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Preparation and characterization of alkoxysilane functionalized isocyanurates

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Abstract

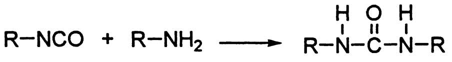
Alkoxysilane functionalized isocyanurates were prepared from hexamethylene diisocyanate (HDI) isocyanurate and 3-aminopropyltriethoxysilane. The reactants and functionalized isocyanurate were characterized by ^{1}H, ^{13}C and ^{29}Si NMR, IR and electrospray ionization-mass spectrometry. Two-dimensional NMR was necessary to accurately assign the proton and carbon spectra for both the reactants and functionalized products. The composition of the HDI isocyanurate was a mixture of oligomers ranging from two to three HDI monomers. The functionalization reaction was performed neat, and as a function of dilution. As expected, substitution on the isocyanurate becomes more uniform with increasing solvent content. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Alkoxysilane; Isocyanurates; Polyurethane

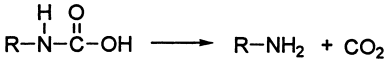
1. Introduction

Polyurethane or polyurea coatings are derived from reaction of an isocyanate with a hydroxy functionalized oligomer forming carbamate structure (–NHCOO–) or a amino functionalized oligomer producing urea group (–NHCONH–), respectively. Polyurethane and polyurea coatings are widely used in the furniture, floor, railway vehicle, automobile, and aerospace industries [1]. Isocyanate based coatings can be classified as aromatic or aliphatic. Compared to the aromatic structures, coating based on aliphatic isocyanates exhibit excellent light and weather stability and as a consequence are principally used for outdoor application. The two main commercial aliphatic isocyanates are hexamethylene diisocyanate (HDI) and isophorone isocyanate (IPDI).

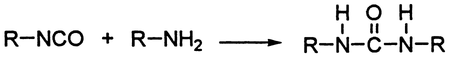
Isocyanate groups can also react with water to produce “moisture curing polyurea coatings”. The chemistry of the moisture curing process is depicted in Eqs. (1)–(3). After reaction with water, an unstable carbamic acid intermediate is formed which decarboxylates into an amine. This amine reacts with another isocyanate group to form the urea cross-link [2]. The reaction rate is controlled by temperature, humidity, and catalysts. Moisture curing polyurethane and polyurea systems have a wide variety of high durability applications for wood, concrete, and metal coatings [3].



$$R{-}NCO + R{-}NH_2 \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R \qquad (1)$$



$$R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow R{-}NH_2 + CO_2 \qquad (2)$$



$$R{-}NCO + R{-}NH_2 \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R \qquad (3)$$

An inorganic moisture curing coating is based on sol–gel precursor. Alkoxysilane groups also have a moisture curing mechanism as depicted in Eqs. (4)–(6). The alkoxy group can react with water to form a silanol and an alcohol (Eq. (4)). The silanol group can then condense to form siloxane groups with the elimination of water or alcohol (Eqs. (5) and (6)). Further hydrolysis and condensation reactions form a silicon oxide network producing silicon ceramer. The processes are determined by many factors including pH, temperature and solvent. Brinker and Scherer [4] summarized the effects of these factors on the hydrolysis and condensation processes, and concluded that the dominant factor was pH. Alkoxysilane hydrolysis is very slow under neutral conditions, however, it can be accelerated either with acid or base catalysts. One of the commonly used sol–gel precursors is tetraethylorthosilicate (TEOS), $Si(OET)_4$, which is used in coatings for preparing zinc-rich primers. After application, TEOS absorbs water from

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the atmosphere and undergoes hydrolysis and condensation reaction in accordance with Eqs. (4)–(6) forming silica gel. It is a widely used method for corrosion protection [5].

$$\equiv\text{Si–OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Si–OH} + \text{ROH} \qquad (4)$$

$$\equiv\text{Si–OH} + \equiv\text{Si–OH} \rightarrow \equiv\text{Si–O–Si}\equiv + \text{H}_2\text{O} \qquad (5)$$

$$\equiv\text{Si–OR} + \equiv\text{Si–OH} \rightarrow \equiv\text{Si–O–Si}\equiv + \text{ROH} \qquad (6)$$

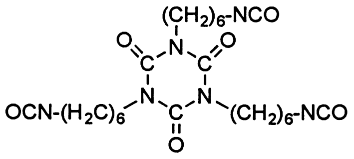
Organofunctional silanes, R'–Si–$(OR)_3$, possess an alkoxysilane group –Si–$(OR)_3$ and an organic group R', which have been used as coupling agents for composites and adhesion promoters for primer coatings [6–8]. Organofunctional silanes are also used in preparing the inorganic/organic hybrid materials called “ceramers”. Oligomers are functionalized with alkoxysilane; sol–gel precursors are added and form a crosslinked inorganic/organic network. The terminated alkoxysilane cocondenses with sol–gel precursor and functions as a coupling agent between the polymer and inorganic phase. Many functionalized oligomers have been reported, including poly(tetramethylene oxide) [9,10], poly(ether ketone) [11], polyimide [12], polyamide [13] and polyurethane [14,15].

The alkoxysilane functionalized polyurethane was reported by Pascault and coworkers [14,15]. In their work, poly(ethylene oxide) (PEO) was terminated with an isocyanate group via the reaction of hydroxy group of PEO and IPDI. The isocyanate group further reacted with aminosilane producing an alkoxysilane terminated urethane macromonomer. The hydrolysis and condensation mechanism of alkoxysilane and water was investigated using ^{29}Si NMR and gel permeation chromatography (GPC). The results showed that condensation reaction was catalyzed by acid catalyst and the condensation rate constants decreased as the degree of condensation increased. Similar to the sol–gel precursors, the alkoxysilane terminated macromonomer can hydrolyze and condense to form a ceramer matrix.

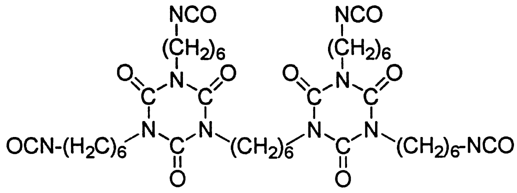
As a result of their superior weatherability, aliphatic isocyanurates are primarily used for exterior coating. The problem with aliphatic diisocyanates, especially HDI, is volatility which exacerbates the inherent toxicity of the isocyanate group. To circumvent this problem, we used the isocyanurate of HDI.

HDI isocyanurate have been studied in the formulation for aircraft, paper and floor coatings [16–18]. They have also been used extensively in high solid and decorative coatings [19,20]. Some results have shown that HDI isocyanurates have advantages over the other aliphatic isocyanates. One instance is in the area of flame-resistant paper coatings. HDI isocyanurate attached with a bromine-containing diol has a much higher tensile strength at high temperature than HDI monomer [17]. The other instance is for the UV-curable floor coatings [18]. HDI isocyanurate, HDI biuret, IPDI trifunctionalized triol and HDI trifunctionalized triol were applied as polyisocyanates in the preparation of urethane acrylates. The coating with HDI isocyanurate provided fairly good tensile strength, hardness, weatherability, and adhesion compared to other polyisocyanates.

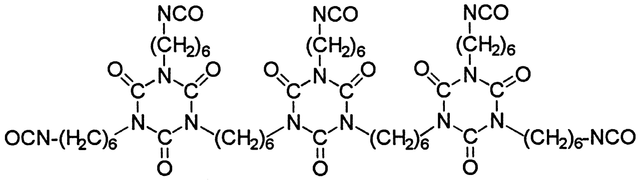
The HDI isocyanurate is a mixture mainly consisting of mono-, di- and tri-isocyanurates. Their chemical structures are shown as follows.



(1)



(2)



(3)

Although many isocyanates have been well characterized, the ^{1}H and ^{13}C HDI isocyanurate have not yet been fully assigned. For example, two-dimensional ^{1}H–^{13}C correlation via long-range coupling (COLOC) NMR experiments have been previously reported for the isocyanate IPDI [21,22]. Compared to IPDI, the isocyanurate of HDI has all primary isocyanate –NCO groups. Consequently, the HDI monomer forms a mixture of oligomers during isocyanurate preparation.

