

Preparation and Characterization of Polysilanes with Electron Donating Substituent

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ABSTRACT: Polysilanes with electron donating substituents such as polymethoxyphenylmethylsilane (II) and polydimethylaminophenylmethylsilane (III) were prepared by the condensation reaction of the corresponding dichlorosilanes with sodium. The absorption band of silicon main chain is shifted to a longer wavelength as the increase of molecular weight up to ca. 4000 and became constant after that. The constant λ_{\max} values are 342, 351, and 361 nm for polyphenylmethylsilane (I), (II), and (III), respectively. The third-order nonlinear susceptibilities ($\chi^{(3)}$) were measured by the Maker fringe technique using Nd-YAG laser at 1064 nm. The $\chi^{(3)}$ values were 2.1, 6.0, and 3.8×10^{-12} esu for polymers (I), (II), and (III), respectively.

KEY WORDS Polysilane / Electron Donating Substituent / Third-Harmonic Generation / Optical Property /

Since polysilanes that are soluble in organic solvent were synthesized in 1981 by West,¹ many kinds of polysilanes have been reported.²⁻⁶ These polysilanes exhibit a number of interesting chemical and electronic properties which have led to potential applications such as photoresists,⁷ photoinitiators in vinyl polymerization,⁸ precursors for SiC fiber,⁹ and dopable semiconductors.¹⁰ Although the backbone of polysilane is composed of only σ bonds, polysilane derivatives show very similar electronic properties as polyacetylene which has a strong bond strength and a high third harmonic wave generation ability. These properties are explained by the electron conjugation among the σ bond of silicon main chain. It is also found that polymethylphenylsilane exhibits unusual red-shift in UV absorption spectra due to the conjugation between σ orbital of silicone atom and π orbital of aromatic group. However, most of the polysilanes prepared hitherto have sub-

stituents of alkyl, aryl, or aralkyl in their side groups. Therefore, there was a limit to broaden the properties more widely.

In this paper we report the synthesis of some polysilanes which have electron donating substituents in a side group such as alkoxy and alkylamino groups. The change of UV absorption maximum and THG efficiency by these substituents were also discussed.

EXPERIMENTAL

Syntheses of Monomers

The Grignard reagent prepared from the corresponding halogenated compound was added dropwise to an ether solution of methyltrichlorosilane for 1 hour at room temperature. As the reaction proceeded, the white salt was precipitated with a slight temperature increase. After removing the salts by decantation and the solvent by evaporation, the monomer was obtained by distillation under

reduced pressure.

Polymer Preparation

The sodium metal suspension, which was dispersed in toluene by ultrasonic probe, was added quickly dropwise to the dichlorosilane monomers. During the addition, the reaction mixture was stirred severely by mechanical stirrer and the color of the mixture turned from gray to dark purple. After refluxing for 3 hours, the reaction mixture was cooled and quenched with methanol and water. The organic layer was separated and washed with a large amount of water to remove any traces of sodium salts. The polymer was obtained by precipitation with methanol, purified by reprecipitation with toluene-isopropanol system and dried *in vacuo* at room temperature.

Characterization

The molecular weight of the polymers were determined by GPC using THF as an eluent at a flow rate of 1 ml min^{-1} and a JASCO MULTI-330 multichannel UV detector. The average molecular weights were calibrated with standard polystyrene samples. NMR spectra in CDCl_3 were recorded on a JEOL FX-200 spectrometer at room temperature.

In order to measure the THG activity, a polymer thin film of 1000–1300 nm thickness was cast on a fused silica substrate from THF solution (5 wt%) using a spin coater. The THG measurements were performed with a *Q*-switched Nd:YAG laser with maximum energy of 200 MW cm^{-2} at the 1064 nm

fundamental wavelength and operated at a repetition rate of 10 Hz with a pulse duration of 10 ns. The fundamental laser beam entered the sample through the substrate. The sample was rotated along an axis parallel to the fundamental beam polarization direction. The third harmonic wave signal generated in the sample was separated from the fundamental wave using IR filter, monochromated (355 nm) and detected by a photomultiplier tube, whose output was averaged in a digital oscilloscope. Third-order nonlinear optical susceptibilities were determined by comparing the susceptibility of the sample with that of the fused silica substrate.

