Introduction

Cyanate ester resins are an important class of thermosetting compounds that have experienced an ever-increasing interest as matrix systems for advanced polymer composite materials, which among other applications, are especially suitable for highly demanding functions in the aerospace or microelectronics industries. Other names for cyanate ester resins are cyanate resins, cyanic esters, or triazine resins. The various types of cyanate ester monomers share the —OCN functional group that trimerizes in the course of resin formation to yield a highly branched heterocyclic polymeric network based on the substituted triazine core structure. The basic reaction sequence leading to the typical cyanate ester polymer molecule is depicted in Figure 11.1. The curing reaction may take place with or without catalyst.

Cyanate esters display a unique property profile. This includes high glass transition temperature, low dielectric loss/dissipation factor, radar transparency, low moisture absorption, low outgassing, good adhesion to metals and other substrates, and relatively high strength and high fracture toughness. Due to the high aromatic content they also show inherently good flame retardancy and rather low smoke generation. Furthermore, cyanate esters usually have good processability since the dicyanate monomers melt at low temperatures and are available in a wide range of physical forms (liquids, low melting solids, prepolymer of different molecular weights), long shelf lives, and good compatibility with a variety of reinforcing materials. The monomers are of exceptionally low toxicity and no volatile compounds are released during thermal curing. They show good compatibility with numerous other thermosetting materials and, hence, have frequently been employed to modify phenol and epoxy resins or for blends and copolymers with bismaleimide resins [1] to, for example, modify their brittleness. Some major distinctive features of cyanate ester monomers are summarized in Table 11.1.

Due to their attractive properties, it does not come as a surprise that cyanate esters have increasingly been investigated during the past years. Numerous novel composite systems have been developed especially for high-performance matrix materials in the aviation, aerospace, and electronics industries. Because of their outstanding thermomechanical and interesting dielectric properties, they are discussed as major future candidates for applications in the electronics sector with the potential to substitute the currently used materials (mainly epoxies) to a great extent. Important applications range from structural composites in aircrafts...
or satellites to products under high temperature and mechanical wear conditions like gas turbines, etc., to printed circuit boards and other electronic parts.

The trend towards increasing industrial demand of cyanate ester-based materials is reflected by a steadily increasing number of scientific studies that have been published on these thermosets during the past years (Figure 11.2). The published data on cyanate ester resins can be roughly categorized into four main topics: (1) new monomers for novel cyanate esters, (2) blends of cyanate ester resins with other polymeric systems, (3) copolymerization of cyanate ester monomers with other types of monomers to yield novel high-performance thermosetting systems, and (4) different kinds of composites of cyanate esters containing micro- and nanoscale reinforcements based on particulate, layered, or fibrous reinforcing materials.

### Table 11.1 Distinctive Features of the Cyanate Ester Monomers [2]

<table>
<thead>
<tr>
<th>Structural Feature</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanate functionality</td>
<td>Low toxicity</td>
</tr>
<tr>
<td></td>
<td>Easy to process</td>
</tr>
<tr>
<td></td>
<td>Reacts with epoxies</td>
</tr>
<tr>
<td></td>
<td>Blends with thermoplastics</td>
</tr>
<tr>
<td>Ring forming</td>
<td>High service temperatures</td>
</tr>
<tr>
<td>−O−linkages</td>
<td>Tough</td>
</tr>
<tr>
<td>Low cross-link density</td>
<td>Tough</td>
</tr>
<tr>
<td>Low polarity</td>
<td>Low dielectric loss</td>
</tr>
<tr>
<td></td>
<td>Low moisture absorption</td>
</tr>
<tr>
<td>High purity</td>
<td>Low dielectric loss</td>
</tr>
<tr>
<td></td>
<td>Low corrosion potential</td>
</tr>
</tbody>
</table>

**Figure 11.1** Basic reaction scheme illustrating the formation of cyanate ester resins. Difunctional monomers containing two cyanate ester groups react via addition polymerization to yield highly branched polymers containing aromatic heterocyclic nuclei. The cyclo-trimerization reaction of three cyanate ester functionalities to yield a triazine ring is highlighted in red in the reaction scheme. The monomers (highlighted in blue) may contain a wide variety of linkage groups X connecting the −OCN functionalities.

**Figure 11.2** Number of scientific publications found in the scientific database Scopus from 1996 to 2013 using “triazine” or “cyanic ester” or “cyanate ester resin” as the search terms.
Numerous composite materials based on cyanate esters have been recently described in the literature where cyanate esters have been combined, blended, and compounded with a wide range of other thermosetting materials such as epoxy [3–5] or bismaleimide resins [6–8], thermoplastics, rubbers, and fillers, modifiers, and reinforcements. Reinforcements include a wide range of organic and inorganic materials and nanomaterials such as aluminum phosphate [9,10], aluminum nitride [11–13], aluminum borate whiskers [14], ceramics like CaCu$_3$Ti$_4$O$_{12}$ [15] or zirconium tungstate [16,17], expanded graphite [18], graphene [19], graphene oxide [20], carbon nanotubes [13,18,19,21,22], carbon fibers [7,8], polycrylnitrile fibers [23], glass fibers [24], glass microspheres [25], alumina nanoparticles [26], silicon nanoparticles [27], sol-gel derived [28] or fumed [29] silica nanoparticles, hollow silica tubes [30], fumed nanoclays [20,31,32], silsesquioxane/POSS [33,34], or bentonite [35,36].

Cyanate ester resins have been thoroughly covered by the seminal book edited by Hamerton (1994) [37,38], which still represents an important reference work for the basic chemistry and technology of cyanate ester resins. More recently, several excellent reviews have been published that cover the scientific and technological progress during the last decade in this rapidly evolving field of high-performance thermosetting polymers, for example, [39,40]. A huge number of scientific reports have been filed that document the progress in the application of cyanate ester/composite systems. To cover all new developments in this broad field would take a complete book chapter in itself. However, due to time and space restrictions, this chapter will only feature a brief outline of the most important aspects of cyanate ester resin chemistry with respect to their main applications, and only some of the most recent developments directly related to cyanate ester resins and their monomers will be highlighted. For a deeper coverage of the topic, especially regarding the wealth of information on blends, copolymers, and composites of cyanate esters, the reader is referred to the above-mentioned monographs and the original literature.

**Chemistry**

Cyanate ester resin monomers can be prepared from various difunctional phenolic starting materials such as, for instance, bisphenol A or similar compounds by reaction with cyanogen chloride or cyanogen bromide to introduce the cyanate functionality into the aromatic core. The general basic structural unit defining a cyanate ester is shown in Figure 11.3. Typically, R consists of a rigid, aromatic structure conferring good mechanical and thermal properties. The aromatic cyanates are then trimerized and cured under formation of a three-dimensional thermosetting network as illustrated in Figure 11.1 to yield highly branched structures containing substituted triazine rings.

One major advantage that has significantly propelled cyanate ester research is the relatively low viscosity of the typical cyanate ester monomer molecules that, hence, can comparatively easily be handled. The heterocyclic aromatic structure that is mainly responsible for the interesting thermomechanical performance is formed only upon polymerization during the final cross-linking and is not yet present in the uncondensed state. This is often not the case with many of the other currently used high-temperature, stable thermosetting materials, which makes cyanate ester monomers more suitable from an application point of view. Also, the pre-polymers usually have favorable physical properties in terms of solubility or low melting points.

The chemical structures of some important monomers used for industrial cyanate ester resin preparations are summarized in Table 11.2. Various types of bisphenols with different substitution patterns are typical raw materials, such as bisphenol A, bisphenol E, bisphenol C, tetramethylbisphenol F, and bisphenol M. Bisphenol A containing perfluorinated methyl groups at the bridging carbon atom (hexafluorobisphenol A) is also used. Besides the bisphenol-based monomers, other important monomers are based on phenolic resin-type structures like novolacs carrying OCN-groups.

