

## **Determining the Extent of Reaction by $^{29}\text{Si}$ NMR of Abrasion-Resistant Hybrid Sol-Gel Coatings Based on Triethoxysilane Functionalized Organics**

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Diethylenetriamine, melamine, and low molecular weight branched polyethyl-enimine were functionalized separately with 3-isocyanatopropyltriethoxysilane. Coatings on polycarbonate were prepared from these compounds through the sol-gel process. The extent of reaction and the relative species concentration of the trifunctional silicon atom were obtained from  $^{29}\text{Si}$  CP-MAS NMR measurements. The sol-gel reaction was found to be limited by vitrification. A variety of silicon species was present in the vitrified coating. The extent of reaction could be increased by increasing the curing temperature, curing for longer times, and increasing the acid concentration. The extent of reaction was also found to be related to the basicity of the functionalized organic backbone.

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**KEY WORDS:**  $^{29}\text{Si}$  nuclear magnetic resonance; extent of reaction; hybrid sol-gel coatings; triethoxysilane functionalized organics.

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### **INTRODUCTION**

Clear thermoplastics such as polycarbonate, polymethylmethacrylate, and poly(4-methyl-1-pentene) are often used in optical applications where abrasion-resistant characteristics would also be desirable. Polycarbonate has a poor abrasion resistance and so coatings are often applied to the surface of polycarbonate to improve its abrasion resistance. Wang and Wilkes [1] have demonstrated that low molecular weight organics endcapped with triethoxysilyl groups when reacted through the sol-gel process can form transparent coatings which adhere well to polycarbonate and plasma-treated poly(4-methyl-1-pentene) and offer abrasion resistance when cured

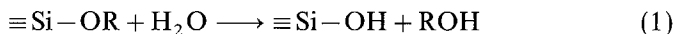
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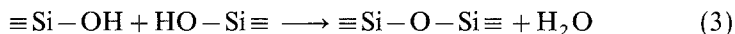
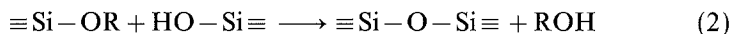
at high temperatures. Increasing the curing temperature has generally been found to improve the abrasion resistance of the coated polycarbonate [2-4]. The present study was undertaken to determine the extent of reaction and the species distribution of coatings prepared from coating precursors of triethoxysilyl functionalized diethylenetriamine, melamine, and polyethyleneimine of number-average molecular weight of 600 gm/mole. The coatings were cross-linked through the sol-gel process as described below.

The sol-gel reaction is said to occur when a metal alkoxide reacts with water to form a metal hydroxide which condenses into a M-O-M bond, with the liberation of water and alcohol. The basic reaction is inherently simple and applicable to several species including the transition metal atoms such as Ti, Al, and Zr and the semi-metal atom Si.

Generally three reactions are used to describe the sol-gel process [5]. The forward reaction in the first step is the hydrolysis step and the reverse reaction is the esterification reaction:



The second step is the condensation step, which can occur along two routes. In the first route, the forward reaction produces an alcohol complimented by the reverse reaction called the alcoholysis reaction. The second route is the water-producing forward reaction; the reverse of this reaction is the hydrolysis reaction and is not to be confused with the hydrolysis reaction in the first step.



Theoretically, 2 mol of water is required for complete conversion of the silicon alkoxide to amorphous silicon dioxide, with a net loss of 4 mol of alcohol. The reaction usually does not go to completion because of vitrification. The rate of the reaction and the species distribution are influenced by a variety of parameters such as the pH of the reaction media, the concentration of the reactants, the solvent medium, and the nature of the alkyoxysilane.

## EXPERIMENTAL

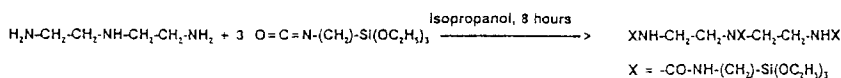
### Synthesis of Coating Precursors

Diethylenetriamine (DETA) of 99%+ purity was obtained from Aldrich. It was diluted with reagent-grade isopropanol to an extent such that after functionalization the concentration would be 18% (w/w). The

clear solution was then jacketed with cold water. The functionalization reagent 3-isocyanatopropyl-triethoxysilane was obtained from Hüls America Inc. The silane reagent was 95% pure, and no attempts were made to purify it further. A schematic of the endcapping reaction is shown in Fig. 1. The silane reagent was added dropwise to the stirred mixture of the DETA in isopropanol to ensure that the temperature of the reactants was never more than warm. The volume of silane added was adjusted to account for the purity and to provide for a slight excess (5%). The entire addition required approximately 30 min. Each batch contained approximately 2.5 g of DETA and 19.8 g of silane reagent. The solutions were allowed to stir 6 h. The endcapping was monitored using FTIR by observing the disappearance of the isocyanate group ( $2270\text{ cm}^{-1}$ ). The endcapping was assumed to be complete when the peak was barely discernible. The endcapping was usually complete within 1 h. The importance of slow addition is a prerequisite for successful endcapping of DETA at such a concentration. Too fast an addition increases the temperature to a level where there is spontaneous hydrolysis and condensation by absorption of water from the atmosphere, resulting in a gel. The clear solution was capped and utilized within a two week period.

The reactivity of melamine is lower than that of an aliphatic amine. As a result, the endcapping reaction of melamine had to be conducted at

Diethylenetriamine (DETA):



Melamine:

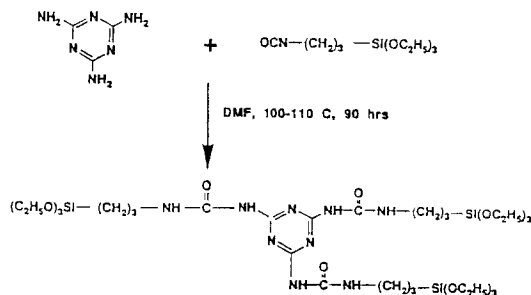


Fig. 1. Functionalization scheme for diethylenetriamine and melamine.

temperatures of between 100 and 110°C. A schematic of the endcapping reaction is shown in Fig. 1. The reaction vessel consisted of a three-necked flask with a magnetic stirrer and jacketed with a heater. The melamine and the *N,N'*-dimethylformamide were charged into the vessel and heated to between 90 and 110°C. The silane reagent was then added to a total of 5% excess, which accounted for the 95% purity level. The functionalization of the melamine makes it soluble in *N,N'*-dimethylformamide. The endcapping at this temperature was complete within 90 hr. The final concentration of the endcapped melamine was 18% (w/w). The stoichiometry of the silane could be adjusted so that an average of two of the three amine groups on the melamine was endcapped. The endcapped melamine solution was stable for up to 2 weeks.

