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~~ALKOXY SUBSTITUTED~~ POLY(DIARYLSILANES): THERMO AND SOLVATOCHROMI~~SM~~ Behavior

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ABSTRACT: The first soluble poly(bis alkoxyphenylsilanes) have been prepared and characterized. The UV spectra of the bis-p-alkoxyphenyl derivatives show a strong absorption at unexpectedly short wavelengths. These materials are thermochromic and at higher temperatures their spectra resemble those reported for the bis p-alkylphenyl derivatives. On the basis of these results, we propose that the silicon backbone of the poly(bis-p-alkoxyphenylsilanes) is substantially nonplanar at room temperature possibly due to unfavorable dipolar substituent interactions in the planar zigzag form. This suggestion is supported by studies on the corresponding m-alkoxyphenyl derivatives and unsymmetrical alkoxyphenyl substituted diaryl polysilanes. These latter materials also show solvatochromic spectral changes due to conformer redistribution.

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Soluble high molecular weight polysilane polymers are attracting attention as an interesting new class of radiation sensitive materials for which a number of applications have been described.[1] The electronic structure of these materials is particularly interesting since the chromophore is the sigma bonded polymer backbone.[2,3,5d] The absorption spectra depend not only on the nature of the substituents but also on molecular weight[3] and the conformation of the backbone.[4]

Recently, we have reported that poly(bis-p-alkylphenylsilanes) are the most red shifted of all polysilane derivatives and have tentatively ascribed this observation to the presence of long all trans backbone segments even in solution.[4c,5] Some further support for this hypothesis based on light scattering studies has recently been reported.[6]

For some time, we have been interested in the chemistry and spectroscopy of substituted poly(diarylsilanes), particularly those which incorporate substituents which would be expected to influence the polymer spectral properties and polarizability. We describe here the synthesis and spectroscopic characterization of a variety of alkoxy substituted diaryl polysilanes and report on their unusual thermo and solvatochromism.

The desired substituted dichlorosilane monomers were prepared by the condensation of the corresponding alkoxyphenyl Grignard or lithium reagents with silicon tetrachloride as previously described for the preparation of the p-alkylphenyl derivatives.[5] The unsymmetrically substituted derivatives were prepared in a stepwise fashion via the corresponding substituted trichlorosilanes. The structures of the monomeric dichlorosilanes were supported by their analytical and spectral data. In this regard, ^{13}C NMR was particularly useful for the characterization of the unsymmetrical derivatives, since all of the carbon resonances were separated and easily identifiable.

The polymerization of the highly purified dichlorodiarylsilanes was performed using commercial sodium dispersion as previously described[5] and the results are shown in Table I. The yields reported for the isolated and purified polymers are low (<10%)

which is typical for the preparation of sterically hindered polysilanes, but the procedure is unoptimized.

The polymer structures were consistent with their analytical and spectral data. For the diaryl derivatives, the proton NMR signals for the aromatic hydrogens and the aliphatic methylene protons α to oxygen were extremely broad and structureless at room temperature. In a typical polymer such as 2, these absorptions appeared as broad featureless resonances around 5.0-6.8 and 3.2-4.0 ppm, respectively. The situation improves somewhat at elevated temperatures (60°C) where these signals narrow to 1.45 and 0.47 ppm and some fine structure appears. In general, the ^{13}C spectra were much more diagnostic, particularly at elevated temperatures. For example, the ^{13}C spectrum of 2 at 60°C showed four separated aromatic carbon resonances at 159.1, 138.9, 120.6 and 113.7 ppm and the methylene adjacent to oxygen appeared at 67.9 ppm. The remaining carbons of the aliphatic chain were also separated and easily identified. The IR spectra of the poly(alkoxyphenylsilanes) are all quite similar with a number of characteristic strong bands in the region from 1000-1600 cm^{-1}, particularly around 1250 cm^{-1}. In fact, the infrared spectra of films of the model monoaryl polymer 1 and the bis p-alkoxyphenyl polymer 2 overlay almost exactly, except in the region from $\sim$750-850 cm^{-1} where some differences are observed.