Electrospray ionization mass spectrometry (ESI-MS) has been used to analyze low molecular weight polymer or macromolecules up to about 10 000 Daltons (Da) [23–25]. It is a soft ionization technique in which exclusively molecular ions are formed with no fragmentation. The data are predictable as both the exact composition mass of the molecular ion and the corresponding isotopic pattern can be computed prior to analysis and compared with the experimental results. ESI-MS has provided predictable compositional information on many types of polymers. Many coating materials such as polyfunctional alkoxysilanes, polyurethane, acrylic copolymers, and epoxide prepolymer have been analyzed using ESI-MS [23–25]. We characterized most of these materials using K^+IDS. Most components in these complex mixtures can be identified by molecular weight and quantified by the abundance on the basis of assumption that the signal strength of abundance is independent of molecular weight.

In this study, HDI isocyanurate was characterized by ESI-MS and 2D NMR experiments. Alkoxysilane functionalized isocyanurates were prepared through the reaction of HDI isocyanurate and 3-aminopropyltriethoxysilane. The reaction was performed neat and as a function of dilution. The products were characterized using ESI-MS and NMR. Two-dimensional NMR experiments were performed to fully assign the ^{1}H and ^{13}C spectra. The product mixtures of the functionalization reactions were also monitored via ESI-MS.

2. Experimental

2.1. General information

The HDI isocyanurate was obtained from Bayer Corporation (Desmodur N-3300, unstabilized). The 3-aminopropyltriethoxysilane (3-APTES, Aldrich) and methanol (Burdick & Jackson) were used as-received. Absolute ethanol (McCormick Distilling) was dried over molecular sieves and acetone (J.T. Baker) was distilled over molecular sieves (Aldrich, 4A bead). All reactions were performed under a dry nitrogen atmosphere. Air-sensitive materials were transferred and weighted under argon in an inert atmosphere dry-box. The solvent, acetone, was transferred via an air tight syringe under dry nitrogen.

A JEOL 400 spectrometer was used to record the ^{1}H, ^{13}C NMR spectra and a JEOL 270 spectrometer used to record the ^{29}Si NMR. All NMR spectra were determined in $CDCl_3$ at ambient temperature. The ^{1}H–^{1}H correlation spectroscopy (COSY) was performed on the JEOL 400, 64 experiments were acquired with X sweep and Y sweep, both of which were 1735 Hz and give a 256×256 data matrix. The ^{1}H–^{13}C heteronuclear correlation spectroscopy (HETCOR) was recorded on the same instrument as the COSY; 128 experiments were acquired with (^{13}C) X sweep = 6583 Hz and Y sweep = 3281 Hz and give a 2048×512 data matrix. FT-IR spectra were obtained from a Bruker IR spectrometer (Equinox 55, resolution: 2 cm^{-1}). The electrospray ionization mass spectrometry experiments were conducted on a Finnigan 3-Tesla 2001 FTMS (Madison, WI) equipped with an UltraSource I assembly. For the electrospray analyses, solutions of the isocyanates under study were prepared in tetrahydrofuran (THF) to a concentration of approximately 0.1 mM. Sodium iodide (Aldrich, Milwaukee, WI), our cationization reagent, was added to the THF to a concentration of 0.25 mM. Our ESI capillary voltage was set to 2800 V. Twenty spectra, 128 K data points each, were zero-filled, apodized and summed to yield the reported spectra. The resolution was about 10 000.

2.2. Preparation of the methanol terminated hexamethylene diisocyanate isocyanurate

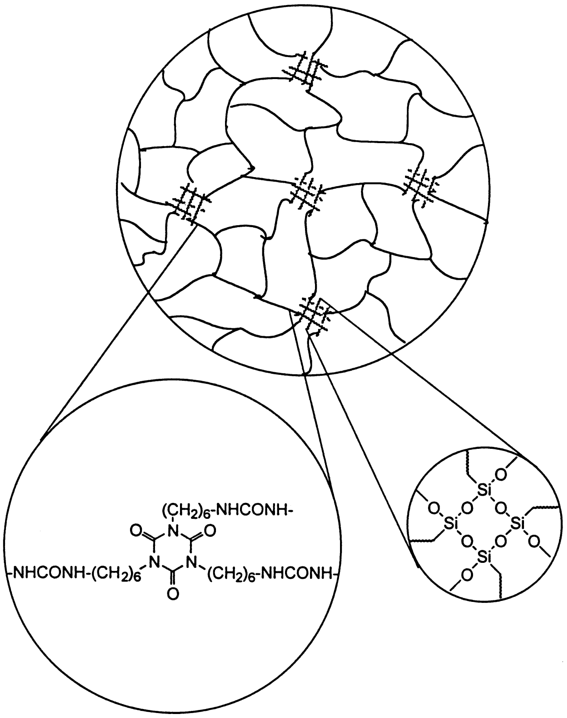
Methanol (32 g, 1 M, molarity) was added into HDI isocyanurate (19.49 g, 0.1 equiv. –NCO, normality) and mixed to form a uniform solution. The reactants were vigorously mixed at 25°C for 168 h. The disappearance of the isocyanurate was monitored by IR. When all the isocyanate (–NCO) group (2270 cm^{-1}) was consumed, the reaction was stopped. The excess methanol was removed by vacuum at ambient temperature to afford **4** (19.81, 100%): ^{1}H NMR, δ 5.10 (singlet, 3H, $-\mathrm{N}\mathit{H}\mathrm{COCH_3}$), δ 3.86 [triplet, 7.3H, $-\mathrm{CO-})_2\mathrm{N-C}\mathit{H}_2-$], δ 3.64 (singlet, 9H, $-\mathrm{NHCOC}\mathit{H}_3$), δ 3.16 (quartet, 6H, $-\mathrm{C}\mathit{H}_2\mathrm{NHCO-}$), δ 1.30–1.70 [multiplet, 28.4H, $-\mathrm{CH_2-(C}\mathit{H}_2)_4\mathrm{-CH_2-}$]; ^{13}C NMR, δ 157.2 ($-\mathrm{NH}\mathit{C}\mathrm{OCH_3}$), δ 149.0 [$(-\mathit{C}\mathrm{O-})_2\mathrm{N-}$], δ 51.9 ($-\mathrm{NHCO}\mathit{C}\mathrm{H_3}$), δ 42.8, 40.9, 29.8, 27.7, 26.3, 26.2 [$-(\mathit{C}\mathrm{H_2})_6-$]; and ESI-MS: base peak 623 Da.

2.3. Synthesis of trifunctionalized hexamethylene diisocyanate isocyanurate

The 3-APTES (6.63 g, 0.3 M, molarity) was dissolved in acetone (33.2 ml) producing a 20% 3-APTES solution. A 20% solution of HDI isocyanurate was obtained by mixing HDI isocyanurate (5.82, 0.3 equiv. –NCO, normality) and acetone (29.1 ml). The 3-APTES solution was added dropwise into the flask containing HDI isocyanurate solution at 25°C. After addition, the reactants were stirred for 1 h. The acetone was then removed by vacuum at ambient temperature to afford **5** (12.45, 100%): ^{1}H NMR, δ 5.84 ($\mathrm{N}\mathit{H}\mathrm{CON}\mathit{H}$), δ 3.87 [$(-\mathrm{CO})_2\mathrm{NC}\mathit{H}_2-$], δ 3.81 [$-\mathrm{Si(OC}\mathit{H}_2\mathrm{CH_3})_3$], δ 3.12 ($-\mathrm{C}\mathit{H}_2\mathrm{NHCONHC}\mathit{H}_2-$), δ 1.42–1.72 [$-(\mathrm{C}\mathit{H}_2)_6-$ and $-\mathrm{C}\mathit{H}_2\mathrm{CH_2Si-}$], δ 1.22 [$-\mathrm{Si(OCH_2C}\mathit{H}_3)_3$], δ 0.62 ($-\mathrm{C}\mathit{H}_2\mathrm{Si-}$); ^{13}C NMR, δ 159.1, ($-\mathrm{NH}\mathit{C}\mathrm{ONH-}$), δ 148.8 [$(-\mathit{C}\mathrm{O})_2\mathrm{N-}$], δ 58.1 [$-\mathrm{Si(O}\mathit{C}\mathrm{H_2CH_3})_3$], δ 42.6, 39.8, 30.2, 27.5, 26.4, 26.2, 23.6 [$-(\mathit{C}\mathrm{H_2})_6-$ and $-\mathrm{NH}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2Si-}$], δ 18.1 [$-\mathrm{Si(OCH_2}\mathit{C}\mathrm{H_3})_3$], δ 7.5 ($-\mathit{C}\mathrm{H_2Si-}$); and ^{29}Si NMR, δ -45 ($-\mathit{Si}-$).