The polyethyleneimine was obtained from Polysciences Inc. and had a number-average molecular weight (as supplied by the manufacturer) of 600 g/mol. The oligomer was endcapped without further purification. The oligomer was dissolved in isopropanol. Due to the uncertainty in the number of accessible amine groups due to branching, a trial and error approach was taken with respect to endcapping. The theoretical dose of the silane reagent required to endcap the amine was calculated from the molecular weight. Fifty percent of the calculated silane was added in a single dose. Thereafter the silane was added incrementally and the  $-NCO$  peak monitored after each addition. The addition was stopped when the isocyanate peak showed no discernible change in intensity after 30 min. The number of actual imine groups reacted based on the volume of the silane added was found to be 83%. Not all the imine groups are accessible to the endcapping reaction. This could be due to the branching of the PEI chains, which reduce accessibility to the bulky silane reagents because of steric hindrance.

### Coating Formulations

The sol-gel reaction was initiated by the addition of water and acid to the coating precursors: 0.5 mol of water and 0.0091 mol of HCl were added per mol of alkoxide. The coatings were then applied to 15-mm-thick samples of polycarbonate (LEXAN) of dimensions  $4 \times 4$  in.<sup>2</sup> by a dipcoating procedure. Up to three layers of coating were applied to each sample to build up the thickness of the coating to approximately 10  $\mu$ m. The polycarbonate substrates were then cured in air-circulating ovens. Most coated substrates were cured at 135°C. The samples were cured in the constant-temperature ovens for the specified time, after which they were removed and allowed to cool to room temperature. The coating was then scraped from the surface of the polycarbonate and ground to a fine powder. It was then packed in a 7-mm-diameter zirconia rotor with a Kel-F cap for NMR studies.

### $^{29}\text{Si}$ Solid-State NMR

The extent of reaction of the triethoxy species was determined by  $^{29}\text{Si}$  solid-state NMR at a silicon Larmor frequency of 59.601 MHz. Data were obtained using a cross-polarization program. An optimum contact time of 3 ms was chosen to obtain a high signal-to-noise ratio and quantitative data. The proton  $90^\circ$  pulse was adjusted to  $6\ \mu\text{s}$ . The delay between consecutive scans was 4 s. The spectrometer was calibrated using a  $\text{M}_8\text{Q}_8$  sample, i.e.,  $[(\text{CH}_3)_3\text{Si}]_8[\text{Si}_8\text{O}_{20}]$ . The Hartmann–Hahn condition was obtained by adjusting the RF power of the silicon channel. Between 200 and 1800 free induction decays (FID) were accumulated for each sample. The FIDs were Fourier transformed using a line broadening of between 50 and 100 Hz. Samples were spun at the magic angle at 5.5 KHz. Actual spectra were simulated with the program GLINFIT installed in the Bruker spectrometer. A three-parameter curve-fitting procedure was utilized to obtain the polarization transfer rate constants ( $T_{\text{Si-H}}$ ), the proton spin-lattice relaxation times in the rotating frame [ $T_{1\rho}(\text{H})$ ], and the peak intensities extrapolated to zero contact time.

## RESULTS AND DISCUSSION

$^{29}\text{Si}$  NMR is a powerful technique that can detect the various silicon species present in the coating. The lower relative gyromagnetic ratio of the  $^{29}\text{Si}$  nucleus with respect to carbon and hydrogen makes this nucleus more difficult to detect. Also spin-lattice relaxation times ( $T_1$ ) for the silicon nucleus are much longer than for the  $^{13}\text{C}$  and  $^1\text{H}$  nucleus, which implies that successive scans must be obtained over larger time intervals. A delay between scans of greater than 100 s is not uncommon. Such long delays between scans results in an inefficient use of spectrometer time. Therefore for practical reasons it is more convenient to use cross-polarization to transfer magnetization to the silicon nucleus.

A preliminary NMR study was done using direct  $90^\circ$  Si pulses. Inversion recovery experiments on a DETA coating sample indicated a  $T_1$  of approximately 21 s, which agrees with the  $T_1$  observations of other researchers [6, 7]. If quantitative data are required, an interval between consecutive scans of at least 5  $T_1$  has to be employed. A sample of the coating had to be run continuously for almost 24 h before a good signal-to-noise ratio could be obtained. Therefore this method was abandoned in favor of the cross-polarization method. In cross-polarization the delay between successive scans is governed by the rate of relaxation of the proton in the rotating frame of reference [ $T_{1\rho}(\text{H})$ ], which is typically of the order of a few milliseconds [8].

Figure 2 shows the  $^{29}\text{Si}$  NMR solution spectra of functionalized DETA and melamine. It may be recalled that the melamine was functionalized in *N,N'*-dimethylformamide, while the DETA was functionalized in isopropanol. The melamine spectrum shows a single peak at ca.  $-45.2$  ppm, which corresponds to the alkyltriethoxysilane [9–11]. All of the silicon is present in the unhydrolyzed and uncondensed state. The DETA spectrum, in contrast, shows two peaks, at ca.  $-45.2$  and ca.  $-45.6$  ppm. The peak at the left corresponds to the triethoxysilane species, while the peak at the right is assigned to a silyl species which is partly transesterified by the isopropanol. Transesterification has been known to occur in alkoxides [12]. This assignment is based on the observation of Van De Ven and co-workers [13], who noticed a ca.  $-4$ -ppm shift if the methyl group on the alkoxy species was replaced by an ethyl group. By analogy, another ca.  $-4$ -ppm shift can be expected for substitution of all the ethoxy groups on the silicon atom by isopropoxy groups. The figure shows that the shift is of the order of ca.  $-0.4$  ppm, which suggests that not all of the ethoxy groups per silicon atom have been substituted.

Figure 3 shows the  $^{29}\text{Si}$  CP-MAS spectrum of the DETA coating cured at  $135^\circ\text{C}$  for 380 min as a function of contact time. The spectra clearly show the presence of three peaks at ca.  $-50$ ,  $-58$ , and  $-66$  ppm, which is attributed to the  $\text{T}^1$  [ $-\text{Si}(\text{OR})_2(\text{O})_1$ ],  $\text{T}^2$  [ $-\text{Si}(\text{OR})(\text{O})_2$ ], and  $\text{T}^3$

