Design, synthesis and properties of new materials based on densely crosslinked polymers for polymer optical fiber and amplifier applications
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Polytrimerization of diisocyanates - Formation of highly transparent polyisocyanurates

ABSTRACT
The polytrimerization of eight difunctional isocyanates has been explored. Polymerization conversion, trimerization reactivity and glass transition temperature are discussed in relation to the molecular structure and the reaction mechanism. The polytrimerization of hexamethylenediisocyanate (HDI), which was the most promising candidate, has been carried out with different types of catalysts. The resulting densely crosslinked materials (based on HDI) are discussed with respect to glass transition temperature, polymerization conversion, mechanical properties and, highly important, the optical quality. Polytrimerization of hexamethylenediisocyanate with a neodymium–crown ether complex as catalyst produced a superior material with excellent optical, thermal and mechanical properties. The material is highly suitable for all kinds of polymeric optical components, such as polymer optical fibers and planar waveguides, which has been the goal of the investigation. The high thermal and dimensional stability make it possible to use the aforementioned polymeric optical components in high-temperature environments.
INTRODUCTION

Isocyanates can undergo a broad spectrum of chemical reactions and are of great importance for contemporary polymer chemistry. Isocyanates can, for instance, be polymerized along the nitrogen-carbon double bond producing substituted polyamides. By far the most important reaction, however, is the reaction between an isocyanate and an alcohol forming an urethane bond. Also the reaction with an amine forming an urea bond is widely used.

\[
\begin{align*}
R-N\equiv C=O + HO-R' & \rightarrow R-N-C-O-R' \quad \text{urethane} \\
R-N\equiv C=O + H_2N-R' & \rightarrow R-N-C-N-N-R' \quad \text{urea}
\end{align*}
\]

Special of isocyanates is that they can react with themselves to form dimers (uretidinones) or trimers (1,3,5-triazine-2,4,6-triones or isocyanurates).

\[
\begin{align*}
2 \, R-N\equiv C=O & \rightarrow R-N\equiv C\equiv N-R \quad \text{uretidinone} \\
3 \, R-N\equiv C=O & \rightarrow \quad \text{isocyanurate}
\end{align*}
\]
Polytrimerization

In case of polytrimerization of diisocyanates a 3-dimensionally crosslinked polymer with tri-functional crosslinks introduced by the isocyanurate rings results. Polytrimerization or polycyclomerization has been extensively used in polyurethane chemistry to improve the thermal stability, flame retardancy, chemical resistance and the film-forming characteristics, which reveals the interesting properties of fully trimerized polyisocyanurates.

The polyurethanes, polyureas and polyisocyanurates all have in common that they are formed by addition reactions, during which no reaction products are split off. This is a great advantage when processing crosslinkable materials. To obtain the aforementioned materials, catalysis is of a vital importance. In general, the catalysis of isocyanate reactions can be grouped into two categories: (1) polymerization of isocyanates, including di- and trimerization; (2) reaction of isocyanates with active hydrogen-containing compounds. Thermoplastic polyurethanes and polyureas or a combination of both, polyurethane-ureas, form microphase-separated systems that are usually opaque materials. For optical applications these materials are not suitable. The formation of microphases can be completely suppressed when synthesizing densely crosslinked systems. Such systems are highly transparent. Still they have two important drawbacks, however. Polyurethanes and polyureas contain a high number of N-H bonds, which are known to lead to strong overtones of the fundamental infrared absorption, resulting in relatively high optical losses at visible and especially at near-infrared wavelengths. Another very important problem is their low photo- and thermal stability, which leads to yellowing of the materials. These drawbacks make them poor candidates for polymer optical fibers. Fully trimerized materials, on the contrary, do not have these drawbacks and are, therefore, promising candidates. The applicability of polytrimerized materials for polymer optical fibers will become clear in this chapter and in more detail in chapter 6 of this thesis.