2.4. Synthesis of monofunctionalized hexamethylene diisocyanate isocyanurate with ethanol termination

An acetone (110.5 ml) solution of 3-APTES (22.1 g, 0.1 M, molarity) was added dropwise into a flask containing HDI isocyanurate (58.2 g, 0.3 equiv. –NCO, normality) dissolved in acetone (291.0 ml) at 25°C. After addition, the reactants were stirred for 1 h. The acetone was removed by vacuum at ambient temperature to afford **6** (80.3, 100%). Product **6** was characterized by ^{1}H and ^{13}C NMR. The peaks of **6** are a combination of **3** and **5**. **6** (8.03 g, 0.02 equiv. –NCO, normality) was dissolved in absolute ethanol (9.2, 0.2 M) and stirred at 25°C for 168 h. The reaction was monitored by FT-IR until isocyanate (–NCO) group (2270 cm^{-1}) disappeared. The remaining ethanol was removed by vacuum at the ambient temperature to afford **7** (8.95, 100%): ^{1}H NMR, δ 5.43–5.78 (multiplet, 4H, $-\mathrm{N}\mathit{H}\mathrm{COOC_2H_5}$ and $-\mathrm{N}\mathit{H}\mathrm{CON}\mathit{H}-$), δ 4.08 (quartet, 4H, $-\mathrm{COOC}\mathit{H}_2\mathrm{CH_3}$), δ 3.77–3.98 [multiplet, 13.3H, $(-\mathrm{CO})_2\mathrm{NC}\mathit{H}_2-$ and $-\mathrm{Si(OC}\mathit{H}_2\mathrm{CH_3})_3$], δ 3.04–3.34



Scheme 1. Proposed crosslinking structure of polyurethane/siloxane hybrid coating.

(multiplet, 8H, $-CH_2COO-$ and $-CH_2NHCONHCH_2-$), δ 1.14–1.74 [multiplet, 45H, $-CH_2(CH_2)_4CH_2-$, $-COOCH_2CH_3$ and $-CH_2CH_2Si(OCH_2CH_3)_3$], δ 0.62 (triplet, 2H, $-CH_2Si-$); ^{13}C NMR, δ 158.6 ($-NHCONH-$), δ 156.6 ($-NHCOOCH_2-$), δ 148.6 [$(-CO)_2N-$], δ 60.0 [$-COOCH_2-$], δ 57.9 [$-Si(OCH_2CH_3)_3$], δ 42.4, 40.4, 39.6, 30.0, 29.4, 27.3, 26.1, 25.9, 23.4 [$-(CH_2)_6-$ and $-NHCH_2CH_2CH_2Si-$], δ 18.0 [$-Si(OCH_2CH_3)_3$], δ 14.4 ($-COOCH_2CH_3$), δ 7.2 ($-CH_2Si-$); ^{29}Si NMR, δ -45 ($-Si-$); and ESI-MS, base peak 840 Da.

3. Results

The overall objective of this study is to prepare an improved unicoat coating system for aircraft. Currently, the coating procedure of aluminum substrate for aircraft includes several steps. A chromate conversion which usually consists of hexavalent chromium in acidic media is applied to prevent corrosion; after which a wash primer of passivating chromium pretreatment is used to aid adhesion of the primer to the surface. A 2 K epoxy-amine system is coated as a primer on the wash primer layer and followed by a topcoat of polyurethane. In this procedure, chromate is a known carcinogen and as a consequence will be limited in application. The concept of unicoat system is to replace the present multi-coat system with a self-priming coating system.

Unicoat coatings are an approach developed for naval aircraft. A two-component polyurethane with a combination of many pigments was applied as self-priming topcoat. The preliminary results indicated a significant reduction in application cost, emissions of hazardous materials and aircraft maintenance [16]. However, adhesive failure has undermined the widespread use of the unicoat system [26]. In this study, the approach to develop a unicoat is to prepare a polyurethane/siloxane system in which polyurethane provides the bulk mechanical properties, and the siloxane is an adhesion promoter. Two crosslinking mechanisms occur simultaneously in the presence of atmospheric water. The organic moisture curing mechanism of isocyanate (Eqs. (1)–(3)) and the inorganic moisture curing mechanism of alkoxysilane (Eqs. (4)–(6)) result in urea/siloxane (organic/inorganic) crosslinked coating (Scheme 1).

The HDI isocyanurate is a mixture, and as a consequence the carbon and proton NMR spectra have never been fully delineated in the open literature. As a strategy to assign the monofunctionalized isocyanurate, the trifunctionalized

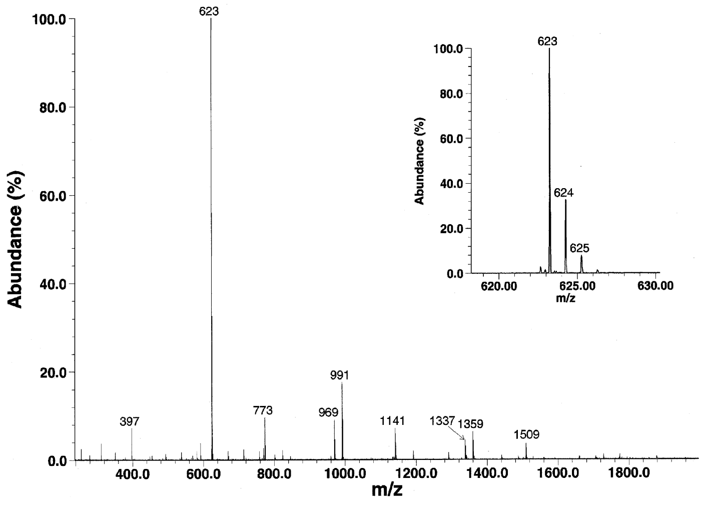


Fig. 1. Na^+ IDS mass spectrum of the HDI isocyanurate terminated with methanol.

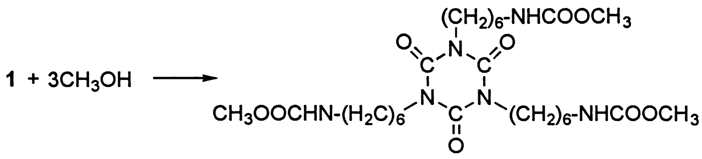
Table 1
Structural units and observed ions of the ESI-MS spectrum for methanol terminated HDI isocyanurate

Peak (Da)	Structural units	Mole percentage (%)
397	2HDI + $2CH_3OH$ + Na^+ + H_2O − CO_2	1.73
623	3HDI + $3CH_3OH$ + Na^+	79.3
773	4HDI + $3CH_3OH$ + Na^+ − H_2O	2.24
969	5HDI + $4CH_3OH$ + H^+	3.14
991	5HDI + $4CH_3OH$ + Na^+	6.12
1141	6HDI + $4CH_3OH$ + Na^+ − H_2O	2.54
1337	7HDI + $5CH_3$ + H^+	1.01
1359	7HDI + $5CH_3OH$ + Na^+	2.47
1509	8HDI + $5CH_3$ + Na^+ − H_2O	0.83

isocyanurate compound was prepared, and both the starting isocyanurate and trifunctionalized product fully characterized. The composition of HDI isocyanurate was first identified and quantified by ESI-MS. Then, the ^{1}H and ^{13}C NMR spectra of HDI isocyanurate (**1**) and trifunctionalized isocyanurate (**7**) were assigned. Combining the peak assignment of **1** and **7**, the NMR spectra of monofunctionalized isocyanurate was also assigned. After the monofunctionalized isocyanurate was prepared neat, the reaction was also investigated with respect to dilution with solvent. The effect of dilution on the monofunctionalization reaction was also investigated by ESI-MS.

