

# Cyanuric Acid–Epichlorohydrin Prepolymers

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**ABSTRACT:** In this study, we investigated the reaction of cyanuric acid and epichlorohydrin (ECH).  $\text{SnCl}_4$  was used as a catalyst. Several reaction conditions were tested, and the products were analyzed by means of Fourier transform infrared and  $^1\text{H-NMR}$  spectroscopy, hydroxyl group content, molar mass, elemental and thermal analysis, viscosity, and density. ECH reacted with the amine groups of the cyanuric acid ring to form lateral chains that contained chloroalkyl and hydroxyl end groups. Full substitution of the amine groups was observed in all of the synthesized products. The solvent used in the synthesis was found to be very important for the structure of the final prepolymers. When *N,N*-di-

methylformamide was used, relatively low-molar-mass prepolymers of cyanuric acid and ECH were obtained. When solvents with low dielectric constants were used, no reaction with cyanuric acid was observed. The prepared prepolymers were thermally stable up to 160°C. At this temperature, degradation started via the lateral chains. The viscosity of the products decreased as the ECH–cyanuric acid ratio increased, whereas the density remained basically constant. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3684–3691, 2006

**Key words:** oligomers; polyurethanes; star polymers

## INTRODUCTION

Cyanuric acid is a well-known compound with a 1,3,5-*s*-triazine ring in its structure. The 1,3,5-*s*-triazine ring is present in cyclo-1,3,5-trimethylene-2,4,6-trinitramine, a widely used energetic material, and in new materials such as 4,6-dinitramino-1,3,5-triazine-2(1H)-one.<sup>1</sup> It confers good properties to these compounds, namely, a high density and thermal stability. Cyanuric acid and its derivatives are used as fuel additives to reduce the nitrogen oxide formation in the escape gases of internal combustion engines.<sup>2</sup> This type of compound also finds applications in low-toxicity and enhanced-burning-rate propellants for airbags<sup>3,4</sup> and low-temperature gas generators.<sup>5</sup> The reaction of cyanuric acid with epichlorohydrin (ECH) in the presence of basic catalysts yields tris(2,3-epoxypropyl)isocyanurate.<sup>6,7</sup> This compound is widely used, especially in electronics and films.<sup>8,9</sup>

In this study, we synthesized prepolymers from cyanuric acid and ECH in the presence of a solvent and the catalyst  $\text{SnCl}_4$ . The synthesized prepolymers were characterized by several techniques. We carried out this study having in view the possible use of the prepolymers as precursors of energetic materials. In this context, it was important to study the possible substitution of the chlorine atoms by azide or other

energetic groups to give energetic prepolymers with the 1,3,5-*s*-triazine ring in their structure. This part of the study will be reported in a forthcoming article.

## EXPERIMENTAL

### Materials and equipment

The following reagents were used: cyanuric acid (>98%), ECH (99%), and propylene glycol (>99.5%) were obtained from Aldrich (St. Louis, MO); tin (IV) chloride fuming and dichloromethane (99.8%) were obtained from Riedel-de-Haen (Hanover, Germany); trifluoroacetic acid (99.5%) was received from Panreac (Barcelona, Spain), *N,N*-dimethylformamide (DMF; 99%) was obtained from Fluka (St. Louis, MO); and toluene (99.5%) was obtained from Merck (New Jersey).

Fourier transform infrared spectra were obtained on a Nicolet 750 instrument with a Golden Gate attenuated total reflection accessory from Specac, where the samples were analyzed as prepared. The resolution was 4, and the number of scans was 64. NMR spectra were obtained on a Varian (Palo Alto, CA) Unity 500 NMR spectrometer operating at 499.824310 MHz and at 25°C with a 5-mm broad band probe. Dimethyl sulfoxide ( $\text{DMSO-d}_6$ ; 99.99% Deuterium) from Riedel-de-Haen was used as solvent.