The curing of cyanate esters can be brought about in the presence or absence of catalysts. Typical curing temperatures are in the range of 170 to 200°C. Typical commercial catalysts used for enhancing polymerization of cyanate esters are
### Table 11.2 Cyanate Ester Monomers [41]

<table>
<thead>
<tr>
<th>Monomer Structure</th>
<th>Material/CAS Registry Number</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Bisphenol M cyanate ester" /></td>
<td>[127667–44–1]</td>
<td>Arocy XU-366</td>
<td>Huntsman, former Ciba</td>
<td>396.49</td>
</tr>
<tr>
<td><img src="image" alt="Dicyclopentadienylbisphenol cyanate ester" /></td>
<td>[135507–71–0]</td>
<td>Arocy XU-71787</td>
<td>Dow</td>
<td>251.32</td>
</tr>
<tr>
<td><img src="image" alt="Bisphenol A cyanate ester" /></td>
<td>[1156–51–0]</td>
<td>Arocy B-10</td>
<td>Huntsman, former Ciba</td>
<td>278.31</td>
</tr>
<tr>
<td><img src="image" alt="Tetramethylbisphenol F cyanate ester" /></td>
<td>[101657–77–6]</td>
<td>Arocy M-10</td>
<td>Huntsman, former Ciba</td>
<td>306.36</td>
</tr>
<tr>
<td><img src="image" alt="Bisphenol E cyanate ester" /></td>
<td>[47073–92–7]</td>
<td>Arocy L-10</td>
<td>Huntsman, former Ciba</td>
<td>264.28</td>
</tr>
<tr>
<td><img src="image" alt="Hexafluorobisphenol A cyanate ester" /></td>
<td>[32728–27–1]</td>
<td>Arocy F-10</td>
<td>Huntsman, former Ciba</td>
<td>386.25</td>
</tr>
<tr>
<td><img src="image" alt="Bisphenol C cyanate ester" /></td>
<td>[not assigned]</td>
<td>RD98-228</td>
<td>Huntsman, former Ciba</td>
<td>331.16</td>
</tr>
<tr>
<td><img src="image" alt="Phenol novolac cyanate ester" /></td>
<td>[30944–92–4]</td>
<td>Arocy XU-371</td>
<td>Huntsman, former Ciba</td>
<td>381.39</td>
</tr>
<tr>
<td><img src="image" alt="Phenol novolac cyanate ester" /></td>
<td>[173452–35–2]</td>
<td>Primaset PT-30</td>
<td>Lonza</td>
<td>381.39</td>
</tr>
</tbody>
</table>
Characterization and Reaction Monitoring

Optical Spectroscopy

Besides structural characterization of the materials by methods such as nuclear magnetic resonance spectroscopy, optical spectroscopy has widely been used to monitor the reactions involved in cyanate ester formation, cure, and thermal degradation [41–46].

For infrared spectroscopic studies, measurement set ups in attenuated total reflectance mode have been widely employed, either by employing off-line devices, where sequential measurements are performed at different reaction times after removing small samples at regular intervals from the bulk reaction mixture and depositing a drop on the ATR crystal, by employing heatable micro-ATR stages onto which the reaction mixture is deposited and that allow curing monitoring in real-time, or by employing in-line measurements, where an ATR sensor probe is immersed into the reaction mixture and infrared spectra are recorded on a continuous basis.

Since polymerization of cyanate esters primarily takes place via cycloaddition of three monomers under formation of a triazine ring, distinct changes in the infrared spectrum are to be expected that can be used for IR on-line monitoring of the curing reaction. Two strong characteristic bands grow during triazine ring formation, the $\nu(C=\equiv N)$ at 1553–1565 and the $\nu(O-C=\equiv N)$ at 1354–1365 cm$^{-1}$, depending on the exact matrix environment [45]. Cyanate conversion is observed by the decrease in absorbance of the C$=\equiv$N stretch mode at 2260/2233 cm$^{-1}$ [45]. For quantification, as a stable reference peak not affected by the polymerization reaction, the aromatic ring out-of-plane bending mode appearing at 1013 cm$^{-1}$ can be used [45].

Naturally, besides formation of the triazine ring that is observed with every kind of cyanate ester, other typical bond formation reactions that take place when copolymerization with other monomers or oligomers is performed can also be followed by infrared. For example, when cyanate esters are covalently reacted with epoxies, new oxazoline functionalities ($-N\equiv C-O-\equiv$) and ether linkages ($-N\equiv C-O-Ar-\equiv$) are formed that result in increasing absorbances at around 1680 cm$^{-1}$ and 1295 cm$^{-1}$, respectively [44].

In-line fiber optical Raman spectroscopy was shown to be an effective real-time monitoring tool, for example, when a bisphenol E dicyanate ester resin was prepared from Arocy L-10 [42]. In a univariate approach, the authors monitored the reaction progress by using indicative changes at specific bands in the Raman spectrum: the shifting of a peak at 801 cm$^{-1}$ into a new mode at 854 cm$^{-1}$ with a low- and a high-energy shoulder (due to branching at the alpha carbon as the first step in the cyclization reaction) and the splitting of the ether linkage mode at 1193 cm$^{-1}$ into two modes at 1172 and 1203 cm$^{-1}$. During curing, the relatively weak signals from the symmetric and asymmetric CN modes at 2239 and 2269 cm$^{-1}$ decrease to zero while the formation of the triazine ring is recognized by a growing peak at 986 cm$^{-1}$, which is characteristic for the symmetric triazine ring breathing mode [42]. Although the univariate (single peak-focused) analysis gave instructive results, multivariate data analysis (see Chapter 18), which utilizes the full spectrum as an information source, was preferred by the authors in determining the cure percentage.

Moreover, with their in-line optical fiber setup, the authors monitored the local sample temperature during curing by comparing the intensities of the (temperature-independent) Stokes and the (temperature-dependent) anti-Stokes Raman peaks originating from the same intense mode, well resolved and unaffected by the curing reaction at 633 cm$^{-1}$ (and, respectively, $-633$ cm$^{-1}$) resulting from the C–H out-of plane deformation of a phenyl ring.

Thermal Methods

The curing kinetics of cyanate esters is also typically studied and modeled using thermal and viscosimetric methods. DSC and TGA are used here as the typical methods to characterize glass
transition temperatures and thermal degradation as well as conversion degree upon curing (see below).

Thermal analysis (dynamic differential scanning calorimetry) in combination with isoconversional kinetic methods as described in Chapter 18 were also applied [47]. The cyanate resin was extracted from quartz-based prepregs and its curing behavior was studied by dynamic DSC scans. Different isoconversional approaches [48,49] were applied to analyze the data and isothermal curing profiles were determined. The authors found the curing reaction to be complex and to consist of four distinct stages, one of which was of a zero-order reaction mechanism.

### Processing of Cyanate Ester Resins

Due to their unique property profile, cyanate esters can be processed using a wide range of standard duroplastic manufacturing technologies including processing technologies of fiber-reinforced composites. For instance, among others, laminates [24,30], prepreg manufacturing, resin transfer molding, filament winding, pultrusion [50], vacuum bag processing, and sheet molding processing are applicable. Foams [31] and foam sandwich composites [51] have also been prepared from cyanate ester resins. This is partly due to the favorable physical state of the monomers or prepolymers employed (typically solids of low melting points, sometimes also liquids such as bisphenol E or bisphenol M dicyanates). Prepolymers are typically obtained by simply heating the monomers. Tacky semi-solids are formed from monomers typically at conversions of around 25–40%, whereas hard solids have conversion degrees of 45 to 55% [52].

The flexibility with regard to processing technologies can further be exploited by using either blends of cyanate ester resins with other high-performance resins (typically epoxy and bismaleimide resins) or by adding toughening polymers such as rubbers or various types of thermoplastics.

Both monomers and prepolymers are usually well-soluble in ketone-solvents such as acetone or methyl ethyl ketone. For sulfur-containing monomers or blends with (for example) BMI, more powerful solvents may be required such as cyclopentanone and mixtures of it with other solvents [52].