3.1. Composition of hexamethylene diisocyanate isocyanurate

The HDI isocyanurate is a mixture and its composition has to be first elucidated in this study. ESI-MS has been shown to be a very efficient characterization tool for polymers under about 10 000 Da. The composition of HDI isocyanurate was determined from the ion abundancies calculated from the electrospray mass spectrum. The HDI isocyanurate was terminated with methanol (Eq. (7)) to eliminate the possible side reactions inherent to the –NCO group.

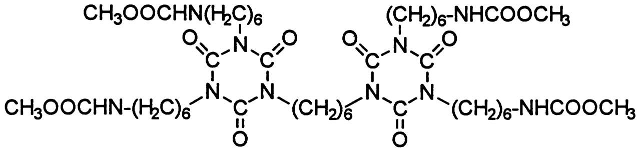


(4)

(7)

The ESI-MS spectra of methanol-terminated HDI isocyanurate is shown in Fig. 1. The observed ions result from sodium attachment to the species originally present in the solution. For example, the base peak seen at 623 Da and the corresponding isotopes (see inset Fig. 1) result from sodium (23 Da) cationization of the methanol-terminated HDI isocyanurate. HDI monomer weighs 168 Da, therefore, the trimer weighs $168 \times 3 = 504$ Da. The three methanol capping groups contribute $32 \times 3 = 96$ Da, and sodium adds 23 Da. Hence, the expected ion is observed at $504 + 96 + 23 = 623$ Da. The isotopic envelope seen in the inset of Fig. 1 supports a species having a molecular formula of $[C_{27}H_{48}N_6O_9]Na^+$, the methanol-terminated HDI isocyanurate. Table 1 lists the relative abundance for several ions seen in Fig. 1. The corresponding isotopic patterns of each species support the assignments listed in Table 1. It is obvious from the spectrum that the HDI isocyanurate is a mixture containing several components.

The base peak at 623 Da can be attributed to the HDI trimer, **4**. The ions at 991 and 1336 Da were attributed to **8** and **9**, respectively. These components were formed by the further isocyanuration reaction of mono-isocyanurate or di-isocyanurate. The peak at 397 Da, 26 Da less than the HDI dimer was attributed to the urea structure, **10**. The urea was formed by the reaction of HDI with water as described in Eqs. (1)–(3). The ion at 773, 1141, and 1509 Da are 18 Da less than tetramer, hexamer and octamer, respectively. Tetramer, hexamer and octamer may possess both the uretidione and/or isocyanurate structures. The ion at 969 Da was surmised to be the combination of **8** and H^+. Indeed, the high resolution data supported this assignment because the peak at 969 Da was 21.949 Da less than the sodiated peak at 991 Da. This deviates by less than 40 ppm from the theoretical difference of 21.982 Da. The composition of **8** should be 3.14% (969 Da) + 6.12%(991 Da) = 9.26%. In the same manner, we determined that the peak at 1337 Da was due to protonated **9** (3.48%) and the peak at 1359 Da due to sodiated **9**, hence the concentration of **9** is a combination of 1337 Da (1.01%) and 1359 Da (2.47%) or 3.48%.



(8)

3.2. NMR resonance assignment of hexamethylene diisocyanate isocyanurate

The major NMR resonances of ^{1}H and ^{13}C spectra were considered to be derived from **1**. As there were six minor products with a combined concentration of less than 20%, it was assumed that the minor products afforded only weak resonances, consequently the resultant contribution of the

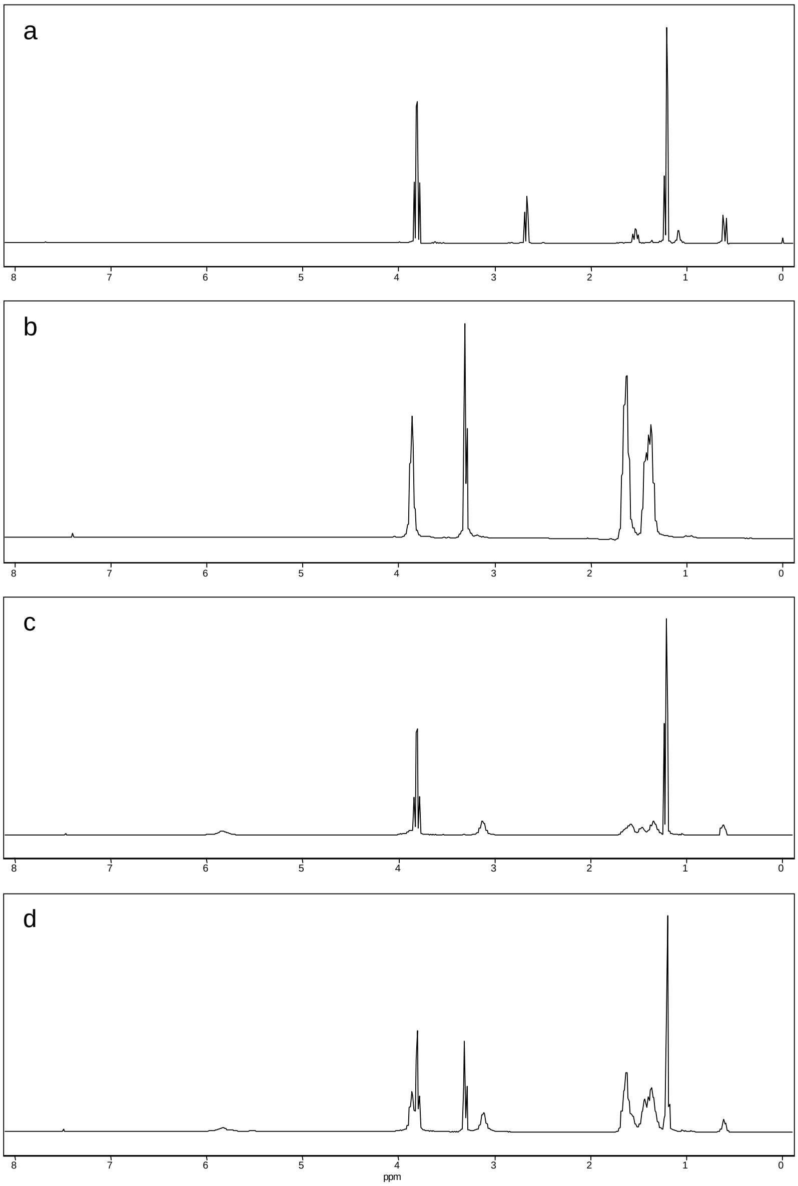
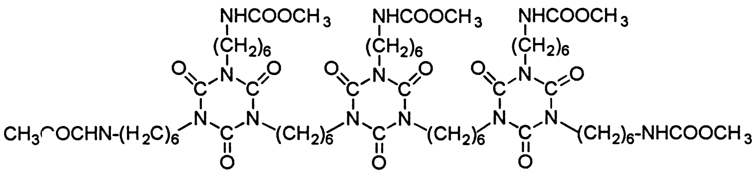


Fig. 2. ^{1}H spectra of (a) 3-aminopropyltriethoxysilane; (b) HDI isocyanurate, **1**; (c) trifunctionalized HDI isocyanurate, **5**; (d) monofunctionalized HDI isocyanurate, **6**.



(9)

CH$_3$OOCNH-(CH$_2$)$_6$-NHCONH-(CH$_2$)$_6$-NHCOOCH$_3$

(10)

