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Absorption Spectra of Radical Ions of Low Molecular Weight Poly(methyl-*n*-propylsilane)s—Chain Length Dependence

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ABSTRACT: Electronic absorption spectra of radical ions, both cations and anions, of various molecular weight poly(methyl-*n*-propylsilane)s were measured in rigid matrices at 77 K. The radical ions were produced by γ-irradiation. The spectra had two peaks in UV and near infrared regions, and the maxima in both UV and near infrared regions shifted to longer wavelengths with increasing chain length until about 16 monomer units and showed saturation above this length. Excellent inverse correlation was obtained between the transition energy and the chain length; this reflects increasing electronic delocalization with increasing number of silicon atoms in the radical anions and cations.

Introduction

Polysilanes make up a new class of polymers which consists of a linear Si−Si catenation in the main chain and organic substituents at each silicon atom.[1] σ-Electrons in the main chain of polysilanes are strongly delocalized.[2a] This delocalization leads to semiconductivity after doping, excellent photoconductivity, and promising nonlinear optical properties.[3]

In order to understand the electrical and optical properties of the polymers in general, information concerning the exciton delocalization in electronic state and excited state dynamics is indispensable. In particular, the electronic structure of the redox states of those molecular subunits which are responsible for the conductivity along the conjugated chains needs to be characterized for controlling the conductive properties.

The electrical, optical, and chemical properties of polysilanes depend upon chain length, substituents at the Si atoms, and chain conformation.[1] This resembles the case for other delocalized systems such as polyenes. A number of studies have dealt with polythiophenes and oligothiophenes in terms of polarons and bipolarons, which constitute a theoretical basis for understanding the conducting polymers.[4−10] The primary species obtained upon oxidative doping of the polymers are radical cations (called polarons in the language of solid-state physics). As discussed in the papers, polarons and bipolarons form the theoretical basis for understanding the electrical conduction in the polymers.

We have focused our attention on the radical cations and anions of polysilanes. In previous papers, we reported the absorption spectra of the radical ions of linear polysilanes and cyclic polysilanes and their dynamic behavior.[11] In this study we examined the chain length dependence of radical ion spectra. The results will give information concerning the dependence of the delocalization length of the radical ions on the silicon catenation.

Experimental Section

Table 1. Absorption Bands of Radical Anions and Cations for Poly(methyl-*n*-propylsilane)s at 77 K

		$\lambda_{\max}$, nm				
		anion		cation		
chain length[a] (NMR)	$M_w \times 10^{-2}$ [b] (GPC)	UV	IR	UV	IR	IR (after thermal annealing)
	120	361	2200	356	2100	1700
107	85	361	2150	356	2100	1700
50	64	359	2100	356	2050	1650
40	48	358	2100	355	1950	1650
30	40	357	2000	353	1900	1650
21	28	354	1950	352	1900	1600
16	20	354	1800	350	1800	1550
11	16	348	1700	344	1700	1450
9	13	345	1550	340	1550	1350
8	10	340	1400	325	1400	1250
7	8	330	1200	318	1200	1100

[a] The chain lengths of the polymers were determined by ^{1}H NMR signal intensities: $SiCH_3/OC_2H_5$ ratio. [b] Based on polystyrene standards.

Various molecular weights of poly(methyl-*n*-propylsilane) were prepared by fractionation of the polymers, synthesized according to the Wurtz coupling method,[1,2] with preparative liquid chromatography (Shodex column H-2001, H-2002, and H-2003). A typical polymerization procedure follows: Methyl-*n*-propyldichlorosilane (31 g, 0.20 mol) was added dropwise to 200 mL of toluene containing dispersed sodium (9.7 g, 0.42 mol) at around 100 °C. After the addition of the monomer, the mixture was refluxed for 5 h and then allowed to cool to 60 °C. The reaction was quenched by the addition of 100 mL of ethanol, and then water was added to the mixture to dissolve the sodium salts. The organic layer was separated, and a large amount of ethanol was added to precipitate the polymers. The fractionated polymers and the molecular weights are summarized in Table 1. The chain length and the molecular weights of the polysilanes were determined by both ^{1}H NMR spectroscopy and gel permeation chromatography. The permethyl oligomer series, Si_3Me_8, Si_4Me_{10}, Si_5Me_{12}, or Si_6Me_{14}, was prepared by coupling of the corresponding chlorosilane with either Li or Na,[12] and the materials were purified by fractional distillation and preparative gas chromatography (GC). Absorption spectra of radical anions and cations were measured in rigid matrices, and the ions were produced using γ-irradiation, as previously reported.[11] The polysilanes were dissolved in the matrix materials and frozen at 77 K. After reference spectra were taken, the samples were exposed to 0.5 Mrad of ^{60}Co γ-irradiation, whereupon the difference spectra (before and after irradiation) were obtained. 2-Methyltetrahydrofuran (MTHF) and *n*-butyl chloride (BuCl) were purified by repeated distillation. All samples were degassed by the

