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## Macromolecular Nanotechnology

## Understanding the role of clay silicate nanoparticles with organic modifiers in thermal curing of cyanate ester resin

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## ABSTRACT

The catalytic effect of montmorillonite clay nanoparticles containing organic modifiers such as quaternary phosphonium salts on cure mechanism of cyanate ester resin (RS-9D) was studied by differential scanning calorimetry (DSC) measurements, FT-IR and NMR spectroscopy as well as mass-spectrometry. The results show that the net catalytic effect arises from the presence of moisture associated with nanoclay particles where organic modifiers act as moisture transport agents. Possible mechanisms for cure pathways are discussed.

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## 1. Introduction

Current interest in cyanate ester resins arises from both their commercial applications [1–3] and their use in studies of non-linear step polymerization [4]. Cyanate ester resin-based materials offer relatively high  $T_g$ , low dielectric loss properties, and relative ease of processing [1]. This combination of properties makes the cyanate ester resins excellent candidates for a wide variety of aerospace applications where temperatures (>400 °C) can initiate material degradation.

In recent years there has been a significant amount of work looking at using layered clay silicate (montmorillonite) fillers to improve thermal stability and mechanical properties of a wide variety of thermoset and thermoplastic resin systems [5]. In the case of thermoset resins, there have been a number of instances reported in the literature that indicate the addition of these highly functionalized fillers can result in significant changes in the rate at which

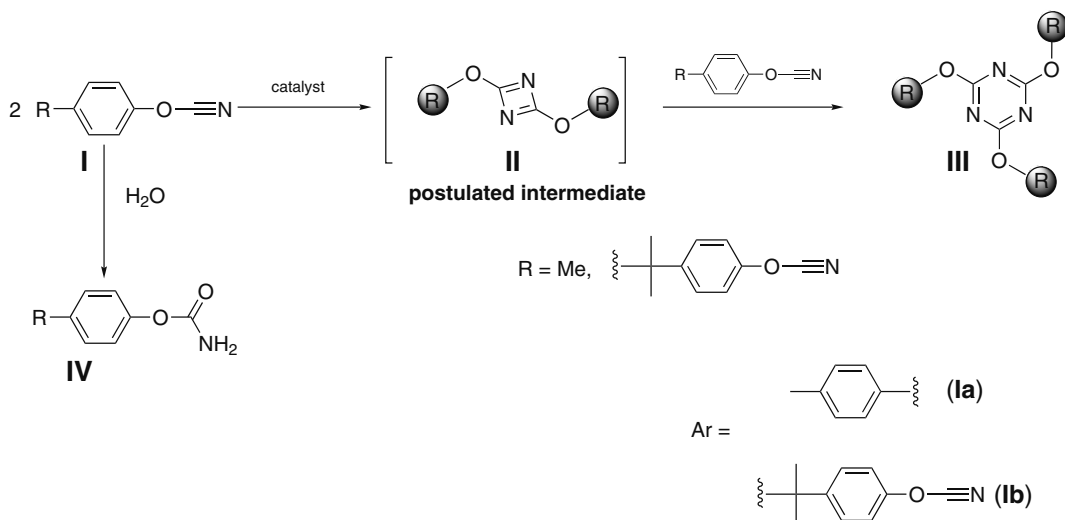
polymerization occurs, as well as the overall degree of polymerization [6]. It is vitally important to identify and understand the mechanisms by which these nanoscale fillers alter the polymerization kinetics of the resins in order to ensure that these materials are processed in a manner that yields consistent properties. The current effort focuses on model system of a commercially available cyanate ester resin (RS-9D) produced by YLA Inc., and a montmorillonite clay filler that has been functionalized with a patented phosphonium-based high temperature organic modifier [7].

The polymerization of cyanate esters via cyclotrimerization mechanism as shown in Chart 1 has become the commonly accepted pathway based on extensive research [2,3,8–11] conducted over the past two decades. This mechanism has been confirmed by FT-IR and NMR spectroscopic methods [9–16], as well as mass-spectrometry [17] and HPLC/GPC chromatography [18].

Despite some earlier NMR evidence for the intermediate **II** formation [18], no further proof has been found. It has also been confirmed that cyclotrimerization process requires the presence of catalyst: either Lewis acids metal

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**Chart 1.** Direct transformation pathways for cyanate esters.

salts such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  [19] or compounds which can act as a source of proton (e.g. water or phenols) [20]. In the latter case the mechanism of cyclotrimerization alters from direct reaction  $\text{I} \rightarrow \text{II} \rightarrow \text{III}$  and undergoes via a multiple step mechanism (Chart 2a).

Thus, the reaction proceeds through initial formation of carbamate **IV** ( $\text{H}_2\text{O}$  catalysis) or iminocarbonate **VI** (phenol **V** catalysis), whereas iminocarbonate **VI** can cyclotrimerize directly into triazine **III** with release of phenol molecule (Chart 2b) [1]. The mechanistic pathway from **IV** to **III** remains somewhat controversial. Several possible routes were proposed including decarboxylation of **IV** into amine **VII**, followed by formation of isourea type intermediate **VIII** [21]. Alternatively, by some accounts carbamate **IV** can decompose directly into phenol **V** and cyanuric acid, with **V** acting as a catalyst for further cyclotrimerization [22]. Another proposed route involves the reaction between **IV** and cyanate ester **I** to give intermediate **X**, which can react with additional molecule of **I** to give **III** and  $\text{H}_2\text{O}$  [13].

Since the pioneering work by Kamigaito et al. there has been a great deal of interest in polymer-organoclay nanocomposites [23]. The specific interest for these composites is due to their improved properties compared to the polymer matrix [24]. The addition of layered silicates (montmorillonite, hectorite or bentonite) was found to have a significant effect on mechanic properties improvement [25,26]; however, the role of the silicate clay in curing mechanism remained obscured. Recent work by Wooster et al. [27–29] on cyanate ester polymerization catalyzed by montmorillonite clay showed a considerable decrease of curing temperature measured by DSC techniques. Even more substantial decrease of curing temperature was found for the silicate nanoclays containing tertiary ammonium modifiers. Such behavior was attributed to quaternary ammonium salt decomposition at elevated temperatures, which generates amines – efficient catalysts for cyanate ester polymerization [1]. In the current work

we present our further investigations into the effect of organic modifiers in clay silicate nanoparticles (sodium montmorillonite) on the thermal curing behavior of a cyanate ester resin. We also evaluate the possibility of the formation of derivatives **IV–X** by applying NMR spectroscopy and mass-spectrometry techniques to small molecules model systems.

