Electronic Spectra of Polysilanes[†]

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ABSTRACT: The absorption, polarized absorption, and fluorescence spectra of a variety of high molecular weight polysilanes in solution are reported. The first absorption maximum of alkyl-substituted polysilanes shifts linearly to lower energies with increasing substituent size. We suggest that this shift stems from steric interference of the substituents which results in straining of the Si–Si backbone bonds and/or a change of the backbone conformational preference. Strong parallel dichroism in stretch-oriented (di-*n*-hexylsilane)$_n$ is observed. Aryl substitution gives rise to additional shifts in the first absorption band to lower energies and introduces parallel dichroism in oriented materials when the substituents are phenyl or *p*-anisyl but not with β-naphthyl. No evidence for vibrational fine structure exists in either absorption or fluorescence in the high polymer spectra even at low temperature. These results are interpreted as evidence for the first transition being $\sigma \rightarrow \sigma^*$ in the alkyl-substituted polysilanes, mixed π-σ-σ^*-like in phenyl- and *p*-anisyl-substituted polysilanes, and $\pi \rightarrow \pi^*$-like for β-naphthyl substitutions.

Introduction

Recently high molecular weight polysilanes have received considerable attention as precursors to silicon carbide fiber production,[1] as photoinitiators in alkene polymerization,[2] as photoresists,[3] and as photoconductors.[4] Although all known polysilanes are photosensitive in solution, a variety of solid-state photochemical behavior, depending upon the substituent nature, has been observed.[3,5] We have studied the photophysical properties of high molecular weight polysilanes with a variety of substituents to both identify the precursors to photochemistry and provide insight into the mechanisms of charge and energy transport in this class of interesting new polymers.

Studies of the UV spectra of oligosilanes were first reported over 20 years ago. Gilman, Atwell, and Schwebke[7] discussed the ultraviolet spectra of a series of silanes with from two to six dimethylsilane units having phenyl terminations and observed that these behaved similarly to the α,ω-diphenyl polyenes in that their absorption position shifted to the red as the silicon backbone length increased.[9] They[8] also examined the disilanes with increasing phenyl substitutions from zero to six phenyls replacing methyl substituents. In these studies, they observed an apparent conjugation of the aromatic ring with the silicon–silicon linkage and suggested that the activity of this linkage arose from the interaction of the vacant silicon d orbitals with the aromatic (or olefinic) π orbitals of the substituent. Hague and Prince[10] examined the spectra of a variety of phenyl-substituted silanes and interpreted the spectral data in terms of a $\pi \rightarrow \pi(\text{dSi})$ transition from the ring π levels to a π level constructed from the vacant dπ orbitals of the silicon chain or states formed from mixtures of these π levels.

Pitt and co-workers[11] showed that HMO theory was successful in treating the energy dependence of the absorption maxima of permethyl polysilanes having from 3 to 10 silane units. If the assumption was made that the upper states of the transition contained some πC–C character when phenyl or vinyl groups were substituted, the same treatment was effective in predicting their absorption maxima. This result suggested that, at least for the short-chain polysilanes, the transition origin was associated with the silicon–silicon bonding orbitals. Ionization potentials for methyl-substituted silanes having up to eight silicons were obtained[13] and also could be fit with simple molecular orbital methods, assuming that these ionization potentials gave the ground-state energy for a delocalized bonding orbital.[14] The results indicated that the shift in HOMO energy accounted for about 60% of the magnitude of the spectral red shifts of the permethylated silanes with increasing chain length.

UV photoelectron spectra,[15] ionization potentials, and half-wave reduction potentials[16] were used to develop a model of bonding in aryl-substituted oligosilanes. In this work it is concluded that the HOMO's are mixtures of the delocalized silicon chain σ-bonding orbitals with the π-bonding orbitals of the aryl substituents. For phenyl substitution, this model suggests that the HOMO is principally σSi–Si and the first transition σ-π^*(ring), but, with the lower ionization potential of *p*-anisyl or naphthyl substituents, the HOMO becomes more π-like and the corresponding spectra arise from $\pi(\text{ring}) \rightarrow \pi^*(\text{ring})$ transitions.

More recently, higher molecular weight oligomers of permethylated[12,17,18] silanes have been synthesized. In studies of the permethyl silanes with chain lengths extending to 24 silane atoms, Boberski and Allred[12] found that the behavior of not only the lowest energy transition but the next observable band as well could be fit with the same parameters using the Sandorfy "C" method. They proposed that both bands originate from transitions that involve delocalized antibonding or bonding orbitals. In the higher members of this series the two transitions become nearly energetically degenerate and would be expected to be unresolvable in the corresponding high polymer. The X-ray photoelectron spectra and NMR spectra of both linear and cyclic oligosilanes[18,26–29] indicate that the σ-bonding orbitals are delocalized in these small molecules. The behavior of the alkyl polysilanes and cyclopolysilanes suggests that the HOMO can be interpreted as a delocalized σ-bonding orbital in the larger linear and cyclic oligosilanes in much the same way as with the lower molecular weight analogues.

Absorption spectra of high molecular weight homo- and copolysilanes with methyl, alkyl, and aryl side chains[3,5,19–23] have been published recently, as has the dependence of the first absorption maximum on chain length for two of these high polymers. Absorption and emission spectra of poly(dimethylsilane-*co*-methyl-(1-naphthyl)silane) in solution have been examined by Todesco and Kamat.[6] Naphthalene-like monomer and excimer emission was observed for both the singlet and triplet states. These workers also presented evidence that photoscission of the

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polysilane backbone occurs mainly at naphthyl-bearing silicon atoms to give silyl radicals.

Solid-state absorption and emission spectra of a fully alkyl-substituted polysilane, poly(isopropylmethylsilane-*co*-*n*-propylmethylsilane) have been discussed by Zeigler et al.[3a] In this case, a narrow high quantum yield (ϕ_f = 0.65) fluorescence was seen. However, the phosphorescent emission was weak ($\phi_f \sim 10^{-4}$), broad, and strongly vibrationally coupled to Si–C vibrations. On the basis of these observations, states in the triplet manifold were suggested as the likely precursors to photochemical bond scission in this "self-developing" resist material.