The UV spectra of the poly(bis-p-alkoxyphenylsilane) derivatives were somewhat unexpected and the spectrum of 2 is shown in Fig. 1, together with that of the monoarylsilane 1 and poly-bis(p-n-hexylphenylsilane) for comparison. The most striking feature in the spectrum of 2 is the appearance of a strong absorption at 326 nm (ϵ $\sim$9000/SiSi). The long wavelength absorption around 400 nm is weak and broad. Similar spectra were obtained for all the poly(bis-p-alkoxyphenylsilanes). These spectra were quite different from those of typical poly(bis-alkylphenylsilanes) which all absorb strongly (ϵ = 20-25,000/SiSi) around 400 nm (25°C) and are pratically devoid of significant absorptions between 320-330 nm.[5] The strong absorption at 326 nm observed for 2 is substantially blue shifted even relative to that observed for the mono alkoxyphenyl derivative 1. It seems unlikely that the large hypsochromic in 2 shift is caused by increased twisting of both of the aryl substituents on each silicon atom of 2 completely out of conjugation with a trans planar silicon backbone, since space filling molecular models suggest that such a structure would be impossibly sterically congested. Furthermore, it is expected that an all trans silicon backbone would absorb at much longer wavelengths even in the absence of any significant electronic substituent effects. In this regard, it has been observed that poly(di-n-hexylsilane) in the solid state, where the backbone has been shown to be planar zigzag, absorbs at ~375 nm. For these reasons, it seems more reasonable to assume that the short wavelength absorption observed for 2 and the other poly(bis-p-alkoxyphenylsilanes) result from a significant distortion of the polymer backbone from a planar zigzag conformation.

Interestingly, the absorption spectra of the poly(bis-p-alkoxyphenylsilanes) are strongly thermochromic both in solution and in the solid state. This is in contrast with the poly(bis-p-alkylphenylsilanes) where the long wavelength maximum around 400 nm merely broadens with increasing temperature with only minor changes in the λ_{max}. Figure 2 shows the thermochromic behavior for a solution of 3 in p-t-butylbenzene. The spectral changes observed with temperature are completely reversible. The implication from the variable temperature behavior of 3 is that backbone conformational changes are occurring and at high temperatures significantly longer planar zigzag segments of the polymer chain are present. The UV spectra of the poly(bis-p-alkoxyphenylsilanes) at elevated temperatures closely resemble those previously reported for the poly(bis-p-alkylphenylsilanes) at ambient temperatures, although the spectral width of the long wavelength absorption is somewhat greater for the p-alkoxyphenyl polymers.

The origin of this unusual substituent effect is interesting to contemplate. It seems unlikely in nonpolar solvents that the steric demands of the p-alkoxy substituents are significantly greater than those of the comparable p-alkyl groups. Furthermore, space filling molecular models suggest that both types of p-aryl substituents can be nicely accommodated into a planar zigzag backbone conformation by a slight twisting of the aromatic rings so that the plane of the ring is not exactly perpendicular to that of the polymer backbone. However, a trans coplanar backbone leads to an alignment of the para alkoxy substituent dipoles on the silicon atoms which are 1,3 to one another. Perhaps, it is this unfavorable dipole alignment rather than steric effects which destabilizes the planar zigzag form and causes it to twist.

If this is the case, substitution at the meta positions on the ring relative to silicon should bring some relief, since the substituent dipoles on the aromatic rings positioned 1,3 to one another could adopt a conformation where they are not in alignment. Consistent with this proposal, the UV spectrum of the meta disubstituted derivative 4 shows a strong, narrow absorption (ϵ/SiSi = 18,300, FWHH = 11 nm) at 403 nm with only a weak, barely detectable shoulder at 325 nm.

Similarly, when the symmetrical, substitution pattern of the bis(p-alkoxyphenylsilane) polymers was disturbed by either the formation of the 1:1 copolymer 6 or by the generation of the atactic, unsymmetrically substituted homopolymer, 5 changes were observed in the UV spectra. In this regard, the UV spectra of both 5 and 6 exhibited absorption maxima around 322 and 400 nm, the intensities of which were comparable. These spectra were also thermochromic in the fashion described earlier. In addition, the absorption spectra of 5 and 6 were both solvent dependent. For example, in 5, the ratio of the absorbance at 324 nm to that at 400 nm changed from a value of 1.3 when measured in hexane to ~0.38 in THF solvent. This solvatochromic behavior is also consistent with the suggestion of a delicate conformational equilibrium which is perturbed by the interaction of the polar solvent with the dipolar substituents.