## 2. Experimental

### 2.1. Materials and preparations

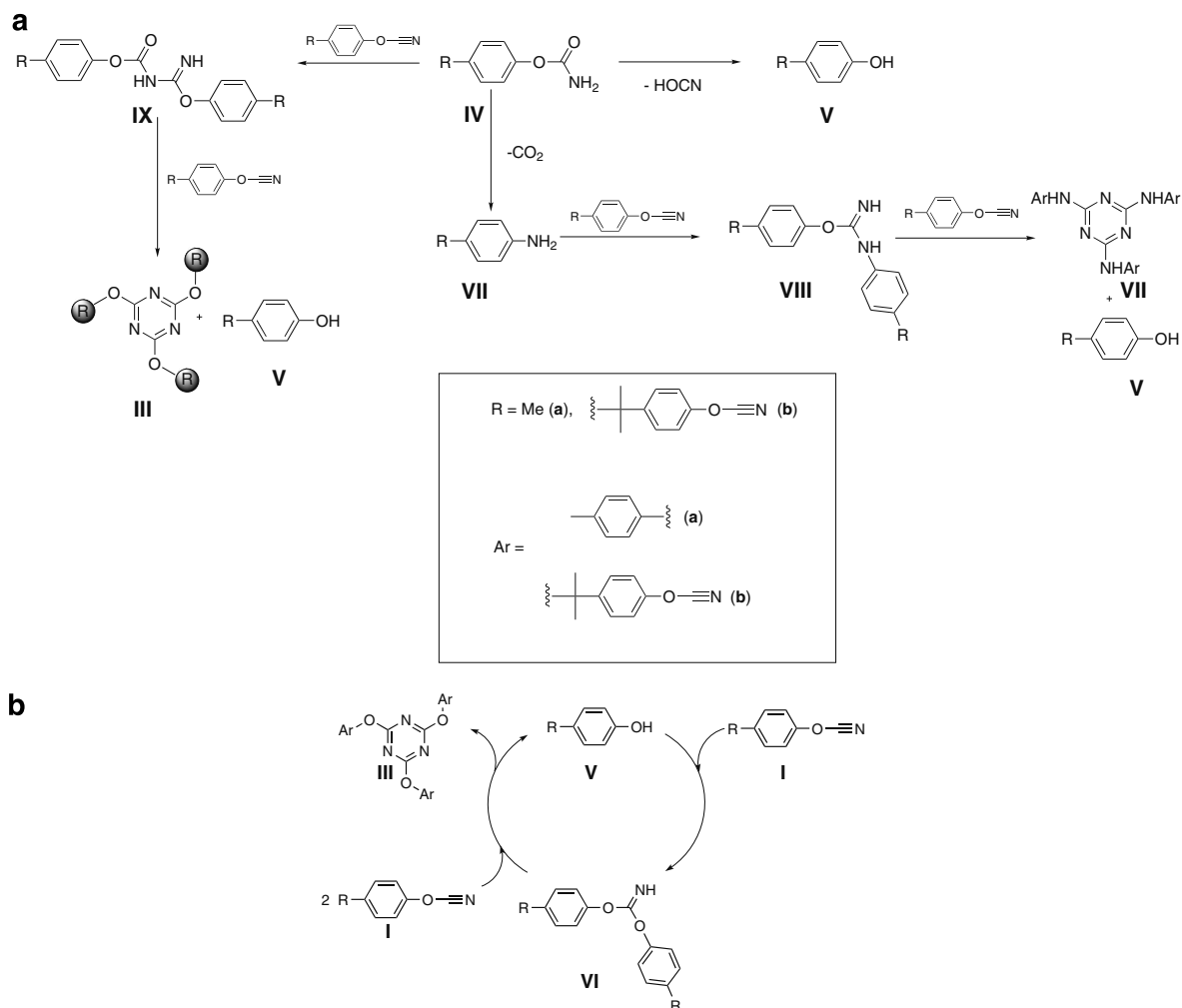
The base resin was a proprietary modified polycyanate resin blend (RS-9D,  $T_g > 350^\circ\text{C}$ ). The nanoclay used in this study was montmorillonite surface treated with tetraphenyl phosphonium bromide. The nanoclay was prepared via ion exchange reactions of sodium montmorillonite with tetraphenyl phosphonium bromide and blended into RS-9D at 2.5 and 5 wt.% by Triton Systems Inc.

Solvents (dry diethyl ether, tetrahydrofuran, hexane, deuteriochloroform, ethanol) and reagents [*p*-cresol (98%), triethylamine (98%), cyanogen bromide (97%), *p*-toluidine (99%), tetraphenylphosphonium bromide (98%), cobalt (III) acetylacetonate (97%)] were purchased from Aldrich or Acros and were used as supplied. *p*-Tolylcyanate ester was prepared according to the literature method [30] and used as 20 wt.% solution in diethyl ether.

Infrared spectra were recorded on a Nicolet Magna-860 Fourier Transform spectrometer ( $4\text{ cm}^{-1}$  resolution) using KBr discs. NMR spectra were recorded using a Bruker AC-300 spectrometer ( $^1\text{H}$  at 300.13 MHz and  $^{13}\text{C}\{^1\text{H}\}$  at 75.47 MHz, referenced to  $\text{SiMe}_4$ ). All spectra were recorded at ambient temperatures.

Chemical ionization (CI) mass-spectrometry measurements were conducted on an AutospecQ instrument.

Calorimetric measurements were performed using a DSC-Q100 differential scanning calorimeter using 40  $\mu\text{l}$



aluminum pans. Samples of cyanate ester resin were heated at 2 °C/min from 50 to 300 °C.

## 2.2. Synthesis

### 2.2.1. Cyanate ester resin curing

Each cyanate ester resin (RS-9D) blend with tetraphenylphosphonium modified montmorillonite clay nanoparticles or neat cyanate ester resin (10 g) were cured in the oven at 120 °C for 1 h followed by the steps at 150 °C for 1 h, at 180 °C for 30 min, and the postcure stage at 200 °C for an additional 2 h. Samples of the resin were taken at each cure step and monitored by FT-IR spectroscopy to estimate the cure completion.

### 2.2.2. Synthesis of triazene **IIIa** ( $R = \text{Me}$ )

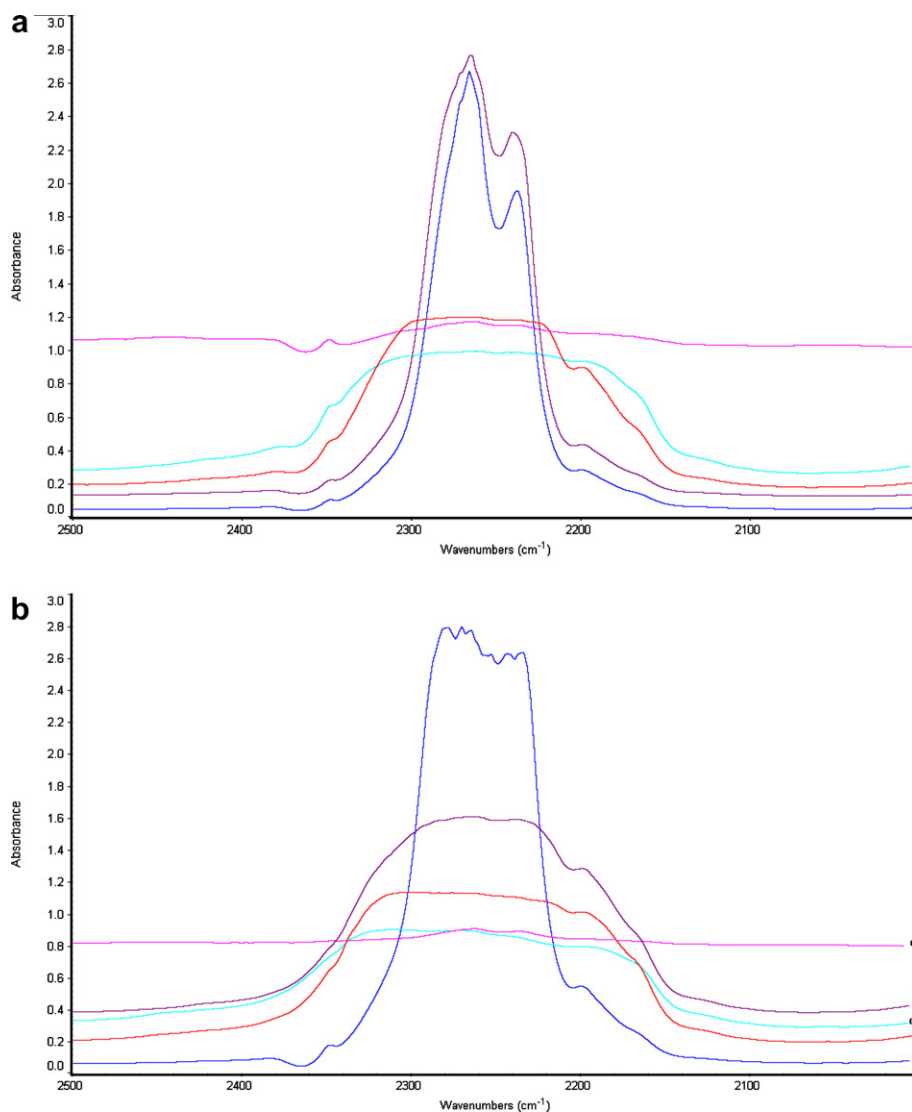
A 20 wt.% solution of *p*-tolyl cyanate ester (10 g) in diethyl ether (15 mmol) was concentrated to ca. 3 mL volume, whereupon cobalt(III) acetylacetonate (0.05 g, 0.14 mmol) was added and the reaction mixture was