A theoretical treatment of the parent polysilane electronic structure has been given by Takeda and Matsumoto[30] and suggests that the HOMO in this material is purely Si–Si σ-bonding, but the LUMO is a mixture of both Si–Si and Si–H antibonding character. This analysis also indicates the presence of a filled band very close to the HOMO for infinite chains with an allowed transition to the LUMO. The existence of this second bonding level may account for the two transitions which merge with increasing chain length in the permethylated silane telomers.

We have synthesized a variety of high polysilanes with both alkyl and aryl substituents and examined not only their absorption spectra in solution but also their spectra as neat solid films and in oriented polymer hosts. Their fluorescence spectra were also obtained to gain additional insight into the nature of the first excited state of these intriguing systems. Kepler et al.[4] have shown that both alkyl- and aryl-substituted polysilanes photoconduct with a quantum efficiency of ≈1% at room temperature. The photocarriers are holes and exhibit high mobility ($\approx 10^{-4}$ cm^2/(V·s)) for amorphous materials. No electron mobility could be detected. This behavior is not in accord with the expectations of the simple delocalized bonding model for the small molecules[15,16] or the nature of the first transition in those telomers, in which electrons and holes would be expected to have similar mobilities. We propose that the evidence favors a first transition in the alkyl-substituted polysilanes that is primarily $\sigma \rightarrow \sigma^*$ in nature overlapped by a transition originating in a second bonding level close to the HOMO. For the aryl-substituted materials, the transitions are similar in origin to the alkyl compounds but both the HOMO and LUMO contain some π character derived from mixing with the ring states. For low energy differences between the ring π and π^* levels, the first transition becomes principally $\pi \rightarrow \pi^*$(ring).

Experimental Section

General. Hydrocarbon solvents were dried over $CaSO_4$ and then refluxed and distilled under argon from NaK alloy. Ether solvents were predried over $CaSO_4$, distilled under argon from Na/benzophenone ketyl to remove residual water and peroxides, and stored under argon until use. A representative synthetic procedure for preparation and polymerization[38] of a noncommercial monomer follows below. Monomer synthesis and polymerizations were performed in dried, N_2-purged glassware. All monomers and polymers were fully characterized (IR, NMR, MS) and gave satisfactory microanalytical results (within 0.3% of theoretical for C, H, and Si). Absorption and emission spectra were obtained on polymers purified by three to four precipitations from toluene or tetrahydrofuran with a nonsolvent (which was specific to the polymer being prepared). For the selected narrow molecular weight poly(phenylmethylsilane), a purified, broad molecular weight range preparation was fractionated on a gel permeation chromatograph in tetrahydrofuran, and the collected fractions were examined without isolating the solid polymers. Solution spectra at room temperature were taken in freshly deoxygenated, distilled tetrahydrofuran or 2-methyltetrahydrofuran for the low-temperature studies.

The spectra were observed by using a combination absorption spectrometer–fluorimeter of our own design. The instrument consists of a xenon (or mercury-xenon) arc lamp, 0.2-m f4.0 Czerny–Turner monochromator/illuminator, and a sample compartment where the sample can be viewed at right angles to the exciting beam or can be illuminated at 180° with a deuterium arc lamp. Detection uses a 0.22-m double Czerny–Turner monochromator equipped with a cooled gallium arsenide cathode photomultiplier. Both photon counting and direct current detection electronics are simultaneously available. In addition, the transmitted exciting beam is continuously monitored by a separate in-line detector to compensate for fluctuations in the lamp output.

Data gathering is controlled by an LSI-11 microcomputer which scans the monochromator and reads the data via a gated 32-bit counter or analogue-to-digital converter. The results are corrected for both excitation intensity and analyzer throughput and recorded on floppy disks for further study.

The sensitivity of the monochromator–phototube combination as a function of wavelength was calibrated by using a ribbon filament tungsten source standardized by NBS. This sensitivity curve is used to correct all fluorescence band shapes.

Low-temperature spectra were obtained by using gaseous nitrogen cooling of the sample chamber. Absorption spectra were obtained by scanning the straight-line deuterium source in the absence of right-angle excitation and can be obtained without movement of the sample under study.

All solution samples studied were extremely photosensitive to light in the region of absorbance. Neutral density filters (OD 2.0–4.0) were used in the exciting beam to minimize photodecomposition during spectrum scans. The absorbance near the long-wavelength transition was very sensitive to the degree of photolysis, and the excitation light transmission was continuously monitored to assure that the spectra were not distorted by photodecomposition. Sufficient reduction of exciting light was used so that the transmitted light varied less than about 1% and the fluorescence spectra on repetitive scans reproduced within instrumental error. Sample solutions were protected from room light prior to spectral determinations.

The neat solid films of poly(phenylmethylsilane) were cast on quartz plates from tetrahydrofuran solution in thicknesses ranging from 6400 Å to greater than 30 μm. The polymer-host-supported films were cast from solutions containing the polymer host (poly(methyl methacrylate) (PMMA) for most systems, poly(*n*-butyl methacrylate) for poly(phenylmethylsilane)). The dried host film containing ≈0.1% polysilane was oriented by straining to ≈700% near its T_g and examined at room temperature.

Fluorescence quantum yields were measured by comparison with the fluorescence intensity of *p*-terphenyl in the same solvent. The quantum yield for *p*-terphenyl was taken as 0.93.[32]

(4-Methoxyphenyl)methyldichlorosilane. A solution of 24.57 g (105 mmol) 4-iodoanisole (Aldrich) in 100 mL of dry benzene was prepared in a dried, argon-purged 3-neck flask equipped with an Allihn condenser, a pressure-equalizing dropping funnel, a gas inlet, and a stirring bar. To this was added dropwise at ambient temperature 100 mL of 2.1 M *tert*-butyllithium (210 mmol) in pentane. A milky white precipitate formed, and a slight exotherm was evident. The mixture was heated at reflux for 2 h after completion of the addition and then allowed to cool to room temperature. Meanwhile, a second flask equipped with a condenser, pressure-equalizing funnel, and gas inlet was readied, and a solution of 15.68 g (105 mmol) of freshly distilled methyltrichlorosilane in 100 mL of dry benzene was prepared in it. The 4-methoxyphenyllithium solution was transferred via double-tipped needles to the dropping funnel and added dropwise to the silane solution. After 2 h, the reaction mixture gave a negative Gilman test for lithium reagent and was worked up by filtration in a nitrogen atmosphere followed by removal of solvent at reduced pressure. The resulting oil was fractionally distilled at a pressure of 1 mmHg to afford 7.6 g (33%) of colorless product, bp 89–92 °C (lit. bp 96 °C (3 mmHg)).[39]