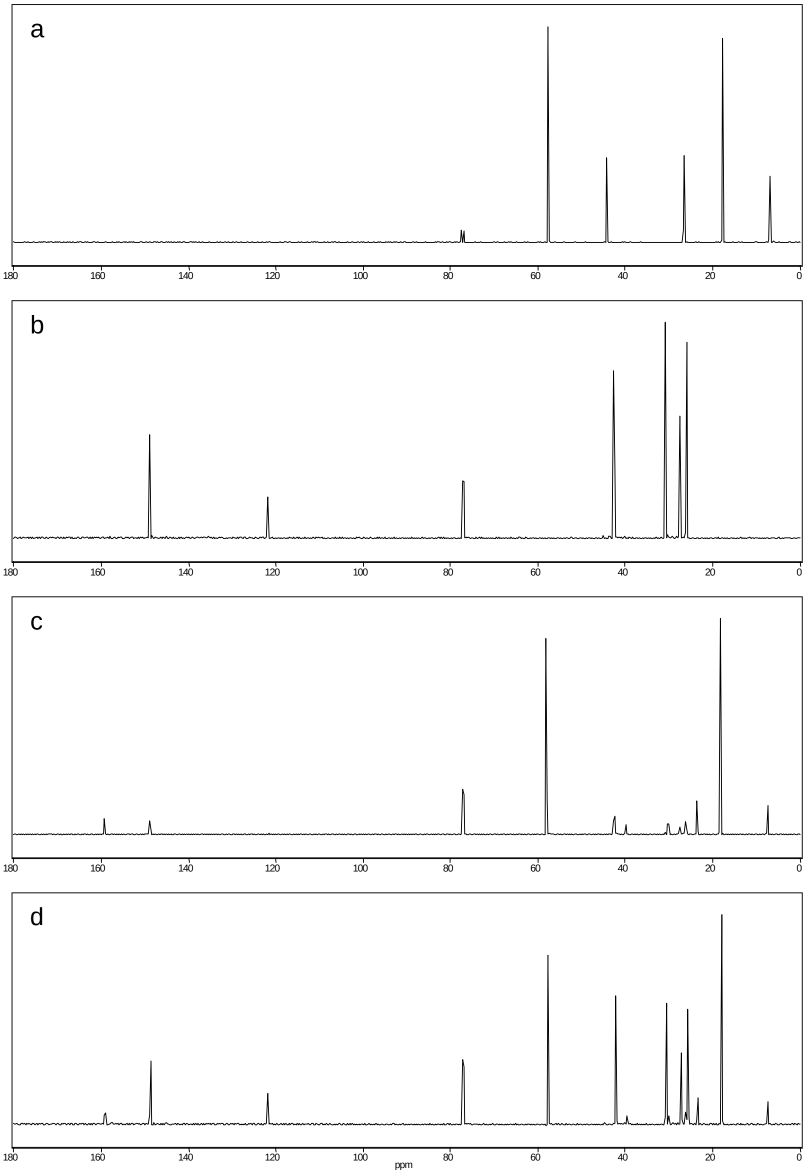


Fig. 3. ^{13}C spectra of (a) 3-aminopropyltriethoxysilane; (b) HDI isocyanurate, **1**; (c) trifunctionalized HDI isocyanurate, **5**; (d) monofunctionalized HDI isocyanurate, **6**.

minor products to the overall NMR spectra assignment of **1** was negligible. The ^{1}H and ^{13}C NMR spectra of **1** are shown in Fig. 2(b) and 3(b). In Fig. 3(b), eight main peaks (strong) corresponding to the eight different carbon in the HDI isocyanurate structure indicated that the assumption is reasonable. Fig. 4 is the 2D ^{1}H–^{1}H COSY NMR experiment depicting the interaction of spin coupling between two protons. Based on the known one-dimensional (1D) proton assignment, the assigning of the ^{1}H NMR spectrum was performed using the ^{1}H–^{1}H COSY experiment. Fig. 5 is the 2D ^{1}H–^{13}C NMR spectrum, by which the correlation between carbon and attached proton can be obtained. The ^{13}C NMR was then assigned using the 2D ^{1}H–^{13}C NMR known as HETCOR. The ^{1}H and ^{13}C assignments are listed in Table 2. The assigned peaks corresponding to the protons and carbons in HDI isocyanurate are shown in Figs. 6 and 7. From Fig. 7, we can observe that the carbons, C7, C6 and C5, on the isocyanurate ring side have greater chemical shift (to downfield) compared to the corresponding carbon on the isocyanate side, C2, C3 and C4. It is caused by the stronger electron-drawing effect from biuret group on the isocyanurate ring compared to the terminal isocyanate groups. The ^{13}C resonance at δ 26.1 ppm (weak) may be attributed to the two middle carbons of hexamethylene between the two

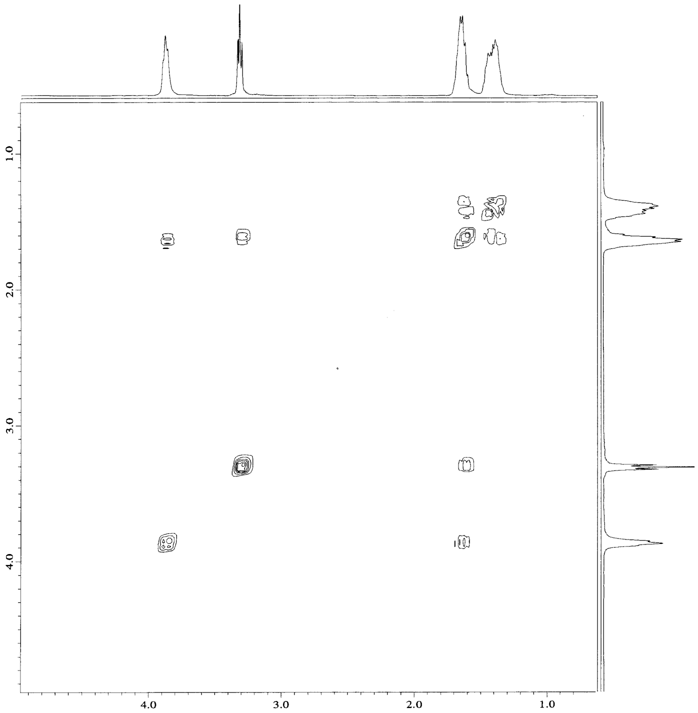


Fig. 4. COSY spectrum of HDI isocyanuarate, **1**.

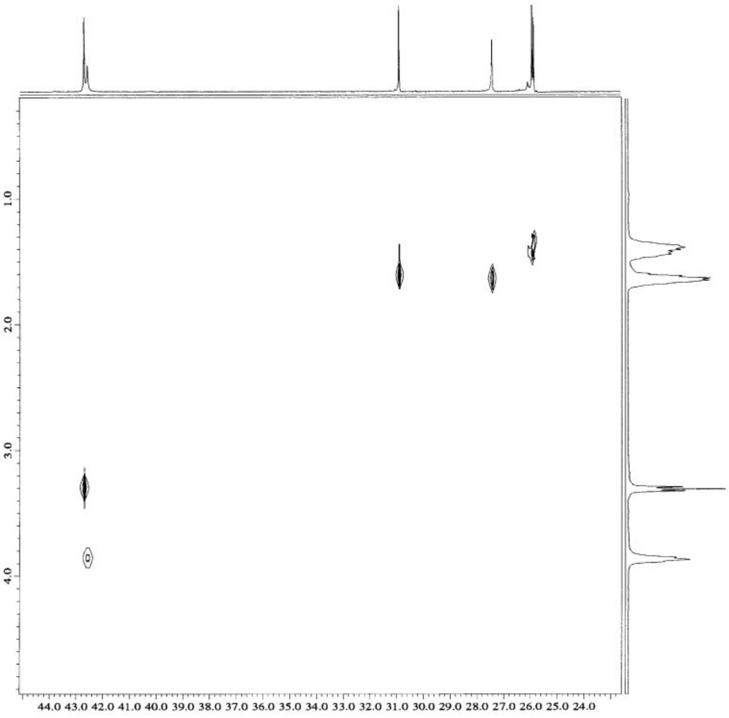
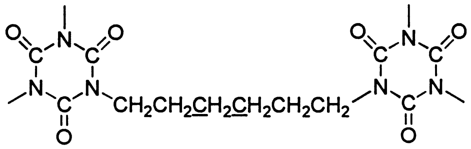


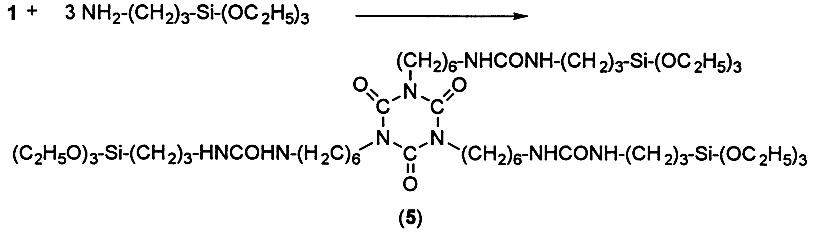
Fig. 5. HETCOR spectrum of HDI isocyanurate, **1**.

trimer rings as shown in the following structure:



3.3. NMR resonance assignment of trifunctionalized hexamethylene diisocyanate isocyanurate

Trifunctionalized HDI isocyanurate was prepared using HDI isocyanurate and excess 3-APTES (Eq. (8)) as a model compound to investigate the chemical shift change of monofunctionalization reaction.



