



## Study of Polysilane Mainchain Electronic Structure by Picosecond Pulse Radiolysis

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### Abstract

The electronic structure of a charged polysilane molecule is studied. The transient absorption spectroscopy was carried out for charged radicals of poly (methylphenylsilane): PMPS by pico-second and nanosecond pulse radiolysis technique. It was observed that the peak of the transient absorption spectra shifted to longer wavelength region within a few nsec, and an increase was observed in the optical density at 370 nm, which had been already assigned to the radical anions of PMPS. It is ascribed to inter-segment electron transfer (intra-molecular transfer) through polymer chain. The nanosecond pulse radiolysis experiments gave similar kinetic traces in near-UV and IR region. This suggests the presence of an interband level, that is, a polaron level occupied by an excess electron or a hole.

### Introduction

Silicon skeleton polymers (for a review, see ref 1) have attracted considerable attention because of the interesting physical properties such as photoconductivity, photosensitivity, and nonlinear optical properties, etc. Recent experimental results and theoretical calculations on polysilanes have suggested that their conjugated  $\sigma$ -bonding in a silicon skeleton ( $\sigma$ -conjugated system) is responsible for their interesting physical properties.

We have already reported the nature of charged radicals in polysilane derivatives.<sup>2)</sup> The radical cations and anions of polysilanes showed strong chromophores in the near-UV and IR regions which were due to the main and sub gap transition between valence band, conduction band, and an interband level. The interband level was predominantly formed by the interaction between an excess electron and backbone phonons, leading to the so-called polaron state. The behavior of the state was also investigated by us in the polysilane with structural defects. The excess electrons relatively localized on the Si backbone, especially around the "defect like" structures, which supported the polaron model for the radical cations and anions of polysilanes. However, the experimental results reveal the final state after the fast relaxation processes, such as the intra-molecular charge transfer (charge transfer between  $\sigma$ -conjugated segments), which is expected to terminate within a few nsec. Thus in the present paper, we discuss the very fast dynamics of the radical anions of polysilane using pico-second pulse radiolysis technique.

### Experimental

Poly(methylphenylsilane): PMPS was synthesized by the conventional Kipping dechlorinate reaction from the methylphenyldichlorosilane monomer. The reaction was carried out in Ar atmosphere, in

dry toluene during 4 h. The polymer was precipitated using isopropyl alcohol after filtration to roughly remove NaCl, and the precipitates were dried under vacuum. Toluene solution of the polymer was washed by water, and precipitated with tetrahydrofuran-isopropyl alcohol mixture.

The pulse radiolysis measurements were performed with L-band electron linear accelerator at the Radiation Laboratory of the Institute of Scientific and Industrial Research, Osaka University. The details in the set of apparatus was described elsewhere. The polymer was dissolved in tetrahydrofuran: THF and CH<sub>2</sub>Cl<sub>2</sub> at 50 mM/dm<sup>3</sup> conc.(base mol unit) for nano-second pulse radiolysis measurement, and degassed before to use. The Ar bubbled solution in THF was used in pico-second pulse radiolysis measurement. The solution flows in a quartz cell (2 cm optical path) at 500 ml/min to prevent the sample from radiation induced damages. All the spectroscopy were done at RT.

### Results and Discussion

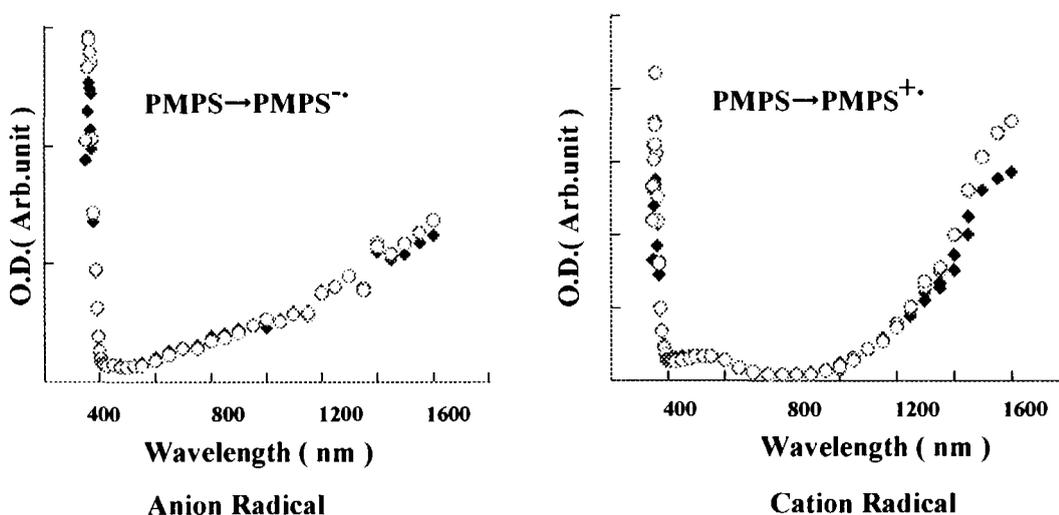


Figure 1. The transient absorption spectra of PMPS radical ions in nano-second pulse radiolysis

Figure 1 shows the transient absorption spectra of PMPS charged radicals obtained by nano-second pulse radiolysis. Two strong chromophores were observed in near-UV and IR regions. Figure 2 indicates the kinetic traces of them. The peak of the IR chromophore was not observable because of the limitation of the present apparatus.

