Electronic Structure of Polysilanes Studied by Femtosecond Laser Flash Photolysis

Yoshinori Matsui, Shu Seki, Toshiyuki Iwamoto, and Seiichi Tagawa
Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 564

(Received April 21, 1998; CL-980302)

Transient absorption spectra were obtained in solution of poly(methylphenylsilylene) (PMPS) and poly(methyl-n-propylsilylene) (PMPrS) at room temperature in the wavelength range 340-500 nm, using femtosecond laser flash photosysis. Transient absorption bands in near UV region, were ascribed to exciton states.

Polysilanes are known as σ-conjugated polymers which consist of saturated silicon chains. These polymers show interesting optical and electronic properties such as photoconductivity and non-linear optical properties, and these properties differ from those of their carbon analogues. These properties are ascribed to σ-electrons delocalized along the silicon main chains.[1] The lowest energy transition displays strong absorption in the near UV leading to delocalized $\sigma\sigma^*$ excitations.[2] The absorption is suggested to an inhomogeneous distribution of main chain length segments having different degrees of excitation localization.[3] The position of absorption maximum depends on the silicon main chain length.[4] The extinction coefficient at the absorption maximum also highly depends on the silicon main chain length. The excited state dynamics is governed by fast competing processes of radiative decay,[1] energy transfer process between σ-conjugated segments,[5,6] and chain scission by photodegradation.[4,7] The emission lifetimes are reported to be very short (75-200 psec),[1] and emission quantum yield increases when excitation wavelength goes from short-wavelength to the red tail of the absorption band. These are regarded as evidence that energy transfer occurs from initially absorbed excitation to longer segments having lower excitation energy. Photochemical reaction is considered to be one of the major processes of decay of excited states, and the quantum yield for main chain scission in solutions was reported to be high, between 0.20 and 0.97.[4] We have examined the transient absorption spectra of polysilanes observed for lasr flash photolysis in order to gain insight into the mechanism of excitation dynamics.

PMPS, PMPrS were prepared by Wurtz-type coupling. Molecular weights of these polymers were determined by gel permeation chromatography(GPC) with polystylene calibration standards. Mw of PMPS was 2.6 x 10^5 with Mw/Mn = 4.8. Mw of PMPrS was 7.9 x 10^5 with Mw/Mn = 4.2. PMPS was dissolved into tetrahydrofuran(THF) at 60 base mmol dm^{-3}. PMPrS was dissolved into hexane at 60 base mmol dm^{-3}. Flowing cell was used to avoid observing photodecomposed products. The light pulse of Ti:sapphire femtosecond pulse laser(Tsunami: 6 nJ/pulse, frequency: 80 MHz, fwhm: 80 fs) was amplified by regenerative amplifier(Spitfire: 0.3 mJ/pulse, frequency: 1.2 kHz, fwhm: 110 fs). Exposure was performed with the third harmonics having wavelength of 267±16 nm. The probe light had the continuous spectrum generated by fundamental light focused into a 1cm H_2O flowing cell. The one-dimensional CCD was used to detect the probe light. The time resolution of this set was calibrated to be about 500 fs from the consequence of measuring H_2O Kerr effect. The details of the femutosecond laser flash photolysis were described elsewhere.[8]

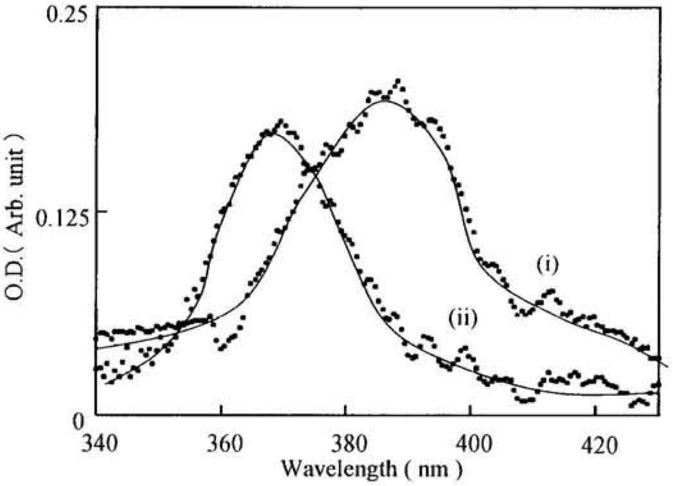

Figure 1. Observed transient absorption spectra immediately after pulses for (i) PMPS in THF at 60 mM (Base. Mol. Unit), (ii) PMPrS in hexane at 60 mM (Base Mol.Unit), excited at 267 ±16 nm

Figure1 shows transient absorption spectra of PMPS in THF and PMPrS in hexane. The transient absorption peaks were observed around 390 nm for PMPS and 370 nm for PMPrS, respectively. For PMPS and PMPrS, the fwhm of transient absorption bands are ca. 0.23 eV and 0.21 eV, respectively. No

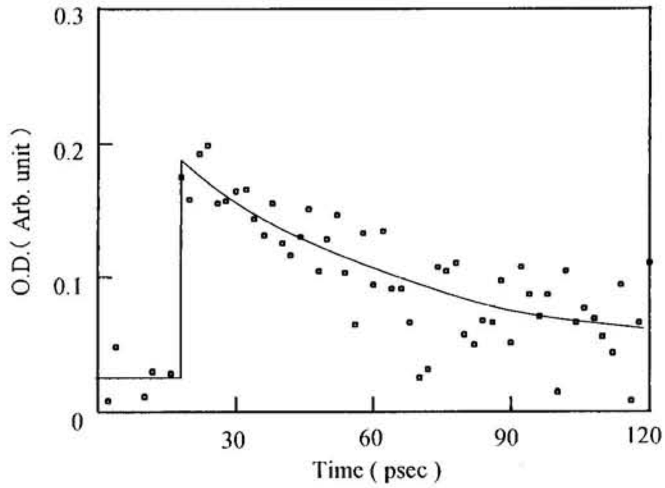

Figure 2. Decay profiles of the transient absorption at 385 nm. observed for PMPS in THF at 60 mM.