heated at 150 °C for 4 h. The residue was recrystallized from ethanol (3 mL) to yield 1.94 g (97%) of triazene **IIIa**.

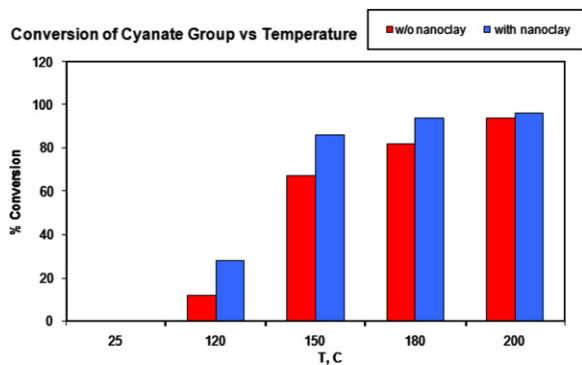
$^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  2.38 (s, 3H,  $\text{CH}_3$ ), 7.01, 7.27 (d, 2H,  $J = 6.5$  Hz,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  24.4 ( $\text{CH}_3$ ), 124.5 130.0, 136.2.0, 149.3 ( $\text{C}_6\text{H}_4$ ), 173.4 ( $\text{C}=\text{N}$ ).  $M/z$ : 400 ( $\text{MH}^+$ , 100%).

### 2.2.3. Synthesis of carbamate **IVa** ( $R = \text{Me}$ )

A 20 wt.% solution of *p*-tolyl cyanate ester (10 g) in diethyl ether (15 mmol) was concentrated to ca. 3 mL volume and diluted by tetrahydrofuran (10 mL), whereupon water (2 mL) was added and the reaction mixture was stirred overnight at ambient temperature (27 °C). Solvents were removed under vacuum and the residue was rinsed with hexane (20 mL) to yield carbamate **IVa** (2.13 g, 94%).  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H,  $\text{CH}_3$ ), 5.16 (br s, 2H,  $\text{NH}_2$ ), 7.18, 7.36 (d, 2H,  $J = 6.8$  Hz,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  22.8 ( $\text{CH}_3$ ), 122.4 128.5, 137.0, 148.4 ( $\text{C}_6\text{H}_4$ ), 155.6 (CO).  $M/z$ : 151 ( $\text{M}^+$ , 100%).



**Fig. 1.** FT-IR comparison of cyanate ester resin cure without (top) and with (bottom) tetraphenylphosphonium modified nanoclay: (a) before the cure cycle; (b) 1 h at 120 °C; (c) 1 h at 150 °C; (d) 0.5 h at 180 °C; (e) 2 h at 200 °C.



**Fig. 2.** Conversion of cyanate group versus time in a cyanate ester resin followed by FT-IR spectroscopy.

#### 2.2.4. Synthesis of isourea **VIIIa** ( $R = Me$ )

To a 20 wt.% solution of *p*-tolyl cyanate (10 g) in diethyl ether (15 mmol), was added *p*-toluidine (1.77 g, 16.5 mmol) and the reaction mixture was stirred overnight at ambient temperature (26 °C). All volatiles were removed under vacuum and the residue was rinsed with hexane (20 mL) to yield isourea **VIIIa** (3.14 g, 87%).  $^1\text{H}$  (CDCl<sub>3</sub>)  $\delta$  2.14, 2.25 (s, 3H, CH<sub>3</sub>), 5.37 (br s, 1H, —NH—), 6.58 (br s, 1H, =NH), 6.84, 7.07, 7.14, 7.30 (d, 2H,  $J = 6.4$  Hz, C<sub>6</sub>H<sub>4</sub>).  $^{13}\text{C}\{^1\text{H}\}$  (C<sub>6</sub>D<sub>6</sub>)  $\delta$  21.5, 23.1 (CH<sub>3</sub>), 120.7, 121.6, 126.6, 129.2, 135.9, 138.4, 150.0, 154.0 (C<sub>6</sub>H<sub>4</sub>NH and C<sub>6</sub>H<sub>4</sub>O), 159.3 (C=NH).  $M/z$ : 241 (MH<sup>+</sup>, 100%).

#### 2.2.5. Thermolysis studies of intermediates **IVa** and **VIIIa** ( $R = Me$ ). General procedure

Each of **IVa** and **VIIIa** ( $R = Me$ ) (2 g) was heated in a sealed glass tube at 150 °C in the oven for 2 h, whereupon

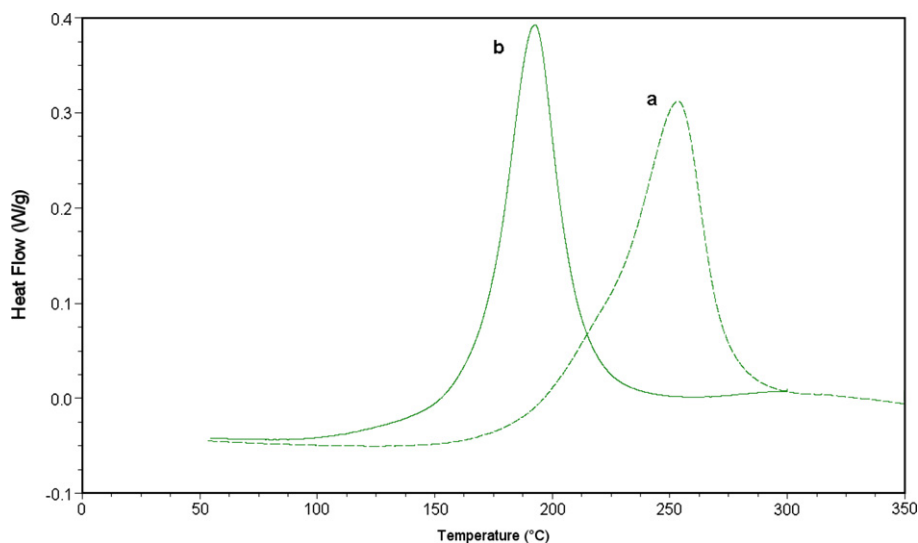


Fig. 3. DSC thermograms for cyanate ester clay systems: (a) neat resin; (b) tetraphenylphosphonium clay.