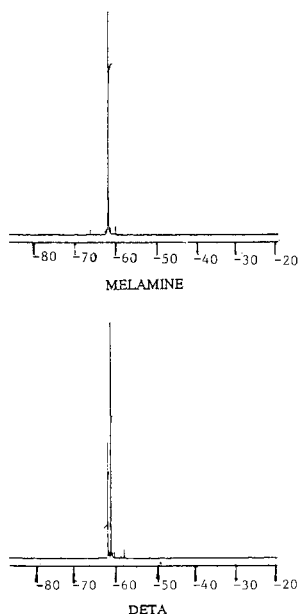
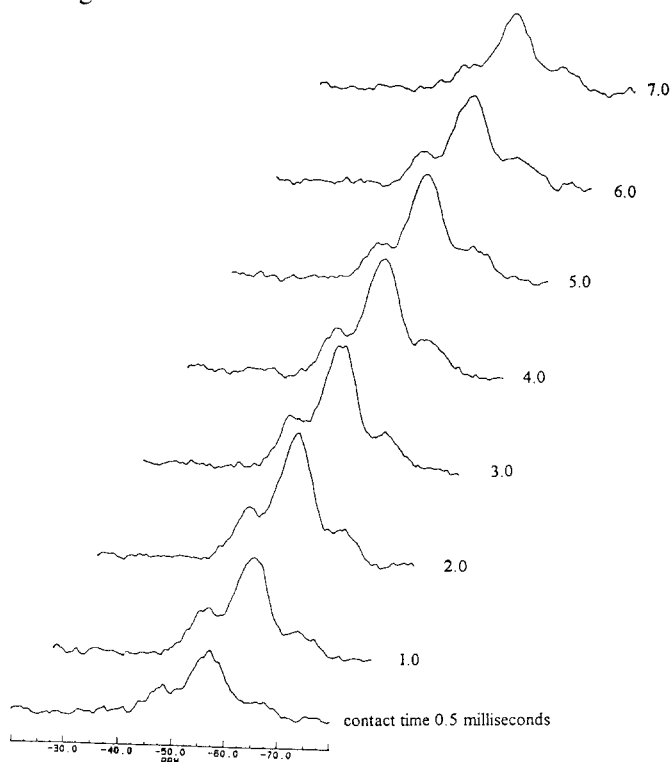


Fig. 2.  $^{29}\text{Si}$  NMR of functionalized DETA and melamine coating precursor.

$[-\text{Si}(\text{O})_3]$  species [9–11]. Although the silicon is not directly bonded to the hydrogen, the presence of protons on the methylene group attached to the silicon alone is in sufficiently close proximity ( $<10 \text{ \AA}$ ) to allow magnetization to be transferred to the silicon nucleus [10]. The spectra qualitatively show that there is no drastic change in the observed spectra of the relative concentration of each species as a function of contact time, although the overall intensity reaches a peak at an approximately 2- to 3-ms contact time. The relative concentration of each species was determined by simulating the actual spectrum utilizing a Bruker software program.

Figure 4 shows an example of a simulated curve for the spectrum in Fig. 3 obtained with a contact time of 3 ms. The simulated curve is designed from three component curves. It must be noted that the left most peak (ca.  $-48 \text{ ppm}$ ), corresponding to the  $\text{T}^1$  peak, is broad enough that it may overlap the  $\text{T}^0$  species which occurs between  $-40$  and  $-45 \text{ ppm}$ . Thus, the simulated curve for the  $\text{T}^1$  peak includes the combined area under the  $\text{T}^0$  and  $\text{T}^1$  peaks. The relative species concentration is contained by the following ratio:



**Fig. 3.**  $^{29}\text{Si}$  NMR spectrum of functionalized DETA coating cured at  $135 \text{ }^\circ\text{C}$  for 380 min.

fraction of  $T^x$  species ( $f^x$ )

$$= (\text{area under } T^x \text{ peak}) / \left( \sum_x \text{area under } T^x \text{ species} \right) \quad (4)$$

The extent of reaction is obtained by the formula ( $R_{\text{ex}}$ )

$$R_{\text{ex}} = \sum_x x \cdot f^x \quad (5)$$

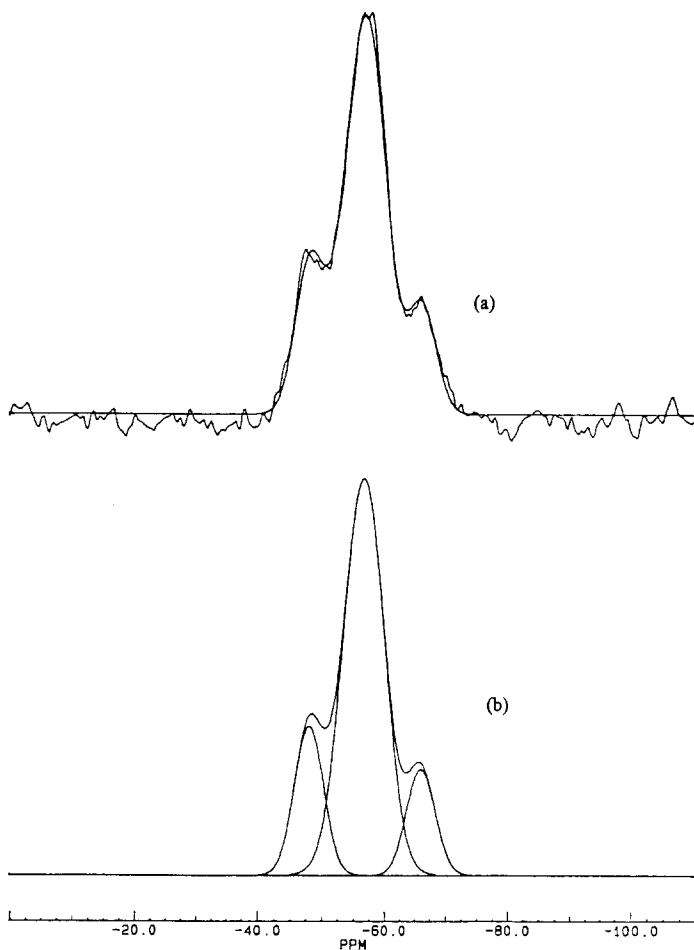


Fig. 4. Simulated spectrum (b) of the functionalized DETA spectrum obtained at a 3-ms contact time (a).

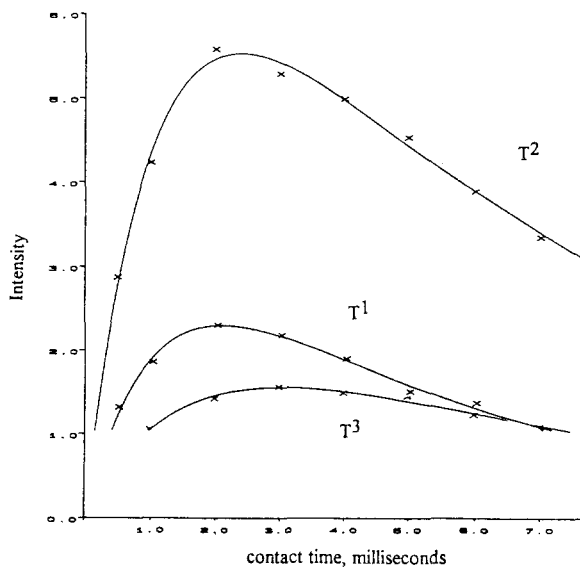


**Table I.** Weighting Factors for the Trifunctional Silicon Species

Species	<i>x</i>
T <sup>0</sup>	0
T <sup>1</sup>	$\frac{1}{3}$
T <sup>2</sup>	$\frac{2}{3}$
T <sup>3</sup>	1

The formula assumes that a reaction is complete when a Si-OR bond is converted into a Si-O-Si bond. Thus, the minimum value of  $R_{ex}$  would be zero, corresponding to a fully uncondensed species such as in the DETA or melamine coating precursor. The maximum value of  $R_{ex}$  would be 1 when all the Si atoms are fully condensed (T<sup>3</sup> stage). The weighting factors (*x*) are provided in Table I. The fractional area under species T<sup>1</sup>, T<sup>2</sup>, and T<sup>3</sup> was determined to be 0.18, 0.68, and 0.13. The average extent of reaction ( $R_{ex}$ ) was calculated to be 0.64.