RESULTS AND DISCUSSION

In order to prepare polysilanes with polar substituents, *p*-substituted polymethylphenylsilanes were synthesized by the condensation reaction of the corresponding dichlorosilane derivatives and sodium dispersion. Table I shows the yields and characteristics of the polymers. The yields and molecular weight

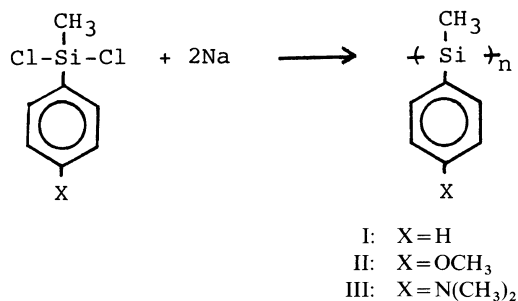


Table I. Yield and molecular weight of the polysilanes^a

Polymer	Substituent (X)	Yield/%		M_w ($\times 10^3$)	M_w/M_n
		Soluble	Insoluble		
I	H	25.8	0.1	33.8	3.6
II	OCH ₃	10.8	0.3	33.2	3.2
III	N(CH ₃) ₂	9.5	27.5	5.0	1.5

^a $-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_4\text{X})-$

All the polymers are white powders. The soluble portion is soluble in toluene, THF, and chloroform.

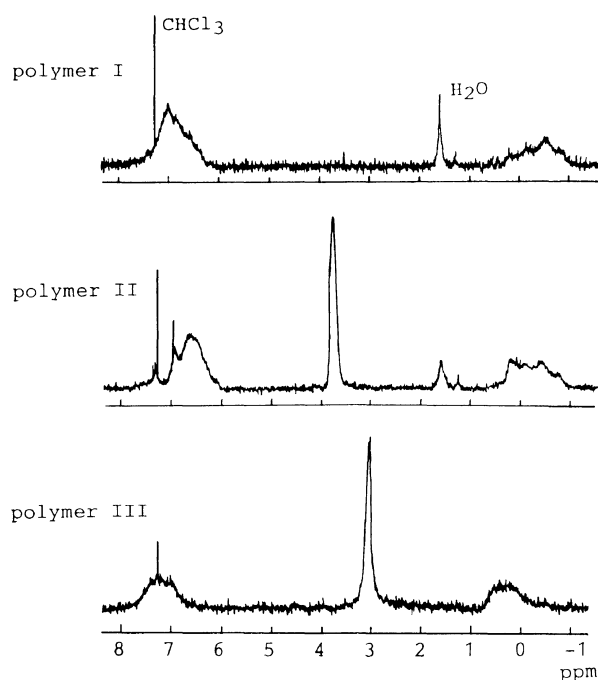


Figure 1. ^1H NMR Spectra of polymers I—III.

distributions were not changed when reaction was carried out for longer than 3 hours. All polymers were soluble in toluene, tetrahydrofuran (THF), and chloroform. However, polymer III alone contained about 27% of insoluble fraction. The insoluble fraction exhibits the same IR spectrum as that of soluble fraction. Zhang and West also observed a small insoluble fraction which is considered to be a crosslinked polymer.⁴ Polymers I and II were obtained in relatively high yields with high molecular weights, while the yield of soluble portion and molecular weight of polymer III was low.

As shown in Figure 1, ^1H NMR spectra of the polymers indicated that all the polymers had the expected structures. Broad signals for the methyl and phenyl protons were observed in the range of -1.0 to 1.0 and 6.2 to 7.8 ppm, respectively. The methyl protons attached to the ether oxygen and amino nitrogen appeared around 3.6 to 3.9 and 2.9 to 3.2 ppm, respectively.

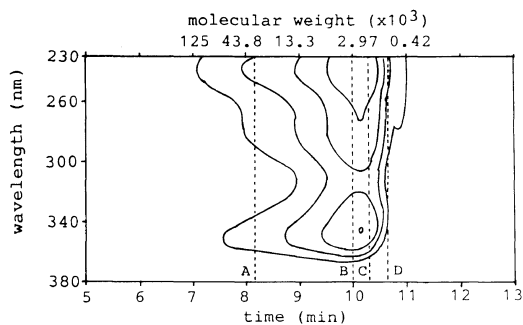


Figure 2. Contour plot of UV absorption for polymer II.