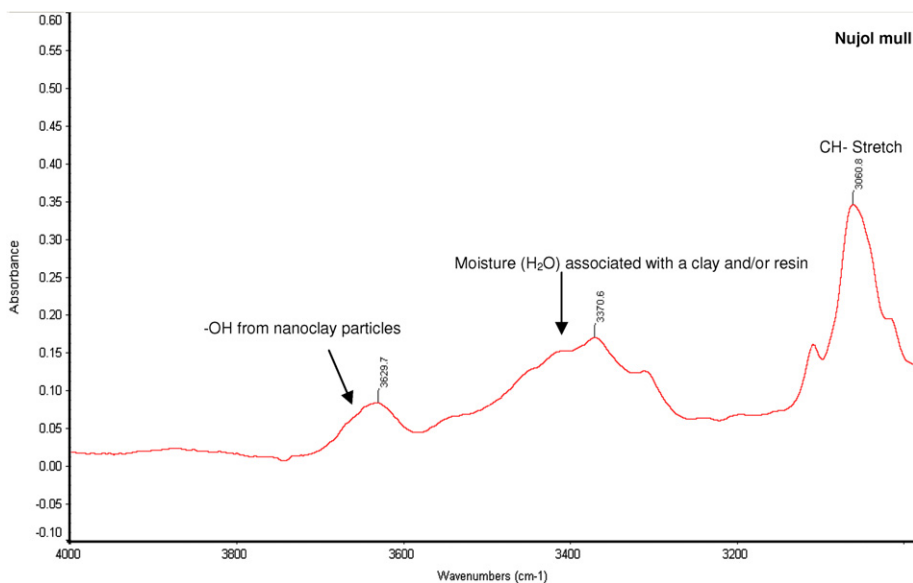


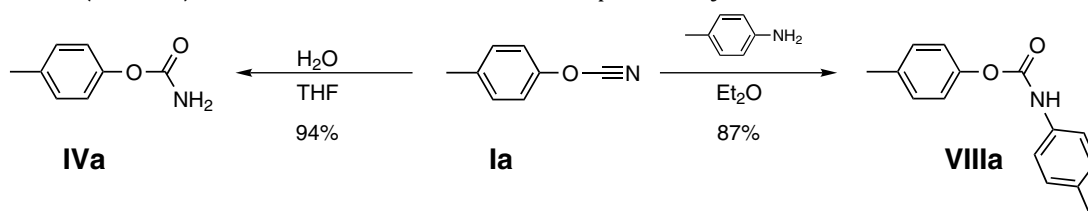
Fig. 4. —OH/H<sub>2</sub>O IR stretches in uncured cyanate resin/clay mixture.

samples were taken, dissolved in CDCl<sub>3</sub> (1 mL) and analyzed by <sup>13</sup>C{<sup>1</sup>H} NMR and mass-spectrometry.

#### 2.2.6. Thermolysis studies of cyanate ester **1a** (*R* = Me)

A 20 wt.% solution of *p*-tolyl cyanate ester (10 g) in diethyl ether (15 mmol) was concentrated to ca. 3 mL

volume, followed by heating in a sealed glass tube under nitrogen either with hydrated Ph<sub>4</sub>PBrx0.7H<sub>2</sub>O, anhydrous Ph<sub>4</sub>PBr or as a neat compound. At certain times and temperatures samples were taken, dissolved in CDCl<sub>3</sub> (1 mL) and analyzed by <sup>13</sup>C{<sup>1</sup>H} NMR and mass-spectrometry.



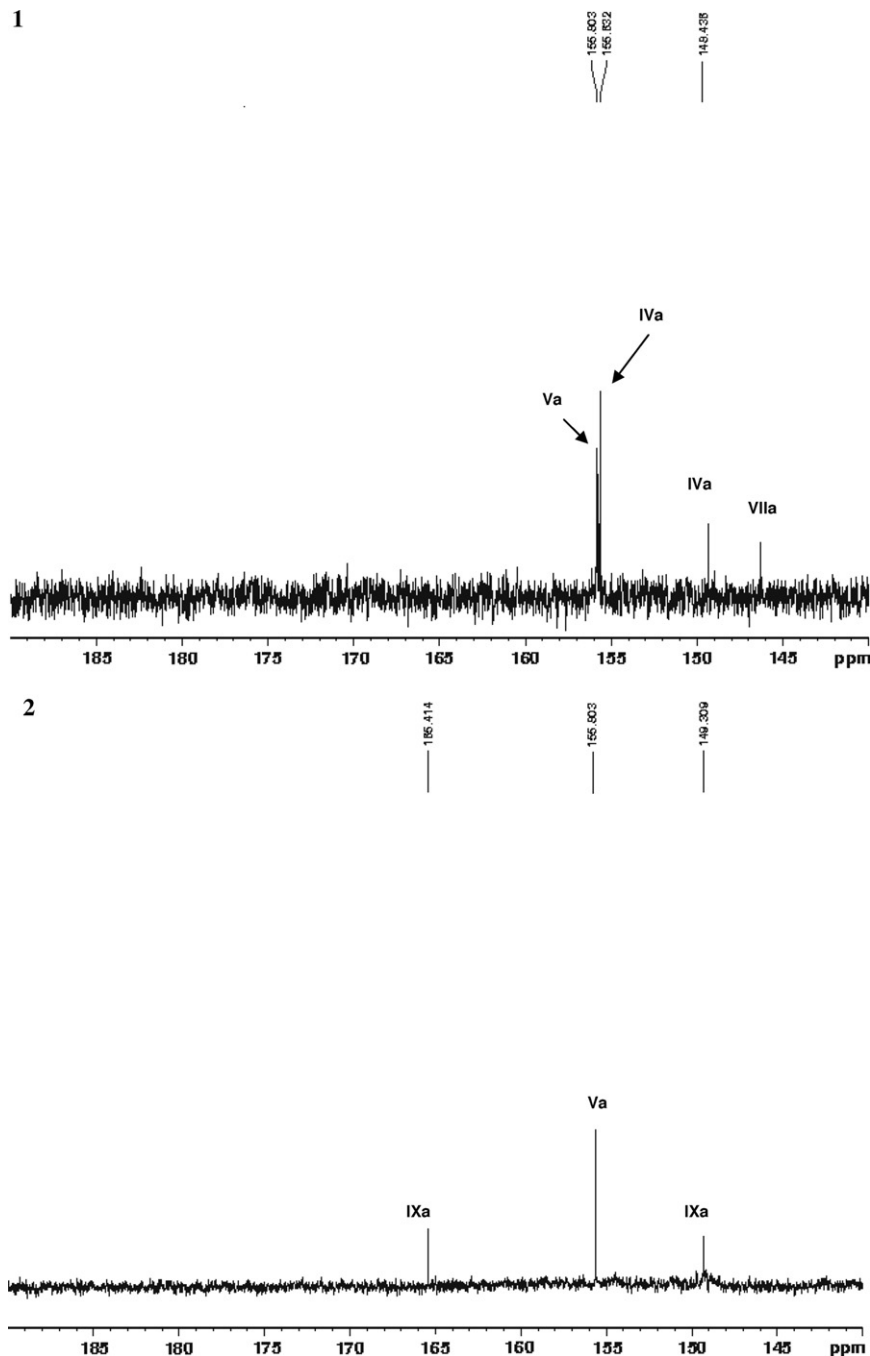
Scheme 1. Synthesis of authentic intermediates **IVa** and **VIIIa**.

### 3. Results and discussion

#### 3.1. FT-IR and calorimetric measurements

Following the earlier results [27–29] the study of cure behavior for cyanate ester resins containing silicate clay nanoparticles with quaternary aromatic phos-

phonium salts was sought in order to avoid Hoffmann-type elimination [31] proposed for the quaternary ammonium analogues [27]. The cure process of the cyanate ester resin (RS-9D) with and without organic tetraphenylphosphonium modified montmorillonite was followed by FT-IR spectroscopy, and results are shown on Fig. 1.