The formation of trimers is highly dependent on the specific reactivity of the particular isocyanate and does not take place spontaneously. For a controlled trimerization a catalyst is necessary, which is the key factor to producing materials with excellent properties. A tremendous amount of catalytic species have been found and described in
literature. Most suitable were found to be Lewis-bases, such as tertiary amines, phosphines, metal or quaternary ammonium salts of alkoxides or Lewis acids such as various organic metal compounds, in particular metal carboxylates. For polytrimerization in the bulk, the catalyst system should be molecularly soluble in the diisocyanate monomer to produce materials with high optical quality. In this study, effective trimerization catalysts are found to be stannous 2-ethylhexanoate, \( N,N,N'' \)-tris(dimethylaminopropyl)hexahydrotriazine and a newly found bimetallic neodymium–crown ether complex. 

If a suitable difunctional isocyanate is used, a three-dimensional network can be made, entirely consisting of thermally stable isocyanurate rings. The polymer is densely crosslinked and, therefore, completely amorphous. These materials possess good mechanical, thermal and optical properties and are very promising candidates for optical applications such as a core material in polymer optical fibers. For processing, the material fulfills all the important requirements: effective purification of the monomers, bulk reaction without production of volatiles and prepolymerization prior to processing to reduce polymerization shrinkage.

Surprisingly, not much has been published about the synthesis and the properties of polyisocyanurates, at least not in the accessible literature (Russian journals excluded).

**EXPERIMENTAL**

**Analysis**

Infrared spectra of the cured materials were recorded with a Bruker IFS 88 spectrometer equipped with an ATR (Attenuated Total Reflection)-unit. For this, fresh samples from the bulk were cut. The reason for this is that long exposure of residual isocyanate groups at the surface to air results in a reaction with the water present in the air. As a consequence of that, the residual isocyanates can not be detected by infrared, anymore.

Glass transition temperatures were determined using a Perkin-Elmer DSC-7 apparatus at a heating rate of 40 °C/min. If a polymerization exotherm was observed another scan was made until an ultimate \( T_g \)-value was found. The glass transition temperature was determined from the midpoint of the DSC-curve.
Mechanical testing was performed on cylindrically shaped samples with an Instron 4301 tensile tester. The measurements were performed at conditioned room temperature (20°C). The crosshead speed was 10 mm/min and the gauge length 25 mm. Tensile measurements were also made at 180°C, to determine the modulus of elasticity at temperatures of \( T \geq T_g + 40°C \). The crosshead speed was 0.5 mm/min in these experiments in order to measure the near-equilibrium modulus of elasticity. The molecular weight between crosslinks (\( M_c \)) was calculated using the formula: \( M_c = \frac{3\rho RT}{E} \).

Measurement of the bulk density was done in absolute ethanol by measuring the exact volume of the sample (≈ 1 g). The values of the density of ethanol and their dependence on temperature were taken from literature.\(^\text{10}\) The density found for polytrimerized hexamethylenediisocyanate was 1.22 g/cm\(^3\).

**Materials**

Hexamethylenediisocyanate (HDI), 2-methylpentane-1,5-diisocyanate (MPDI), butanediisocyanate (BDI), dodecanediisocyanate (DDI), 1,3-bis(isocyanatomethyl)benzene (BMDI), phenyldiisocyanate (PDI), 1,3-bis(isocyanatomethyl)cyclohexane (BMCDI) and isophoronediisocyanate (IPDI) were obtained from Aldrich Chemical Company and distilled before use.

Stannous (II) bis(2-ethylhexanoate) (stannous octoate) was obtained from Sigma Chemical Company. \( N,N',N''\)-tris(dimethylaminopropyl)hexahydrotriazine (polycat) was kindly supplied by Air Products. Both catalysts were used as received. Lanthanide–crown ether complexes were carefully dried under vacuum at 20 - 60°C before use. The synthesis is described in appendix D of this thesis.\(^\text{11}\)

**Polytrimerization (stannous octoate and polycat)**

4 to 5 grams of distilled diisocyanate was taken and put in a dry reaction tube under a nitrogen atmosphere and 2 - 3 drops (≈ 1.5 - 2 wt. %) of catalyst was added. In the case of HDI, pretrimerization was allowed to take place at 60°C. After the viscosity had increased to a moderate level (before the gel point) the mixture was put in a syringe under a nitrogen flow and injected in a Teflon tubing. Curing was accomplished at 60°C for 24 h and at 110°C for another 24 h. The residue was cured further in the reaction tube.
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The series of diisocyanates trimerized by stannous octoate were cured in a reaction tube under a dry nitrogen atmosphere at the above-mentioned temperatures.