Figure 5 shows the variation of peak intensity of the T<sup>1</sup>, T<sup>2</sup>, and T<sup>3</sup> species as a function of the contact time. The curves for each species exhibit a maximum, which implies that there are two opposing functions that control the intensity. At low contact times the magnetization transfer from the proton to the silicon nucleus has a dominant influence on the intensity.



**Fig. 5.** Plot of peak intensity with contact time of functionalized DETA coating spectra in Fig. 3.

**Table II.** Calculated Rate Constants of Each Species for the Functionalized DETA Coating

Species	$T_{\text{Si-H}}$	$T_{1\rho}(\text{H})$	$I(0)$
T <sup>1</sup>	1.04	4.99	3.46
T <sup>2</sup>	1.06	7.18	7.71
T <sup>3</sup>	1.59	6.98	2.41

The longer the contact time, the greater is the transfer of magnetization. A measure of the rate of magnetization transfer is the  $T_{\text{Si-H}}$ , the cross-polarization transfer rate constant. As the contact time increases further, the relaxation of the protons in the rotating frame of reference begins to influence the intensity. At long contact times the intensity is governed by the proton spin-lattice relaxation time in the rotating frame [ $T_{1\rho}(\text{H})$ ]. A biexponential curve-fitting procedure [14] of the form shown below for each species yields the value of the rate constants shown in Table II.

$$I(t) = I(0) \cdot (\exp(-t/T_{1\rho}(\text{H})) - \exp(-t/T_{\text{Si-H}})) / (1 - (T_{\text{Si-H}}/T_{1\rho}(\text{H}))) \quad (6)$$

Typically the  $T_{\text{Si-H}}$  rate constant is governed by the proximity of the proton to the carbon atom and the molecular motion of the bonds. The polarization transfer of magnetization is inversely proportional to the sixth power of the Si-H distance [8]. Thus, silicons with directly bonded protons cross-polarize faster than silicon atoms with unbonded protons [8]. The values obtained for the polarization transfer rates are comparable to the values obtained by other researchers. Glaser [15] obtained a value of 3 ms for the T<sup>3</sup> species. Hoh *et al.* [10] obtained  $T_{\text{Si-H}}$  values of less than 100  $\mu\text{s}$  for the T<sup>3</sup> species in silica gels treated with aminopropyltriethoxysilane. In comparison,  $T_{\text{C-H}}$  times for carbon directly bonded to hydrogen are of the order of microseconds, while those for nonbonded carbons are of the order of 1–5 ms [9]. One would expect the  $T_{\text{Si-H}}$  times to decrease due to increasing rigidity around the vicinity of the Si atom at the number of Si-O-Si species on the silicon atom increased. However, the trend (if any) shows the opposite behavior. An explanation of this behavior may be obtained by considering the atoms around the vicinity of the silicon atom. The partially condensed silicon atom has hydroxyl groups in its vicinity. The protons of these hydroxyl groups might conceivably contribute to the polarization transfer [16], counteracting the effect of increasing rigidity. The  $T_{1\rho}(\text{H})$  relaxation times are between 4.99 and 7.18 ms. In comparison Glaser [14] obtained a value of 19.3 ms for the T<sup>3</sup> species. Caravajal *et al.* [9] obtained a value of 4.4 ms for the  $T_{1\rho}(\text{H})$  from a <sup>13</sup>C spectra of aminopropyl modified silica. Maciel and Sindorf [17] obtained values

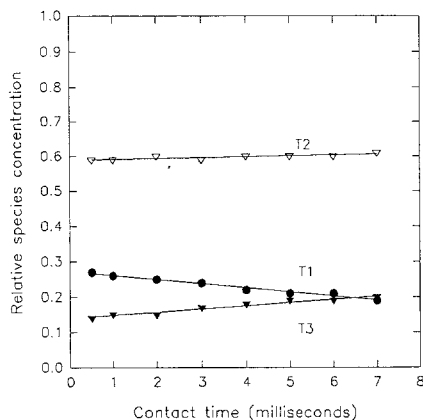


Fig. 6. Relative species concentration of functionalized DETA coating as a function of contact time.

between 20 and 22 ms for silica gels. Thus, there seems to be a narrow variation in the  $T_{1\rho}(H)$  values for all species.

Figure 6 shows the relative species concentration of the functionalized DETA coating as a function of contact time. With increasing contact time the relative concentration of the T<sup>3</sup> species increases at the expense of the T<sup>1</sup> and the T<sup>2</sup> species. This is due to the slight differences between the rate constants of the individual species. As a result of these differences, the maximum intensity for each species occurs at different contact times. The actual intensity can be estimated by extrapolation to the Y axis of the part of the spectrum where  $T_{1\rho}(H)$  dominates. The species concentration calculated from the  $I(0)$  values together with the species fractions obtained using a 3-ms contact time is tabulated in Table III. The data are in close agreement, which implies that a 3-ms contact time can provide quantitative information about relative species concentration. Thus, a contact time of 3 ms was used in later experiments.