Hydroxyl group content was measured by the acetic anhydride in pyridine method, with a 1-h reaction time at 98°C.<sup>10</sup>

For the chromatographic studies, the following equipment was used: a Knauer (Berlin, Germany) des-

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**TABLE I**  
**Reagents and Their Respective Amounts Used in the Syntheses of the Prepolymers**

	PC14	PC15	PC17	PC13	PC18	PC19	PECH1-PECH2	SOLV1-SOLV8
Cyanuric acid (mmol)	199.86	168.14	117.11	91.34	91.40	54.54		7.20
DMF (mL)	109.0	92.0	64.0	58.9	59.0	40.0		
Solvent (mL) <sup>a</sup>							8.0	9.0
ECH (mmol)	1000	1682	1754	1883	1880	2199	601	639
Propylene glycol (mmol)							12.5	
SnCl <sub>4</sub> (mmol)	6	10	11	11	28	28	0.85	0.72
CF <sub>3</sub> COOH (mmol)							3.79	3.53
ECH-cyanuric acid (mol/mol)	5.0:1	10.0:1	15.0:1	20.6:1	20.6:1	40.0:1		89:1

<sup>a</sup> Dichloromethane for PECH1 and toluene for PECH2. See Table II for SOLV1-SOLV8.

gasifier, a Knauer K-1001 pump, a Polymer Laboratories (Shropshire, UK) PL gel 10- $\mu$ m 500- $\text{\AA}$  column in an Eldex CH-150 oven at 70°C, and a RI Knauer K-2301 detector. Osmometry was carried out in a Gonotec (Berlin, Germany) Osmomat 070. The temperature was set at 100°C, and the sampling time was 10 min. DMF (99.9+ %, high performance liquid chromatography grade from Aldrich) was used as a solvent in both cases.

Elemental analysis was performed in a Fisons Instruments EA 1108. Differential scanning calorimetry (DSC) tests were done on a Polymer Laboratories differential scanning calorimeter (model PL DSC) at 10.0°C/min. Dynamic mechanical thermal analysis (DMTA) experiments were performed in a Triton (Notts, UK) Tritec 2000 dynamic mechanical analyzer. A steel plate in a closed V shape was used to hold the samples. A single-cantilever free-sample length of 14 mm, a displacement of 50  $\mu$ m, a frequency of 1 Hz, a heating rate of 2.0°C/min, and a still-air atmosphere were used in all of the experiments.

The viscosity was measured in a Haake Rheostress 1. Parallel plates geometry was used with a lower plate diameter of 60.0 mm, an upper plate diameter of  $10 \pm 0.002$  mm, a gap of 1.000 mm, and a temperature of 45°C. The density was measured in an Accupyc (Monchengladbach, Germany) 1330 helium pycnometer at 25°C.

## Syntheses

As a first step, the compatibility of cyanuric acid with SnCl<sub>4</sub> was tested in DMF at 70°C for 2 h. The products

were analyzed by IR spectroscopy, which showed that no reaction occurred.

All syntheses were carried out in 50- or 100-mL glass reactors equipped with a magnetic stirrer and a reflux condenser in a temperature-controlled oil heating bath. Predetermined quantities of cyanuric acid and solvent were added to the reactor. Stirring and heating were started, and ECH was then added. The catalyst was gradually added for a period of 5 min. Table I shows the reagents and respective amounts used in the syntheses of the prepolymers. The syntheses of samples PECH1, PECH2, and SOLV1-SOLV8 were carried out to study the influence of the solvent in the reaction products. Trifluoroacetic acid was used as a cocatalyst. Polyepichlorohydrin (PECH) was synthesized in dichloromethane (PECH1) and DMF (PECH2), with propylene glycol as an initiator. The experimental conditions for SOLV1-SOLV8 are shown in Table I, and Table II presents the solvents used. All reactions were carried out at 70°C for 24 h. The exceptions were those of PECH1 and PECH2, which had reaction times of 1.5 and 4 h, respectively. The syntheses of samples PC26 and PC27 were carried out to study the influence of the temperature on the reaction. The same conditions as those used for PC13 synthesis were used, with the exception of the temperature, which was in this case, 100 and 40°C, respectively.

When the reactions were finished, 50 mL of distilled water was added to the reaction products. After some minutes of agitation, the two phases were allowed to separate. The upper aqueous phase was removed. These steps were repeated twice, and the products were dried

**TABLE II**  
**Solvents Used in the Syntheses of SOLV1-SOLV8**

	SOLV1	SOLV2	SOLV3	SOLV4	SOLV5	SOLV6	SOLV7	SOLV8
Toluene (mL)	9.0	4.5	6.0	8.0				
DMF (mL)		4.5	3.0	1.0		4.5	1.0	9.0
Dichloromethane (mL)					9.0	4.5	8.0	

overnight at 60°C in a ventilated oven. A final drying was carried out in a vacuum oven at 50°C and 1 Pa.