Poly(4-methoxyphenylmethylsilane). A 40 wt % sodium dispersion (2.69 g, 46.9 mmol) was added dropwise to a refluxing solution of 4.71 g (21.3 mmol) of (4-methoxyphenyl)methyldichlorosilane in 100 mL of dry toluene contained in a foil-covered reaction vessel. The addition was maintained at the highest rate allowed by the strongly exothermic reaction. Reflux was continued

Table I
Summary of Absorption and Emission Spectral Data for Poly(dialkylsilanes)

substituents	λ_{max1}	ϵ_{max1}	λ_{max2}	ϵ_{max2}	F_{max}	ϕ_{fl}	no. of units
n-hexyl, methyl	3060	6500			3360	0.61	660
cyclohexyl, methyl	3170	6540			3450	0.42	40
n-dodecyl, methyl	3100	6340	2240	2930	3370	0.67	155
di-*n*-hexyl	3180	10500	2200	2870	3420		5100
β-phenethyl, methyl	3050	9950	2140	17140	3375		6700
dimethyl[a]	2960	45500	2280	28000			24

[a] From extrapolated values, ref 12.

for 4 h after completion of the Na addition, whereupon the dark blue slurry was cooled to room temperature and sufficient methanol added cautiously to react with the excess sodium. A volume of saturated aqueous $NaHCO_3$ equal to that of the reaction mixture was added in a single portion, and, after complete dissolution of the blue NaCl byproduct had taken place, the layers were separated. Removal of solvent from the organic phase afforded 5.08 g of crude product as a viscous oil. Two precipitations of this from toluene with hexane and one from tetrahydrofuran (THF) with methanol gave 130 mg of pure white powdered polymer. Size exclusion chromatography of this material (THF, 1.0 mL/min, Zorbax bimodal column set) indicated a modal molecular weight relative to polystyrene standards of 30 000 with a shoulder at 5000: ^1H NMR ($CDCl_3$) δ −0.2 (br s, 3 H, Si–CH_3), 3.8 (br s, 3 H, OCH_3), 6.6 (br m, 4 H, aryl H); IR (KBr) 3010, 2940, 2850, 1595, 1275, 1250, 1090, 1030, 810, 750, and 685 cm^{-1}. Anal. C, H, Si.

Results

Spectra of Alkyl Polysilanes. The observed solution spectra of the alkyl polysilanes are summarized in Table I. The spectra of poly(β-phenethylmethylsilane) are included with the data on alkyl-substituted silanes since both the absorption and fluorescence spectra and their maxima and widths suggest that the aromatic ring insulated from the chain by the two methylene groups is not important in determining the states involved in the transition. Figure 1 compares the spectra of poly(β-phenethylmethylsilane) with poly(*n*-hexylmethylsilane).

The positions of the first absorption maxima in alkyl polysilanes suggest that, in the high molecular weight limit, the transition energy is determined primarily by the size of the substituent groups. Figure 2 shows the relationship between absorption position and an estimated size based on the sum of the radii of the groups attached to the silicon-bonded carbons. For this estimate, only the first three carbons and their associated hydrogens are considered, and the conformation is taken to separate the third carbon the maximum distance from its associated silicon. This estimate ignores the remainder of the chain and may underestimate somewhat the effective size of the dodecyl group. Nevertheless, it does suggest that the limiting long-chain transition energy is related linearly to an effective side-group size. Note that, again, the size of the β-phenethyl and methyl substituents places the corresponding polymer clearly in this series.

The widths of both the absorption and emission spectra in poly(dialkylsilanes) are substantially greater than those of high molecular weight poly(phenylmethylsilane) and poly(*p*-anisylmethylsilane). No evidence for vibrational fine structure is shown in any of the high polymer solution spectra. Below −100 °C both the absorption and emission bands narrow in the alkyl-substituted polymers.

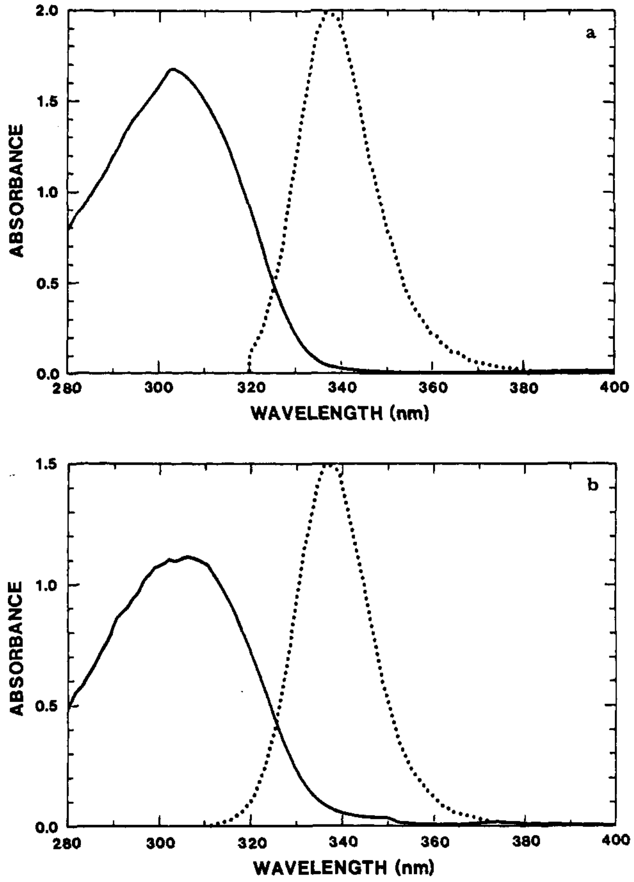

Figure 1. Absorption and emission spectra of (a) poly(β-phenethylmethylsilane) in THF and (b) poly(*n*-hexylmethylsilane) in THF.