GPC measurements were carried out using a multichannel UV detector. Figure 2 shows contour plot of the GPC measurements for polymer II with elution volume on the horizontal axis and wavelength for the vertical axis. The absorption of silicon backbone and phenyl ring of side chain were both observed in the range of 350 nm and 270 to 280 nm, respectively. When a slice parallel to the

vertical axis is drawn, the UV spectrum of any elution volume, *i.e.*, any molecular weight, is obtained as shown in Figure 3 in the spectral range of 300 to 380 nm which is assigned to the σ conjugated silicon main chain. As the molecular weight increases, the absorption band is shifted toward longer wavelengths.

In Figure 4, the maximum absorption is plotted against molecular weight for each polymer. As the molecular weight increases, wavelength at the maximum (λ_{\max}) for all three polymers increase until the values become

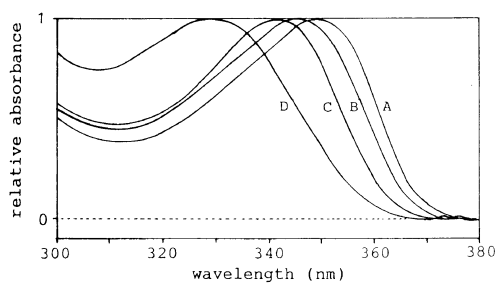


Figure 3. UV Spectra for polymer II having molecular weights of 30.0×10^3 (A), 2.9×10^3 (B), 1.6×10^3 (C), 0.85×10^3 (D).

nearly constant around a molecular weight of 4,000. This observation is consistent with that reported by Trefonas *et al.*¹¹ for polydialkylsilanes and it means that silicon σ electrons are delocalized over at least 25–30 monomer units.¹² The limiting absorption maximum increased with increasing electron donating power of the substituent on the phenyl ring; I (342 nm) < II (351 nm) < III (361 nm). Therefore it is possible to say that electron donating effects through the phenyl ring have an influence on the electronic properties of the main chain and results in a red-shift of UV absorption band.

Figure 5 shows the Maker fringe pattern of the third harmonic wave for polymer I. From the intensity of Maker fringe pattern, the third-order susceptibilities of these polymers can be estimated using the equation of Kubodera¹³ assuming that the effects of refractive index differences and transmission factors are negligible. Using the value of $\chi^{(3)} = 3.1 \times 10^{-14}$ esu¹⁴ for the silica substrate, the $\chi^{(3)}$ values of polymers I, II, and III were determined to be 2.1×10^{-12} , 6.0×10^{-12} , and 3.8×10^{-12} esu, respectively. The $\chi^{(3)}$ value of

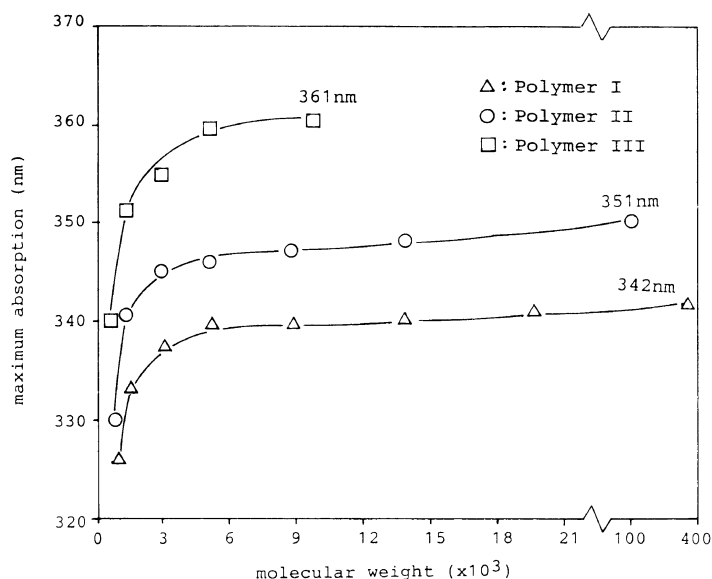


Figure 4. Progression of λ_{\max} vs. molecular weight for polymers I–III.