**Fig. 5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the 140–190 ppm region for: (1) thermal decomposition of IVa; (2) thermal decomposition of VIIa; (3a) thermolysis of Ia was heated at with a catalytic amount of  $\text{Ph}_4\text{PBr}\cdot 0.7\text{H}_2\text{O}$  after 20 min at 150 °C; (3b) thermolysis of Ia was heated at with a catalytic amount of  $\text{Ph}_4\text{PBr}\cdot 0.7\text{H}_2\text{O}$  after 2 h at 150 °C; (3c) thermolysis of Ia was heated at with a catalytic amount of  $\text{Ph}_4\text{PBr}\cdot 0.7\text{H}_2\text{O}$  after at 2 h 200 °C; (4a) authentic IIIa; (4b) authentic IVa; (4c) authentic VIIa.

The direct comparison of two IR kinetic stack plots confirms the catalytic effect of tetraphenylphosphonium modified nanoclay on the cyanate ester resin cure behavior by showing nearly twofold of the initial rate increase (for the temperature range between 25 and 120 °C). The overall conversion of the cyanate ester monomer (calculated by

relative integrations of  $\text{—OCN}$  group absorbance at  $2260\text{ cm}^{-1}$  in IR spectra) versus the temperature is illustrated on Fig. 2. The diagram shows the considerable increase in cyanate ester monomer consumption (ca. 20%) at earlier cure stages for the system containing tetraphenyl phosphonium modified clay.

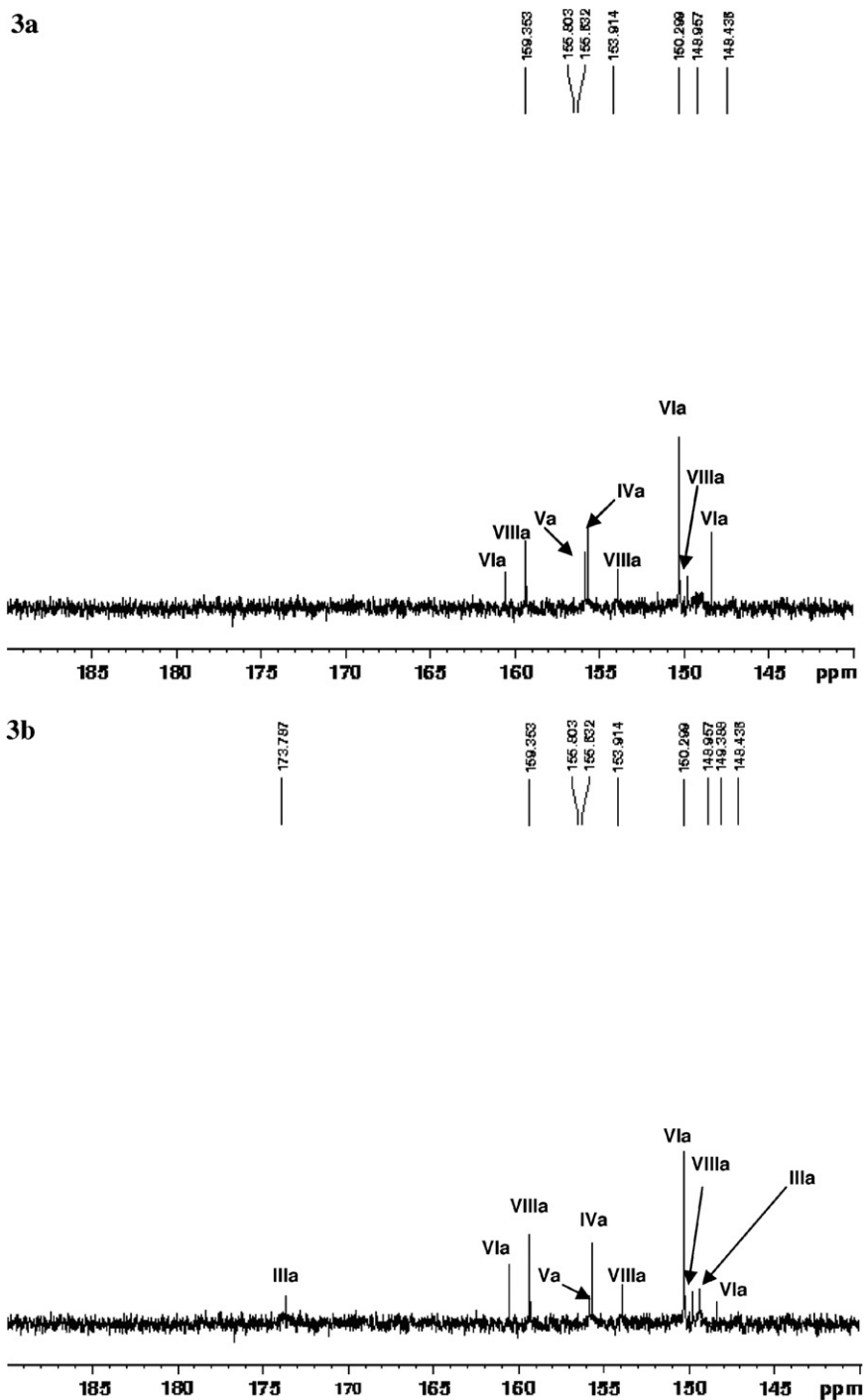


Fig. 5 (continued)

The series of DSC experiments for the same set of resins also exhibit a significant drop in a cure temperature indicative of a lower activation barrier for the process (Fig. 3). Overall cure heat for the resin without nanoclay is 458 J/g and decreases slightly to 429 J/g in a presence of tetraphenyl phosphonium modified nanoclay. This corresponds to the 62 °C decline in a peak cure temperature (from 254 °C for neat resin to 192 °C in a presence of modified nanoclay). A similar decline in cure heat was observed for a neat cyanate ester resin (298 °C, [27]) versus cyanate ester/montmorillonite blend suggesting that the presence of the nanoclay contributes to the overall catalytic effect

on the cyanate ester resins. It has been proposed that the catalytic effect may arise from moisture associated with nanoclay particles and/or Bronsted acid [Si–OH, Al–OH] surface hydroxyl groups present on the edges of the aluminosilicate particles. The latter hypothesis was also supported by examining the IR spectrum of uncured cyanate ester resin with nanoclay particles, which shows two distinct absorbance peaks at 3371 and 3630  $\text{cm}^{-1}$  corresponding to the moisture ( $\text{H}_2\text{O}$  molecules) and –OH groups, (from the aluminosilicate edge hydroxyls), respectively (Fig. 4).