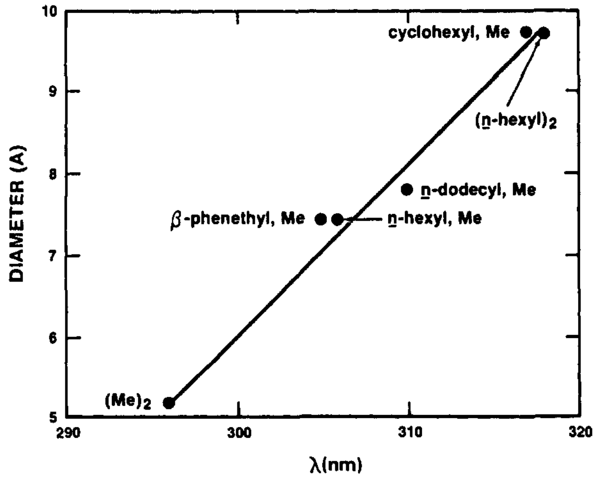

Figure 2. Wavelength of the first band maximum vs. the radius sum of substituents on the silicon chain (see text).

The spectral width of these transitions is probably due to both the existence of two closely spaced lower levels, perhaps the two transitions of the permethyl series unresolved, and inhomogeneous broadening related to conformational energy dependence of the transitions. In dilute solutions at approximately −31 °C, poly(di-*n*-hexylsilane) is seen to undergo a rod–coil transition,[33a] where the absorption line widths increase by a factor of about 3. Most

Table II
Summary of Absorption and Emission Spectral Data for Poly(arylmethylsilanes)

substituents	λ_{max1}	ϵ_1	λ_{max2}	ϵ_2	λ_{fl}	ϕ_{fl}	no. of units in chain
phenyl, methyl	3420	12000	2720	4300	3525	0.084–0.3	4200
p-anisyl, methyl	3440	8180	2720	7450	3605	0.2–0.5	340
β-naphthyl, methyl	3500	2800	2270	17000	4370		300

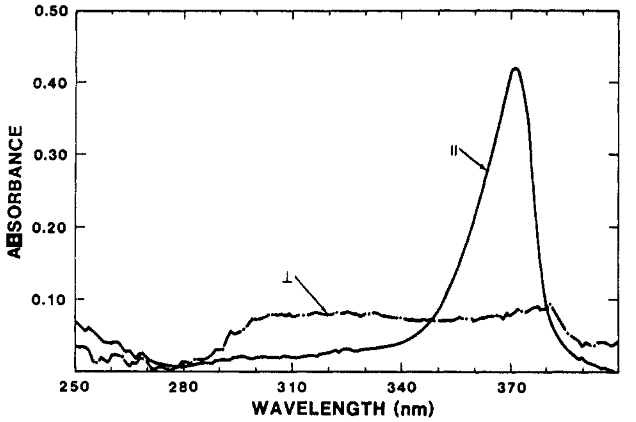

Figure 3. Polarized absorption spectra of a stretch-oriented (draw ratio ~20) film of poly(di-*n*-hexylsilane) on poly(methyl methacrylate).

asymmetrically substituted alkyl polysilanes and alkyl polysilane copolymers also exhibit either substantial thermochromism or rod–coil transitions at low temperatures, depending upon solvent, with band narrowing and bathochromic shifts as the temperature is lowered. A few polysilanes (e.g., poly(cyclohexylmethylsilane)) exhibit hypsochromic shifts with decreased line widths on cooling which are observable both in absorption and emission. We have suggested[33c] that this effect may be due to a change in the conformational preference of the polymer chain from trans in those polysilanes showing bathochromic shifts to gauche or pseudogauche in those polysilanes displaying hypsochromic shift behavior. Unsymmetrically substituted polysilanes show greater line widths than the symmetrically substituted polymers. Since the rod form must be substantially more ordered than the random coil and has considerably narrower spectra, the wide bands in the alkyl-substituted polysilanes are likely to result primarily from inhomogeneous (conformational) broadening.

Polarized absorption spectra were taken for both poly(β-phenethylmethylsilane) and poly(cyclohexylmethylsilane) by doping the polymers into high molecular weight poly(methyl methacrylate). No visible scattering was observed in these doped films either before or after straining at T_g to ≈700%. The resulting films exhibited no dichroism from 275 to 400 nm. However, when an approximately 2000-Å-thick film of poly(di-*n*-hexylsilane) cast onto a 100-μm film of poly(methyl methacrylate) was similarly oriented (draw ratio >20), it displayed the expected strong dichroism parallel to the draw direction, presumably parallel to the chain. The spectrum from this film (Figure 3) was that of a nearly 100% crystalline material and, subsequent to the draw, showed no detectable absorption in perpendicularly polarized light (i.e., essentially complete parallel orientation was achieved). This observation suggests that the failure to detect orientation in the host solutions of the other poly(dialkylsilanes) examined is either a result of segregation of the solute or, more likely, that the solute is present in a globular, noninterpenetrated conformation which cannot undergo sufficient orientation for the dichroism to be detectable by these techniques.