Polytrimerization (HDI – neodymium–crown ether complex)

To 4 to 5 grams of distilled hexamethylenediisocyanate was added 2 wt. % based on neodymium of neodymium–crown ether complex. After stirring for 1 - 2 h, the insoluble part was filtered off over a 0.2 µm Teflon membrane filter. From elemental analysis was determined that around 40 % of complex was dissolved in the diisocyanate. The trimerization was allowed to take place at room temperature for about 4 - 6 h. After the viscosity had increased to a moderate level (before the gel point) the mixture was put in a syringe under a nitrogen flow and injected in a Teflon tubing. Further gelation was allowed to take place overnight at room temperature. Hereafter, postcuring was accomplished at 60ºC for 24 h and at 110ºC for another 24 h.

RESULTS AND DISCUSSION

Polytrimerization of diisocyanates - mechanism

The polycyclomerization mechanism of diisocyanates is not fully elucidated as is the case with the cyclomerization reaction of their look-alikes, the dicyanates. Several studies have been published describing the trimerization of monofunctional isocyanates or the oligotrimerization of diisocyanates.5,7,8,12-14 These studies revealed that the trimerization reaction starts with an induction period. This induction period is best explained as the time necessary for the formation of catalyst–isocyanate complexes. Hereafter, the cyclomerization proceeds via propagation, transfer and termination steps (Figure 1).7,14

During polytrimerization, first the trimer, is formed followed by oligomerization and polymerization (Figure 2).8,15 Monomer and trimer are present during the whole stage of polymerization, also after gelation.15

The polyfunctional oligomers will grow further into dendritic-like polymers. The rigidity of the rings formed, spatial hindrance and diffusion limitations, suggest that after a certain level of reaction the NCO-groups leftover cannot react further. Although this is likely, it is not always true.
Figure 1. Mechanism of the trimerization of diisocyanates, catalyzed by tertiary amines.
Conversions of 100% with respect to NCO-groups have been found during our study, which is illustrated by an infrared spectrum taken from the bulk of polytrimerized dodecyldiisocyanate (Figure 3). This may be explained by the fact that monomer and trimer present during the entire duration of polymerization are able to diffuse to and to react with the numerous NCO-endgroups and complete the formation of a fully converted three-dimensional isocyanurate network. Also, the curing temperature should be close to or, preferably, higher than the $T_g$ of the crosslinking polymer.

**Figure 2.** *Oligotrimerization of diisocyanates, the initial stage of the polytrimerization.*

**Figure 3.** *Infrared spectrum taken from the bulk of polytrimerized dodecyldiisocyanate.*
Trimerization of diisocyanates - reactivity and catalysis

The ability of an isocyanate to trimerize is strongly dependent on the electronic structure and thus on the electronic environment of the isocyanate group. The double bonds between the nitrogen, carbon and oxygen atoms are polarized, because of the difference in electronegativity.

In fact, the electronic configuration of the isocyanate group is an average of the mesomeric forms.

Due to the resonance, averaged over time, the carbon atom is positively charged making it sensitive to an attack by nucleophilic species. Such nucleophilic addition reactions can be catalyzed either by Lewis bases by opening the $\pi$-system of the isocyanate group (e.g. tertiary amines) or by Lewis acids through an interaction which deforms the $\pi$-electron cloud and perturbs its symmetry (e.g. organic metal compounds)\(^5,7\).

According to the proposed mechanisms, the reactivity is strongly dependent on the group connected to the isocyanate group. Electron-withdrawing groups adjacent to the NCO-group enhance the reactivity by making the isocyanate-carbon atom more electrophilic. Electron-donating groups, on the other hand, will lower the reactivity. This means that aromatic isocyanates will react (trimerize) significantly better and faster than aliphatic or cycloaliphatic isocyanates. By replacing hydrogen atoms by more electronegative atoms such as fluorine or chlorine, enhancement of the reactivity of the isocyanate is expected\(^16\). Steric hindrance of the NCO-group by bulky side groups will undoubtedly influence the reactivity by lowering it through a shielding effect.
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effect. A further influence is the rigidity of the connected group, which becomes extremely important for polytrimerization of difunctional isocyanates in the bulk. The longer the spacer group between the isocyanates, the better the polytrimerization will run.