In summary, the poly(bis alkoxyphenylsilanes) constitute another class of substituted silane polymers with interesting spectroscopic properties. The unexpected spectral effects caused by the presence of p-alkoxy substituents appear to be conformational in origin as suggested by their thermochromism. In addition, certain of the unsymmetrically substituted materials are solvatochromic due to conformational changes induced by solute-solvent interactions.

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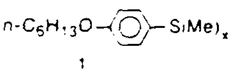
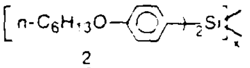
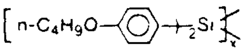
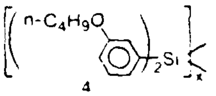
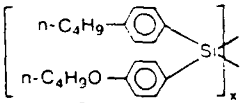
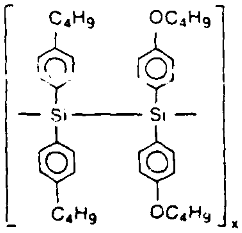
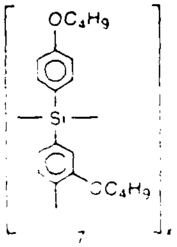
Table I. Polymerization of alkoxyphenyl dichlorosilanes: (a) molecular weights were determined by GPC analyses and are relative to polystyrene standards.

$$R^1R^2SiCl_2 \xrightarrow[\Delta]{Na} (R^1R^2Si)_x + 2NaCl$$

Entry	Polymer	Solvent	Yield (%)	$\overline{M_w} \times 10^{-3a}$	$\overline{M_n} \times 10^{-33}$	Molecular Weight Composition (%)
1.	 1	Toluene	10	44.6 2.1	24.7 1.2	82 18
2.	 2	Toluene	5	416.5 3.2	151.8 2.4	38 62
3.	 3	Toluene	8.5	1247.5 2.6	441.0 2.4	46 54
4	 4	Toluene Diglyme (10%)	7.0	822.7 1.7	220.7 1.6	50 50
5.	 5	Toluene Diglyme (10%)	7.5	800.3 18.4 2.6	367.9 14.5 2.3	33 33 33
6.	 6	Toluene	5.0	38.9	21.8	—
7	 7	Toluene	5.0	617.9 25.7 3.2	252.0 22.5 2.8	11 4 85

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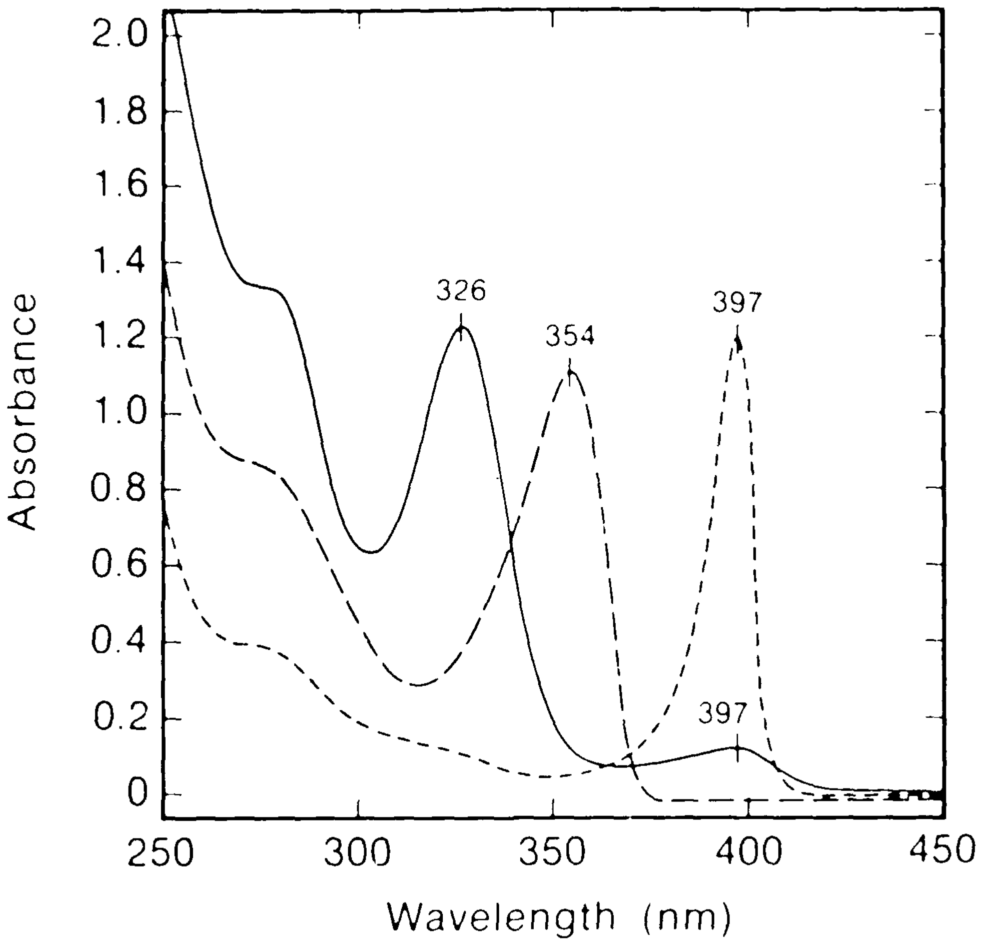