Figure 7 shows the effect of curing time at 135 °C on the DETA species concentration. The figure does not show much change in the relative species concentration with time, implying that the hydrolysis and condensation reactions are retarded by gelation and subsequent low mobility of

Table III. Comparison of the Species Fractions Obtained by Extrapolation and Those Obtained from a 3-ms Contact Time

	T <sup>1</sup>	T <sup>2</sup>	T <sup>3</sup>	$R_{ex}$
From extrapolated values	0.25	0.57	0.17	0.63
From 3-ms contact time	0.24	0.59	0.17	0.64

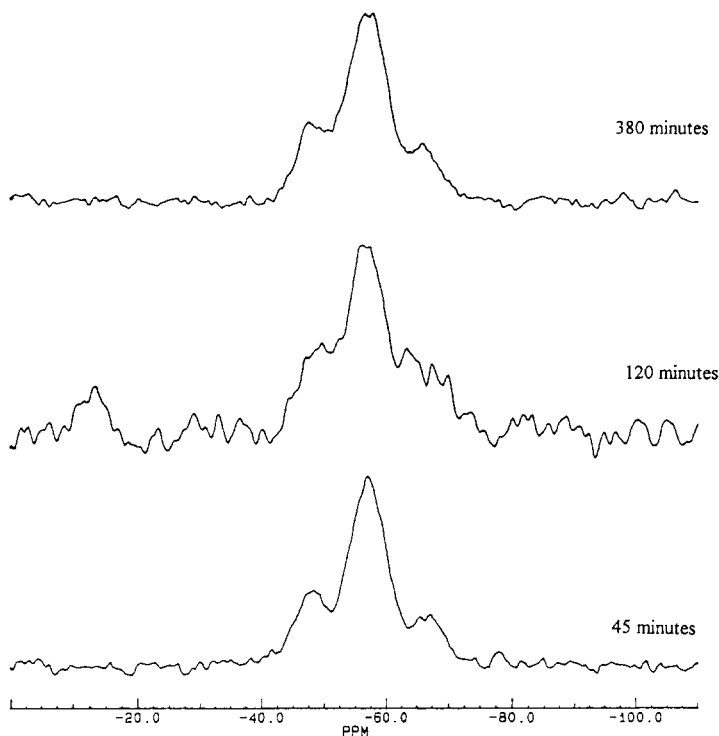


Fig. 7. Evolution of NMR spectra as a function of time for a functionalized DETA coating cured at 135 °C.

the reactive groups. This suggests that the coating is very close to vitrification even at the lowest curing times. In order to prove that the extent of reaction was limited by vitrification, a sample of the DETA coating previously subjected to a 380-min cure at 135 °C was subjected, in addition, to a temperature of 175 °C for a period of 4 h.

Figure 8 shows the NMR spectra of both samples and the relative species concentrations are tabulated in Table IV. In the sample cured at 175 °C, the silicon species are present in the predominantly the T<sup>2</sup> and T<sup>3</sup> form. Thus the reaction has progressed to a more condensed stage.

Table IV. Concentration of DETA Coating Subjected to an Additional Higher Temperature

Conditions of cure	T <sup>0</sup>	T <sup>1</sup>	T <sup>2</sup>	T <sup>3</sup>	R <sub>ex</sub>
135 °C, 380 min	—	0.18	0.68	0.14	0.65
135 °C, 380 min + 175 °C, 240 min	0.07	0.09	0.39	0.43	0.75

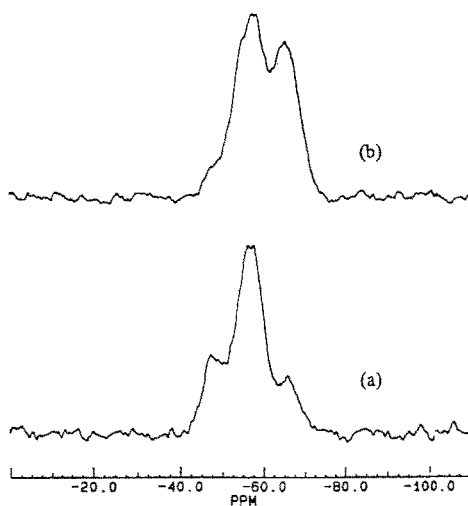
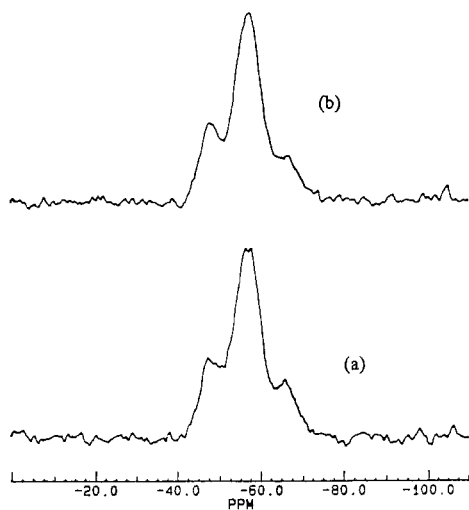
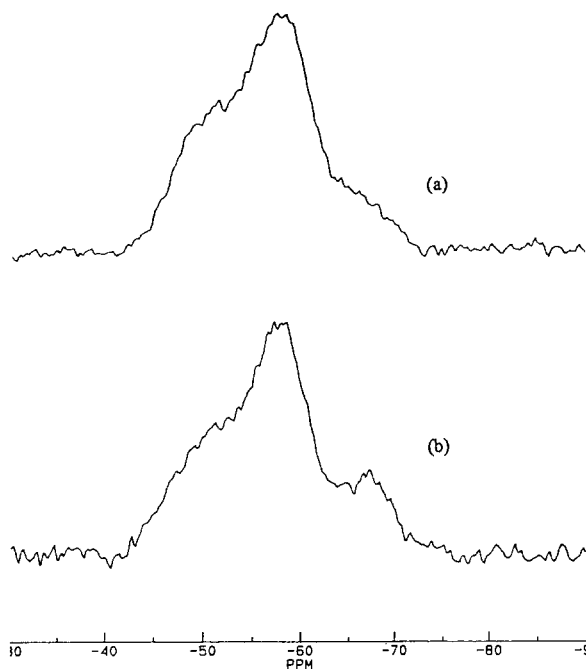


Fig. 8.  $^{29}\text{Si}$  NMR spectra of functionalized DETA coating cured at (a)  $135^\circ\text{C}$ , 380 min, and (b)  $135^\circ\text{C}$ , 380 min +  $175^\circ\text{C}$ , 240 min.

It may be recalled that water is a coreactant in the sol-gel process. The water added to the coating precursor is less than stoichiometric proportions ( $0.5 \text{ mol H}_2\text{O/mol}$  of alkoxide). Conceivably the overall extent of reaction could be increased by increasing the water added to the coating precursor. Accordingly the water dose was doubled, i.e.,  $1 \text{ mol}$  of water was added per mol of alkoxide. Figure 9 shows the NMR spectrum of the coating. The spectrum of the control ( $0.5 \text{ mol/mol}$  alkoxide) is shown for the purpose of comparison and Table V provides the species concentrations. The spectra show that there is not much effect of additional water on the overall extent of reaction, i.e., the water content does not determine the extent of reaction because it is present in sufficiently large quantities and therefore the water concentration does not control the kinetics. However, a very low water concentration does decrease the extent of reaction slightly as shown in Fig. 10. The figure shows the spectra of a DETA coating which had an initial water concentration of  $0.1 \text{ mol}$  of water/mol of alkoxide and  $0.018 \text{ mol}$  of acid/mol of alkoxide, which is slightly greater than the acid concentrations of the coating spectra in Fig. 9. The coating was cured at  $135^\circ\text{C}$  for a period of 8 h. The lower water content spectrum shows arguably a slightly greater concentration of the  $\text{T}^1$  species, which indicates only a slightly lower extent of reaction. These observations suggest that the water content does not play a major role in deciding the extent of the reaction, at least under these conditions. Possibly at the high reaction temperatures the species can react with moisture in the



**Fig. 9.**  $^{29}\text{Si}$  NMR spectra of functionalized DETA coating: (a) 0.5/1.0 water-to-alkoxide ratio; (b) 1/1 water-to-alkoxide ratio.