(8)

The ^1H and ^{13}C NMR spectra of **5** are shown in Figs. 2(c) and 3(c). The ^1H and ^{13}C NMR spectra were assigned with reference to NMR spectra of 3-APTES and HDI isocyanurate, and the COSY and HETCOR NMR spectra of **5**. The details of assignment are listed in Table 3. The assigned peaks corresponding to the protons and carbons in trifunctionalized isocyanurate are shown in Figs. 8 and 9. The ^1H and ^{13}C NMR spectra of 3-APTES, HDI isocyanurate and **5** are listed together in Figs. 2 and 3 to compare the chemical shift attributed to alkoxysilane functionalization of HDI isocyanurate. The change can be observed in both ^1H and ^{13}C NMR spectra. The H5 (δ 2.67 ppm) of 3-APTES and H2 (δ 3.30 ppm) of **1** are both shifted to 3.12 ppm due to the adjacent group variation caused by the reaction of amine

Table 2
^1H and ^{13}C chemical shift (ppm) of HDI isocyanurate (**1**)

Proton	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
H2	3.30 (triplet)	C1	121.7
H3 and H6	1.51–1.73 (multiplet)	C2	42.7
H4 and H5	1.25–1.51 (multiplet)	C3	30.9
H7	3.87 (triplet)	C4	26.0
		C5	25.9
		C6	27.4
		C7	42.6
		C8	148.8

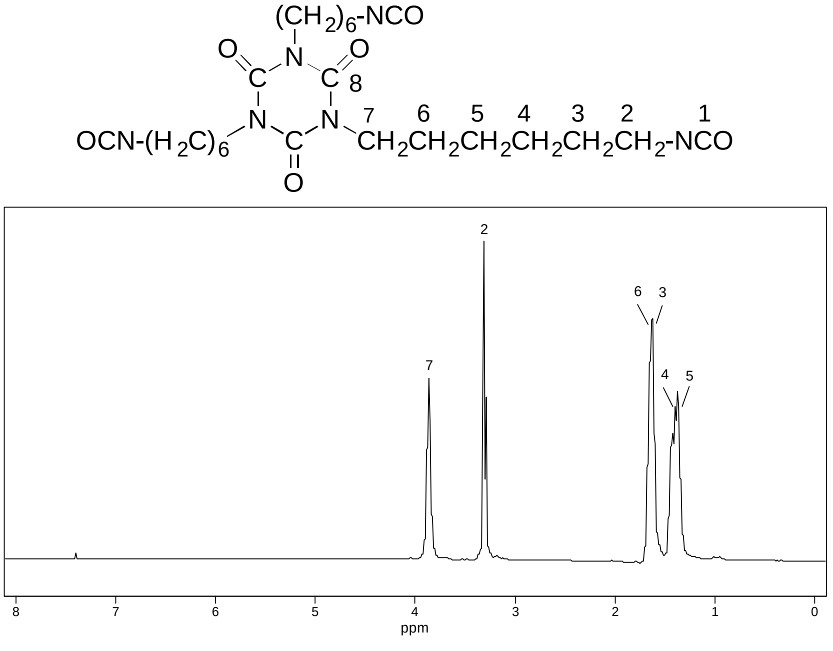


Fig. 6. ^1H NMR spectrum of HDI isocyanurate, **1**.

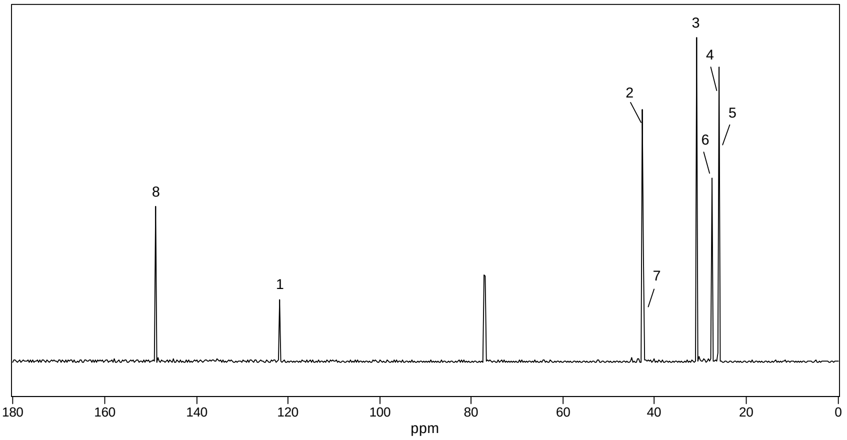
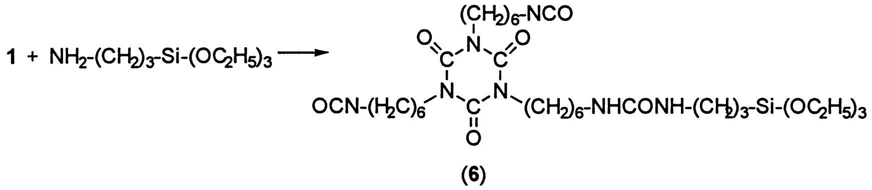


Fig. 7. ^{13}C NMR spectrum of HDI isocyanurate, **1**; the marked numbers are correspond to the carbons in Fig. 6.

and isocyanate groups. In this reaction, primary amine group of 3-APTES (δ 1.10 ppm) changed to a urea group (–N*H*CON*H*–, δ 5.84 ppm). This reaction was also expressed in the ^{13}C NMR. The resonance of isocyanate group (–N*C*O, δ 121.7 ppm) of **1** disappeared after reaction with 3-APTES. The new group (–NH*C*ONH– 159.1 ppm) formed. After functionalization reaction, the chemical shifts of C4 and C5 of the 3-APTES and C2, C3 and C4 in **1** shifted to reflect the formation of the urea group.

3.4. NMR resonance assignment of monofunctionalized hexamethylene diisocyanate isocyanurate



(9)

Monofunctionalization reaction (Eq. (9)) is similar to trifunctionalization reaction, but the products still possess unreacted isocyanate groups. Figs. 2(d) and 3(d) are the ^{1}H and ^{13}C NMR spectrum of **6**. Comparing the three ^{1}H spectra of Fig. 2(a), (b) and (d), it can be observed that there is a new peak appearing at 3.12 ppm from the urea group formation (–C*H*$_2$NHCONHC*H*$_2$–); and also the characteristic peak at 3.31 ppm from the protons next to isocyanate group (–C*H*$_2$NCO) remain in the spectrum. A similar pattern can be observed in ^{13}C NMR in Fig. 3(a), (b) and (d). After monofunctionalization reaction, the new resonance at 159.0 ppm (–NH*C*ONH–) formed from the reaction of HDI isocyanurate and 3-APTES. The resonance at 121.6 ppm remain in the spectrum from the unreacted isocyanate group (–N*C*O). The new peak formation from functionalization in ^{1}H and ^{13}C NMR in monofunctionalized isocyanurate is the same as trifunctionalized isocyanurate; the remaining peaks of monofunctionalized isocynurate from HDI isocynurate are the same as HDI isocyanurate. The ^{1}H and ^{13}C NMR spectra of **6** should be a combination of HDI isocyanurate (**1**) and trifunctionalized isocyanurate (**5**) with some overlapping peaks. The assigned peaks corresponding to the protons and carbons in monofunctionalized isocyanurate are shown in Figs. 10 and 11. The ^{29}Si NMR spectra of 3-APTES, trifunctionalized isocyanurate and monofunctionalized isocyanurate are shown in Fig. 12 for comparison. As expected, the silicon resonance did not shift in tri- and monofunctionalization reactions indicating that the alkoxysilane group remained intact.