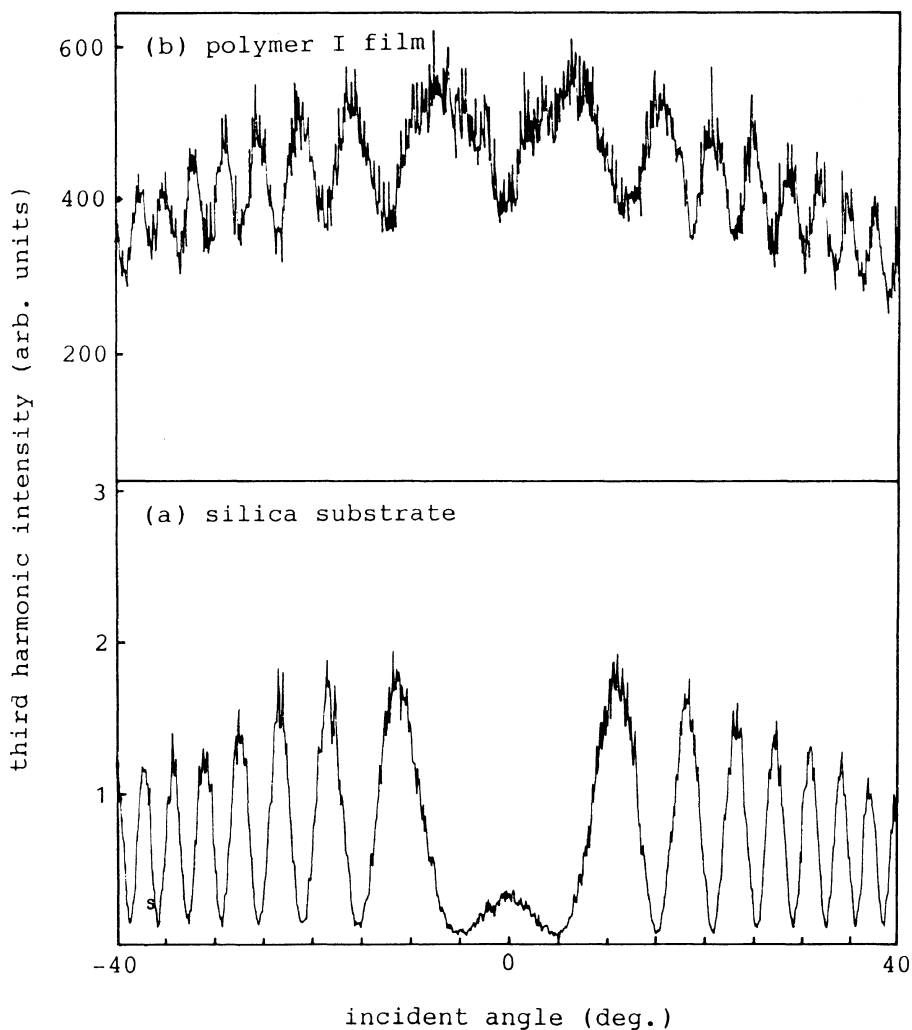


Figure 5. Third harmonic intensities at 1064 nm as a function of incident angle for (a) silica substrate of 1 mm thick and (b) polymer I film of 1300 nm thick.

polymer I is almost the same as that reported by Kajzar *et al.*¹³ The $\chi^{(3)}$ value of polymer II is about 3 times higher than that of polymer I, indicating that the electron donating substituents enhance the third harmonic generation. Since we did not obtain any detectable harmonic signal using 1.9 μm fundamental wavelength, we are considering that the $\chi^{(3)}$ value of polysilane is due to the three-photon resonance effect because of the overlapping of third harmonic wavelength and polymer

absorption band. However, the exact nature of this resonance is unknown. The $\chi^{(3)}$ value for polymer III is smaller than that for polymer II, although the amino substituent is a more efficient electron donor than the ether group. This may be attributed to the low molecular weight of polymer III.

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