## RESULTS AND DISCUSSION

### Spectroscopic analysis

Figure 1 presents the IR spectra of PC14 and PC19, corresponding respectively to the lower and the higher ECH–cyanuric acid ratios of the compounds synthesized in DMF (except SOLV8).

The broad band at about 3300  $\text{cm}^{-1}$  showed the presence of hydroxyl groups in the prepolymers. The bands observed between 2960 and 2870  $\text{cm}^{-1}$  were due to the stretching vibrations of the alkyl groups introduced from ECH. These bands were stronger in the spectra of the prepolymers synthesized with higher ECH–cyanuric acid ratios. The band at 1310  $\text{cm}^{-1}$  was also due to alkyl groups. The band at 1090  $\text{cm}^{-1}$  was attributed to the stretching vibration mode of COH groups and the band at 1060  $\text{cm}^{-1}$  to COC groups.<sup>11</sup> These two bands widened and the band at 1060  $\text{cm}^{-1}$  became more intense with increasing ECH–cyanuric acid ratios, whereas the band at 3300  $\text{cm}^{-1}$  became weaker.

The band at 1685  $\text{cm}^{-1}$  was due to the stretching vibration of the cetonic groups bound to the triazine ring.<sup>11</sup> This band became weaker in the spectra of the prepolymers synthesized with higher ECH–cyanuric acid ratios because of the lower concentration of these groups in comparison with the part of the molecules formed from ECH. The bands at 1455, 1385, and 850  $\text{cm}^{-1}$  were due to the triazine ring. The bands at 760 and 698  $\text{cm}^{-1}$  corresponded to the stretching vibration of chloroalkyl groups.<sup>11</sup> The band at 1385  $\text{cm}^{-1}$  could also be attributed to these groups. The weak band at 1255  $\text{cm}^{-1}$  could be attributed to epoxide groups. To investigate the presence of these groups, the compounds were treated with HCl, and the IR spectra of

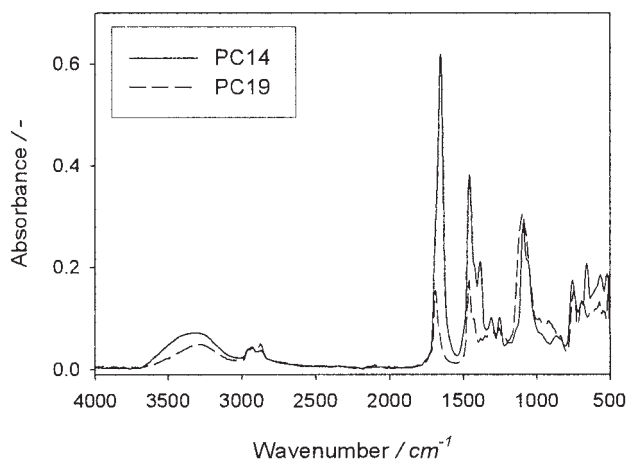


Figure 1 IR spectra of PC14 and PC19.

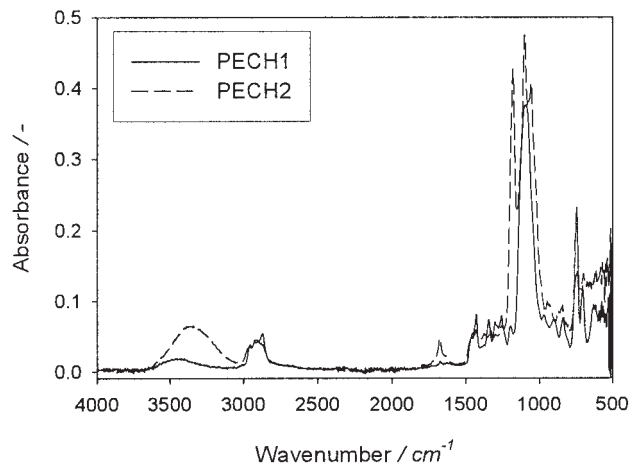
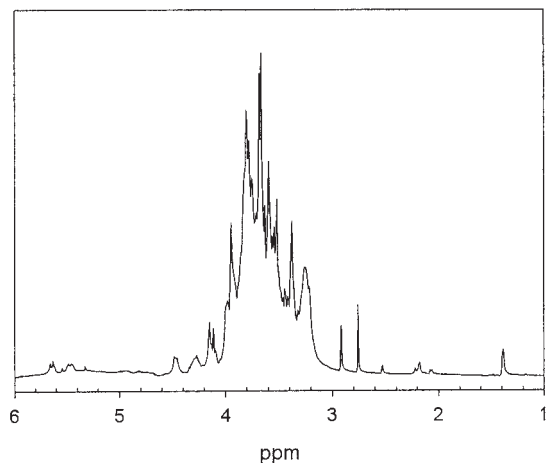