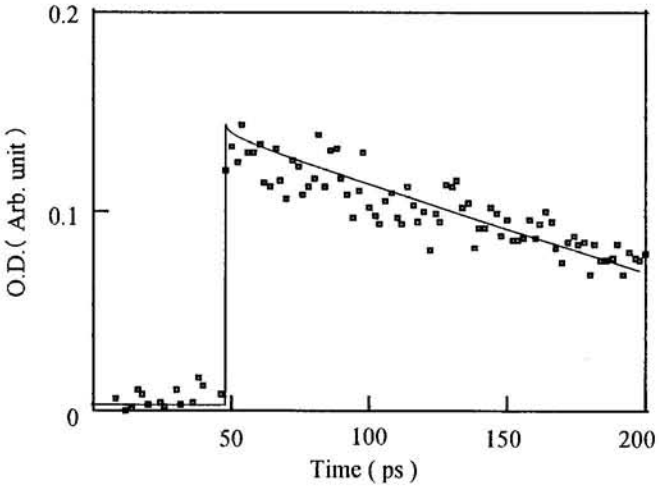

Figure 3. Decay profiles of the transient absorption at 375 nm. observed for PMPrS in hexane at 60 mM.

other transient absorption bands are observed at longer wavelength region(430~500 nm) in both solutions.

Figure2 shows the decay of transient absorption observed for PMPS in THF. Figure3 shows the decay of transient absorption observed for PMPrS in hexane. Though signal-to-noise ratio of this system is low, measured life times of transient absorption bands are 91 ps for PMPS and 2.8 x 10^2 ps for PMPrS, respectively. The kinetic traces of the transient absorption were fitted by a single exponential function for both polymers. Emission lifetimes of these polymers are 73 ps for PMPS and 3.3 x 10^2 ps for melted PMPrS.[5,9] Emission lifetime should correspond to that of observed transient absorption. Therefore transient absorption bands in near UV region in picosecond time range are predominantly ascribed to exciton states for PMPS and PMPrS, although it is reported that the absorption bands of excited states were not observed because of high yield of photodecomposition products for PMPS in THF solution.[6]

However, the possibility exists that the transient absorption bands are partially correspond to photochemical products and/or ionic species by electron photoejection. Silylenes and silyl radicals were investigated as neutral species produced by photochemical reactions by other groups.[10,11,12] The transient absorption of methylphenylsilylene (MePhSi:) is observed at 480 nm by a laser flash photolysis technique.[11,12] No transient absorption bands are observed at this wavelength region in the present experiment. The rate constant of coupling reaction for silyl radicals of PMPS was suggested to be ca. 3 x 10^3 mol^{-1}dm^{-3}s^{-1},[12] indicating quite slower reaction than the reaction observed in the present paper. Generation of ionic species by laser flash photolysis is also reported by other group.[13] The transient absorption is located around 370 nm for ionic species of PMPS. The transient absorption of ionic species was observed at a few hundreds of microsecond.[13] Therefore the transient absorption observed should not be ascribe to photochemical products and ionic species.

In conclusion, transient absorption bands in near UV region in picosecond time range are ascribed to exciton states for PMPS and PMPrS.

This work was supported by a Grant-in-aid for scientific research No.09239230 from the Ministry of Education, Science and Culture. The authors acknowledge Prof. Y. Yoshida at ISIR Osaka University for useful discussion.

References and Notes

1 R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).
2 C. G. Pitt, L. L. Jones, and B. G. Ramsey, *J. Am. Chem. Soc.*, **89**, 5471 (1967).
3 K. A. Klingensmith,. J. W. Downing, R. D. Miller, and J. Michl, *J. Am. Chem. Soc.*, **108**, 7438 (1986).
4 P. Trefonas, R. West, R. D. Miller, and D. J. Hofer, *Polm. Sci., Polm. Lett. Ed.*, **21**, 823 (1983).
5 Y. R. Kim, M. Lee, J. R. G. Thorne, and R. M. Hochstrasser, *Chem. Phys. Lett.*, **145**, 75 (1988).
6 J. R. G. Thorne, S. T. Repinac, S. A. Abrash, J. M. Zeigler, and R. M. Hochstrasser, *Chem. Phys.*, **146**, 315 (1990).
7 P. Trefonas, R. West, and R. D. Miller, *J. Am. Chem. Soc.*, **107**, 2737 (1985).
8 Toshiyuki Iwamoto, Seiji Nagahara, and Seiichi Tagawa, *Photopolymer Sci. Tech.*, **11** (1998) in press.
9 S. Seki, Y. Yoshida, H. Shibata, S. Tagawa, and K. Ishigure, *Polymer Preprints Jpn* ,342 (1995).
10 Y. Ohsako, J. R. G. Thorne, C. M. Phillips, J. M. Zeigler, and R. M. Hochstrasser, *J. Phys. Chem.*, **93**, 4408 (1989).
11 A. Watanabe and M. Matsuda, *Macromolecules*, **25**, 484 (1992)
12 A. Watanabe, H. Miike, Y. Tsutsumi, and M. Matsuda, *Macromolecules*, **26**, 2111 (1993).
13 A. Eckhardt, and W. J. Schnabel, *Inorg. Organomet. Polym.*, **6**, 95 (1996).