Photo-Induced Reaction Dynamics in Poly(di-*n*-hexylsilylene) by Excimer Laser Flash Photolysis

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KrF excimer laser induced photo-dissociation reaction was observed for poly(di-n-hexylsilylene) (PDHS) in several solvents at room temperature by using transient absorption spectroscopy technique within the wavelength range at 340-1600 nm. Transient absorption strongly depended on solvents suggesting that observed near UV absorption was ascribed to polysilylated silyl radicals in cyclohexane and tetrahydrofran (THF), and electron photoejection was also observed in CH_2Cl_2 giving radical cations of PDHS.

The polysilylene derivatives show interesting optical and electronic properties.[1] In the polymers the σ-bonded main chain is made up entirely of Si atoms, and σ-electrons are delocalized along the silicon chains. Hence, many properties of the polymers are found differ from analogous carbon-based polymer systems showing high hole mobility,[2] electro-luminescence,[3] high nonlinear optical coefficient,[4] etc. The σ-conjugated main chain acts as an intense UV chromophore, and the maximum absorption energy and extinction coefficient strongly depend upon the conjugated chain length.[5] The lowest energy transition is considered to give delocalized σ–σ* excitation, that is excitons followed by radiative energy relaxation with high quantum efficiency.[5,6] The excited state dynamics is governed by fast competing processes of radiative decay,[5] energy transfer process between σ-conjugated segments,[6] and chain scission by photodegradation.[7] Photochemical reaction is one of the most important processes of energy relaxation, and silylenes,[8,9] polysilylated silyl radicals,[10,11] and ion species[12,13] were reported to be produced as reactive intermediates upon exposure to UV light and radiation sources. However the mechanism of photodegradation reactions is complicated, and has not elucidated yet. In the present letter, direct observation of the reactive intermediates is carried out using KrF excimer laser flash photolysis technique, and predominant species are discussed in each solution system.

PDHS was prepared by Wurtz-type coupling of di-n-hexyldichlorosilane (purchased from Shinetsu Chemical Co. LTD.) using sodium metal. Molecular weights of the polymer were Mn=3.8x10^4 and Mw=8.7x10^4, respectively determined by GPC with polystylene calibration standards. PDHS was dissolved into THF, cyclohexane, and CH_2Cl_2 (Dojin Chemicals) at 10 mM conc.(Base Mol Unit), and the solutions were Ar bubbled prior to use.

Excimer laser was driven with KrF gas at 248 nm, and the laser pulses were attenuated down to 20 mJ/cm^2•pulse. Exposure was performed with the pulse of which fwhm was 5.4~8.2 nsec. Xe flash lamp was used as a source of analyzing light with continuous spectrum from 250 nm to 1600 nm. The analyzing light was monitored with a Ritsu MC-10N monochromator, and detected by a PIN-Si (Hamamatsu S1722) or a PIN-InGaAs (Hamamatsu G3476) photodiode. Signals were corrected by a Sony/Tektronics SCD1000 transient digitizer.

Pulse radiolysis experiments were also performed with the same detection system using a LINAC accelerator at ISIR Osaka University. Transient spectra were measured for an evacuated solution of PDHS in CH_2Cl_2 at 50 mM conc. Radical cations of CH_2Cl_2 were produced by ionization and extract electrons from PDHS molecules giving radical cations of PDHS.

Figure 1 shows transient absorption spectra of PDHS

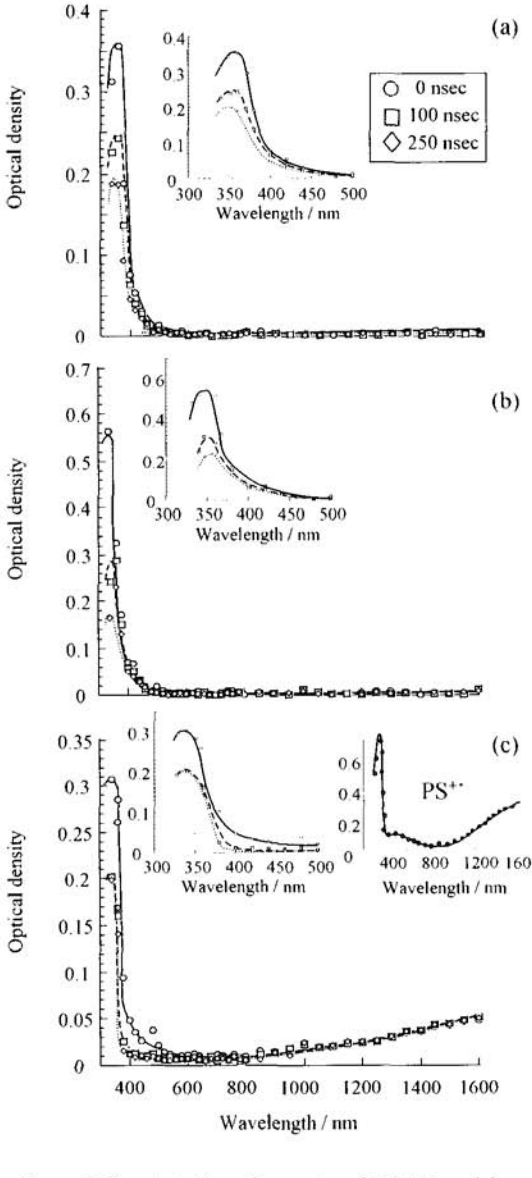

Figure 1. Transient absorption spectra of PDHS in cyclohexane(a), THF(b), and CH_2Cl_2 at immediately after a pulse (solid), 100 nsec (dashed), and 250 nsec (dotted). Superimposed figures show detailed structure of near UV absorption band, and also show transient absorption spectrum of PDHS radical cations obtained by pulse radiolysis technique in (c).