**Fig. 10.**  $^{29}\text{Si}$  spectra of functionalized DETA coating with an initial water/alkoxide ratio of 0.1/1, cured at 135°C; HCl ratio of (a) 0.0018 mol acid/mol alkoxide and (b) 0.018 mol acid/mol alkoxide.

**Table V.** Effect of Higher Water Concentration on the Species Distribution in a DETA Coating

Ratio of water to alkoxide	T <sup>1</sup>	T <sup>2</sup>	T <sup>3</sup>	R <sub>ex</sub>
0.5/1.0	0.18	0.68	0.14	0.65
1.0/1.0	0.20	0.66	0.13	0.64

air if additional water is needed. This is certainly possible as demonstrated by Besland and co-workers [18], who prepared gels from mixtures of alkylalkoxysilanes and titanium isopropoxide without the addition of water by subjecting them to temperatures between 80 and 150 °C.

The next coating studied was the functionalized melamine coating. Figure 11 shows the spectrum of melamine coating cured at 135 °C for 45 min over a range of contact times. The spectrum shows three distinct peaks, at ca. -49.9, -58.2, and 66.4 ppm, which are attributed to the T<sup>1</sup>, T<sup>2</sup>, and T<sup>3</sup> species, respectively [18, 19]. The spectrum shows no drastic change in the species concentration with varying contact time, suggesting that the rate constants  $T_{\text{Si-H}}$  and  $T_{1\rho}(\text{H})$  of all the species are of the same magnitude. Figure 12 shows the variation in peak intensity with contact time for each species. The T<sup>3</sup> species shows only three points due to a problem in the plotting program. The data were fitted with the biexponential equation. The  $I(0)$ ,  $T_{1\rho}(\text{H})$ , and  $T_{\text{Si-H}}$  values obtained from the fitted curves are provided in Table VI. The  $T_{\text{Si-H}}$  values vary from 1.23 to 2.15 ms, while the  $T_{1\rho}(\text{H})$  values vary from 5.52 to 7.59 ms. The values for the  $T_{\text{Si-H}}$  and  $T_{1\rho}(\text{H})$  are in the same range as the corresponding values obtained from the DETA spectrum. This implies that the magnetic environment around the silicon species is little influenced by the differences in chemical structure of the organic that comprises the coating. The lack of influence is probably due to the large distance (>7 C-C bond lengths) between the silicon atom and the organic moiety. The species distribution calculated from the intensities of the individual peaks in each spectrum is plotted against contact time as shown in Fig. 13. The figure again shows that the relative concentration of the T<sup>3</sup> species increases slightly with an increase in contact time at the expense of the T<sup>1</sup> species. The actual species distribution calculated from the  $I(0)$  values is presented in Table VII, together with the values determined from the spectrum obtained with a 3-ms contact time. The table shows a good agreement between the individual species, which implies that a 3-ms contact time would provide a spectrum in which the species fractions are representative of those in the actual sample. Figures 14 and 15 show the spectra and species distribution (Table VIII) at 3-ms contact time of the functionalized melamine for various curing

times at 135 °C. The spectrum shows that there is a decrease in the T<sup>1</sup> and the T<sup>2</sup> species with curing time and a concurrent increase in the T<sup>3</sup> species concentration. By comparing the 45-min spectra of functionalized melamine and DETA, it is seen that there is a higher fraction of the T<sup>1</sup> species in the melamine coating. Thus, the melamine has a lower extent of reaction at the shorter curing times. It may be recalled that the acid and water added per mole of alkoxide were the same for the functionalized melamine and DETA solutions. The solvent has been known to influence the hydrolysis and condensation rates in the sol-gel reaction. Substitution of a protic, polar solvent such as isopropanol with a polar, aprotic solvent such as DMF should increase the hydrolysis and condensation rate. The DMF is comparatively inert in comparison with the isopropanol [19]. Isopropanol tends to hydrogen bond with the nucleophile (hydronium ion) and reduces the reactivity of the nucleophile [5]. Based on these

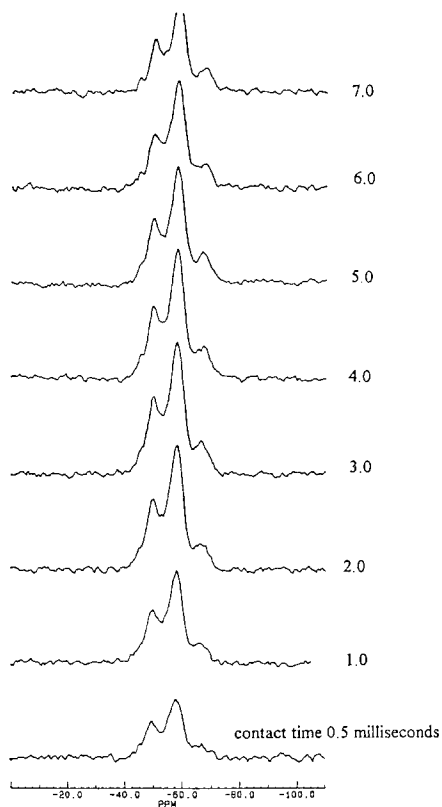


Fig. 11. <sup>29</sup>Si spectra of functionalized melamine cured at 135 °C, 45 min, as a function of contact time.



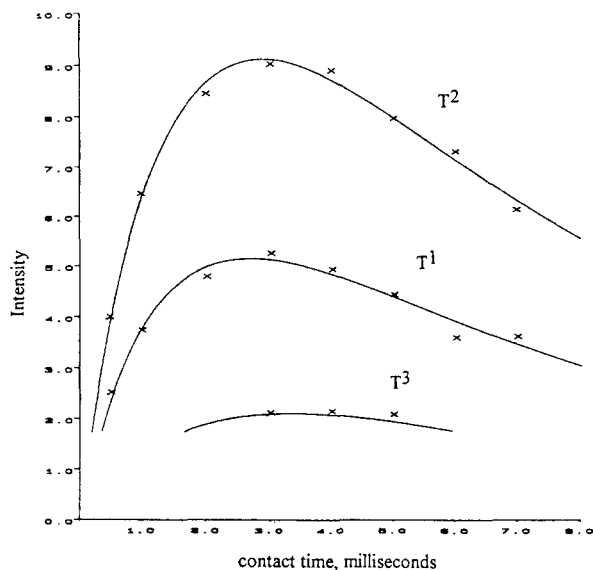


Fig. 12. Variation in peak intensity of each species as a function of contact time for the functionalized melamine coating in Fig. 11.