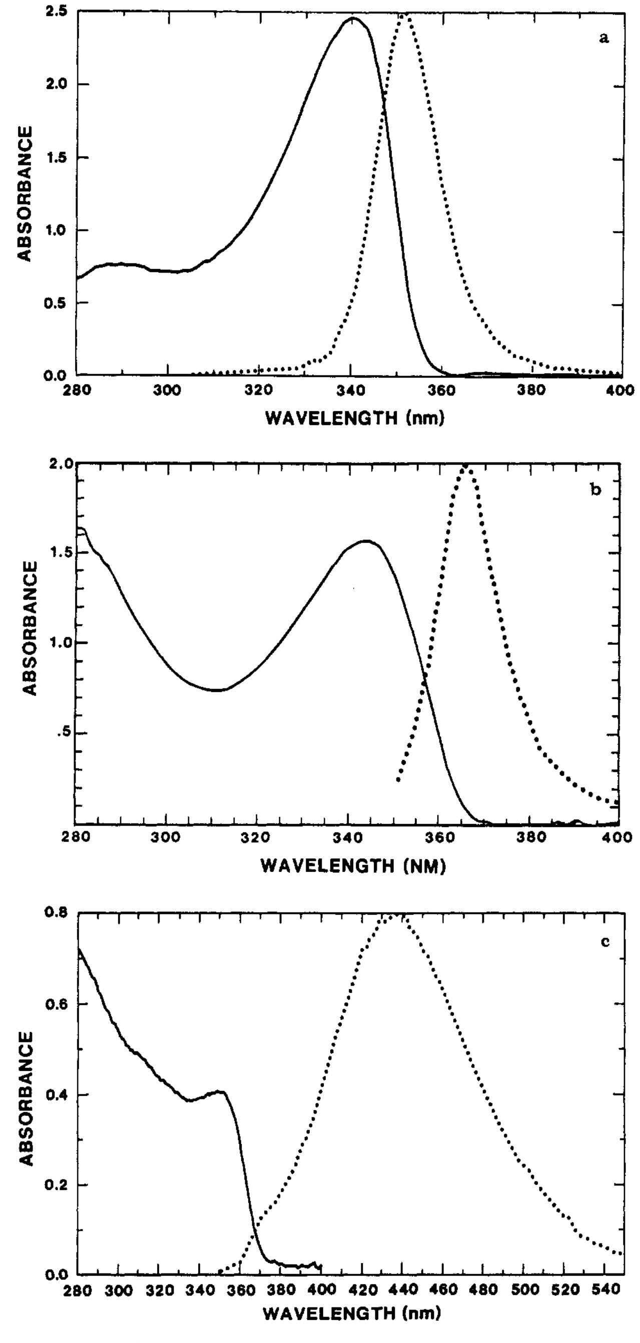

Figure 4. Absorption and emission spectra of aryl polysilanes in THF solutions: (a) poly(phenylmethylsilane); (b) poly(*p*-anisylmethylsilane); (c) poly(β-naphthylmethylsilane).

Spectra of Aryl Polysilanes. The solution spectra of the three aryl polysilanes studied are summarized in Table II and their spectra shown in Figure 4. Here, two distinctly different spectral types are apparent. For both phenyl and *p*-anisyl substitution, the spectra are narrow both in absorption and emission, while β-naphthyl substitution gives weak absorption and a very broad emission spectrum. This broad emission spectrum is similar in shape to the spectrum observed from poly(2-vinyl-

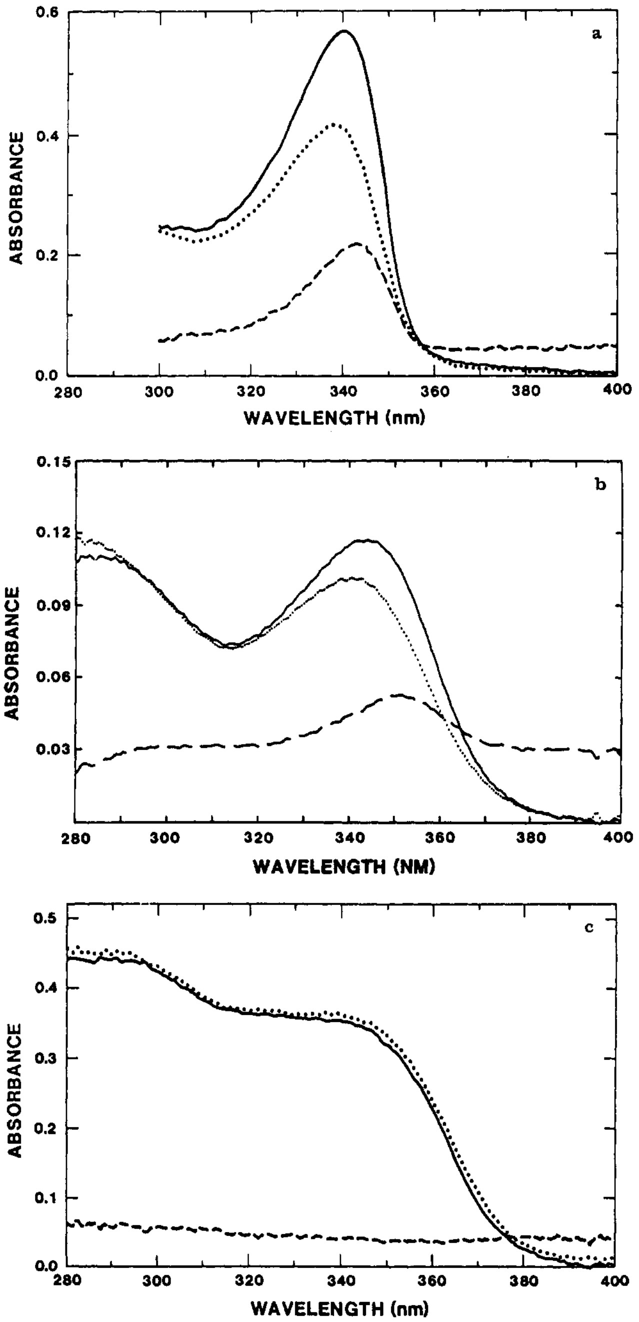

Figure 5. Polarized absorption spectra of aryl polysilanes in oriented polymer hosts: (solid curve) parallel orientation; (dotted curve) perpendicular orientation; (dashed curve) parallel–perpendicular); (a) poly(phenylmethylsilane) in poly(*n*-butyl methacrylate); (b) poly(*p*-anisylmethylsilane) in PMMA; (c) poly(β-naphthylmethylsilane) in PMMA.

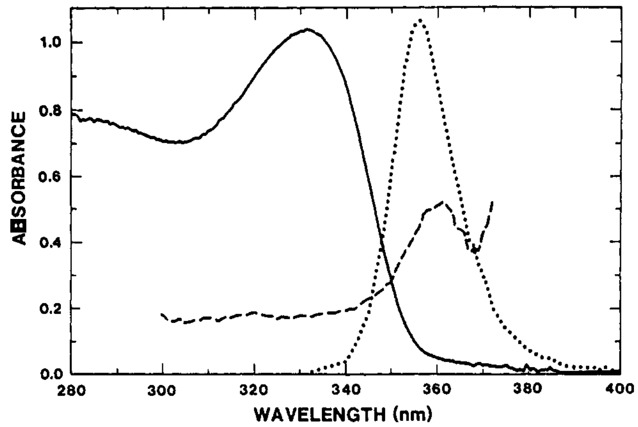

Figure 6. Absorption spectrum, emission spectrum, and emission quantum yield of cast neat poly(phenylmethylsilane). The emission quantum yield scale is linear with a value of 0.5 at the emission peak.

naphthalene) in 2-methyltetrahydrofuran. This emission has been attributed to intramolecular excimer formation[34] prior to emission. Near the high-energy region a small subsidiary shoulder is apparent, again similar to the case of poly(2-vinylnaphthalene) and attributed in that polymer to fluorescence from unassociated excited naphthalene moieties.