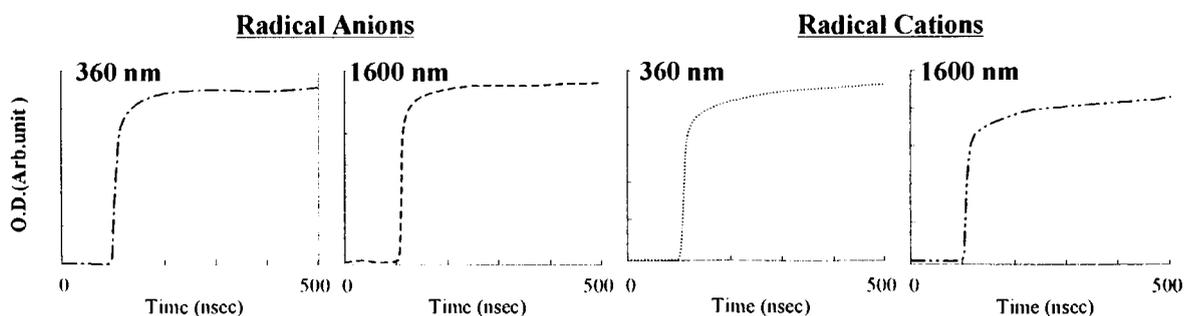
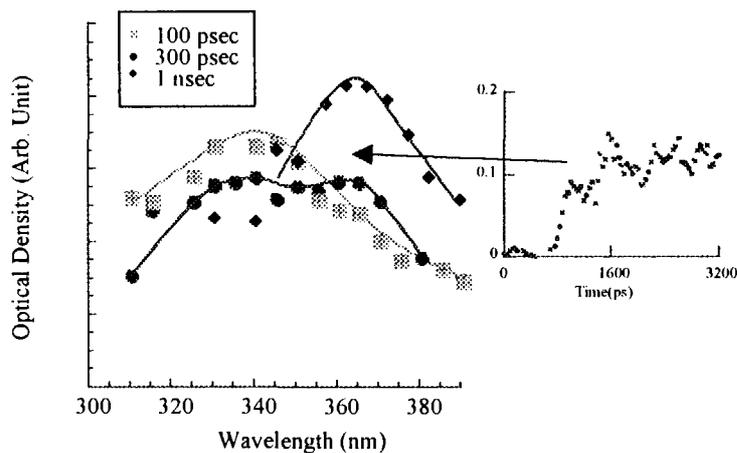


Figure 2. The kinetic traces of the transient chromophores at near-UV and IR for PMPS charged radicals

The transition energy was already confirmed by low temperature matrix experiment to be 0.5-0.6 eV. The kinetic trace in the near-UV and IR absorption can be overlapped each other, suggesting that the transient absorption originates from a single reactive intermediate, i.e., radical anion or cation of PMPS. This result also implies the presence of an interband level occupied by an excess electron or a hole. The level already revealed to be formed by the interaction between an excess electron and 1-D Si backbone phonons.



**Fig.3** Transient absorption spectra of PMPS radical anion in THF by pico-second pulse radiolysis

The sum of the transition energy at near-UV and IR absorption was estimated about 4.0 eV., which shows good agreements with the theoretical calculations.

Figure 3 showed the transient absorption spectra of PMPS radical anion by pico-second pulse radiolysis, together with the kinetic traces at 370 nm during a few nsec. The peak of transient absorption spectra shifted toward longer wavelength region with an increase in the optical density at 370 nm. The radical anions of PMPS are clearly formed at 1 nsec after an electron pulses, and the yield is saturated after a few nsec. A polysilane molecule has already been revealed to have a backbone consisting of conjugated helical segments joined to each other by a disordered Si conformation. A solvated electron is promptly captured by any one conjugated segment, because the each segment in a Si backbone has enough electron affinity to form an radical anion. However, an excess electron should migrate into the segment which has relatively large catenation of Si atoms, thus the anion is stabilized and gives a chromophore at 370 nm.

### Summary

The behavior of charged radicals is studied on polysilane by using pulse radiolysis technique. The prompt red shift in the near-UV chromophore indicates that inter-segment electron transfer (intra-molecular transfer) occurs between the conjugated Si segments within a few nsec. The formation processes of PMPS radical anions may competes with the intra-molecular charge transfer processes.

### References

- 1) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, 89, 1359.
- 2) Seki, S.; Yoshida, Y.; Tagawa, S.; Asai, K. *Macromolecules* **1999**, 32, 1080.