Catalysts are seldom completely specific to one reaction but mostly catalyze a spectrum of reactions. Side reactions like the production of cyclic dimers and carbodiimides may take place during the trimerization reaction. Both side reactions lead to chain extension and are not necessarily detrimental for the final properties. In fact, this may explain the high conversions of isocyanates without encountering the problem of spatial hindrance. However, dimers from aliphatic isocyanates are not very stable and at higher temperature they split into the original isocyanates or react further into a carbodiimide and carbondioxide.3 Further, if the splitting reaction occurs the formed isocyanates can react with each other to form directly a carbodiimide (Figure 4). The latter event is not unlikely, because in a strongly confined network structure, such as a polyisocyanurate, the individual groups are not able to diffuse away from each other. If a third isocyanate group would be in close proximity, trimerization can occur. However, the strong diffusion limitations make such an event unlikely. Dimerization is catalyzed by Lewis bases, such as pyridine.17 Reactions in which carbodiimides are formed needs to be completely suppressed when high optical quality is the objective as they will likely play an important role in the yellowing mechanism of polyurethanes and polyisocyanurates. As far as yellowing is concerned, monomers and catalyst should be very dry. The presence of water can also lead to a yellowing, which is faster and more severe with aromatic isocyanates than with aliphatic isocyanates.18

In Table 1 the diisocyanates that were tested in the polytrimerization with stannous-2-ethylhexanoate as the catalyst, are listed. The table shows the $T_g$ of the resulting networks. If the glass transition temperature has its final value and no increase is found after further curing, the reaction is assumed to be at its maximum conversion. The glass transition temperature is, therefore, given as the ultimate $T_g$. 
Stannous octoate was highly soluble in all diisocyanate monomers. Hexamethylenediisocyanate polytrimerized at slightly elevated temperatures, whereas butanediisocyanate (BDI) did not. The four spacing carbon atoms of BDI do not provide sufficient spatial mobility to form a network structure. Dodecanediisocyanate (DDI) polytrimerized very well (faster than HDI), resulting in a material with a significantly lower $T_g$ than HDI-based networks due to the longer flexible aliphatic portion of the molecule. 2-Methylpentanediisocyanate reacted comparably to HDI. The lower $T_g$ of the polymer with respect to polytrimerized HDI indicates a lower conversion to trimer. At first sight one would expect a higher $T_g$ due to the shorter connecting chain of five carbon atoms and moreover, due to the presence of the methyl group on the second carbon atom. According to an infrared spectrum full conversion of isocyanate groups has taken place (Figure 5). Possibly, side reactions are involved. A very small infrared absorption at 1756 cm$^{-1}$ has been observed indicating the possible presence of some dimer structures (uretidinones). If dimers are present they act as chain extenders, resulting in a higher $M_c$ and as a consequence in a lower $T_g$. The results described here lead to the conclusion that for polytrimerization of linear aliphatic diisocyanates the number of spacing carbon atoms between the two isocyanate groups should be five or higher.
Table 1. *Diisocyanates tested in the polytrimerization in the bulk with stannous (II) octoate.*