Storage stability of cyanate ester monomers and prepolymers is also generally very good and can easily reach 6 months (at room temperature) or more (upon cooling). Low percentages (0.01 to 0.1 weight percent) of acidic stabilizers such as para-toluene sulfonic acid or polyphosphoric esters may be added to further increase the storage times. However, impurities or blending with other materials may significantly reduce the storage stability.

Curing under cyclo-trimerization can be brought about with or without catalysts; however, thermally induced curing without catalysts usually does not yield satisfactorily high degrees of conversion. Therefore, typically curing catalysts are used. The most common systems are carboxylate salts and chelate complexes of transition metals, which mainly act by facilitating the cyclization reaction by forming coordination compounds with the monomers [37–39]. Many different metal cations can be used. Since solubility of the metal catalysts is usually not too good in the monomer mixtures, the catalysts are usually applied in a co-solvent based on an alkyl phenol such as, for instance, nonylphenol. This co-solvent also assists in the ring formation reaction [52]. Besides transition metals, urea compounds [53] and 2,2'­diallyl bisphenol A [54] have also been used as catalysts.

The processing properties of the cyanate ester resin system (pot life, gel time, total cure time) depend on the catalyst composition, i.e. type and concentration of the transition metal ion and application form (salt, complex). Table 11.3 summarizes some effects of the catalyst mixture on the processing properties. As a rule of thumb, the preference for selecting a specific metal ion has been suggested in the order $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+}$, based on the thermal stability properties of the achieved cyanate ester resins (Table 11.3) [37,38,55]. However, the effect of the catalyst strongly depends on the nature of the dicyanate ester system used and choice of the appropriate systems needs to be carefully checked individually. More information on catalyst selection is available in Hamerton, 1994 [37,38], Lin et al., 2004 [6], and Li et al., 2006 [56].

The presence of residual metal catalyst is undesired in the final resin since the metal ions decrease both the hydrolytic [52] and thermal [57] stability of the resin.

A typical casting procedure for cyanate resins is as follows [37,38,52,53]:

"Zinc naphthenate (60–150 ppm metal) is dissolved into the nonylphenol co-catalyst
(2 phr). The resulting catalyst solution is added to the molten cyanate ester monomers or prepolymer at 90 to 110°C. The molten mixture is degassed under vacuum and cast into an aluminium plate mold with Teflon gaskets and treated with silicone mold release. The resins are gelled at 104 to 150°C and cured for 1 h at 177°C plus 1 h at 250°C [37,38].”

### Properties of Cyanate Esters

The general property profile of cyanate ester resins lies somewhere between that of BMI and that of epoxy resins. This was nicely illustrated by Hamerton in 1994 [37,38], who published the following, Figure 11.4. This figure displays the relationship of the glass transition temperature and tensile elongation-at-break properties for these families of high-performance resins. It can be seen that cyanate esters are well suited to fill in a technological gap between the BMI and epoxy resin families.

#### Thermal, Mechanical, and Electrical Properties

Cyanate esters display good mechanical properties; for example, their tensile strength is typically in the range of ca. 70 to 90 MPa, their tensile modulus is within 3.1 and 3.4 GPa, and their tensile strain at break is between 2 and 5% [39]. Hence, while tensile modulus is approximately in the order of magnitude of typical epoxy and toughened bismaleimide resins, the values for both tensile strength and especially for the tensile strain at break are on average higher than the respective values for typical epoxies and bismaleimide resins. Furthermore, cyanate esters display unusually high values for the glass transition temperature. Additionally, compared to epoxy resins, cyanate esters show improved behavior when subjected to UL-94 burning tests (V-0 classification). The thermal behavior of a variety of standard commercially available cyanate ester resins as determined by thermogravimetric analysis in the temperature range from 300 to 900°C is reproduced in Figure 11.5 [41]. It is seen that all cyanate ester samples displayed a significant weight loss only at temperatures significantly above 400°C; at average, the cyanate esters had a peak mass loss rate temperature of ca. 468°C [41]. The highest char yields at 900°C of ca. 62% were obtained with novolac-based cyanate esters whereas the lowest char yields of around 30% were observed with the bisphenol M and the dicyclopentadienyl cyanate ester resins.

The values of the dielectric constants for typical cyanate ester resins lie in the range of 2.6 to 3.1, which is comparatively low. Moreover, the loss

---

### Table 11.3 Effect of Metal Catalyst on BADCy Resin Properties [37,38,52,55]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cu^{2+}</th>
<th>Co^{2+}</th>
<th>Zn^{2+}</th>
<th>Mn^{2+}</th>
<th>Fe^{3+}</th>
<th>Al^{3+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal concentration (ppm)</td>
<td>360</td>
<td>160</td>
<td>175</td>
<td>435</td>
<td>65</td>
<td>250</td>
</tr>
<tr>
<td>Gel time (min)&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 105°C</td>
<td>60</td>
<td>190</td>
<td>20</td>
<td>20</td>
<td>35</td>
<td>210</td>
</tr>
<tr>
<td>at 177°C</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>Conversion (%)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>96.6</td>
<td>95.7</td>
<td>95.8</td>
<td>93.8</td>
<td>96.5</td>
<td>96.8</td>
</tr>
<tr>
<td>Heat distortion temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry</td>
<td>244</td>
<td>243</td>
<td>243</td>
<td>242</td>
<td>239</td>
<td>238</td>
</tr>
<tr>
<td>wet&lt;sup&gt;c&lt;/sup&gt;</td>
<td>175</td>
<td>193</td>
<td>182</td>
<td>163</td>
<td>143</td>
<td>157</td>
</tr>
<tr>
<td>Moisture absorption (%)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.4</td>
<td>2.3</td>
<td>2.5</td>
<td>2.6</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Thermal stability (hours)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>400</td>
<td>400</td>
<td>375</td>
<td>300</td>
<td>250</td>
<td>200</td>
</tr>
</tbody>
</table>

<sup>a</sup>Nonyl phenol system used, nonyl phenol concentration not specified.
<sup>b</sup>Cure cycle 1 h/150°C + 2 h/250°C.
<sup>c</sup>Moisture conditioned 64 h/92°C + > 95% relative humidity.
<sup>d</sup>After 500 h at 100°C.
<sup>e</sup>In 235°C/air, expressed as time required to reduce flexural strength by 50%.
Figure 11.4 Relationship of the glass transition temperature and tensile elongation-at-break for BMI, epoxy, and cyanate ester resins [37,38].

Figure 11.5 Thermal behavior of various commercial cyanate ester resins as determined by thermogravimetric analysis. The monomers used in the study were as follows: PT 30, phenol novolac cyanate ester [58]; XU-371, phenol novolac cyanate ester [59]; BPCCE, bisphenol C cyanate ester; F-10, hexafluorobisphenol A cyanate ester; L-10, bisphenol E cyanate ester; M-10, tetramethylbisphenol F cyanate ester; B-10, bisphenol A cyanate ester; XU-71787, dicyclopentadienylbisphenyl cyanate ester; XU-366, bisphenol cyanate ester.
factors are also quite low, between 1 and $6 \times 10^{-3}$. This renders them suitable for applications in the electronics industry.

Table 11.4 summarizes some important physical properties of commercially available cyanate ester resins. These properties can further be modified, for instance, by toughening the cyanate ester with elastomeric additives.

**Gelation of Cyanate Ester Resins**

The gelation behavior of cyanate esters is also influenced by the type of monomers used. Based on Flory’s mean-field theory [58], the gelation point of dicyanate ester/polycyanurate resins should occur at a conversion of 0.5 [59]. However, in most cases delayed gelation is observed depending on the monomers used and in some cases gelation occurs at conversions as high as 0.80 to 0.95 [59,60]. Typically, delayed gelation occurs when monomers are used that have rigid backbone structures or lower accessibility due to the steric demands of bulky substituents. In contrast, flexible alkyl backbone structures or alkyl chains carrying electron-withdrawing substituents often cause gelation more closely to the expected theoretical value of 0.5. Delayed gelation is also observed when monomer concentrations are rather low. Among other causes, intramolecular cyclization of the difunctional cyanate ester monomers has been suspected to be a major reason for this behavior, and for the case of bisphenol M dicyanate ester, it was experimentally found that such monomer cyclization is very likely to explain the observed behavior [59]. A detailed literature survey covering the gel points of a wide variety of monomers and a thorough discussion on this subject is provided by Li and Simon 2007 [59].

