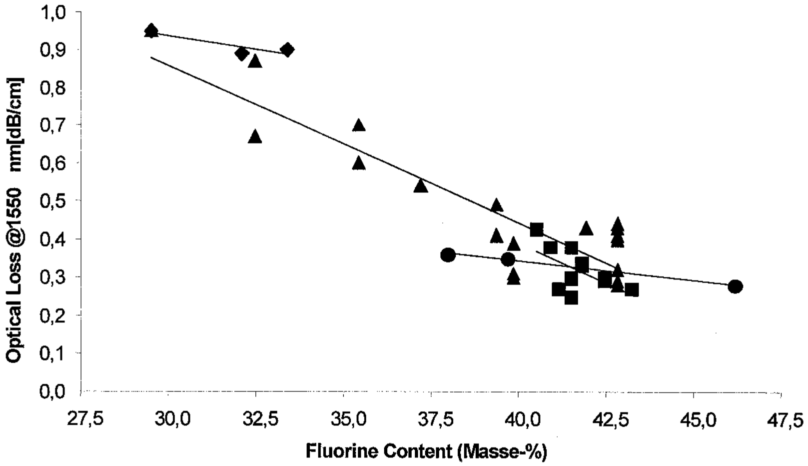


Fig. 7. Optical loss of different polycyanurate copolymers vs. fluorine content (mass-%). ■-HpFBC = constant (≈ 31.7 mol-%), DCFO-content variable. ◆-DCFO-content variable, 0 % HpFBC. ▲ - HpFBC-content variable, 0 % DCFO. ●-other mixtures.

## New Triazine Containing Polymers

Our present work is also focused on triazine-polymers with alternate structures with the goal of solving some of the disadvantages of the polycyanurate systems described above, like high curing temperatures and high birefringence on inorganic substrates. Figure 8 exhibits our strategy for obtaining these new materials. In the first step we incorporate fluorinated or partially fluorinated chains ($R^1$, $R^2$, $R^3$) into the triazine-branchend network, which is still soluble and therefore not fully crosslinked. In a second step we are linking additional reactive groups (X) with the network. These give us the possibility to crosslink the network even further, which is then insoluble and stable. The final crosslinking can be done thermally or by UV-radiation, depending on the particular reactive group.

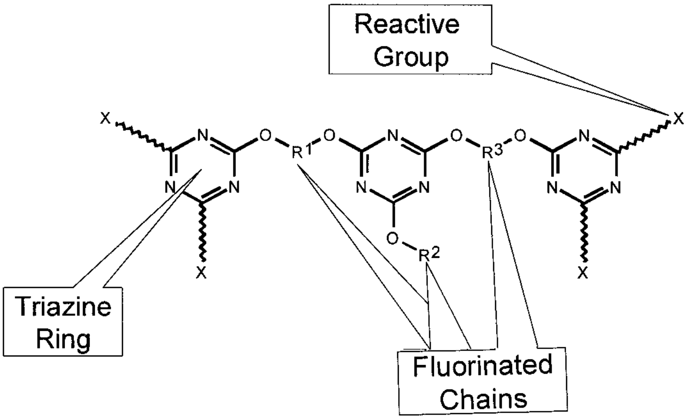


Fig. 8. Alternate triazine containing structures.

We synthesized several polymers using the route described above. The first results appear to be very promising. The films obtained from these new polymers show a good quality and low optical loss. The refractive index is reproducible (with regard to different batches and different curing runs). By varying the chains ($R^1$, $R^2$, $R^3$) and their compositions we can change the fluorine content and thus adjust the refractive index accurately. The chemical structure is only marginally changed.

Using these materials a core/cladding system with a refractive index-contrast of about 0.011 is available. The optical loss of the cladding material is about 0.41 dB/cm; the core material shows a slightly higher absorption of 0.44dB/cm, due to its lower fluorine content. The loss measurements were carried out by using the sliding prism method.

The new system is cured 60 minutes at 180°C under nitrogen atmosphere. The obtained layers are highly crosslinked and unsoluble in common organic solvents.

The best loss-values of our established polycyanurate systems were 0.28 dB/cm - after several years of optimization - thus we are optimistic about obtaining loss values better than 0.3 dB/cm with our new triazine-containing polymers.

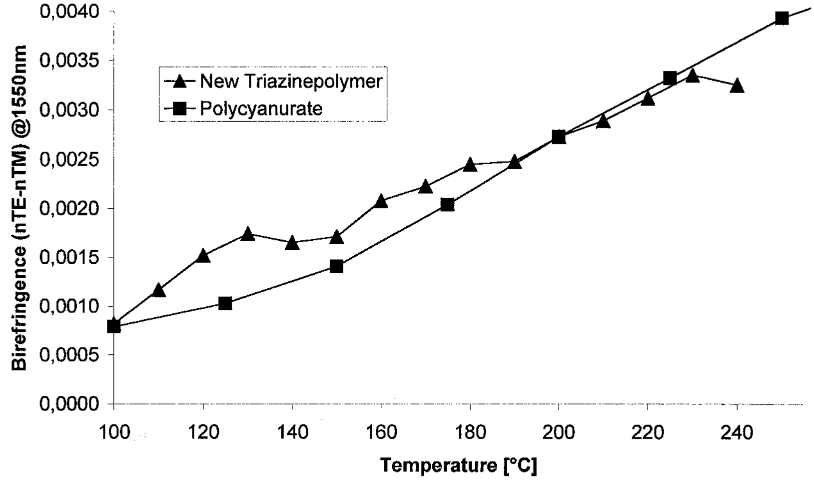


Fig. 9. Dependence of the birefringence of the core material and of a fluorinated polycyanurate on silicone.

Also, an important part of our research is the investigation of birefringence. Figure 9 shows the dependence of the birefringence of the new core material and the ternary polycyanurate copolymer (DCHFBA:DCFO:HpFBC, 61,99:6,28:31,74 mole-%). The birefringence is increasing almost linearly with temperature, as an effect of the different CTE-values of silicone substrate and polymeric layer. It is remarkable that despite the different structures of the polymers the birefringence is almost identical for both systems. Thus, birefringence could not be reduced by this change of the chemical structure. However, as the curing temperature to obtain stable films of the new triazine containing polymers (180°C) could be lowered in comparison to the polycyanurates (250°C), the birefringence of the fully cured layers has been reduced from 0.0039 to 0.0025. This is still too high for polarization sensitive devices, like multiplexers. Therefore further improvement is required.

## Comparision of Polycyanurates and the New Triazine Polymers

Table 1 shows some selected properties of the ternary polycyanurate copolymer and the new triazine polymers. These preliminary results are very promising. The lower curing temperatures allow combinations with temperature sensitive materials, which could not be used together with the polycyanurates.

Table 1. Selected properties of the ternary polycyanurate copolymer (DCHFBA:DCFO:HpFBC, 61,99:6,28:31,74 mole-%) and the new triazine polymers (core and cladding material).

| Property | Polycyanurate (DCHFBA:DCFO:HpFBC) | Triazine Polymer |
|---|---|---|
| Optical Loss @1550nm | 0.28 dB/cm | 0.44 dB/cm (cladding) |
| | | 0.41 dB/cm (core) |
| Birefringence on Silicone | 0.0039 | 0.0025 |
| Birefringence on (adjusted) Polymer | < 0.0001 | work in progress |
| Thermal Stability | > 250°C | > 180°C |
| Curing Temperature | 250°C | 180°C |
| Structurizability | good | work in progress |
| Layer Quality | good | good |

Our work is now focused on the minimizing of the birefringence and the reduction of the optical loss.

## Acknowledgements

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