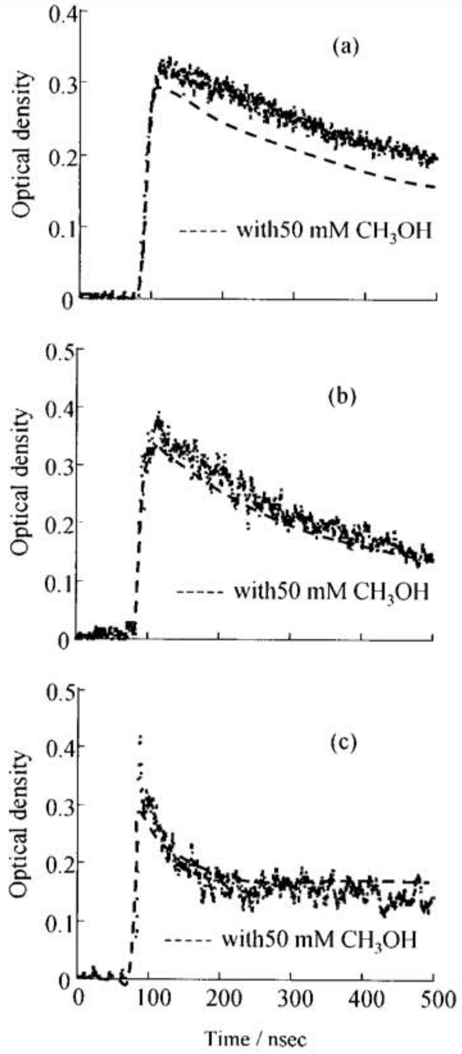

Figure 2. Kinetic traces of optical density observed at 360 nm in cyclohexane(a), THF(b), and at 345 nm in CH_2Cl_2(c). Dashed lines indicate kinetic traces in the solutions with 50 mM CH_3OH.

solutions in cyclohexane, THF, and CH_2Cl_2. All absorption spectra have a strong maximum at 358, 360, and 345 nm, respectively with 0.6~0.8 eV red shift from the steady state absorption ascribed to σ-σ^* transition. The obtained spectra in cyclohexane resemble that in THF though the optical density shows little difference in the two solvents. However remarkable difference is observed in the spectra obtained in CH_2Cl_2 showing stable absorption band in IR region over 1000 nm. The UV absorption maximum also indicates ca. 15 nm blue shift to that observed in cyclohexane and THF. Figure 1 also shows a transient absorption spectrum of PDHS radical cations obtained by pulse radiolysis. The spectrum has two absorption bands at 347 nm and over 1000 nm, indicating good correspondence to the spectra obtained by the flash photolysis in CH_2Cl_2. Figure 2 shows kinetic traces of the UV transient absorption band observed for PDHS in the solvents. Observed transient species are formed within the time range of laser pulse duration. In spite of psuedo-first order decaying in cyclohexane and THF during the time range, the kinetic trace apparently has two components in CH_2Cl_2. Because of similarity in kinetic trace observed in near UV and IR region, these two transient absorption bands should be due to the same reactive intermediates. The kinetic traces are not changed by the presence of 50 mM CH_3OH which is the typical quencher for silylenes.

Transition of exciton states was considered to display transient absorption band in near UV region. However the lifetime of the transient was ca. 300 psec[14] suggesting that the transients were due to photochemical reactive intermediates formed after extinction of excited states.

Reactive intermediates produced by photodissociation of polysilylenes are predominantly silylene and polysilylated silyl radicals. The observed UV transient chromophore is not quenched by the presence of excess CH_3OH in the solutions. Previous studies also reported that the lifetimes of silylenes were much longer than that of the reactive intermediates observed in the present study.[8] In contrast, polysilylated silyl radicals were reported to be produced within a few nsec. Our previous study on EPR spectroscopy of polysilylenes suggested that the polysilylated silyl radicals had unpaired electrons localized on a Si atoms, and computed SOMO levels were expected to display the transition at near UV region.[11] Thus, transient species observed in cyclohexane and THF are ascribed to polysilylated silyl radicals in the present study.

Radical cations of PDHS are responsible to the transient absorption observed in CH_2Cl_2, which is supported by the correspondence between the results of flash photolysis and pulse radiolysis. The long-lived portion of the transient spectra obtained in CH_2Cl_2 is exactly same as that of radical cations having sharp UV absorption at 345 nm and broad IR absorption over 1000 nm. Especially the IR transient chromophore is the typical characteristics of polysilylene radical cations which has been already reported.[12] In spite of lower photon energy (ca. 5 eV at 248 nm) than ionization potential of PDHS, photo-induced electron ejection occurs upon exposure to laser light.

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