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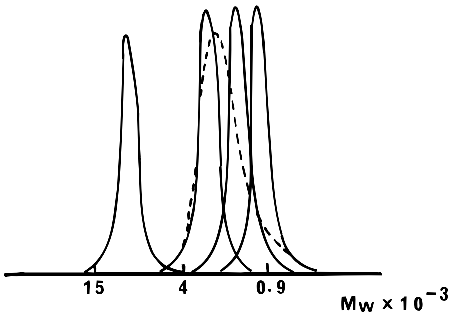

Figure 1. Gel permeation chromatography curves of poly(methyl-*n*-propylsilane)s (—) and a polystyrene standard sample (- - -, $M_w = 2100$; $M_w/M_n = 1.1$).

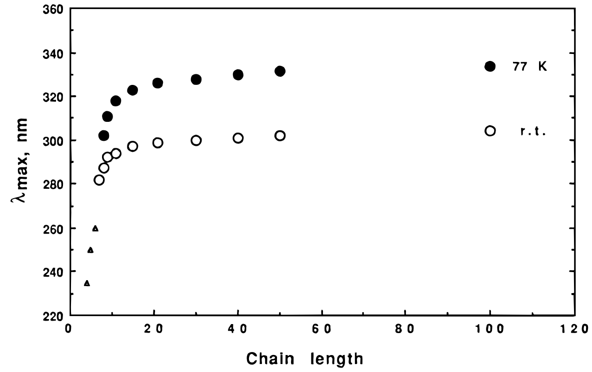

Figure 2. Chain length (determined by NMR) dependence of UV absorption maxima (λ_{max}) at 77 K (●) and at room temperature (○) for poly(methyl-*n*-propylsilane)s. Triangles are for permethyl oligomers ($n = 4-6$).

freeze–thaw cycle method. Electronic absorption spectral measurements were carried out with a Shimadzu UV-3100PC spectrophotometer. The ^1H NMR spectra were measured on a JEOL JNM-GSX500HI instrument.

Results and Discussion

Polysilanes were fractionated carefully with preparative liquid chromatography as described above. The molecular weight distributions of several poly(methyl-*n*-propylsilane)s used in this experiment are shown in Figure 1. The molecular weight distribution was measured by gel permeation chromatography and is compared with those of polystyrene standards. The dotted line in Figure 1 shows the molecular weight distribution of a commercially available polystyrene standard sample ($M_w = 2100$) with $M_w/M_n = 1.1$. The molecular weight distributions of the polysilane samples are narrower than that of the polystyrene standard sample. This indicates that the M_w/M_n values of the polysilanes are lower than 1.1. The chain lengths of the polysilanes were determined by ^1H NMR signal intensities: $SiCH_3$ (of the side chain)/OC_2H_5 (in the chain ends). The chain lengths obtained by the NMR measurement along with the molecular weights measured by gel permeation chromatography (based on polystyrene standards) are summarized in Table 1.

The absorption spectra of these poly(methyl-*n*-propylsilane)s were measured in MTHF rigid matrices at 77 K and in MTHF solution at room temperature. Figure 2 shows the progression of λ_{max} in the UV region versus chain length for the poly(methyl-*n*-propylsilane)s measured at room temperature or at 77 K. The triangles in the figure are for the permethyl oligomer series, Si_4Me_{10}, Si_5Me_{12}, and Si_6Me_{14}. The spectral shift of the permethyl oligomers is similar to that reported by Michl et al.[13] As can be seen from Figure 2, each λ_{max} both at room temperature and at 77 K increases initially with an increase in catenation but approaches a limiting value around a chain length of 10–20. This behavior is in accord with that reported previously by Trefonas et al.[2a] and Michl et al.[13] It should be noticed that the λ_{max} at 77 K is around 25 nm longer than that at room temperature for each oligomer. The λ_{max} of the absorption measured at 77 K also became constant at a slightly longer chain length compared with the λ_{max} at room temperature. This result suggests that the electron delocalization length at 77 K is longer than the length at room temperature.