Figure 2 IR spectra of PECH1 and PECH2.

the products were recorded. The referred band was again observed with the same characteristics, and thus, it could not be attributed to epoxide groups, which would open by reaction with the acid. This band was attributed to chloroalkyl groups.<sup>12</sup> None of the signals from N–H groups in the cyanuric acid IR spectrum were observed in the synthesized prepolymer spectra. The IR spectrum of PC27 (40°C) showed stronger bands for cetonic groups and for the triazine ring when compared to the spectrum of PC13. The bands attributed to alkyl groups were weaker in PC27 spectrum. This indicated a higher concentration of the part of the molecule formed from cyanuric acid in PC27. The IR spectra of PC26 (100°C) and PC13 were similar. Samples from the synthesis of PC13 were analyzed at various reaction times. The bands attributed to groups from cyanuric acid became weaker with reaction time, whereas the hydroxyl and alkyl bands became stronger, which confirmed the attributions made before.

Figure 2 shows the IR spectra of PECH1 and PECH2. The spectrum of PECH1 was compared with the spectrum of a commercial PECH, and good agreement was observed. The spectrum of PECH2 showed a stronger hydroxyl band over 3000  $\text{cm}^{-1}$ . The analysis of the spectra between 1200 and 1050  $\text{cm}^{-1}$  indicated that the hydroxyl groups and ether bridges had fewer interactions in PECH1 compared to PECH2. The band at 740  $\text{cm}^{-1}$ , attributed to chloroalkyl groups, was weaker in PECH2.

The IR spectra of SOLV1, SOLV5 (not shown), and PECH1 were similar, which showed that the groups from cyanuric acid were not present. This was attributed to the very low solubility of cyanuric acid in the solvents used in SOLV1 and SOLV5. The spectra of SOLV2–SOLV4 (not shown) revealed that cyanuric acid reacted with ECH. SOLV6 and SOLV7 had similar IR spectra to SOLV2–SOLV4, with the spectra of all of these compounds similar to the spectrum of SOLV8

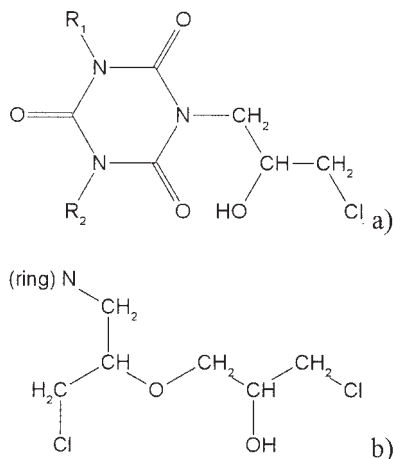


**Figure 3**  $^1\text{H-NMR}$  spectrum of a  $\text{DMSO-d}_6$  solution of PC13 at 499.824310 MHz and  $25^\circ\text{C}$ .

(not shown). This showed that the presence of DMF as a cosolvent in toluene or dichloromethane gave products that were nearly identical to those synthesized in DMF.

Figure 3 shows the  $^1\text{H-NMR}$  spectrum of PC13 in  $\text{DMSO-d}_6$ . The peaks at 2.76, 2.92, and 7.97 (not shown) were assigned to the solvent DMF, which could not be completely removed.