The polarized absorption spectra of these three polymers were examined in a high molecular weight polymer host following strain alignment. Both poly(*p*-anisylmethylsilane) and poly(β-naphthylmethylsilane) were miscible at the 0.1% level with poly(methyl methacrylate). The phenyl, methyl-substituted polymer precipitated in this host, but was found compatible with poly(*n*-butyl methacrylate) and was observed in that host. The spectra obtained are shown in Figure 5 together with the difference $\epsilon_{\parallel} - \epsilon_{\perp}$. Poly(phenylmethylsilane) and poly(*p*-anisylmethylsilane) exhibit substantial dichroism with the maximum transition moment in the strain direction (presumably the chain axis direction). Poly(β-naphthylmethylsilane) shows no detectable dichroism. Clearly, either the upper or lower orbital type has changed in going from *p*-anisyl to naphthyl substitution. Both polymers displaying dichroism exhibit a maximum in the difference spectrum which does not coincide with the maximum in the first absorption band. This observation, coupled with the substantial width difference between absorption and emission, suggests that the first absorption band is complex, consisting of at least two components with different origins.

The relative quantum yield for fluorescence in poly(phenylmethylsilane) thick films ($\approx$50 μm) was determined as a function of wavelength in the region of the first absorption. Figure 6 shows these spectra and quantum yields. The absorption is taken from a thin film (6500 Å) and the fluorescence quantum yield from a thick sample to simplify yield measurement in the weakly absorbing tail. The quantum yield rises by a factor of $\approx$3 from the short-wavelength edge of the band to the long-wavelength tail, again suggesting that the band is resolvable into at least two transitions. An alternative rationalization for this observation, that longer wavelength excitation selects polymer chains with higher degrees of delocalization, thereby leading to more efficient fluorescence, accounts for the shift of the polarization difference curve with respect to the absorption maximum only if the longer all-trans chain segments are selectively oriented in the drawing process.

We have examined the quantum yields in solution for poly(phenylmethylsilane) at modal molecular weights of 450 000 and near 30 000. The high molecular weight material excited at 302 nm emits with a yield of 0.112 ± 0.01 and the lower molecular weight with a yield of 0.093 ± 0.01. The nearly equal quantum yields observed support our suggestion of the complex band origin for the wavelength dependence of the quantum yield and seem to rule out the photoselection alternative. An attempt was made to resolve the two postulated transitions by subtracting progressively larger fractions of a band with the shape of $\epsilon_{\parallel} - \epsilon_{\perp}$ from the parallel spectrum for the *p*-anisylmethyl polymer in poly(methyl methacrylate). A reasonable fit was obtained when the intensity of the two components was approximately equal (Figure 7). A similar procedure performed with the phenyl,methyl polymer gives about a

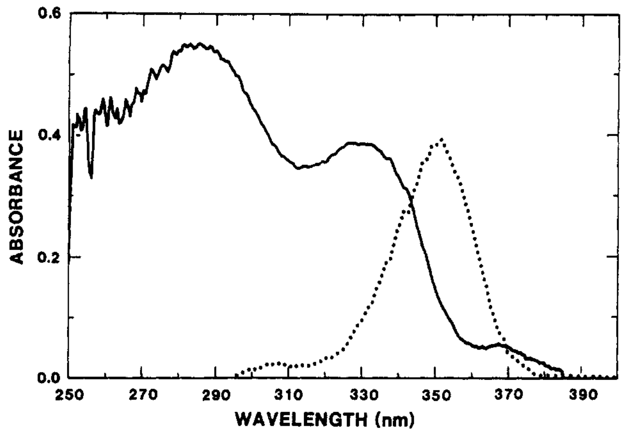

Figure 7. Spectrum of poly(*p*-anisylmethylsilane) in PMMA taken with polarization parallel to draw direction showing the result of partial resolution of the first absorption band by subtraction of the difference spectrum, parallel–perpendicular: (solid curve) parallel orientation spectrum–difference spectrum; (dotted curve) difference spectrum).

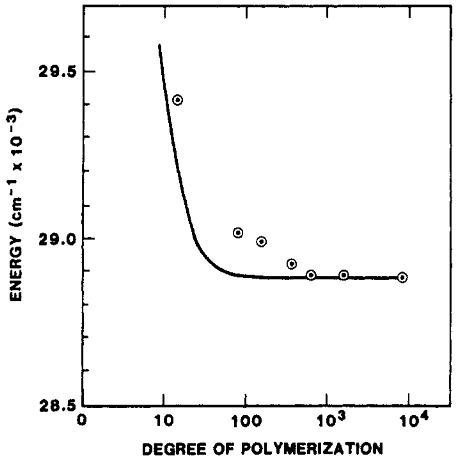

Figure 8. Transition energy in THF solutions of poly(phenylmethylsilane) vs. degree of polymerization. Solid line is calculated from $E = \alpha + 2\beta \cos (J\pi/N + 1)$ (see ref 17).

3:1 ratio for the two components.

Narrow molecular weight fractions of trimethylsilyl-terminated poly(phenylmethylsilane) were separated and their solution spectra measured. As the molecular weight increases, the transition energy decreases as in the permethyl series,[12] but the decrease is not well fit by the MO predictions[15,16] in the region beyond ≈12 chain units (Figure 8).

Among the aryl polysilanes, we have characterized the thermochromic behavior only for poly(phenylmethylsilane). Solutions of this material exhibit a slight hypsochromic shift and a decrease in line width of absorption on cooling. Whether this behavior is associated with conformational changes in the polymer backbone, as in the alkyl polysilanes, or stems from some other source is not known at this time.