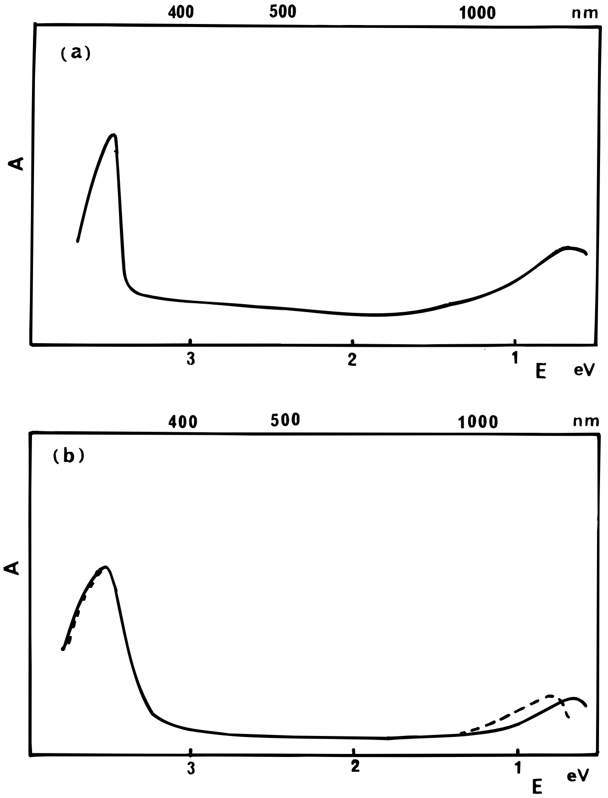

Figure 3. (a) Absorption spectra of poly(methyl-*n*-propylsilane) ($M_W = 2800$) irradiated with a dose of 3×10^{19} eV/g at 77 K in MTHF. The concentration of the polymer in MTHF was 1×10^{-2} M. (b) Absorption spectra of poly(methyl-*n*-propylsilane) ($M_W = 2800$) irradiated with a dose of 3×10^{19} eV/g at 77 K in BuCl. The concentration of the polymer in BuCl was 5×10^{-2} M: (—) immediately after irradiation; (- - -) after thermal annealing at 100 K.

On the basis of the above fundamental knowledge of the absorption spectra of the neutral state, we studied the absorption spectra of the corresponding radical anions and the radical cations. In a previous paper,[11b] we have reported the absorption spectra of radical anions and cations of various linear polysilanes in rigid matrices using γ-irradiation. It is well established that a solute radical anion is produced in irradiated MTHF by the reaction of an electron with a solute molecule.[14] A solute radical cation is produced in irradiated BuCl by the reaction of a positive hole with a solute molecule.[14] Figure 3a shows the absorption spectrum of a MTHF solution (1×10^{-2} M) of poly(methyl-*n*-propylsilane) ($M_w = 2800$) at 77 K irradiated with a dose of 3 $\times 10^{19}$ eV/g after photobleaching the trapped electrons. The spectrum has two bands at 354 and 1950 nm. In a previous paper,[11b] we could not clearly assign the near infrared band because of overlap with that of the trapped electrons. The absorption spectrum of 2×10^{-2} M poly(methyl-*n*-propylsilane) ($M_w = 2800$) in a BuCl

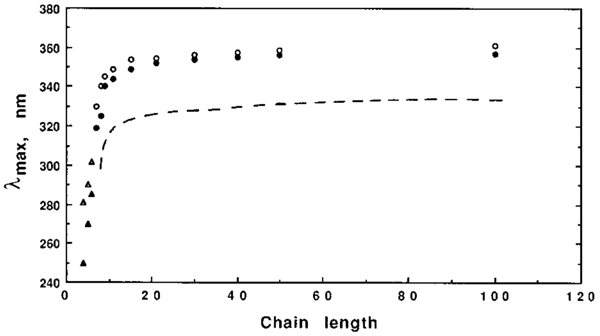

Figure 4. Chain length (determined by NMR) dependence of the absorption maxima (λ_{max}) of radical cations (●) and anions (○) for poly(methyl-*n*-propylsilane)s at 77 K. (- - -) λ_{max} of the absorption of neutral molecules at 77 K. Triangles are for permethyl oligomers ($n = 4-6$).

matrix irradiated with a dose of 3×10^{19} eV/g at 77 K is shown by the solid curve of Figure 3b. Two absorption bands appear at 352 and 1900 nm. Both the radical anion and cation of poly(methyl-*n*-propylsilane) each have two absorption bands at similar positions in the UV and near infrared regions.