The protons bound to nitrogen in cyanuric acid show a signal at 11.9 ppm.<sup>13</sup> In the PC13 spectrum, no signal in that region was observed, even after strong amplification. Therefore, in PC13, all of the protons of cyanuric acid were substituted by lateral chains, which confirmed the IR analyses. The peaks between 5.6 and 4.6 ppm corresponded to protons of the hydroxyl end groups in the lateral chains. This assignment was based on the  $^1\text{H-NMR}$  spectra of melamine-ECH prepolymers<sup>14-17</sup> and of tris(2-hydroxyethyl)iso-



**Figure 4** Proposed structures for the lateral chains of PC13.  $\text{R}_1$  and  $\text{R}_2$  are lateral chains. The N atom in part b is part of the triazine ring.

**TABLE III**  
Hydroxyl Group Contents of the Prepolymers (massic %)

Prepolymer	OH (%)	Standard deviation
PC14	8.82	0.374
PC13	7.99	0.0405
PC18	6.64	0.0500
PC19	4.48	0.121

cyanurate.<sup>18</sup> For these protons, the  $^1\text{H-NMR}$  spectrum of PC17 (not shown) revealed more intense peaks, from 5.8 to 4.6 ppm.

In Figure 4(a,b), the proposed structures for the lateral chains of PC13 are shown. The most intense peaks of the spectrum were observed between 4.5 and 3.2 ppm (see Fig. 3) and were due to protons of these chains formed from ECH. In the PECH  $^1\text{H-NMR}$  spectrum, these peaks were observed between 3.8 and 3.4 ppm,<sup>19</sup> with the broadening of the signals attributed to the presence of the triazine ring. By comparison with ECH,<sup>18</sup> the signals between 3.7 and 3.4 ppm were assigned to the protons of the  $\text{CH}_2\text{Cl}$  groups. Comparison of the  $^1\text{H-NMR}$  spectra of PC13 and tris(2-hydroxyethyl)isocyanurate<sup>18</sup> showed that the signals at 3.8–3.9 ppm were due to the protons of the methylene groups bound to the ring. The protons of the methylene or methyne groups bound to ether bonds or hydroxyl groups showed signals at 3.5 ppm.<sup>18</sup> The overlapping of these signals with the signals corresponding to the protons of the  $\text{CH}_2\text{Cl}$  groups did not allow a clear assignment. The broad signal at 3.2–3.3 ppm was attributed to water traces in the solution. The  $^1\text{H-NMR}$  spectrum of PC17 displayed the same characteristic features of the spectrum of PC13 and led to the structures proposed in Figure 4.

Epoxide end groups were present in the products when basic catalysts are used.<sup>6,7</sup> In our case, a Friedel-Crafts catalyst was used, and hydroxyl end groups were expected.<sup>20</sup> In the  $^1\text{H-NMR}$  spectra of PC13 and PC17, no peaks could be assigned to the protons from epoxides, as expected.

#### Determination of hydroxyl group content

Table III shows the results for hydroxyl group content in the prepolymers. Two analyses were performed for each compound. A decrease in hydroxyl content was observed as the ECH-cyanuric acid ratio increased. The comparison between PC13 and PC18 showed that a higher catalyst concentration led to a lower OH content.

#### Molar mass

Table IV shows the molar masses of the prepolymers synthesized in DMF (except SOLV8) as measured by

chromatography and osmometry techniques. Broad peaks were obtained in the chromatography analyses, with this reflected in the differences among the weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and mass of the peak ( $M_p$ ). This could be explained by the relatively high mass of the ECH monomer when compared to the mass of the prepolymers. Slightly higher  $M_n$  values from osmometry were obtained. Although the highest molar masses were found for higher ECH–cyanuric acid ratios, it was not possible to identify a general trend for the lower ratios. The value of  $M_p$  of PC14 was higher than the corresponding values for PC15, PC17, and PC13, whereas the  $M_w$  values were all similar with the exception of PC17. The higher molar mass value for PC18 compared to that of PC13 was attributed to the higher catalyst concentration in the first case. The results for PC26 show that the increase in the reaction temperature from 70 to 100°C led to a decrease in the molar mass of the products. However, the values for PC26 were mainly due to a sharp peak at 307 g/mol in the chromatogram (not shown), with the remaining chromatogram similar to PC13. PC27 and PC13 showed similar values.

The similarity of the molar mass values for the synthesized prepolymers with different ECH–cyanuric acid ratios indicated that another factor or factors controlled this property. Table V shows the molar masses of PECH1, PECH2, and SOLV1–8 as measured by chromatography.