Fluorescence spectra of poly(phenylmethylsilane) were obtained over the temperature range 299–77 K in 2-methyltetrahydrofuran solution. The full width at half-maximum decreases from 17.0 nm at 299 K to 7 nm at 77 K with no observable fine structure. The poly(*p*-anisylmethylsilane) and poly(β-naphthylmethylsilane) polymers were also examined in rigid 2-methyltetrahydrofuran at 77 K. In steady-state measurements, neither the phenyl,methyl nor the *p*-anisyl polymer showed resolvable phosphorescence, while the β-naphthyl polymer phosphoresced with an emission characteristic of the isolated naphthyl substituent. In time-resolved measurements, the phenyl,methyl polymer exhibits weak phosphorescence, consistent with the extremely weak phosphorescence reported for poly(isopropylmethylsilane-*co*-*n*-propylmethylsilane).[3a]

Discussion

The spectral behavior of the alkyl polysilanes suggests that the lowest energy absorption arises from a $\sigma \rightarrow \sigma^*$ transition from a delocalized silicon–silicon bonding orbital to a delocalized antibonding level. The widths of the fluorescence spectra relative to the absorption spectra suggest that the observed absorption band may be complex; perhaps it is a combination of the two transitions observed to be coalescing in the discrete permethyl telomers.[12] In the alkanes, the lowest excited state has been assigned to a Rydberg level which lies very close to the first antibonding σ-state.[35] The presence of an aromatic ring, even removed from the chain by an insulating ethylene linkage, should still substantially lower a Rydberg excitation energy but the consistency of the spectrum of poly(β-phenethylmethylsilane) with the similarly sized poly(*n*-hexylmethylsilane) would seem to exclude the $\sigma \rightarrow$Rydberg origin of the first transition in polysilanes. Recent calculations on the electronic states of the parent polysilane $(SiH_2)_x$[30] indicate that the first transition is to a σ^* level consisting of a mixture of silicon–silicon antibonding and silicon–substituent antibonding character. These arguments and the observed spectra would seem to favor an assignment of the first band to a $\sigma \rightarrow \sigma^*$ transition. If the observed band is a combination of the two transitions observed in the permethyl telomers, both are likely to be $\sigma \rightarrow \sigma^*$. Our finding of strong parallel dichroism in stretch-oriented poly(di-*n*-hexylsilane) is completely consistent with and a necessary consequence of the $\sigma \rightarrow \sigma^*$ interpretation for the transition.

The high quantum yield for fluorescence (up to 67% for poly(*n*-dodecylmethylsilane)) is curious in light of the extreme photosensitivity of these polymers. The fluorescence yield and lack of vibrational coupling in the fluorescence emission at low temperatures suggest that the singlet state is highly delocalized. These observations argue for a photochemically stable material, yet poly(diorganosilanes) are usually high photosensitive in solution and solid state. The low quantum yield of phosphorescence in low-temperature glasses, short (≈1 ms) triplet lifetime, and strong vibrational coupling in the triplet imply a high degree of excitation localization in the triplet manifold relative to that observed for the singlet states, suggesting that triplet states are probably responsible for photochemical backbone scission in these materials. Photochemical depolymerization quantum yields were measured in solid films of poly(cyclohexylmethylsilane-*co*-dimethylsilane) to be ≈6, consistent with a previously proposed chain decomposition mechanism involving multiple silylene expulsions from the radical chain ends generated by the initial backbone scission.[3a]

The large shift associated with the rod–coil transition in poly(di-*n*-hexylsilane) solutions as well as the absorption narrowing in the rod form indicates that a large fraction of the bandwidth in the alkyl polymers may result from conformational inhomogeneity, a not unexpected result even for σ-bonded systems.[36] The substituent size dependence apparently is due to steric interference between pendant groups either 1,2 or 1,3[33c] to each other, which can result in Si–Si bond lengthening and/or a change in the equilibrium content of the trans and gauche conformers.

The spectra of the poly(arylsilanes) can be interpreted in the following manner: both phenyl- and *p*-anisyl-substituted polymers have similar ground and excited states; in the naphthyl-substituted material, either the ground state or the excited state or both have changed character. The absorption spectrum of the β-naphthyl polymer is substantially different in character from either phenyl- or *p*-anisyl-substituted polymers. Several overlapping transitions are found in the β-naphthyl material, while only three well-separated bands are evident in the phenyl and *p*-anisyl spectra. The fluorescence of the β-naphthyl-substituted polymer occurs from both naphthalene-like excimer and naphthalene-like monomer. Phosphorescence is strong and is naphthalene-like. The transition in the β-naphthyl polymer, therefore, must be predominantly $\pi \leftrightarrow \pi^*$(ring). This conclusion is in accord with the analyses of Pitt et al.[15,16] and the recent observations by Todesco and Kamat[6] on poly(dimethylsilane-*co*-1-naphthylmethylsilane).

The behavior of the *p*-anisyl polymer, by Pitt's analysis, would be predicted to follow that of the β-naphthyl-substituted material rather than that of the phenyl-substituted material. Yet the spectral shifts, shapes, and polarizations clearly associate the *p*-anisyl behavior with the phenyl. From the arguments of Pitt and Bock[15] and Pitt et al.,[16] the poly(phenylmethylsilane) transition should be $\sigma \rightarrow \pi^*$(ring) or π(ring) $\rightarrow \sigma^*$, depending on the relative mixtures of character in the excited state. The parameter affecting ground-state mixing of the π(ring) and σ Si–Si bonding levels is related to the substituent ionization potential. Both *p*-anisyl and β-naphthyl groups have ionization potentials of about 8.12 eV,[16] and the ground state would be expected to be roughly the same mixture of ring and chain levels in the high polymer. Certainly the phenyl polymer with a side-group ionization potential of 9.25 eV[15] would have substantially different ground-state character than either the *p*-anisyl or the β-naphthyl. However, the nature of the transition depends on the relative mixing in the upper level as well as in the ground state. Here it is evident that raising the side-group ground-state energy alone did not result in a change in the transition character but lowering the excited-state energy did.