Figure 1. The UV spectra of some aryl substituted polysilane derivatives in cyclohexane: – – – poly(n-hexyloxyphenyl methylsilane; ----- poly(bis-p-n-hexylphenylsilane); —— poly(bis-p-n-hexyloxyphenylsilane).

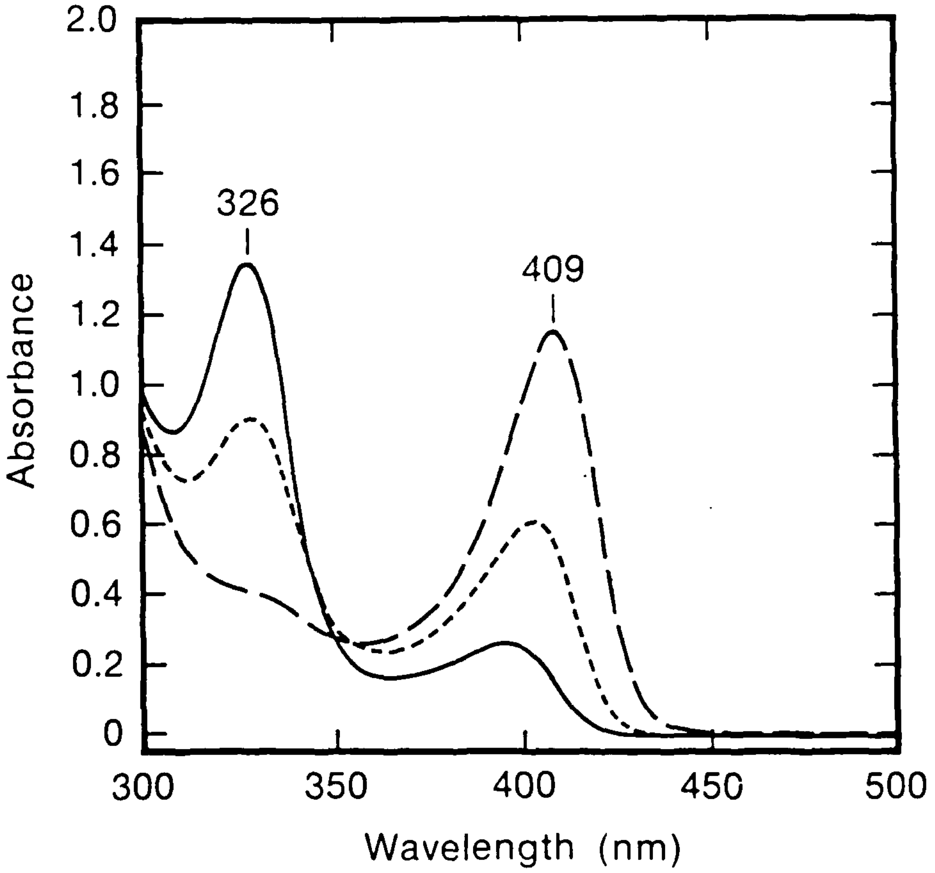

Figure 2. Thermochromism of poly(bis-p-n-butoxyphenylsilane) in p-tert-butylbenzene: —— 35°C, ----- 75°C, – – – 150°C.