Dichloromethane and DMF were used in the PECH1 and PECH2 syntheses, respectively. The PECH1 molar mass was significantly higher than the PECH2 molar mass. The SOLV1 and SOLV5 molar mass values were significantly different from those of the other SOLV samples. However, the differences between SOLV8 (DMF only) and the other syntheses where DMF was used as a cosolvent were not significant. In the presence of DMF, lower molar masses were always obtained. This was due to the high dielectric constant of DMF, as compared to toluene or

**TABLE IV**  
Molar Masses of the Prepolymers Synthesised in DMF (Except SOLV8)

Prepolymer	Chromatography			Osmometry
	$M_w$ (g/mol)	$M_n$ (g/mol)	$M_p$ (g/mol)	Mn (g/mol)
PC14	360	188	516	—
PC15	354	203	512	—
PC17	295	179	333	—
PC13	375	235	470	406
PC18	499	437	606	520
PC19	480	394	652	501
PC26	314	142	307	—
PC27	461	396	425	—

**TABLE V**  
Molar Masses of the Prepolymers of the Syntheses of PECH1, PECH2, and SOLV1–SOLV8

Prepolymer	$M_w$ (g/mol)	$M_n$ (g/mol)	$M_p$ (g/mol)
PECH1	998	766	956
PECH2	271	210	243
SOLV1	1640	707	631
SOLV4	379	237	416
SOLV3	409	261	408
SOLV2	386	251	404
SOLV5	3452	1476	2198
SOLV6	376	238	425
SOLV7	390	231	408
SOLV8	371	182	451

dichloromethane. This parameter influences ion solvation in solution,<sup>21</sup> and the alkoxide ions that result from epoxide ring opening may not take part in subsequent polymerization reactions. When a low dielectric constant solvent is used, the propagating species exist as ion pairs.<sup>20</sup> During chain growth, it is probable that these ion pairs form agglomerates and eventually micelles, and the reaction becomes heterogeneous and proceeds within the agglomerates.<sup>20</sup> When a solvent with a high dielectric constant is used, for example, DMF, the solvation is more intense and creates different reaction conditions.

These results show that the relatively low molar masses found for the syntheses in DMF could be attributed to the solvent. The syntheses of SOLV1 and SOLV5 showed that cyanuric acid did not take part in the reaction when toluene or dichloromethane were used without DMF. This could be explained by the very low solubility of cyanuric acid in these solvents and the absence of reaction between ECH and solid cyanuric acid.

### Elemental analysis

Table VI shows the elemental analysis results for the syntheses in DMF (except for SOLV8). Nitrogen content decreased as the ECH–cyanuric acid ratio increased. As nitrogen came exclusively from cyanuric acid, this result shows that more ECH was incorporated in the prepolymers with higher ECH–cyanuric acid ratios in the respective syntheses. Oxygen, which is at a higher content in cyanuric acid compared to ECH, showed a similar trend. The carbon values were all similar. The column Other in Table VI is expected to account only for chlorine because no other elements were expected. Chlorine came from ECH, and its content increased with the ECH–cyanuric acid ratio in the syntheses. A comparison of PC26 with PC13 showed lower N and O contents and a higher Cl content for PC26. The inverse was true for PC27. Therefore, a

TABLE VI  
Elemental Analysis Results and ECH–Cyanuric Acid Molar Ratios of the Prepolymers

Prepolymer	C (%)	N (%)	H (%)	O (%)	Other (%)	ECH–cyanuric acid
PC14	37.723	9.628	6.411	23.333	22.903	3.4:1
PC15	37.798	7.241	5.911	23.138	25.910	4.9:1
PC17	37.983	6.885	5.789	22.200	27.142	5.2:1
PC13	37.909	5.115	5.338	23.222	28.414	7.5:1
PC18	36.536	3.914	5.819	20.828	32.902	10.2:1
PC19	37.230	2.859	5.810	19.637	34.463	14.5:1
PC26	38.394	3.983	6.233	20.714	30.676	10.0:1
PC27	37.558	7.078	5.829	28.017	21.518	5.1:1

higher reaction temperature led to the incorporation of more ECH in the prepolymers.