**Dimensional Stability Upon Curing—Shrinkage Behavior**

An important feature of cyanate ester resins is their dimensional behavior upon cross-linking. Typically, cyanate esters show an increase in specific volume at high conversion degrees. For instance, when BADCy is cross-linked at 200°C the forming polymer experiences a minor loss in specific volume only until a degree of conversion of approximately 60% is reached; after solidification at the gel point the solid mass slightly expands again thereby counteracting potential inaccuracies in mold reproduction and preventing shrinkage-induced mechanical stresses in the network [39]. The relative changes in specific volume in dependence on the conversion are reproduced in Figure 11.6 [39]. Here, cyanate ester resins behave very much unlike many other thermosetting systems like, for instance, unsaturated polyester resins which show extraordinarily high shrinkage upon cure especially after solidification and which therefore require the addition of significant amounts of specially developed anti-shrink additives.

From the shape of the function of density versus conversion depicted in Figure 11.6 it is immediately evident that suitable cyanate ester prepolymer of low conversion degrees between 20 and 40% can be selected or prepared that show no overall volume change at all upon being cured to the final degree of cross-linking.

**Hydrolysis Behavior**

Hydrolytic stability is an important prerequisite for cyanate ester resins to be used as polymer matrices in, for instance, printed circuit boards. When stored under humid conditions and used without prior drying, cyanate ester-based products may delaminate or form blisters upon rapid heating to elevated temperatures of around 250°C, which are common when soldering such boards for electronic applications. Although one of the advantages of cyanate esters is their low water absorption (see Table 11.5 for representative values of commercial cyanate esters) compared to other high-performance materials, they still may tend to blister more frequently after shorter solder float times than do epoxy resins [61]. The ultimate cause for this blistering and delaminating is hydrolysis of the network under formation of phenols, cyanuric acid, and carbon dioxide [61–63]. Kasehagen et al. [61] related the blistering behavior of a cyanate ester resin to dependence of the kinetics of the hydrolysis reaction of the neat resin. For the cyanate ester resin based on the 2,2’-bis(4-cyanatophenyl)isopropylidene (DCBA) monomer cured with Mn$^{2+}$ octoate, the authors found that up to temperatures $<220°C$ no blistering occurred since the loss of water from the laminate was sufficiently fast to prevent blistering [61]. Although drying of the cyanate ester-based materials before exposure to high peak temperatures in the process is always an option to minimize
<table>
<thead>
<tr>
<th>Name</th>
<th>Linkage (X)</th>
<th>Physical State, Viscosity</th>
<th>Properties of the Cured Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T_g$</td>
</tr>
<tr>
<td>Bisphenol A dicyanate</td>
<td><img src="https://example.com/structure1.png" alt="Structure" /></td>
<td>Crystalline (MP = 79 °C)</td>
<td>257, 289</td>
</tr>
<tr>
<td>Bisphenol E dicyanate</td>
<td><img src="https://example.com/structure2.png" alt="Structure" /></td>
<td>Supercooled liquid (MP = 29°C) 100 cP at 25°C</td>
<td>258</td>
</tr>
<tr>
<td>Bisphenol M dicyanate</td>
<td><img src="https://example.com/structure3.png" alt="Structure" /></td>
<td>Supercooled liquid (MP = 68°C) 8000 cP at 25°C</td>
<td>192</td>
</tr>
<tr>
<td>Dicyclopentadienyl bisphenolcyanate</td>
<td><img src="https://example.com/structure4.png" alt="Structure" /></td>
<td>Semisolid 1000 cP at 82°C</td>
<td>244, 265</td>
</tr>
<tr>
<td>Novolac cyanate ester phenolic triazine</td>
<td><img src="https://example.com/structure5.png" alt="Structure" /></td>
<td>Semisolid 20–40 cP at 80°C (for PT-15) 250,000 cP at 25°C (for PT-30)</td>
<td>300 to 400</td>
</tr>
</tbody>
</table>

*a Glass transition temperature [39,41].
*b Heat density
*c Water absorption at saturation (100°C) [39].
*d Dielectric constant [39].
*e Dielectric loss (tanδ) [Kessler 2012] [39].
*f 5% weight loss temperature [41].
*g Peak mass loss temperature [41].
*h Char yield at 900°C [41].
hydrolysis and hence delamination and blistering, appropriate design of the polymer network may in itself improve hydrolytic stability sufficiently well. For instance, incorporating sterically demanding substituents in the cyanate ester backbone (such as methyl groups in para position to the cyanate group) of the monomer has been shown to effectively improve hydrolytic stability [61,64,65].

Properties of Cyanate Ester Blends with Epoxy and BMI

Cyanate ester resins are very often used in combination with numerous other high-performance polymers [66,67,68,69], the most important being duroplastic systems such as epoxy [3,4,21,69,70–78] or bismaleimide resins [6–8,79–81,81a], or rubber [82] of various thermoplastics [82] for improved toughness.

Bismaleimide (BMI) resins are often modified by cyanate ester resins to reduce the brittleness of the BMI networks. To optimize the compatibility between cyanate esters and other resins, special monomers may be designed. For instance, monomers that allow ready co-condensation with bismaleimide resins have recently been prepared. The novel cyanate ester monomers carried allyl functionalities in order to improve formation of interpenetrating networks with BMI [83]. Other cyanate ester monomers have especially been developed for tailored composites such as, for instance, cyanate ester-modified epoxy resin/glass fiber composites [4]. An interesting strategy towards high-performance epoxy/cyanate ester systems has been described recently [5,25,71,72] where micro-capsulated composites of cyanate and epoxy resins have been prepared and shown to be of good mechanical and electrical performance. Furthermore, cyanate ester systems containing both epoxy and BMI resins such as bismaleimide-modified bisphenol dicyanate epoxy matrices have also been studied [84].

Epoxy resins are also known to catalyze cyanate ester cure. This latter effect has been ascribed to

![Figure 11.6](image_url) Relative changes in specific volume of cyanate ester resin based on BADCy monomer cured at 200°C.
the hydroxyl groups present as impurities in virtually all epoxies [37,38]. The preparation of blends from cyanate ester resins with epoxy resin can be performed quite easily by blending the two resins at elevated temperatures between 80 and 100 °C, adding the catalyst formulation, degassing the mixture by applying vacuum, pouring the resin blend into a mold, and curing the system by, for instance, heating to about 180 °C. As in the above case of neat cyanate resin cure, a post-curing phase at even higher temperatures above 200 °C can follow. With increasing amounts of cyanate ester resin in the blend the more likely a post-curing phase needs to be included in order to bring about complete resin conversion [37,38].

For processing cyanate ester resins and cyanate ester resin blends, the following components may be present in the cyanate ester resin formulations [85]:

- Cyanate monomer and its prepolymerms.
- Epoxy prepolymerms such as bisphenol A diglycidyl ether (BADGE); N,N,N′,N′-tetruglycidyl diamino-4′-diphenylmethane (TGDDM); N, N,O-truglycidylamino-4-phenol (TGAP).

- Bismaleimides (BMI, BT resins).
- Catalyst.
- Thermoplastics.
- Core-shell rubbers.
- Reactive rubbers.
- Reactive diluents.
- Fibers: glass, carbon, aramid, or other.
- Other fillers or reinforcements (see Introduction).

Since it is impossible to summarize and appropriately acknowledge all major developments that have taken place during the past decades, some typical properties of selected examples of classic BMI and epoxy-based blends shall be given in Table 11.5 to illustrate the range of application properties possible.