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>Trimerization*</th>
<th>Ultimate $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCN — (CH$_2$)$_6$ — NCO</td>
<td>+</td>
<td>140</td>
</tr>
<tr>
<td>hexamethylenediisocyanate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN — (CH$_2$)$_4$ — NCO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>butanediisocyanate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN — (CH$<em>2$)$</em>{12}$ — NCO</td>
<td>+</td>
<td>40</td>
</tr>
<tr>
<td>dodecanediisocyanate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN — CH$_2$ — CH$_2$ — CH$_2$ — CH — CH$_2$ — NCO</td>
<td>+</td>
<td>115</td>
</tr>
<tr>
<td>2-methylpentanediisocyanate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN —</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,4-phenyldiisocyanate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN — CH$_2$ — NCO</td>
<td>+</td>
<td>200</td>
</tr>
<tr>
<td>1,3-bis(isocyanatomethyl)benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN —</td>
<td>+/-</td>
<td>80</td>
</tr>
<tr>
<td>1,3-bis(isocyanatomethyl)cyclohexane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$ CH$_2$ — NCO</td>
<td>+/-</td>
<td>Semi-solid</td>
</tr>
<tr>
<td>isophoronediisocyanate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* + : effective trimerization, - : no trimerization, +/- : incomplete trimerization.*
Polytrimerization

1,4-Phenyldiisocyanate did not polytrimerize at all. Although the aromatic ring next to the NCO-groups would give rise to a high reactivity towards trimerization, the molecule is too small and too rigid to form a network structure. On the contrary, 1,3-bis(isocyanatomethyl)benzene polytrimerized to a high-$T_g$ network. The two methylene units between the NCO-groups and the aromatic ring give enough flexibility to form a three-dimensional network. Furthermore, the electron-withdrawing capability of the benzene ring may influence the rate of trimerization, positively. 1,3-Bis(isocyanatomethyl)cyclohexane showed only partial trimerization. Due to the conformations of the cyclohexane ring the 3-substituted methylisocyanate group is less accessible and, thereby, the polytrimerization is hindered. This is enhanced by the fact that the 1,3-bis(isocyanatomethyl)cyclohexane was a mixture of cis and trans. Incomplete polytrimerization was also found for isophoronediisocyanate (IPDI). IPDI is too bulky to polytrimerize effectively and does not have reactivity-enhancing groups.

Figure 5. Infrared spectrum of polytrimerized 2-methylpentanediisocyanate. Note the small peak at 1756 cm$^{-1}$ indicating a dimer structure (uretidinone).
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Properties of polytrimerized hexamethylenediisocyanate

Hexamethylenediisocyanate proved to polytrimerize efficiently and resulted in a densely crosslinked polymer with interesting properties. For the trimerization three different types of catalysts have been used, being stannous bis(2-ethylhexanoate) (a metal carboxylate), \( N,N',N''\)-tris(dimethylaminopropyl)hexahydrotriazine (a tertiary amine) and a bis(neodymium-8-crown-5) complex (a bimetallic lanthanide complex). The neodymium-complex proved to be the most efficient and selective catalyst for polytrimerization of HDI. Gelation occurred within about 4 - 6 hours at room temperature. Curing at higher temperatures to obtain maximum conversion of the polytrimerization reaction resulted in a material with excellent optical quality. Such results can be obtained with polycat and stannous octoate also, but yet with a small yellowing effect in most cases. It should be mentioned here that the latter has been evaluated in fiber configuration, implying long optical path lengths. Yellowing is then immediately visible. It seemed that stannous octoate and polycat are less selective catalysts and catalyze side reactions, possibly the carbodiimide formation.

The good catalytic properties of the neodymium–crown ether complex can be better explained when we take a closer look at the molecular structure of the complex. It was possible by a very slow recrystallization process to obtain well-formed, cubic shaped crystals from the neodymium complex. The crystals were large enough to investigate them by x-ray diffraction. This gave us the structure as shown in Figure 6. Synthesis, experimental data and the lattice parameters can be found in appendix D of this thesis.\(^{11}\)
Figure 6. A three-dimensional depiction (PLUTO) of the crystal structure of the neodymium-8-crown-5 complex \( \text{(C}_{16}\text{H}_{32}\text{N}_{4}\text{Nd}_{2}\text{O}_{22}) \). A single neodymium atom is surrounded by a crown-5-ether fragment and by two bidentate nitrate ligands.