The actual ECH–cyanuric acid molar ratios in the prepolymers was calculated from the N content. The values are shown in Table VI. A clear trend for the higher incorporation of ECH in the prepolymers synthesized with higher ECH–cyanuric acid ratios was confirmed. A comparison between PC13 and PC18 showed a higher ECH content in the latter due to the higher catalyst concentration. PC19 showed a slightly higher value than PC18, which indicated that doubling the content of ECH in the synthesis led to a much smaller increase of ECH in the final product.

The low N content of the prepolymers with higher ECH–cyanuric acid ratios compared to the measured molar masses led to question whether a mixture of ECH–cyanuric acid prepolymers and PECH was present. PC19 was mixed with THF, and part of the prepolymer was soluble in this solvent. The two fractions were collected and analyzed by IR and elemental analysis. The IR spectra of the two compounds showed only minor differences, namely, higher bands around  $920\text{ cm}^{-1}$  for the nonsoluble part. These bands were attributed to H bonds to nitrogen<sup>12</sup> and showed that the nonsoluble part had a slightly higher concen-

tration of cyanuric acid. However, the differences were negligible and showed that cyanuric acid was in both fractions. The nitrogen content in the two fractions was similar. PC13 was also tested with the same results.

### Thermal analysis

Figure 5 shows the DSC analysis of PC19. The onset temperature of the endothermic decomposition was  $161.9^\circ\text{C}$ . The first peak occurred at  $211.5^\circ\text{C}$  and was attributed to the decomposition of the lateral chains. A second peak was observed at  $296.4^\circ\text{C}$  and was due to the decomposition of the triazine rings. Below  $161.9^\circ\text{C}$ , no thermal events were observed. The other prepolymers showed an identical decomposition onset temperature. For the prepolymers with lower ECH–cyanuric acid ratios, the first endothermic peak was narrower, and the peak at about  $300^\circ\text{C}$  was more pronounced due to the higher triazine ring content.

Figure 6 shows the DMTA analysis of PC19. The values of  $E'$  (storage modulus = amplitude of stress/amplitude of in-phase strain) and  $\tan \delta$  only had an indicative value due to the steel support used. Because it had no influence on the variation of  $E'$  and  $\tan \delta$ , the variations in the curves were attributed to the sample

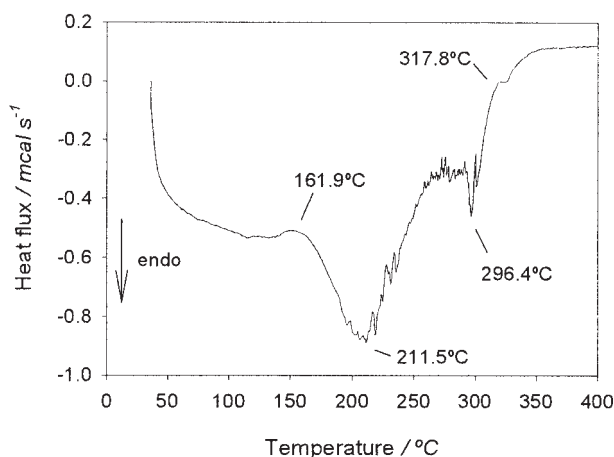


Figure 5 DSC analysis of PC19.

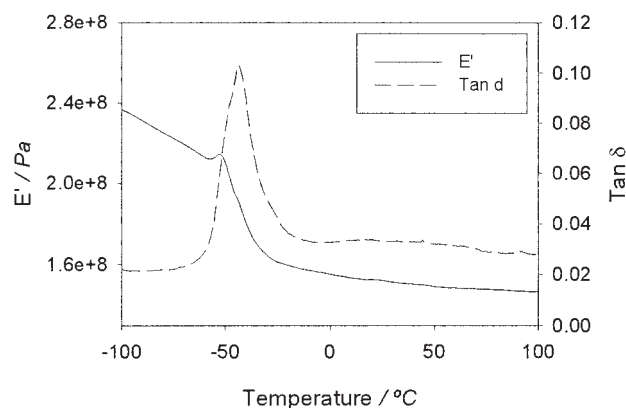


Figure 6 DMTA of PC19.