The synthesis and characterization of different novel cyanate/epoxy and cyanate/BMI blends have also been described more recently. For example, the results reported by Sarodajevi et al. [1] illustrate very well the great potential that cyanate esters do have with respect to modifying the property profile of epoxy and BMI resins. The authors synthesized

### Table 11.5 Properties of Three Cured Cyanate Ester Resin Blends Based on BADCy Monomer and Either Epoxy (BADGE, DGETBBPA) or BMI [52]

<table>
<thead>
<tr>
<th></th>
<th>BADGEa (57%)</th>
<th>DGETBBPAb (25%)</th>
<th>BMIc (10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanate ester (weight %)</td>
<td>43</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Catalyst type</td>
<td>Cu acetylacetonate</td>
<td>Cu naphthenate</td>
<td>Zinc octoate</td>
</tr>
<tr>
<td>Catalyst amount</td>
<td>0.05</td>
<td>0.24</td>
<td>0.02</td>
</tr>
<tr>
<td>Nonylphenol</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Maximum cure temperature (°C)</td>
<td>177</td>
<td>215</td>
<td>232</td>
</tr>
</tbody>
</table>

**Cured resin properties**

<table>
<thead>
<tr>
<th></th>
<th>Dry</th>
<th>Weta</th>
<th>Water absorptiond(%)</th>
<th>Flexural strength (MPa)</th>
<th>Flexural modulus (GPa)</th>
<th>UL 94 flammability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>192</td>
<td>178</td>
<td>1.31</td>
<td>117</td>
<td>3.1</td>
<td>Fails</td>
</tr>
<tr>
<td>Dry</td>
<td>192</td>
<td>178</td>
<td>1.31</td>
<td>117</td>
<td>3.1</td>
<td>Fails</td>
</tr>
<tr>
<td>Weta</td>
<td>192</td>
<td>178</td>
<td>1.31</td>
<td>117</td>
<td>3.1</td>
<td>Fails</td>
</tr>
<tr>
<td>Water absorptiond(%)</td>
<td>1.31</td>
<td>1.65</td>
<td>2.02</td>
<td>173</td>
<td>131</td>
<td>Fails</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>117</td>
<td>173</td>
<td>131</td>
<td>Fails</td>
<td>V-0</td>
<td>Fails</td>
</tr>
<tr>
<td>Flexural modulus (GPa)</td>
<td>3.1</td>
<td>3.3</td>
<td>3.3</td>
<td>Fails</td>
<td>Fails</td>
<td>Fails</td>
</tr>
<tr>
<td>UL 94 flammability</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|aBADGE: bisphenol A diglycidyl ether. |
bDGETBBPA: diglycidyl ether of tetrabromobisphenol A. |
cBMI: bismaleimide. |
dMoisture conditioned 64 hours at 93 °C plus > 95% relative humidity.
a series of novel cyanate ester resins, performed blending experiments with epoxy and BMI resins, and characterized the resulting materials with regard to the mechanical and thermal properties [1].

With all blends based on new monomers studied by the authors, the performance of the cyanate-modified epoxy resin systems was generally significantly better than that of the neat epoxy or BMI materials. For instance, in the case of the epoxy systems, the tensile strength of the cyanate ester blends varied between 55 to 76 MPa (compared to 52 with the neat epoxy); the flexural strength varied between 96 and 169 GPa (neat epoxy: 89 GPa); and the impact strength varied between 1.3 and 4.5 J/m (neat epoxy: 0.67 J/m). With respect to the thermal properties, the temperature stability was improved in most cases by up to 30°C higher temperatures as expressed by the $T_{10}$ value (358°C for neat epoxy, 390°C for BCAM-modified cyanate ester/epoxy product). Also the char yield typically increased [1].

Similarly, the mechanical and thermo-mechanical performance of BMI was greatly improved upon blending with a newly prepared cyanate ester. The effect depended strongly on the amount of cyanate ester used. By addition of 9 parts cyanate ester resin to 91 parts of BMI, the tensile strength, for instance, was enhanced from 418 MPa to 461 MPa. At lower levels, performance improvement was accordingly less pronounced. A similar trend was found with other mechanical characteristics like tensile modulus, flexural strength, flexural modulus, fracture toughness, and impact strength. The findings are summarized in Table 11.6. As evident from the data given in the table, only minor amounts (<10%) of the cyanate ester are needed to significantly influence, i.e. improve, the overall performance of the BMI. The chemical structure of the novel monomer used in this work for the BMI blending experiments is given in Figure 11.7.

### Recent Developments

#### Novel Cyanate Ester Monomers

Besides those materials that are already used on a large scale, a huge number of special monomers have been prepared during the past decades and are described in the scientific literature to further enhance specific property profiles. Although they are mostly not yet employed commercially, a few recent examples are briefly addressed in this section to illustrate some rationales behind the design of such monomers with respect to their modifying effect on the material properties. Often, blends and composites are produced from the novel cyanate esters and only the performance of the overall system is given in the scientific literature. Hence, unfortunately, it is difficult to compare the performance of all monomers and resin systems described in the literature within one single table. The following examples feature new monomers that have been shown to influence network rigidity and in turn toughness and thermo-mechanical behavior of the polymer, and the flammability of cyanate ester resins. In addition, following the increasing trend towards sustainable manufacturing technologies in the chemical industry (“green chemistry,” “bio-based materials,” etc.), a subsection has been added that features some recent developments with regard to the use of renewable resources to prepare novel bio-based cyanate resins.

#### Monomers Modifying Flexibility

Anuradha and Sarodajevi prepared a series of structurally closely related novel cyanate ester monomers containing propylene chain segments between the aromatic cores of the diphenylecyanate units in order to improve the flexibility of the obtained cyanic ester resin networks [83]. The chemical structure of the newly prepared monomers is depicted in Figure 11.8. The idea was that the flexible aliphatic methylene spacer should lead to a moderate improvement in toughness of the resulting thermoset accompanied by a decrease in dielectric properties [83]. It has been shown that increasingly bulky or longer hydrocarbon bridges between the aromatic rings lower the dielectric properties; the dielectric constant progressively decreased when the alkyl bridges were changed from methylene to isopropylene to dicyclopentadiene to meta-disopropenylbenzene. The reason for this is that alkyl substituents of increasingly demanding steric requirements reduce the spatial density of highly polar groups responsible for the dielectric interactions present in the volume unit of the polymer network and, additionally, decrease the electronegativity of the benzene rings by their electron-donating capacity [37,38]. It was found furthermore in earlier studies that especially substitution by methyl groups in the ortho position to the cyanate...
Table 11.6 Improvement of Properties of BMI by Modification with Different Amounts of Cyanate Ester Resin [1]

<table>
<thead>
<tr>
<th>BT Ratio</th>
<th>Mechanical Properties</th>
<th>Dynamic Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanate**:BMI</td>
<td>Tensile Strength (MPa)</td>
<td>Tensile Modulus (GPa)</td>
</tr>
<tr>
<td>100:0</td>
<td>516</td>
<td>48</td>
</tr>
<tr>
<td>9:91</td>
<td>461</td>
<td>35</td>
</tr>
<tr>
<td>6:94</td>
<td>442</td>
<td>33</td>
</tr>
<tr>
<td>3:97</td>
<td>422</td>
<td>32</td>
</tr>
<tr>
<td>0:100</td>
<td>418</td>
<td>29</td>
</tr>
</tbody>
</table>

*Cyanate resin based on bis(4-cyanato-3'-methoxybenzal)-4,4'-diaminodiphenyl methane (BCDM) as the monomer.
group significantly lowered the overall dielectric constant by shielding and weakening the C–O, C–N, and C≡N dipoles [37,38,83].

With the new monomers Cy(a), Cy(b), Cy(c), Cy(d), and Cy(e), it was found that both the glass transition temperature and the thermal stability followed the trend Cy(b) > Cy(c) > Cy(a) > Cy(e) > Cy(d). The authors explained their findings by the symmetry of the used structures, the \( T_g \) being higher for those structures with the \textit{para}-substituted rings. Higher symmetry is also directly correlated to a higher cross-linking density, and in turn, to better thermal stability. Although all prepared cyanate esters displayed LOI values in the range from 36.1 to 38.7 and hence were considered to be sufficiently thermally stable, the cyanate esters derived from the monomers Cy(b) and Cy(c) having the highest degree of symmetry were thermally the most stable within the series [83].