3.5. Effect of dilution on monofunctionalized reaction

The functionalization reaction of the primary amine and isocyanate is fast. In monofunctionalization reaction (Eq. (9)), it was anticipated that the difunctionalization and trifunctionalization (Eq. (8)) would also occur, and these three reactions will kinetically compete with each other. For the neat reaction, the resultant products are determined by the diffusion process of aminosilane into HDI isocyanurate. Dilution decreases the viscosity of the overall media. More importantly, dilution decreases the concentration of reactants, and thus increases the effective mixing of the reactants. The reaction was performed at three different concentrations of acetone, 0, 20 and 80%. The product mixtures were terminated with ethanol (Eq. (10)) to eliminate the side reactions emanating from the unreacted

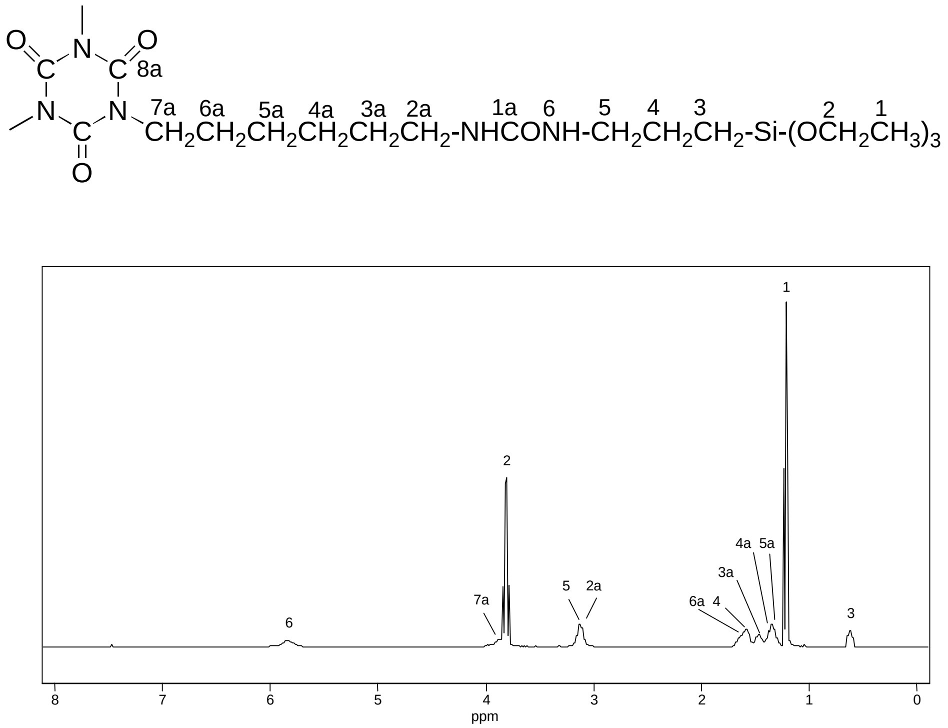
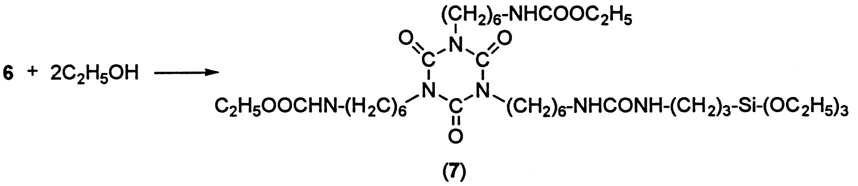


Fig. 8. ^{1}H spectrum of trifunctionalized HDI isocyanurate, **5**.

isocyanurate groups and subsequently evaluated using ESI-MS.

Unfortunately, the mole percentage derived from the ESI-MS data as a function of acetone concentration was only semi-quantitative. However, the relative ratio of mono-, di-, and tri-functional products were consistent with the expected outcome of the experiments. The monofunctionalized isocyanurate increases as a function of dilution, whereas, the trifunctionalized product decreased.



(7)

(10)

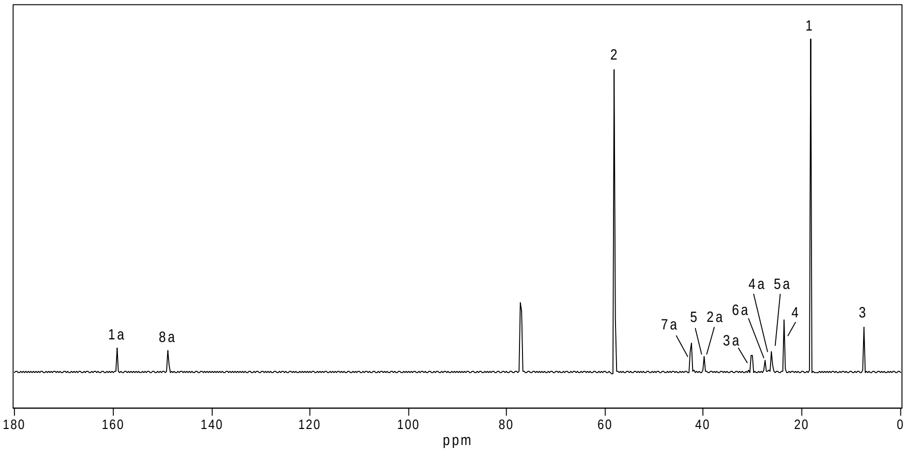


Fig. 9. ^{13}C spectrum of trifunctionalized HDI isocyanurate, **5**; the marked numbers correspond to the carbons in Fig. 8.

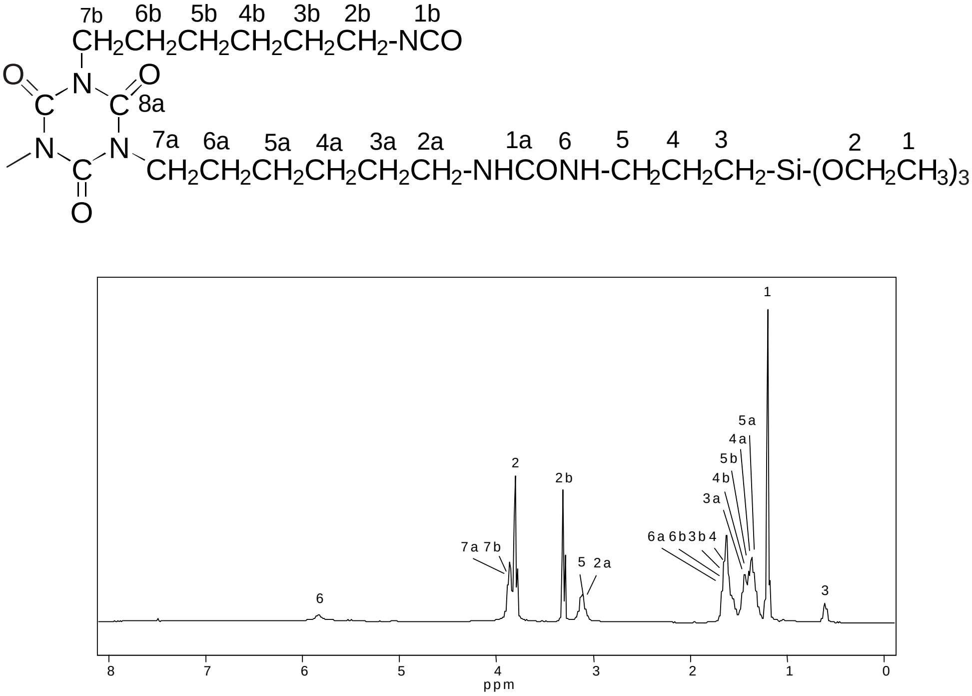


Fig. 10. ^{1}H spectrum of monofunctionalized HDI isocyanurate, **6**.

4. Discussion

The components of HDI isocyanurate were identified and quantified by ESI-MS. The major component was identified as **1** (79.3 mol.%). Two-dimensional NMR experiments were performed on the isocyanurate mixture to delineate the previously unreported assignment of all the proton and carbon resonances for **1** in situ. The assignment of spectra is a crucial step in the ability to monitor the various crosslinking reactions which occur within a fully formulated HDI isocyanurate based unicoat coating system. As the inorganic and organic crosslinking reactions are competitive in coatings developed from functionalization of the isocyanurate, it is necessary to fully delineate this spectra for further studies as well.