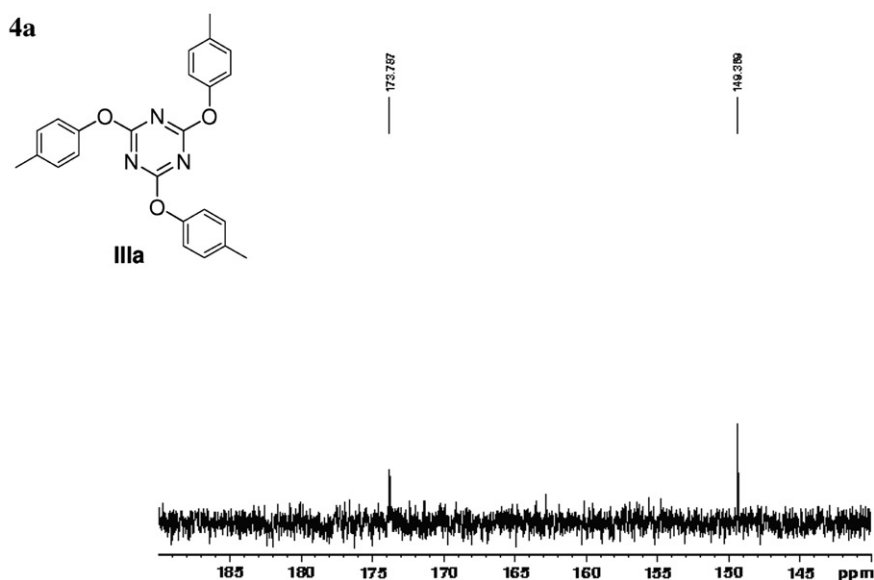
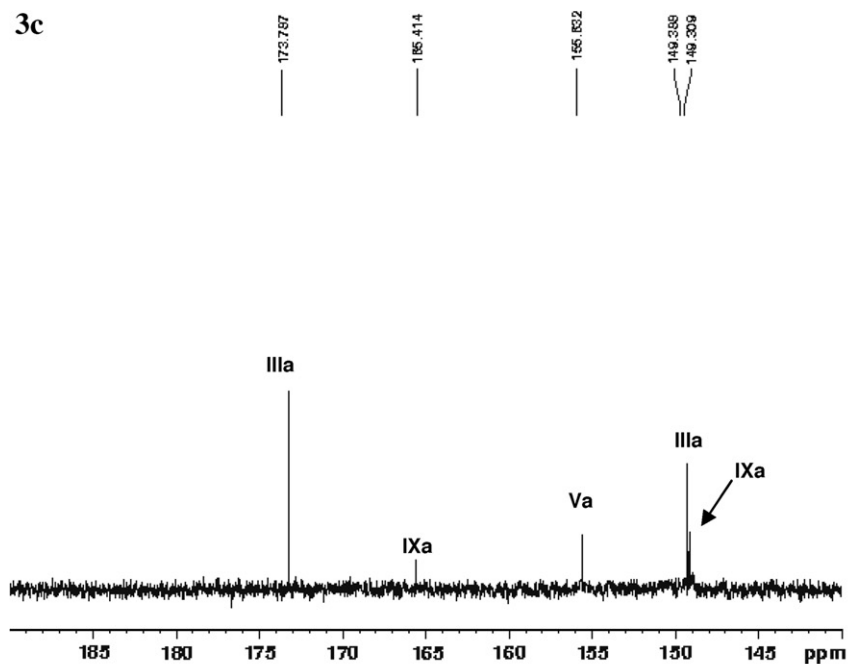
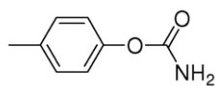


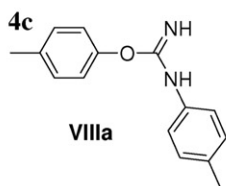
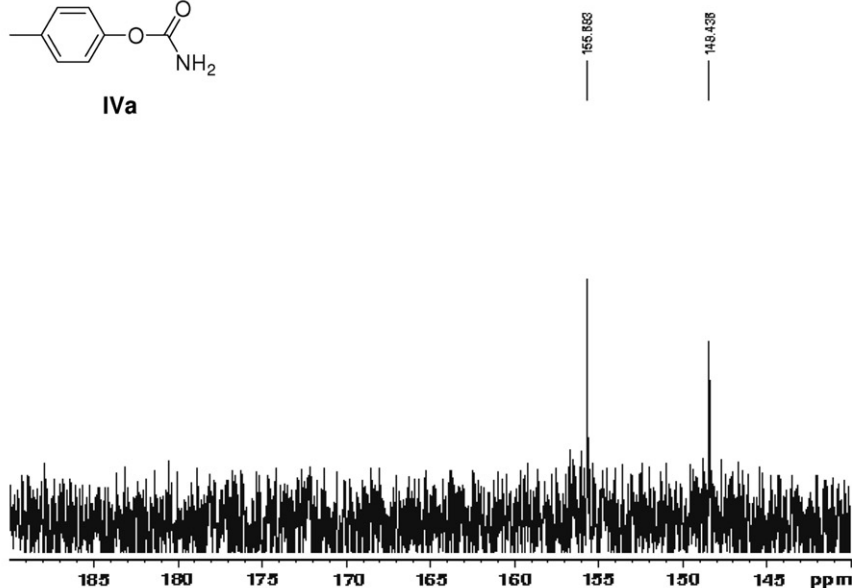
Fig. 5 (continued)