arguments, the extent of reaction would be expected to be higher in the functionalized melamine coating, which is clearly not the case. This suggests that another factor may be responsible for the lower extent of reaction in melamine. From an inspection of the chemical structures of melamine and DETA, it is apparent that melamine would be more basic

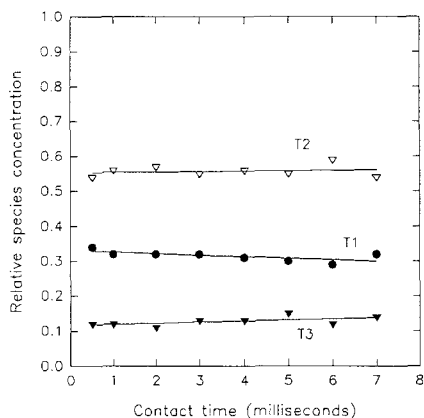


Fig. 13. Relative species concentration of functionalized melamine coating as a function of contact time.

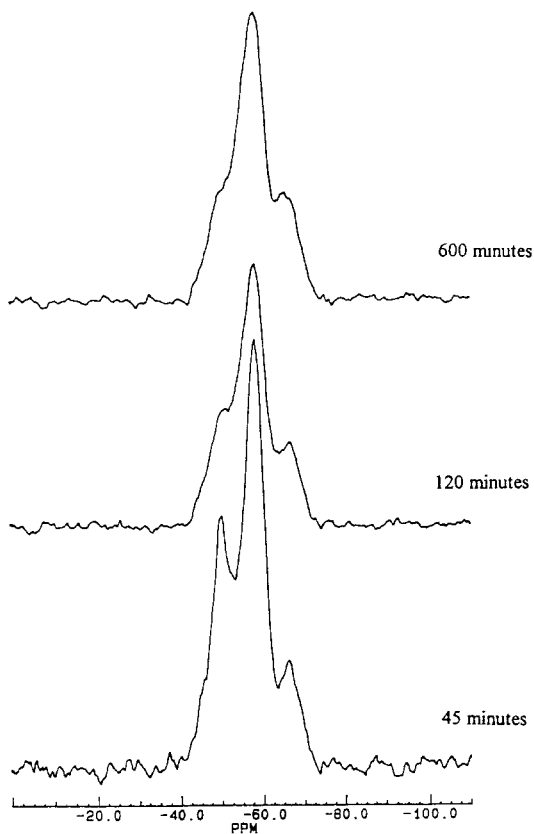


Fig. 14. Evolution of NMR spectra as a function of time for a functionalized melamine coating cured at 135 °C.

than DETA. It may be recalled that the hydrolysis rate under acid catalysis decreases as the basicity of the reaction medium increases. Thus, it is possible that the higher basicity of the melamine has retarded the hydrolysis step. It follows that a higher concentration of acid should increase the overall extent of reaction. Figure 16 shows the effect of higher acid concentration on the functionalized melamine coating. When the acid concentration is increased by an order of magnitude, the silicon species in the functionalized melamine coating are predominantly in the form of  $T^2$  and  $T^3$  species, implying a higher extent of reaction. The extent of reaction is higher than the functionalized DETA coating. Thus, a higher initial acid concentration can increase the extent of reaction.

Figure 17 shows the spectrum of the functionalized polyethyleneimine coating at varying curing times at 135 °C. The species distribution is shown

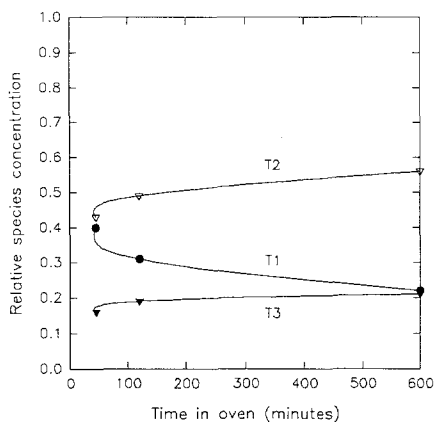


Fig. 15. Relative species concentration of functionalized melamine coating determined from Fig. 14.

in Fig. 18 and tabulated in Table IX. The spectrum shows four peaks, at ca.  $-44$ ,  $-52$ ,  $-58$ , and  $-65$  ppm, which are assigned to the  $T^0$ ,  $T^1$ ,  $T^2$ , and  $T^3$  species. The figure shows that as the curing time increases, the relative concentration of the  $T^1$ ,  $T^2$ , and  $T^3$  species increases at the expense of the  $T^0$  species. A characteristic of the functionalized PEI spectrum is the significant concentration of the uncondensed silanols present even at the longest curing times, which contributes to a lower extent of reaction as

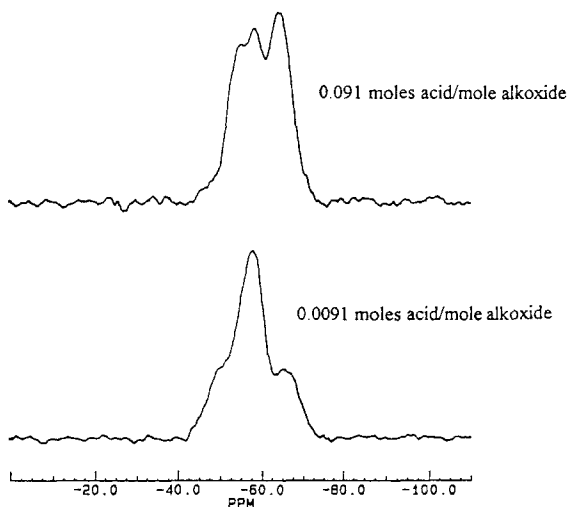


Fig. 16.  $^{29}\text{Si}$  spectra of functionalized melamine cured at  $135^\circ\text{C}$ : effect of acid concentration.

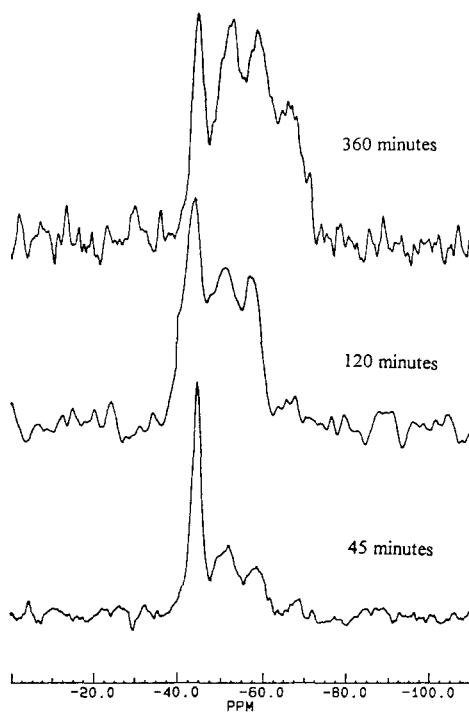


Fig. 17.  $^{29}\text{Si}$  spectra of functionalized polyethyleneimine at various curing times at 135 °C.