As previously stated, the ESI-MS was applied to identify each component of HDI isocyanurate mixture. The HDI isocyanurate mixture was previously evaluated using GPC [19]. Unfortunately, the individual components could not be separated yielding only the polydispersity index (1.21), the ratio of the weight average molecular weight to the number molecular weight. The quantification of ESI-MS was based on the assumption that signal strength is independent of molecular weight, or the detector response factor (DRF)

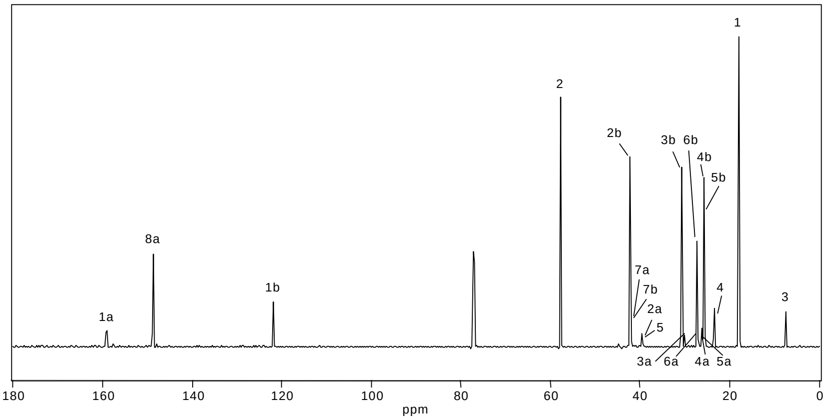


Fig. 11. ^{13}C spectrum of monofunctionalized HDI isocyanurate, **6**; the marked numbers correspond to the carbons in Fig. 10.

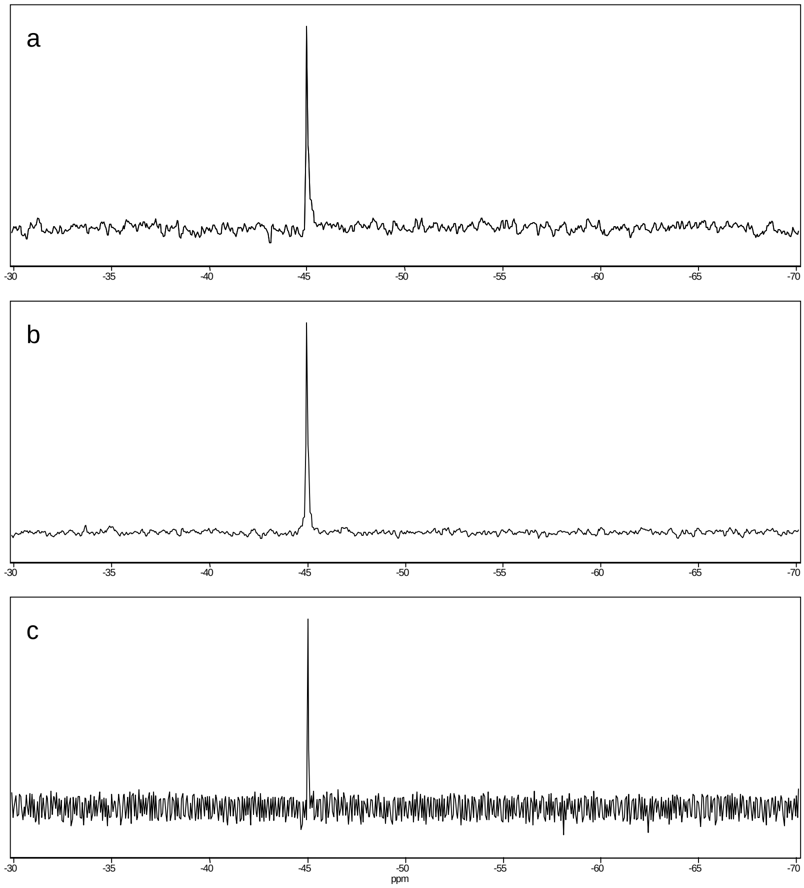
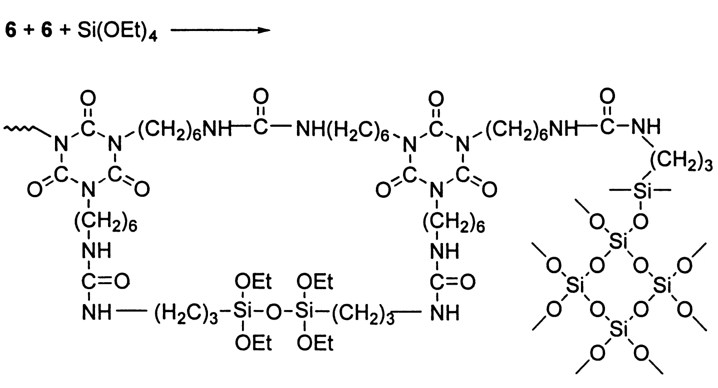


Fig. 12. ^{29}Si spectra of (a) 3-aminopropyltriethoxysilane; (b) trifunctionalized HDI isocyanurate, **5**; (c) monofunctionalized HDI isocyanurate, **6**.

was similar for all the ions. This assumption seems to fit the HDI isocyanurate system well. The composition quantified by ESI-MS is consistent with the molecular weight distribution measured by GPC. The results indicated that compositions of mono-, di- and tri-isocyanurate are 79.3, 9.26 and 3.48%, respectively. Thus, different information can be obtained by ESI-MS from GPC. However, the accuracy of the quantification needs to be further confirmed by other techniques. The absolute quantification of the ESI-MS data for functionalized system cannot be claimed. The assumption that the detector response factor of measured species was the same is not valid. From the data, it is clear that the trifunctionalized isocyanurate has a higher DRF than the monofunctionalized product. Therefore, the alkoxysilane group is responsible for the deviation in the mass spectra detector response factor. But, ESI-MS successfully identified each component, and yielded relative quantitative data for the system. In monofunctionalization reaction, the monofunctionalized product increased with solvent concentration. It corresponds well with the expected product ratio. The products of monofunctionalized isocyanurate without solvent and with 20% acetone are generally



Scheme 2. Crosslinking structure of polyurethane-silica ceramer.

Table 3
^{1}H and ^{13}C chemical shift (ppm) of trifunctionalized HDI Isocyanurate (**5**)

Proton	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
H1	1.22	C1	18.1
H2	3.81	C2	58.1
H3	0.62	C3	7.5
H4 and H6a	1.53–1.72	C4	23.6
H5 and H2a	3.12	C5 and C2a	39.8
H6	5.84	C1a	159.1
H3a	1.47	C3a	30.2
H4a and H5a	1.42–1.53	C4a	26.4
H7a	3.87	C5a	26.2
		C6a	27.5
		C7a	42.6
		C8a	148.8

insoluble, because of this higher percentage of the trifunctionalized product. The trifunctionalized isocyanurate is not even compatible with the parent HDI isocyanurate or compatible. As a consequence, the functionalized isocyanurate without solvent and with 20% solvent cannot be used in coating formulation. The monofunctionalized product prepared in 80% acetone contained mostly the mono-product, and consequently were reasonably soluble in most solvent. To achieve a high solid coating, this mono-product mixture could also be formulated into the parent HDI isocyanurate. Therefore, the dilution of the functionalization reaction is crucial with respect to the usage in coating formulation.

The alkoxysilane functionalized isocyanurate was synthesized with this approach to prepare a moisture curing unicoat coating system. The alkoxysilane functionalized isocyanurate will function as a coupling agent between organic and inorganic phases. Functionalization reaction gives chemical bond between the organic and inorganic portion, that is similar to alkoxysilane termination reaction for most of the reported ceramer preparation [11–15]. The research can be expanded to an organic and inorganic ceramer system, in which polyurethane functions as organic phase, siloxane as inorganic phase, and functionalized isocyanurate as coupling agent between the two phases. HDI isocyanurate and TEOS can be applied as oligomer and precursor, respectively. After moisture curing, the crosslinking structure of the ceramer can be described in Scheme 2. This system is being currently investigated in our research.

5. Conclusions

The alkoxysilane functionalized isocyanurate was prepared by the reaction of HDI isocyanurate and 3-aminopropyltriethoxysilane. The reaction was characterized by NMR experiments and ESI-MS. Increasing solvent content prefers to the formation of monofunctionalized isocyanurate in monofunctionalization reaction. The components of HDI isocyanurate were quantitatively evaluated using ESI-MS. The ESI-MS technique could not be used to quantitatively evaluate the alkoxysilane functionalized HDI isocyanurate.

Acknowledgements

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