After thermal annealing, the absorption band of the radical cation showed a blue shift, as shown in Figure 3b. This result is similar to that observed for linear polysilanes but is in contrast with that for the cyclic polysilanes, which do not show the shift.[11c] In comparison with the case for the radical cations of the polysilanes, the shift of the radical anions upon annealing was negligible.

Table 1 summarizes the absorption spectral data of the radical anions in MTHF solution and the radical cations in BuCl solution for various molecular weight poly(methyl-*n*-propylsilane)s at 77 K. It is apparent that the absorption bands in the UV−visible and near infrared regions both vary with the chain length and shift to longer wavelengths with increasing chain length of poly(methyl-*n*-propylsilane)s.

It has been reported that, in the case of thiophene oligomer cation radicals, the spectra have bands in the visible and near infrared regions.[4,6−8] Both bands shifted to longer wavelengths with increasing oligomer chain length due to the greater charge delocalization. The spectral shift observed for poly(methyl-*n*-propylsilane)s is thus similar to that for the oligothiophenes.

Figure 4 shows the plot of λ_{max} of the radical anions and cations in the UV−visible region versus chain length. The permethyl oligomers are also shown in the figure (triangles). Shown on the broken line are the absorption maxima of neutral molecules at 77 K. As observed for the neutral polymers, the λ_{max} of the radical anions and cations increased rapidly for the short catenates region and then increased gradually, approaching a constant value above a chain length of about 16. The initial spectral shifts of both radical anion and cation are however much steeper in comparison with the shift of neutral polymers. The correlation between the λ_{max} of the radical ions and the chain length enabled us to estimate the delocalization length of the radical ions in the silicon catenates. An extension of the radical ion chain beyond 16 silicon units hardly affects the delocalization of spin and charges. Similar results are observed for the photoluminescence.[15,16]

The absorption energy (E) of the radical anions and cations of the polysilanes was plotted against the inverse chain length, as shown in Figure 5. The transition energy decreases linearly with the decreasing inverse chain length up to a chain length of 16. For longer chains, the transition energy is almost constant. The inverse dependence of the absorption maxima in conjugated systems on chain length has also been reported for oligothiophenes.[4,8] The linear relationship observed between $E(\lambda_{max})$ and $1/N$ until $N = 16$ for the polysilane radical ions implies that the charge is delocalized over a 16 silicon segment.

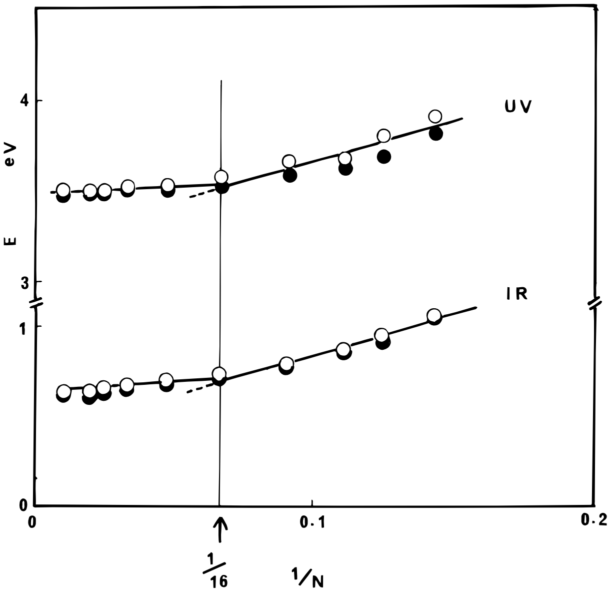

Figure 5. Relation between the electronic transition energies of the radical anions (●) and cations (○) (UV and IR regions) at 77 K and the reciprocal of the number of chains (determined by NMR) for poly(methyl-*n*-propylsilane)s.

Recently it has been reported that the unpaired electron of polysilane radical anions is not delocalized along the Si−Si main chain but is confined in the branched polymer chain.[17a] The radical cation has been reported to delocalize over only six silicon atoms.[17b] These results are in marked contrast with our observations. Hochstrasser et al. have sought the conditions that need to be satisfied for excitation delocalization in σ-conjugated systems and found that at least 10 silicon atoms are required for large polaron formation.[18] It is reported that the lowest excitonic state has been shown to delocalize over several tens of monomer units from time-resolved and steady-state fluorescence measurements of poly(methylphenylsilane).[19] Consistent with these results, the present observations suggest that the charges of the radical anions and cations in poly(methyl-*n*-propylsilane) delocalize over ~16 monomer units.

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