TABLE VII  
 $T_g$  Values of the Prepolymers

	PC14	PC15	PC17	PC13	PC18	PC19
$T_g$ (°C)	-18.8	-10.3	-13.5	-33.6	-26.0	-43.2

alone. The glass-transition temperatures ( $T_g$ 's) of the prepolymers synthesized in DMF are shown in Table VII. These were measured by the loss modulus ( $E''$ ) peak temperature and were unique for all of the prepolymers.

Figure 6 shows a peak in the  $E'$  curve just before the  $\tan \delta$  peak, which was caused by the relaxation of the chains that occurred near  $T_g$ .<sup>22</sup> Thereafter, a decrease in  $E'$  values was observed due to the transition from the glass to the liquid state. This behavior was supported by the  $\tan \delta$  curve. The curves showed no other events, which proved the homogeneous nature of the prepolymer. If a mixture of different, nonmiscible molecules were present, the DMTA results would clearly have shown the different phase transitions for each fraction. However, the broadness of the  $\tan \delta$  peak showed that small differences existed in the molecules of the prepolymer. This was in accordance with the broad molar mass distribution found by chromatography. The analyses of the other prepolymers showed the same characteristics as those of the PC19 analysis, with shifts in the temperature of the events and different widths of the  $\tan \delta$  peaks.

The measured  $T_g$  values showed the effect of the lateral chains formed by ECH. A trend was observed for lower values with increasing ECH–cyanuric acid ratio, with the exception of PC14 and PC18. The comparison between PC13 and PC18 showed that a higher catalyst concentration led to higher  $T_g$  values. PC14 had a higher molar mass than PC15 or PC17, and this may have been responsible for its lower  $T_g$  value, due to the effect of longer amorphous lateral chains.

### Viscosity and density

Table VIII shows the viscosity of the prepolymers. The high viscosity of PC14 was out of the range of the equipment used. A clear trend for lower viscosity with increasing ECH–cyanuric acid ratio was observed.

TABLE VIII  
Viscosities of the Prepolymers at 2 s<sup>-1</sup> and 45°C

Prepolymer	Viscosity (Pa s)
PC15	1375
PC16	1295
PC13	593
PC18	245
PC19	156

TABLE IX  
Densities of the Prepolymers at 25°C

Prepolymer	Density (g/cm <sup>3</sup> ) <sup>a</sup>
PC13	1.3986 ± 0.000216
PC18	1.4154 ± 0.001114
PC19	1.3926 ± 0.000993

<sup>a</sup> The uncertainties refer to a confidence level of 95%.

This showed that the incorporation of more ECH into the prepolymers led to a higher mobility of the molecules.

Table IX shows the densities of the prepolymers. Ten analyses of each compound were performed. The values were between the densities of ECH and cyanuric acid but closer to the ECH density. This was explained by the liquid state of the prepolymers, which was different from the crystalline cyanuric acid, and by the higher ECH content. A comparison between PC13 and PC18 showed that a higher catalyst concentration led to a higher density. PC19 showed a lower viscosity than PC18 due to a higher ECH content. However, the differences were small.

### CONCLUSIONS

ECH–cyanuric acid prepolymers were synthesized with SnCl<sub>4</sub> as a catalyst. Different reaction conditions were used, and the products analyzed. ECH was shown to react with the amine groups of the triazine ring to give lateral chains. These had hydroxyl end groups, which could be used for cure reactions. The solvent was shown to be of crucial importance in the synthesized products. Low-dielectric-constant solvents led to the synthesis of PECH, without cyanuric acid. When DMF was used as a solvent or cosolvent, cyanuric acid took part in the reaction, but the molar masses obtained were relatively low. This was attributed to the different solvation of the alkoxide negative ions of the growing ends of the chains in the high-dielectric-constant solvent. The synthesized prepolymers decomposed thermally at 160°C and had  $T_g$  values from -10 to -43°C.

In the light of the use of the prepolymers in the energetic materials area, the presence of the 1,3,5-s-triazine ring and the lateral chains with hydroxyl end groups curable by isocyanates was accomplished with success. The chlorine atoms in the lateral chains could be substituted by energetic groups such as azides. A good feature of these prepolymers was their high density, which was higher than most current energetic prepolymers. Their high viscosity may be limiting for the processing of some energetic formulations. However, the introduction of energetic groups can lead to lower viscosities and reduce the need for solid oxidizers.

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