Possibly the higher symmetry of the cyanate ester monomer packing units also led to the highest glass transition temperature observed with the \textit{para}-tetraaryl cyanate ester monomer within the series of structurally related monomers investigated by Reams and Boyles [86] and depicted in Figure 11.9. Again, the more symmetrical tetraaryl monomers yielded significantly higher glass transition temperatures, storage moduli, and cross-linking densities than the corresponding triaryl monomers of lower symmetry. Within each series, the \textit{para}-substituted monomers showed larger values than the \textit{meta}-substituted, and in turn, higher values than the \textit{ortho}-substituted monomers [86].

Guenthner et al. recently prepared a cyanate ester resin of greatly improved flexibility that was based upon the novel monomer 1,2,3-tris(4-cyanatophenyl) propane [87]. The approach used by the authors illustrates nicely a general strategy to improve the flexibility in rigid aromatic three-dimensional polymer networks by incorporation of a monomer of improved molecular mobility. The three-dimensional polymer network obtained with the new monomer resulted, according to the authors, in a “checkerboard”-like network architecture in which flexible juncture points alternated with rigid juncture points.

**Figure 11.7** Chemical structure of bis(4'-cyanato-3'-methoxybenzal)-4,4'-diaminodiphenyl methane (BCDM) [1].

**Figure 11.8** Series of structurally related cyanate ester monomers used by Anuradha and Sarodajevi [83].
Figure 11.10 shows an ideal representation of the resulting molecular framework in comparison to the network structure obtained from polymerization of the commercially available, novolac-based cyanate ester monomer Primaset® PT-30 [87]. The new material had the same cross-linking density compared to the Primaset® PT-30 polymer, but displayed several advantages over the commercial material: under identical curing conditions, the activation energy for autocatalytic thermal cure at 210–290°C was lower by 14 kJ/mol, the overall extent of cure was higher with the new material while cross-link density at full cure (3.811 + / − 0.004 × 10⁻¹¹) and wet glass transition temperature (ca. 245°C) was approximately the same. The novel material had higher molar volume and lower density.

More details on the influence of chemical structure of monomers on the resin performance are available in Hamerton and Nair et al. [37,38,40]. The structure-reactivity and structure-property relationships between a wide range of different cyanate ester monomers studied until 1994 has been extensively discussed in Hamerton [37,38]; the literature until 2001 has been covered well by Nair et al. [40]. Since then, most work on cyanate esters has focused on formulation and development of cyanate ester blends with other duroplastic polymers and on the characterization of a wide range of cyanate ester composite materials including nanocomposites and comparatively less effort has been invested in the characterization and design of new monomers.

Monomers Conferring Flame Retardance

The flame retardancy of cyanate esters is frequently being improved by incorporation of bromine-substituents into the polymeric network or by formulation of cyanate ester resins with bromine-based additives. Due to the inherent temperature stability of cyanate esters, generally, lower bromine levels are required as for other polymers. Compared to, for instance, covalently bromine-modified epoxy resins which require about 20% of bromine to yield a flame retardant material, only ca. 12% of bromine are required with cyanate esters, and in unmodified cyanate resin formulations lower levels of brominated additives are usually required as well to achieve a UL94 V-0 rating [88].

Figure 11.9 Series of structurally related cyanate ester monomers used by Reams and Boyles [86].
Figure 11.10 Structural comparison of idealized network architectures obtained with Primaset® PT-30 monomer and the novel monomer 1,2,3-tris(4-cyanatophenyl)propane [87].
However, incorporation of bromine into cyanate esters not only improves polymer performance but has some drawbacks as well, such as the potential corrosion of metal components in composites due to halide ion liberation, a decrease in glass transition temperature leading to a softening at already lower temperatures, a possible reduction of the thermo-oxidative stability, a deterioration of the dielectric loss properties, and, due to the high atomic weight of bromine, an increase in the specific weight of the polycyanurates [88].

As an alternative, it has been shown that incorporation of phosphorous can also greatly enhance the flame retardant properties of cyanate ester resins and many phosphorous-containing compounds have been prepared [6,89,89a,90].

Other novel cyanate ester monomers with promising flame retardant properties that carry phosphorous moieties have been synthesized more recently. For example, Hamerton et al. [88] in a four-step synthesis prepared 2,2,4-tri(4-cyanatophenoxy)-4,6,6-trisphenoxy-2\(\lambda^5,4\lambda^5,6\lambda^5\)-[1,3,5,2,4,6]-triazatriphosphine (compound x, Figure 11.11), a new monomer containing a six-membered ring consisting of phosphorous and nitrogen atoms that confers improved flame retardancy to the cured cyanate ester network and simultaneously avoids the aforementioned drawbacks caused by bromine substituents. The new synthetic route yielded the monomer with a yield of ca. 35%.

A one pot-synthesis leading to phosphinated bisphenols by addition of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) to either 1,1,1-tris(4-hydroxyphenyl)ethane or diaminophenylmethane- and diaminophenylether-based benzoxazines with subsequent conversion of the bisphenols to the corresponding dicyanate derivatives has been described [91,92]. The structures of the obtained cyanate ester monomers are depicted in Figure 11.12. The latter two compounds can be prepared without any catalyst at room temperature in high purity without particular purification that holds some promises for the procedure for larger scale applications. The resulting polycyanurates showed good flame retardancy as well as good dielectric properties.

Zhang et al. [12] prepared a novel substituted biphenyl-based cyanate ester resin (Figure 11.13). The monomer, 4,4’-bis(4-cyanatobenzyl)biphenyl (BBPCy) does not contain any phosphorous or halogen atoms and hence, avoids the drawbacks involved with such compounds like, for instance, the generation of toxic fumes upon thermal combustion of halogen-containing compounds. Compared to a resin derived from the commercially available monomer BADCy, with the new monomer a UL-94 rating of V-0 was reached and both glass transition and thermal stability were slightly better (Tg = 258°C). The low water absorption (1.08 %) and excellent dielectric properties (Dk: 2.94, Df: 0.0037 at 1 GHz) achieved with this material provide promising properties for applications in electronic encapsulation and printed circuit board manufacturing [12].

Bio-Based Raw Materials

Currently much research work is performed with the general direction of modifying the raw material basis of the chemical industry with regard to re-generable resources. Raw material shortages and raw material costs are an important incentive to exploit natural resources (plants and plant oils) as the basis for new materials in many fields. This trend is also affecting the research work in the cyanate ester resin field where monomers based on natural resources are increasingly being investigated.

Recently, strategies to prepare cyanate esters from fully or partly re-generable raw materials have been proposed [93—95]. For example, one approach recently described uses epoxidized soybean oil (ESO) as a bio-based modifier for commercial cyanate ester monomers [95]. The authors reacted 1,1’-bis(4-cyanatophenyl)ethane with ESO together with a silicon-organic compound that led to in situ generation of nanosilica in a sol-gel process. The nanocomposites thereby accessible are
partly based on renewable resources and showed improved storage moduli and thermal stability compared to neat cyanate ester reference material. A different approach was described by Meylemans et al. [93]. The authors ultimately used lignin as a polymeric raw material basis that is accessible from the wood-based industry; it represents a natural polyphenolic resin of varying constitution and composition. Lignin has since long been tested as a natural-based substitute for phenolic monomers or oligomers in phenolic resins [96,97] and numerous other polymers such as polyesters [98,99], polyurethanes [100], and epoxy resins [101–103]. Due to its high carbon-content, it has also been investigated as a precursor for carbon fibers [104]. Hence, it seems reasonable to investigate this versatile raw material as a source for monomers applicable in cyanate ester resin production.