The nucleophilic oxygen atom of the isocyanate group can strongly coordinate with an electrophilic neodymium atom. Such an interaction with a metal is often proposed for isocyanates (Figure 7). The second neodymium center in the bimetallic complex makes it possible to interact with a second isocyanate group. Both isocyanate groups are herethrough brought into close proximity, making it possible to form an intermediate complex. At the same time a third isocyanate group can interact with the unoccupied neodymium atom, making it possible to react with the intermediate complex. The unstable intermediate reacts further to a stable trimer.
Figure 7. Proposed catalytic mechanism for the trimerization of isocyanates by bis(neodymium-8-crown-5). For reasons of clarity the nitrate ligands are not drawn.

The ultimate reachable glass transition temperature is a good indication for the polymerization conversion and with that also for the molecular weight between crosslinks. From measurements of the molecular weight between crosslinks, only slight differences are found between the polycat, stannous octoate, and neodymium-catalyzed polyhexamethylene-isocyanurates (Table 2). The neodymium–crown ether complex and stannous octoate are most comparable and yield higher conversions in the polytrimerization than polycat, as is reflected in the values for $T_g$ and $M_c$. The polymer
**Polytrimerization**

formed by stannous octotate, however, is less ductile than the neodymium–crown-catalyzed polyisocyanurate. The neodymium-catalyzed polytrimerization of HDI resulted in a material that not only has the best mechanical properties, but also has the best optical properties. The polymerization proceeds most selectively to trimers and no yellowing effect due to side reactions has been found. Stannous octoate and tertiary amines are also highly selective catalysts, but are more sensitive to side reactions, still. It should be noted here that the final optical properties, and thus the yellowing effect, are dependent on the curing process. Temperatures should be low in the beginning (RT) to reduce the chance of side reactions. Gradually, the temperature can be increased to cure the material to maximum conversion. Only two publications dealing with the properties of polytrimerized HDI are known.4,15. The catalytic systems used in those studies result in physical properties that are far inferior to those obtained with the systems used in this study (Table 2).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_g$, ultimate ($^\circ$)</th>
<th>$M_c$ (g/mol)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$E$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd-crown</td>
<td>140</td>
<td>295</td>
<td>85</td>
<td>60</td>
<td>1000</td>
</tr>
<tr>
<td>Polycat</td>
<td>130</td>
<td>315</td>
<td>76</td>
<td>80</td>
<td>1125</td>
</tr>
<tr>
<td>Sn(Oct)$_2$</td>
<td>140</td>
<td>236</td>
<td>64</td>
<td>32</td>
<td>1740</td>
</tr>
<tr>
<td>TMHAE*</td>
<td>-</td>
<td>-</td>
<td>60</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>HBSO**</td>
<td>80</td>
<td>480</td>
<td>29</td>
<td>18</td>
<td>360</td>
</tr>
</tbody>
</table>

* TMHAE: trimethyl-2-hydroxypropyl ammonium 2-ethylhexanoate
** HBSO: hexa-$n$-butyldistannum oxide

The conversion of isocyanate (N=C=O, 2275 cm$^{-1}$) to isocyanurate (C=O, 1675 cm$^{-1}$) is evidenced by infrared spectroscopy as presented in Figure 8. Full conversion of isocyanate groups was observed for all three catalysts.
CONCLUSIONS

Polytrimerization in the bulk of a number of difunctional isocyanates has been explored. Aliphatic diisocyanates trimerized to densely crosslinked materials if the number of carbon atoms between the two isocyanate groups was higher than 4. Conformational influences, rigidity and bulkiness of cycloaliphatic and aromatic spacers had a large effect on the ability to polytrimerize.

The selectivity of the molecularly soluble catalyst system had a significant effect on the transparency of the ultimate material. For these materials transparency is strongly related to the extent of yellowing. It has been found that polytrimerization of hexamethylenediisocyanate with a bimetallic neodymium–crown ether complex produced a material with superior mechanical and optical properties.

$M_c$-values below 300 g/mol (theoretically: 170 g/mol) for polytrimerized hexamethylenediisocyanate have been reported for the first time.

Polytrimerization of diisocyanates can be a controllable process and has promising applicability for polymer optical components.
REFERENCES AND NOTES

6)  Chapter 6 of this thesis.
9)  Chapter 1 of this thesis.
11)  Appendix D of this thesis.
16)  Appendix A of this thesis.
18)  Internal unpublished results.