4b



IVa



VIIIa

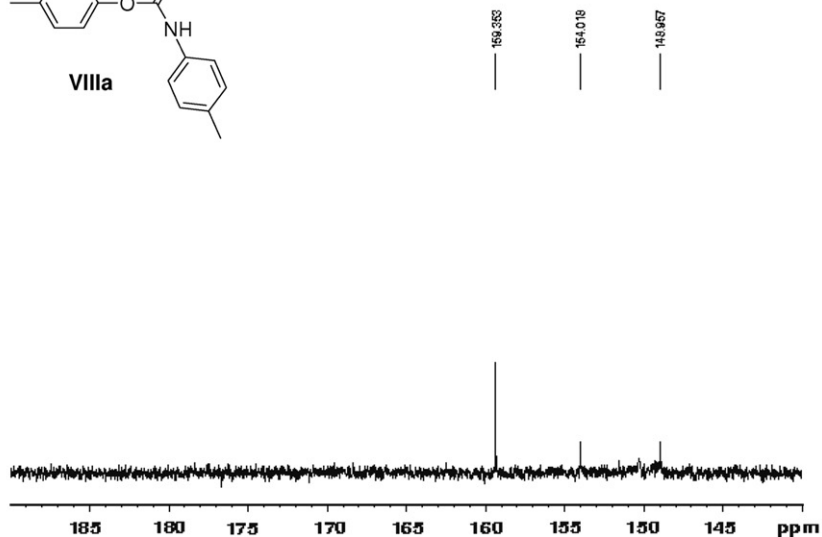


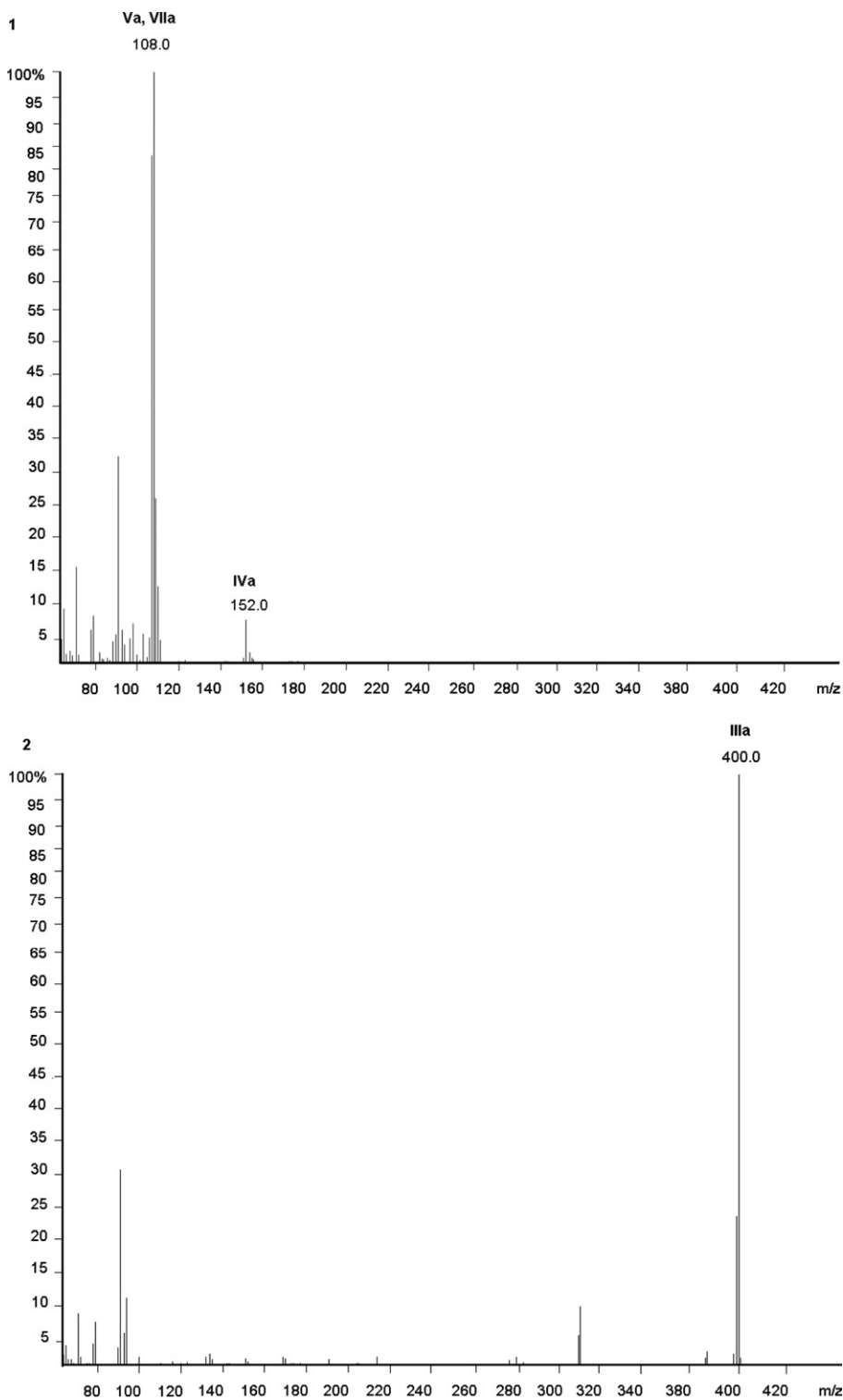
Fig. 5 (continued)

Although such additional decline in both cure temperature and cure heat for cyanate ester resins containing aluminosilicate nanoparticles with organic modifiers is reminiscent of earlier precedents reported in the literature [27]; the process occurs through a different mechanism proposed for ammonium-based modifiers, since the Hoffmann-type elimination for tetraarylphosphonium salts can be completely ruled out [31]. The data presented clearly suggest the existence of a pre-cure stage (prior to triazine formation) occurring at temperatures below 150 °C in the presence of organic modified clay. Hence, a mechanistic study using a model small molecule system was carried

out to establish the possible cure pathway of cyanate ester resins in the presence of nanoclays that do not undergo Hoffmann elimination.

### 3.2. Mechanistic studies

In order to assess the nature of the cure pathway resulting from the organically modified nanoclays net catalytic effect on the curing of cyanate ester resin, the series of experiments were undertaken with *p*-tolylcyanate ester [30] as a convenient small molecule to model the behavior of dicyanate ester monomer. Anhydrous Ph<sub>4</sub>PBr was



**Fig. 6.** CI mass-spectra for: (1) thermolysis of **IVa**; (2) thermolysis of **VIIa**; (3a) thermolysis of **Ia** with a catalytic amount of  $\text{Ph}_4\text{PBr} \cdot 0.7\text{H}_2\text{O}$  after 20 min; (3b) thermolysis of **Ia** with a catalytic amount of  $\text{Ph}_4\text{PBr} \cdot 0.7\text{H}_2\text{O}$  after 1 h.

exposed to air overnight; the total weight increase was recorded at 2.4%, which corresponds to a formulation ca.  $\text{Ph}_4\text{PBr} \cdot 0.7\text{H}_2\text{O}$  [32]. Both anhydrous and hydrated  $\text{Ph}_4\text{PBr}$

(2.5 wt.%) were heated with a monomer **Ia** ( $R = \text{Me}$ , Chart 1) at 150 °C, and samples were taken from each reaction at certain moments and examined by  $^{13}\text{C}\{^1\text{H}\}$  NMR spec-

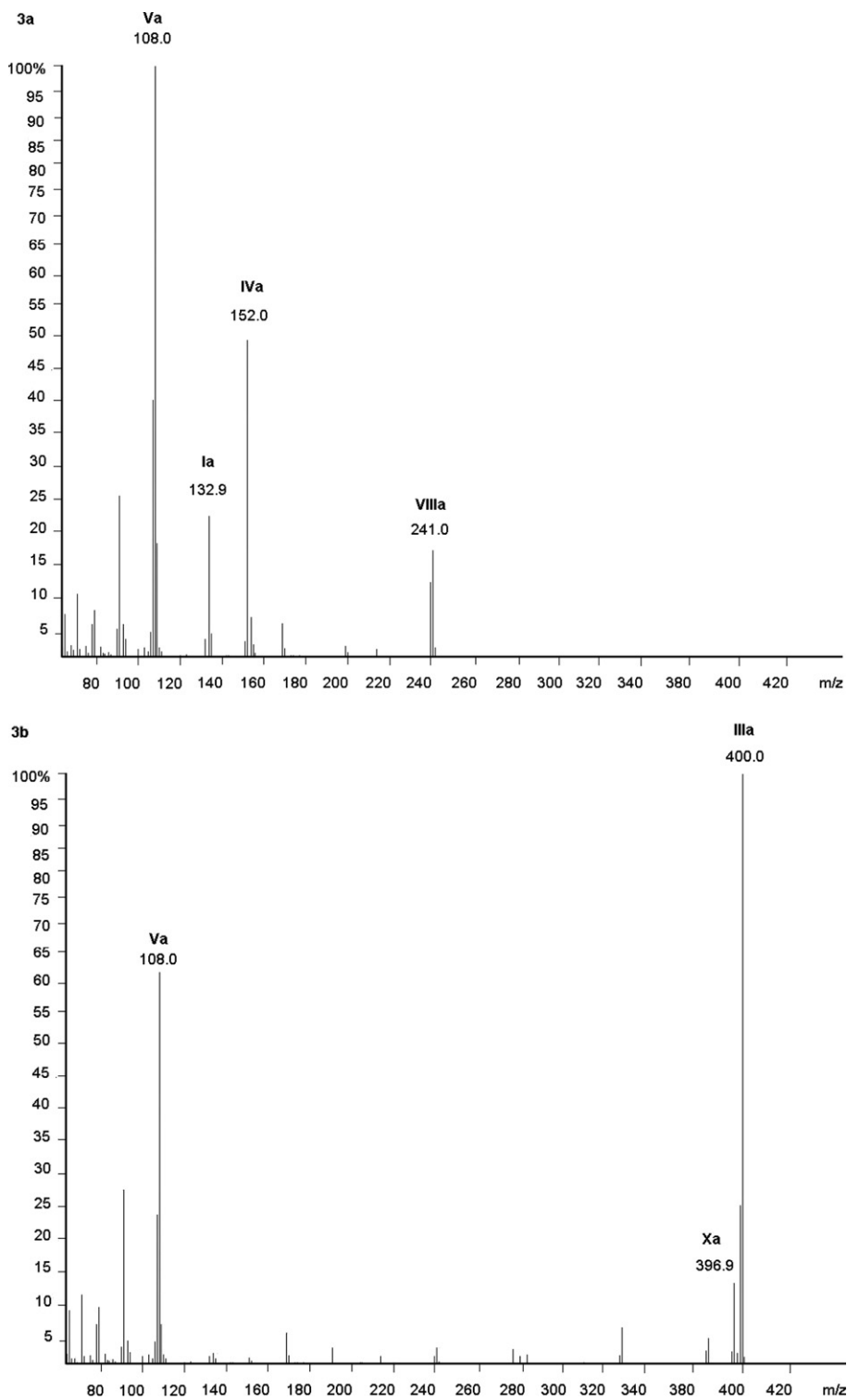


Fig. 6 (continued)

troscopy and CI mass-spectrometry. In a control experiment neat **1a** was heated under similar conditions, and the reaction was monitored by  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy after the same intervals as for **1a**/phosphonium salt mix-

ture. To establish the nature of intermediates on firm bases, authentic compounds **IVa** and **VIIIa** were synthesized as shown on Scheme 1 and characterized by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy and CI mass-spectrometry.