The authors suggest producing well-defined phenolics such as vanillin and, in turn, creosol, from conversion of lignin (Figure 11.14a), and, by dimerization, further transforming these into bisphenols, which are then suitable as cyanate precursors for resin production (Figure 11.14b) [93,105].

Davis et al. recently demonstrated that trans-anethole can be chemically transformed into suitable precursor molecules for the preparation of cyanate ester resins that show a technological performance comparable to currently available commercial resins [94]. This approach is highly interesting since it exploits re-generable plant oil as an alternative resource for phenolic compounds. Trans-anethole is the major ingredient (to about 90%) of the essential oil of star anise (*Illicium verum*) and can be obtained from the crude oil.
Figure 11.14 Conversion of lignin into re-generable precursor molecules (a) that are suitable for producing cyanate monomers (b).
The oil is produced in amounts of approximately 400 metric tons per annum for the preparation of flavor and fragrance products, which of course is not much compared to the petrochemical-based manufacturing of phenols or even to the amounts of lignin that are amounting as byproducts from the wood industry; however, exploiting new high-performance applications of high added value might possibly act as an incentive to increase the crop production and hence improve availability in the long term.

The chemical structure of trans-anethol and the cyanate ester monomers obtained by chemical transformation are given schematically in Figure 11.15. Especially the properties of the cyanate ester resin obtained from RRR/SSS 1-ethyl-2-methyl-3-(4-cyanatophenyl)-5-cyanatoindane displayed a remarkably high glass transition temperature of 313°C, which was superior to the LECy-based commercial reference cyanate ester; further, it had a lower water uptake (1.66 %) than for the two LECy and BADCy reference cyanate esters. The glass transition temperature measured after 96 h immersion in water at 85°C was still 223°C, which was somewhat lower than for the commercial reference materials, but still within an acceptable range. The cyanate ester resin obtained from the other monomer, racemic 1,3-bis(4-cyanatophenyl)-2-methylpentane, displayed comparatively inferior properties [94].

**Recently Covered Aspects of Processing Cyanate Ester Resins**

In the following subsections, a selection of a few recent developments in alternative processing methods of cyanate esters are briefly discussed, including the preparation of cyanate ester resins via frontal polymerization, microwave-assisted polymerization, plasma polymerization of cyanate monomers, and the preparation of cyanate esters under steric restrictions with nanoconfinement in the presence of controlled porous glass.

**Frontal Polymerization**

The curing of cyanate esters is accompanied by the development of high exothermic enthalpies. The reaction heat generated is usually dissipated by appropriate tooling design to avoid inhomogeneous curing or defect formation. However, the curing...
exothermy may also be used with advantage for inducing and advancing the thermal cure in a cyanate ester reaction system. Frontal polymerization is a technique that makes use of the reaction exothermy generated during polymerization. Hence, recently, frontal polymerization technology has been described and studied for the preparation of cyanate esters [106,107].

Frontal polymerization means that within a solid or highly viscous polymerization system the reaction heat generated within a distinct reaction zone where polymerization has been initiated by, for instance, an external heat source, serves as the thermal stimulus to initiate and propagate the polymerization further throughout the rest of the system. The external heat source starting the overall reaction sequence may be either some sufficiently hot object such as, for instance, a soldering iron that is being contacted with the outer zone of the solid reaction system, or it may be another chemical reaction system in close proximity that is able to deliver sufficient exothermal reaction enthalpy for initiating the polymerization reaction in question.

Figure 11.16a schematically shows an example for the experimental set up of a typical frontal polymerization system. Figure 11.16b illustrates the propagation of the polymerization front of thermally induced formation of Primaset LeCy cyanurate ester polymer [106].

In Figure 11.16a, the two highly viscous reaction mixtures are brought into close contact and an external heat source (which is on a laboratory scale, for instance, a heated soldering iron) is contacted at the juncture where the two phases meet. Typical contact times may be a couple of seconds [106]. This initial introduction of heat is sufficient to start the polymerization sequence of the initiator system, which delivers sufficient exothermal energy to initiate the polymerization of the cyanate ester polymerization. Acrylate systems may generate interface temperatures around 250°C [108]. Since for cyanate ester resin formation initial reaction temperatures > 200°C are required [109,110], acrylate polymerization may be a suitable initiator system. As the front of the initiator chemical reaction proceeds horizontally, the cyanate ester polymerization is progressively initiated and develops a vertical propagation zone.

Figure 11.16b shows an example where no chemical initiator system is used but the reaction front of cyanate ester polymerization is started by short contact with a heated surface of a temperature > 500°C. The progression zone is clearly visible from the photograph. The author has found that chemical initiation is of advantage in cases where too much heat is introduced into the reaction system. In such cases the excess energy introduced leads to solvent or monomer evaporation, which causes bubbles that in turn act as heat sinks and hamper homogenous propagation of the reaction front [106].

The potential advantages of frontal polymerization techniques are that rapid curing of polymers can be achieved without the need for external heat sources. Frontal polymerization may provide homogenous curing of thick samples of highly viscous systems. It may be applied as a means of curing solvent-free systems that may be applied to fill or seal structures with cavities of arbitrary shapes that are otherwise difficult to appropriately seal off. By utilizing the reaction enthalpy as a self-sustaining energy source, the need for external heat sources is circumvented.

**Microwave-Assisted Polymerization of Cyanate Esters**

Conventionally, the energy required to initiate polymerization is introduced thermally. However, an interesting option may also be to use microwave radiation to bring about polymerization. Since the electromagnetic radiation completely penetrates the bulk material, the energy is introduced more uniformly and the batch is heated throughout the bulk more homogeneously than with convection. The thermal conductivity of the material is also not of importance. Since heating of the whole bulk is brought about instantaneously upon switching on the microwave generator, the curing reaction should be accelerated as compared to conventional heating. Microwave-assisted curing hence may lead to more quickly and uniformly cured cyanate ester products. However, it was found that microwave radiation was not feasible for the processing of unmodified cyanate ester resins [111]. It was found that either charred or incompletely cured products were obtained. Obviously, by microwave radiation the reaction was accelerated so much that the liberated exothermal energy caused complete thermal degradation of the formed material. On the other hand, when the reaction conditions were more moderately selected to contain microwave-assisted auto-acceleration, only
incompletely cured products were the result. However, when the authors used thermoplastic-modified networks by co-reacting phenolphthalein-based poly(arylene ether) as a reactive thermoplastic toughness modifier, the reaction was much more controllable and led to resin materials of very high degrees of conversion (97–98%) within minutes of reaction time. Furthermore, it was found that by applying microwave heating, defined morphologies of the thermoplastic-modified cyanate ester resins could be obtained independent of the applied microwave input power. In general, the faster the curing took place, the finer was the resulting network morphology [111]. Hence, microwave-assisted processing of cyanate ester resin systems may in some cases be employed beneficially in order to further reduce the processing times and create products of defined morphology.

Figure 11.16 Schematic representation (a) of the frontal polymerization principle using an exothermal chemical reaction (e.g. in this case an acrylate polymerization) for the thermal initiation of cyanate ester resin synthesis [106], and (b) specific example for the reaction sequence during frontal polymerization of a thermally induced cyanate ester reaction [106].
Nanoconfinement

Cyanate esters have been synthesized using nanoporous templates based on controlled pore glass of different pore sizes [112–114] to modify the properties of the resulting polymers. Nanoconfinement often leads to distinct differences in the reaction rates at which a synthesis takes place and due to the imposed steric restrictions within the nanoreactor systems often results in reaction pathways that cannot be realized via traditional bulk synthesis. For instance, when oxirane-modified fullerene molecules (C_{60}) are intercalated and trapped within single-wall carbon nanotubes that then act as nanoreactors, unusual reactions are possible such as the formation of linear, unbranched polymeric chains of C_{60}O-molecules. Without nanoconfinement, three-dimensional products are obtained [115].