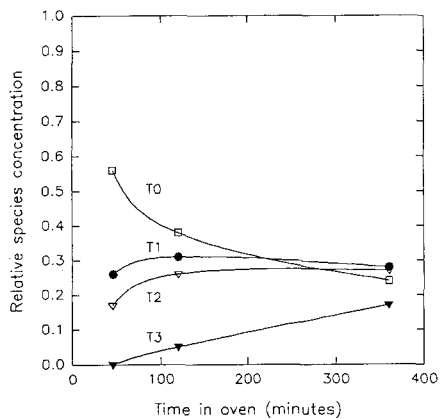


Fig. 18. Series distribution of functionalized polyethyleneimine as a function of curing time at 135 °C.

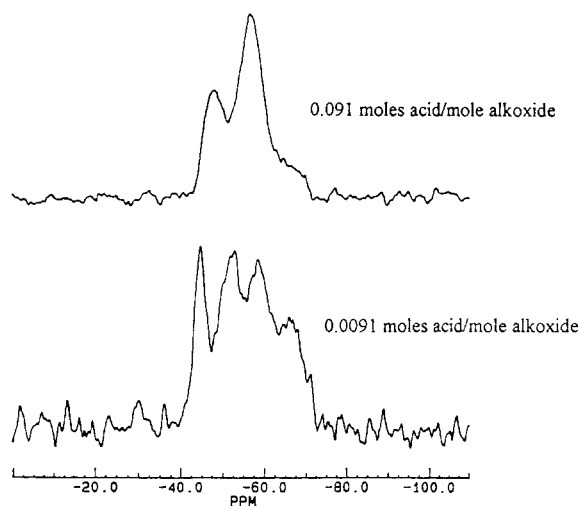


Fig. 19.  $^{29}\text{Si}$  of functionalized polyethyleneimine coating: effect of acid concentration.

shown in Fig. 20. The PEI coating may best be compared with the functionalized DETA coating. The functionalized DETA coating is similar to the functionalized PEI coating in a sense that the solvent system and the repeat unit of the organic backbone is the same. These factors can be discarded as the cause of the discrepancy in the extent of reaction. In view of the observations in the melamine system it would seem likely that the effect on the reaction of the unreacted imine groups would also have to be considered. It may be recalled that a fraction of the imine groups remain

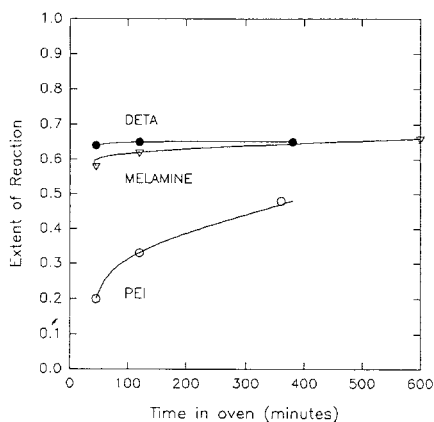


Fig. 20. Extent of reaction as a function of curing time at  $135^\circ\text{C}$  for the functionalized DETA, melamine, and polyethyleneimine.

**Table VI.** Values of the Rate Constants Calculated from Curve-Fitting Data in Fig. 12

Species	$T_{Si-H}$	$T_{1\rho}(H)$	$I(0)$
T <sup>1</sup>	1.23	7.59	7.29
T <sup>2</sup>	1.41	7.31	13.52
T <sup>3</sup>	2.15	5.52	3.80

**Table VII.** Species Distribution at a 3-ms Contact Time and That Calculated from Curve-Fitted Constants of the Melamine Coating

	T <sup>1</sup>	T <sup>2</sup>	T <sup>3</sup>	$R_{ex}$
From extrapolated values	0.32	0.55	0.13	0.59
From 3-ms contact time	0.30	0.55	0.13	0.59

**Table VIII.** Species Distribution in the Functionalized Melamine Coating as the Curing Time Is Varied

Time in oven (min)	T <sup>1</sup>	T <sup>2</sup>	T <sup>3</sup>	$R_{ex}$
45	0.40	0.43	0.16	0.58
120	0.31	0.49	0.19	0.62
600	0.22	0.56	0.21	0.66

**Table IX.** Species Distribution of Polyethyleneimine as the Curing Time is Varied

Time in oven (min)	$T_0$	T <sup>1</sup>	T <sup>2</sup>	T <sup>3</sup>	$R_{ex}$
45	0.56	0.26	0.17	0.00	0.20
120	0.38	0.31	0.26	0.05	0.33
600	0.24	0.28	0.27	0.21	0.48

unreacted during the endcapping reaction. These free imines could potentially act as basic sites and retard the rate of hydrolysis in a manner analogous to the effect of melamine in melamine based systems. In PEI, the retarding effect seems to be higher as evidenced by the significant fraction of the  $T^0$  species. The effect of a higher acid concentration is also similar to melamine-based systems. Figure 19 shows the effect of increasing the acid concentration by an order of magnitude. The line shape of the functionalized PEI coating at the higher acid content now shows a closer resemblance to the functionalized DETA coating in Fig. 6. The  $T^2$  species is predominant followed by the  $T^1$  and the  $T^3$  species. The peaks of the  $T^0$  and  $T^1$  species have merged, resulting in a hybrid peak which is located between the  $T^0$  and the  $T^1$  peaks. Despite the 10-fold increase in acid concentration, the extent of reaction is lower than that of the DETA coating. This suggests that an even higher concentration of acid is needed for the PEI spectrum to match the DETA spectrum. Figure 20 summarizes the extent of reaction as a function of time for the various functionalized organics. The figure clearly shows the effect of the backbone structure on the extent of the reaction.

## SUMMARY AND CONCLUSIONS

Diethylentriamine, melamine, and polyethyleneimine were functionalized with triethoxysilane and reacted through the sol-gel process to obtain clear coatings on polycarbonate. The concentration of the individual silicon species and the overall extent of reaction were determined by  $^{29}\text{Si}$  CP-MAS solid-state NMR. The data show that the reaction of the functionalized coatings is limited by vitrification. A broad spectrum of species is present in the coating at vitrification. The extent of reaction was found to differ for the various coatings. The difference was attributed to the basicity of the organic backbone which helped to retard the sol-gel reaction. The extent of reaction could be increased by curing at a higher temperature, curing for longer times and by increasing the acid concentration. The water concentration in the coating precursor did not play a significant role in the range of water concentrations studied.

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