Both compounds **IVa** and **VIIIa** were then heated in a sealed tube at 150 °C; reaction mixtures were taken into CDCl<sub>3</sub>, and analyzed by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and mass-spectrometry. The results were further compared to the spectroscopic data obtained for the thermal studies of both neat **la** and **la**/Ph<sub>4</sub>PBrx0.7H<sub>2</sub>O blend in order to provide a reliable peak assignment. Whereas the <sup>1</sup>H NMR spectroscopy data were not conclusive, the analysis of the region between 140 and 190 ppm for <sup>13</sup>C{<sup>1</sup>H} NMR spectra (quaternary carbon region) proved to provide the best interpretation for the mixtures compositions. The corresponding spectra expansions with peaks assignment are presented on Fig. 5.

Thus, <sup>13</sup>C{<sup>1</sup>H} NMR spectra **1** and **2** (Fig. 5) and mass-spectra **1** and **2** (Fig. 6) confirm the decomposition pathways for the key intermediates **IVa** and **VIIIa** to form a mixture of *p*-cresol **Va** and *p*-toluidine **VIIa**, and (tris-*p*-tolyl)melamine **IX** [33,34] and *p*-cresol **Va**, respectively. The formation of **Va** in both cases is crucial for understanding the mechanism of moisture-based catalysis during cyanate ester curing process; hence, phenols were proven to be one of the most efficient Lewis acid catalysts for such reactions [20].

When model compound **la** was heated at 150 °C with a catalytic amount of Ph<sub>4</sub>PBrx0.7H<sub>2</sub>O the buildup of the isourea **VIIIa** type intermediate along with carbamate **IVa** were observed by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy as shown on spectra **3a** and **3b**, recorded after 20 min and 2 h for **la**/Ph<sub>4</sub>PBrx0.7H<sub>2</sub>O mixture. Also, the surge of iminocarbonate intermediate **VIa** becomes noticeable with resonances at 160.5 and 149.4 ppm (Fig. 4) [18]. The latter intermediate could arise from the reaction between cyanate ester monomer **la** and *p*-cresol **Va** upon thermal decomposition of **IVa**. The assignment was made by direct comparison of the chemical shifts to those observed in authentic samples of **IIIa**, **IVa** and **XIIIa** (spectra **4a–4c**, Fig. 5). The latter spectra exhibit resonances at 173.8 (**IIIa**), 159.4 (**VIIIa**), and 155.7 ppm (**IVa**), which correspond to –C(O)=X (X = O, NH) quaternary carbon group. The resonances at the range of 148–150 ppm were assigned to the C–O *ipso*-carbon of a phenyl ring. The nature of compounds **IVa**, **Va**, **VIIIa** was also confirmed by CI mass-spectrometry showing the molecular peaks at *M/z* of 152 (**IVa**, MH<sup>+</sup>, 64%), 108 (**Va**, M<sup>+</sup>, 100%), and 241 (**VIIIa**, MH<sup>+</sup>, 26%) (mass-spectrum **3a**, Fig. 6). No imidocarbonate type intermediate **Xa** (Chart 2) proposed earlier by some accounts [13] was detected by spectroscopic methods. Also, no further changes were observed when the reaction mixture was heated for additional 2 h at 150 °C bringing the total heat time to 4 h. Further heating the mixture at 200 °C for 4 h led intermediates **IVa** and **VIIIa** to convert into a mixture of triazine **IIIa**, *p*-cresol **Va** and **IXa** (Fig. 4, spectrum **3c**). Thus, in <sup>13</sup>C{<sup>1</sup>H} NMR spectrum the peaks at 173.8 and 165.4 ppm were assigned to the compounds **IIIa** and **IXa**, respectively. The presence of **IIIa**, **Va** and **IXa** was also supported by CI mass-spectrometry as shown on mass-spectrum **3b**, Fig. 6 [*M/z* of 400 (**IIIa**, MH<sup>+</sup>, 100%), 397 (**IXa**, MH<sup>+</sup>, 13%), and 108 (**Va**, MH<sup>+</sup>, 62%)]. In a control experiment, when neat **la** was heated under similar conditions without a phosphonium salt or with

anhydrous Ph<sub>4</sub>PBr no detectable transformations of the cyanate ester molecule were detected. Although no amine intermediate **VIIa** was observed by spectroscopic methods in all experiments, we speculate that this could be attributed to the fact that such species once formed would immediately react with a cyanate ester molecule [31]. Moreover, the formation of isourea **VIIIa**, which occurs as a product from the reaction of cyanate ester and amine, also confirms that amine **VIIa** should exist as a short-living intermediate. These experiments simulate the important role played by moisture impurities associated with organic modifiers such as quaternary phosphonium salts in cyanate ester curing process. Further investigations are on the way to understand the effect of organic clay modifiers on the mechanical properties of polycyanate esters and polycyanate-ester-based composite materials. Also, we are evaluating the role of surface hydroxyl groups on montmorillonite nanoparticles in overall cyanate ester resin cure process.

#### 4. Conclusions

The data reported here significantly advance our understanding of the role of organically modified clay nanoparticles in a cyanate ester resin cure process. Overall, their presence in a cyanate ester resin leads to a significant decrease of both cure heat and temperature as well as enhance in initial cure rate almost twofold. Thus, it has been shown that the traces of moisture associated with organic modifier molecule can alter the polymerization mechanism by forming a carbamate intermediate **IV**, which then can undergo thermal decomposition by the dual pathway: either forming a molecule of phenol **V** and cyanuric acid (HOCN) or undergo decarboxylation to yield an amine **VII**, which further reacts with a molecule of a cyanate ester to give a isourea derivative **VIII**, followed by thermal decomposition of **VIII** into cyclic melamine-type product **IX** and phenol **V**. The formation of phenolic species **V**, which are known to catalyze cyanate ester resin cure, ultimately attributes to the net catalytic effect of organically modified nanoclay. The nature of intermediates **IV**, **V**, and **VIII** as well as the final cyclic products **III** and **IX** were confirmed by NMR spectroscopy and mass-spectrometry techniques. We also speculate that the moisture could directly arise from montmorillonite clay nanoparticles with phosphonium modifier acting as a carrier of water molecule from heterogeneous solid particles into the resin. There is also a distinct possibility that surface hydroxyl groups on montmorillonite nanoparticles can engage directly into the cure process. As has been shown in prior work [27], non-modified montmorillonite clay particles are capable of catalyzing the cyanate resin cure, although not nearly as effectively as their organically modified analogs. Hence, we conclude that organic modifiers in silicate nanoclays play a pivotal role in both reduction of the cyanate ester resin cure temperature and enhancement of the cure rate by associating with water and/or acting as moisture carrier into the resin. The results obtained are in good accord with previously postulated mechanism for the cyanate ester cure.

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