If the ground state is π(ring)-like in character in the β-naphthyl and *p*-anisyl polymers, the excited-state character changes from σ^* Si–Si-like in phenyl and *p*-anisyl polymers to π^*(ring)-like in β-naphthyl. A transition from a localized ring state to a delocalized chain state would be expected to have the major transition moment parallel to the polymer chain (as would the $\pi \rightarrow \pi^*$ predicted by Pitt et al.).[15,16] While the polarization observation alone cannot distinguish between the π(ring)-σ^*(chain) and the σ(chain) $\rightarrow \pi^*$(ring) possibilities, when coupled with the fluorescence and absorption spectra character changes, it provides convincing support for the argument that the transition is $\pi \rightarrow \sigma^*$. We have carried out simple MO calculations on a short-chain model of the poly(phenylmethylsilane) that also indicate a flow of electron density from the ring to the chain on excitation. It is possible that the observed dichroism results not from chain alignment in our experiments but from side-group organization. Two observations argue against this possibility: (1) the largest side group, β-naphthyl, shows no dichroism and (2) the direction of the maximum transition moment should be perpendicular to the chain orientation for $\pi \rightarrow \pi^*$-like transitions[37] for the polysilanes with phenyl, *p*-anisyl, and naphthyl side chains. It should be noted that our assignment of the nature of the transitions in polysilanes is supported by recently reported photoelectron spectroscopy studies of Loubriel and Zeigler[41] on polysilanes which show that alkyl and naphthyl side group binding energies are nearly unperturbed by the presence of the silicon backbone. The phenyl binding energy is strongly affected, indicative of considerable cross-hybridization of the phenyl with the polysilane backbone.

We conclude that the first transition in alkyl-substituted polysilanes arises from a delocalized $\sigma \rightarrow \sigma^*$ transition which is inhomogeneously broadened by chain conformational defects in solution and amorphous solids. The first transition in the small-ring aryl polysilanes is probably $\pi \rightarrow \sigma^*$ in character (charge transfer, ring to chain) and is less affected by conformational defects. In the amorphous solids this transition may lead to a charge-transfer exciton band. In the large fused aromatic ring substituents (β-naphthyl), the transition is best characterized as a localized π-π^* naphthalene-like excitation.

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Registry No. (4-Methoxyphenyl)methyldichlorosilane, 18236-55-0; 4-iodoanisole, 696-62-8; methyltrichlorosilane, 75-79-6; poly(4-methoxyphenylmethyldichlorosilane) (homopolymer), 97464-14-7; poly(hexylmethyldichlorosilane) (homopolymer), 88002-83-9; poly(cyclohexylmethyldichlorosilane) (homopolymer), 88002-85-1; poly(dodecylmethyldichlorosilane) (homopolymer), 88002-84-0; poly(dihexyldichlorosilane) (homopolymer), 97036-67-4; poly((β-phenethyl)methyldichlorosilane) (homopolymer), 88002-80-6; poly(dimethyldichlorosilane) (homopolymer), 30107-43-8; poly(phenylmethyldichlorosilane) (homopolymer), 31324-77-3; poly((β-naphthyl)methyldichlorosilane) (homopolymer), 100894-75-5.

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Solid-State NMR Study of the Hexamethylenetetramine Curing of Phenolic Resins

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ABSTRACT: The curing of a phenolic resin by hexamethylenetetramine (HMTA) is elucidated through the use of ^{13}C and ^{15}N CP/MAS NMR spectroscopy. The cure was shown to result in increased cross-linking, with the bridging carbons originating from the curing agent. Intermediates involved in the curing process are identified, with species having structures of the benzoxazine and tribenzylamine types being the major components. The results are compared to previous studies on model systems, and the power of solid-state NMR to probe chemistry in complex macromolecules is again clearly demonstrated.

Introduction

In 1907 a technique for processing phenol–formaldehyde resins, the first wholly synthetic commercial polymer material,[1] was developed by Baekeland. Today, phenolic resins have great commercial applications, especially as molding compounds, coatings, and industrial bonding resins. Details of the curing process are responsible for many of the important physical and mechanical characteristics of these materials. Thus, an explicit knowledge of the curing process is essential for understanding and improving the use of phenolic resins.

Although the curing of phenol–formaldehyde resins has received a great deal of attention,[1-12] most of the previous studies have suffered from experimental limitations, chiefly due to solubility limitations, dissolution uncertainties, and heavy reliance on model systems. Recent studies[13-16] have demonstrated the use of solid-state ^{13}C NMR with cross polarization (CP) and magic-angle spinning (MAS)[17-19] for systems warranting such concerns. The ^{13}C CP/MAS technique has proven to be a powerful tool for structural elucidation in macromolecular systems. It is the application of this technique to the investigation of the hexamethylenetetramine (HMTA) curing of a phenol–formaldehyde resin of the novolak type on which this paper focuses.

Experimental Section

NMR Measurements. ^{13}C CP/MAS spectra were obtained at 25.1 MHz on a home-built spectrometer that utilizes a Nicolet 1180 data system and a Nalorac 4.7-T magnet operated at half field. Spectra were obtained at numerous contact times, ranging from 0.5 to 4 ms, and the relative peak intensities showed no major dependence on contact time over that range. Spectra of the cured resins presented here were obtained with a 2-ms contact time and a 1-s repetition time. Samples were spun at 3.2–3.5 kHz, using spinners of the Windmill type.[20] The magic angle was adjusted to within 0.1° by using the ^{79}Br spectrum of KBr placed in a spinner.[21]

^{15}N CP/MAS spectra were obtained at 20.3 MHz on a modified wide-bore Nicolet NT-200 spectrometer. The NMR parameters used to accumulate the spectra presented here were a 4-ms contact time and a 15-s repetition time. Samples were spun at 2.2 kHz, using bullet-type spinners,[22] and the magic angle was again set by the KBr method.

Proton-decoupled solution-state ^{13}C spectra were obtained on an IBM WP-200SY spectrometer at a carbon frequency of 50.3 MHz, while ^{15}N solution-state spectra were obtained at 36.5 MHz on a Nicolet NT-360 spectrometer. All ^{13}C spectra were referenced externally to tetramethylsilane at 0 ppm and all ^{15}N spectra to liquid NH_3, also at 0 ppm.

Samples. The test resin used in this study was a novolak phenolic resin prepared at the Durez Division of the Occidental Chemical Corp. under conditions believed to produce a "random resin". The details of the ^{13}C CP/MAS spectrum of this resin have been reported previously.[13] The test resin was cured by heating a mixture of 90% resin plus 10% HMTA for 1 h at the temperature noted in the text. Both the ^{13}C- and ^{15}N-labeled HMTA used in this study were prepared by the method of Bulusu and co-workers,[23] using 99% ^{13}C-enriched CH_2O or 99% ^{15}N-enriched ammonium acetate, respectively.

Model compounds used in this study were either obtained commercially from Aldrich Chemical Co. or synthesized by using literature preparations, as noted in the text.

Results and Discussion

The key types of molecular structures that are known or suspected to be involved or of interest in this study are

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