When cyanate ester synthesis is performed under such restricted steric conditions, the reaction rate of cyclotrimerization was found to be greatly enhanced by a factor of ca. 20 when hydrophobic pores of 11.5 nm diameter were used as confinement with bisphenol M dicyanate as the monomer [113,114]. The authors found that no alteration of the reaction mechanism took place and they also excluded that intramolecular cyclization of the difunctional monomers was mainly responsible for the observed effects [112]. The glass transition temperatures of the obtained cyanate ester products were lower as compared to the bulk polymerized compounds, and the T_{G} depression increased with increasing degree of conversion. Since it was greatest with the fully reacted product (i.e. the resin where the maximum achievable conversion was obtained), the authors concluded that the molecular stiffness influenced the magnitude of the nanoconfinement effects.

Synthetic routes to cyanate esters using nanoconfinement may be of future use to prepare novel and yet unexpected thermal properties by appropriate modification of the reaction conditions. Thus, not only modification and substitution of cyanate ester monomers and co-monomers, but also novel preparation techniques may yield interesting new properties.

An interesting example for producing a nano-structured material with high potential for the use in biosensing from cyanate esters via nanoconfinement of the cyanate ester monomers within a template has recently been described by Gitsas et al. [116]. The researchers produced a nanorod array from cyanate ester resins by using self-ordered anodic aluminum containing arrays of aligned nanopores of defined pore diameter. The monomer formulation was loaded into the nanoporous template and cured at high temperature. The polycyanurate nanorod array was used for optical waveguide spectroscopy of taurine binding to the surface groups of the nanorod assembly [116].

Plasma Polymerization

Cyanate ester resins may also be generated as thin surface films on various substrates using plasma polymerization techniques. For instance, thin films of polymeric polynitrides based on 4-cumylphenol cyanate ester (PPCPCE) were deposited onto silicon wafers and quartz glass [117,118]. The smooth and homogenous PPCPE films showed low dielectric constant (\(\varepsilon_r = 2.51\)) and have some potential as novel intermetallic dielectrics in microelectronics. The dielectric constant of the thin film was lower when lower (5 W) rather than higher (10, 20 W) discharge power was used for the deposition; this was attributed by the authors to the higher retention of aromatic structure and lower concentration of radicals in the deposited film at the lower discharge power [118]. Furthermore, at higher discharge powers, the observed films had a significantly rougher surface [117].

Applications

Cyanate esters are mainly employed in electronics, aerospace, space, transportation, and industrial applications as matrices for composites, coatings, adhesives, and encapsulating resins. Although they have a favorable combination of properties, so far, the use of cyanate esters, due to their comparatively high cost, is restricted mainly to high-performance applications in sectors where cost is a secondary concern. A typical product area for cyanate esters, hence, is as structural parts in aerospace applications. Many primary and secondary structures in military aircraft are produced from cyanate ester-based composites; for example, the Dassault Rafale fighter jet incorporates high-temperature stable cyanate ester resin in its composite parts (Figure 11.17a).
Other examples for applications of cyanate esters in airplanes are air ducts or critical electrical components close to the engine where they are exposed to temperatures as high as 235°C. Cyanate esters are also found in high-speed vehicles such as Formula One racing cars or in motorbikes as, for instance, muffler systems [120].

Radomes are also frequently based on cyanate ester resins due to their favorable dielectric behavior. Other aerospace applications include structural parts for satellites (Figure 11.18a), antennas, reflectors, optical elements, high-precision detectors, solar array substrates, and other components. For instance, NASA has based space carriers that are used to transport cargo into space on cyanate ester-based composite materials. As an example, the Super Lightweight Interchangeable Carrier (SLIC) shown in Figure 11.18b relied largely on carbon fiber-reinforced cyanate ester resin. By employing such reinforced cyanate ester materials, lower launch costs (due to the lower weight) and better dimension stability can be achieved as compared with metals. Compared to epoxy-based systems, cyanate esters display lower tendency towards micro-crack formation, especially when they are toughened by addition of minor amounts of an appropriate toughening agent. Furthermore, cyanate esters show much greater stability towards ionizing radiation in comparison to other high-performance polymers; they can withstand irradiation dosages as high as 10^9 rads [120].

Interesting cyanate ester [122] and cyanate ester/epoxy blends [46] have recently been described that display shape memory behavior. In the latter case, to obtain the shape memory characteristics, poly(tetramethylene oxide) was functionalized with phenol and incorporated into the three-dimensional epoxy/cyanate network. Such shape memory high-performance polymers are very promising for space applications as components made therefrom can be compacted during the launch phase and unfolded in space.

However, perhaps at present the most commercially important field of applications include the manufacturing of electronic and low-dielectric semiconductor devices. An example for a cyanate ester-based electronics enclosure is given in Figure 11.19a. Approximately 70% of the manufactured high-speed printed circuit boards are already based on cyanate ester resins [40]. For applications in the microelectronics industry, the low dielectric constant and low dissipation factor of cyanate ester resins plays an important role for their widespread application. These special dielectric properties allow for better electrical performance, higher signal speed, and lower power loss as compared with other materials [40]. Hence, the single largest use for CEs is the lamination of substrates for printed circuits and their assembly via prepreg adhesives into high-density, high-speed multilayer boards (Figure 11.19b) [37,38,40].

Future applications of cyanate esters are seen as aircraft interiors (Figure 11.17b) such as flooring, ceiling, and walls with tight smoke and heat regulations, as high-performance powder coatings, automotive electronics (navigation) systems, as next generation materials for high voltage industry (e.g. generators, etc.), as shielding materials in nuclear plants (due to their extraordinary radiation resistance), as high-end friction materials, and as adhesives especially for lightning strike applications or in high-temperature rapid bonding [120]. Cyanate esters will also find applications as wave guides and in non-linear optics.
Figure 11.18 Use of cyanate ester-based materials in space applications [120,121].
Trade Names

Only a few companies are currently capable of producing cyanate ester resins on a commercial scale; one reason for this may be the extremely hazardous nature of the starting materials (cyanogen bromide or cyanogen chloride) used to obtain the monomeric compounds and the correspondingly demanding production technology [39]. Table 11.7 lists the most common trade names for commercial cyanate ester resins. Only the economically most important suppliers are considered.

Table 11.7 Trade Names and Basic Structural Elements of Some Commercial Cyanate Ester Resins [16,39]

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Structural Characteristics</th>
<th>Supplier</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primaset™ BADCy</td>
<td>Bisphenol A dicyanate ester</td>
<td>Lonza</td>
<td>Kessler (2012) [39]</td>
</tr>
<tr>
<td>Primaset™ LECy</td>
<td>Bisphenol E dicyanate ester</td>
<td>Lonza</td>
<td>Kessler (2012) [39]</td>
</tr>
<tr>
<td>AroCyL-10</td>
<td>Bisphenol E dicyanate ester</td>
<td>Huntsman</td>
<td>Kessler (2012) [39]</td>
</tr>
<tr>
<td>EX1510</td>
<td>Bisphenol E cyanate ester</td>
<td>Tencate</td>
<td>Badrinarayan et al. (2012)</td>
</tr>
<tr>
<td>Primaset™ METHYLCy</td>
<td>Tetramethyl bisphenol F dicyanate ester</td>
<td>Lonza</td>
<td>Kessler (2012) [39]</td>
</tr>
<tr>
<td>AroCy XU 366</td>
<td>Bisphenol M dicyanate ester</td>
<td>Huntsman</td>
<td>Kessler (2012) [39]</td>
</tr>
<tr>
<td>Primaset™ DT 4000</td>
<td>Dicyclopentadienyl bisphenol cyanate ester</td>
<td>Lonza</td>
<td>Kessler (2012) [39]</td>
</tr>
<tr>
<td>Primaset™ PT</td>
<td>Novolac cyanate ester phenolic triazine (PT)</td>
<td>Lonza</td>
<td>Kessler (2012) [39]</td>
</tr>
<tr>
<td>AroCy XU 371</td>
<td>Novolac cyanate ester phenolic triazine (PT)</td>
<td>Huntsman</td>
<td>Kessler (2012) [39]</td>
</tr>
</tbody>
</table>

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