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Radical Ions of Polysilastyrene

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ABSTRACT: The absorption spectra of radical ions of polysilastyrene have been measured in rigid matrices at 77 K as well as in solution at room temperature by using γ-irradiation and pulse radiolysis methods. The radical anion with λ_{max} at 365 nm was observed in irradiated 2-methyltetrahydrofuran, while the radical cation with two absorption bands at 358 and 2000 nm was observed in irradiated *n*-butyl chloride at 77 K. Upon thermal annealing, the infrared band showed a blue shift to 1700 nm, which is attributed to the geometrical reorientation of pendant phenyl groups from the unrelaxed to relaxed dimer radical cation conformation. A silyl radical bearing a phenyl group, produced from dimethylphenylchlorosilane by the dissociative electron capture reaction, was found to have absorption bands at 300 and 420 nm. The half-life of the radical anion and cation in solution at room temperature were measured to be 30 and 85 μs, respectively, by the pulse radiolysis method.

Introduction

Polysilanes in which the main chain is composed of covalently bonded silicon atoms have recently attracted a great deal of renewed attention.[1,2] These polymers possess interesting properties (e.g., sensitivity to UV irradiation and potential semiconductivity) and are used as UV photoresists,[3] precursors to β-SiC fibers,[4] and dopable semiconductors.[5] If we pay attention only to the chemical structure of the main chain, the linear polysilanes are analogues of saturated alkanes. The polysilanes, however, have the distinct advantage, at least to the experimental spectroscopist, that their lowest lying electronic transition is strongly red-shifted into the easily accessible near-UV region.

In previous papers,[6,7] we have shown that the radical anions and cations of vinyl polymers having aryl pendant groups, polystyrene and poly(2-vinylnaphthalene), are produced by radiation in rigid matrices at 77 K as well as in solution at room temperature and the absorption spectra measured by the pulse radiolysis method can give invaluable information concerning the intramolecular interaction of the pendant groups. In the present paper, we extended the spectroscopic study of radical ions of the vinyl polymers to the organosilane polymer with aryl groups, poly[(dimethylsilylene)-*co*-(methylphenylsilylene)](polysilastyrene), by employing the rigid matrix method and the pulse radiolysis technique.

Experimental Section

Poly[(dimethylsilylene)-*co*-(methylphenylsilylene)](polysilastyrene) was synthesized from equal moles of dimethyldichlorosilane and methylphenyldichrolosilane (Shin-Etsu Silicon Chemicals) according to the method of Zhang and West.[8] The molecular weight of the polymer was estimated by gel permeation chromatography by comparison with that of polystyrene standard samples. 2-Methyltetrahydrofuran (MTHF), and *n*-butyl chloride (*n*-BuCl) were purified by repeated distillation. The solution in a Suprasil cell (optical path length, 2 mm) was degassed, and the frozen solution was γ-irradiated at a dose rate of 1.2×10^{19} eV/g·h at 77 K. The optical absorption change induced by irradiation and by subsequent warming was measured with a Hitachi 323 spectrophotometer. Details of the present pulse radiolysis system, used for the room temperature studies, have been reported previously.[9] The energy of the electron pulse was 10 MeV, and the duration was 0.5 μs.

Results and Discussion

Absorption Spectra of Radical Ions at 77 K. According to Shida and Hamill,[10] reactions in γ-irradiated MTHF ($C_5H_{10}O$) matrices are represented as follows:

$$C_5H_{10}O \rightsquigarrow C_5H_{10}O^+ + e^- \qquad (1)$$

$$C_5H_{10}O^+ + C_5H_{10}O \rightarrow C_5H_{11}O^+ + {}^{\bullet}C_5H_9O \qquad (2)$$

$$e^- + s \rightarrow s^- \qquad (3)$$

where e^- and s denote electrons and solute molecules, respectively. The electrons migrate in the matrix to be captured by the solute molecules, while positive ions of MTHF decompose by reaction 2. Consequently, solute anions are selectively produced in MTHF matrices. On the other hand, reactions in *n*-BuCl (RX) matrices are as follows:

$$RX \rightsquigarrow h^+ + e^- \qquad (4)$$

$$e^- + RX \rightarrow R^{\bullet} + X^- \qquad (5)$$

$$h^+ + s \rightarrow s^+ + RX \qquad (6)$$

where h^+ denotes holes; e^-, electrons, and s, solute molecules. Solute anions are not formed because of the predominant reaction 5, i.e., electron removal, and accordingly solute cations are selectively produced in *n*-BuCl matrices.

Figure 1a shows the absorption spectrum of MTHF solution containing 2×10^{-2} M polysilastyrene (MW = 6.7×10^4) at 77 K irradiated with a dose of 3×10^{19} eV/g. The spectrum with λ_{max} at 365 nm is ascribable to the radical anion of polysilastyrene.

Radical cation of a solute molecule is produced in irradiated *n*-BuCl by the reaction of a positive hole with a solute molecule.[10] Figure 1b shows the absorption spectrum of *n*-BuCl solution containing 2×10^{-2} M polysilastyrene at 77 K irradiated with a dose of 3×10^{19} eV/g. The absorption bands at 358 nm is ascribable to the radical cation of polysilastyrene. In the spectrum of the *n*-BuCl solution, another band was observed in the infrared region, which is similar to the band detected in irradiated *n*-BuCl solution containing polystyrene.[6] According to the assignment of Brocklehurst,[11] the band in the infrared region is due to the charge resonance interaction between two phenyl groups in the radical cation and ground states. The appearance of this band is clear evidence that the interaction of two pendant phenyl groups exists in the radical cation state in polysilastyrene.

Shida has shown that the conformational change in the radical ion state can be detected by measuring the absorption spectrum.[12] We carefully examined the spectral change of the radical ions induced by thermal annealing. Although no spectral change was observed in the radical

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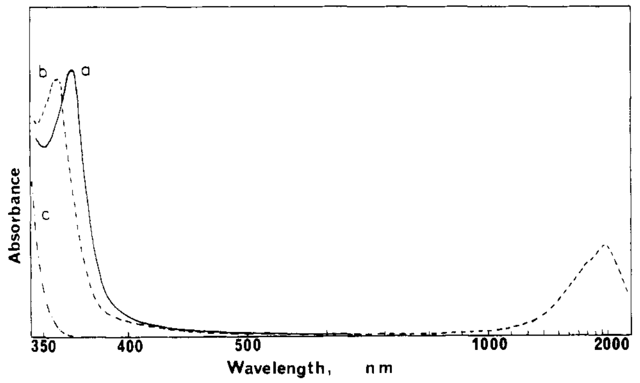

Figure 1. Absorption spectra of MTHF (a) and *n*-BuCl (b) solutions containing 2×10^{-2} M polysilastyrene irradiated with a dose of 3×10^{19} eV/g at 77 K. (c) Absorption spectrum of the unirradiated sample.

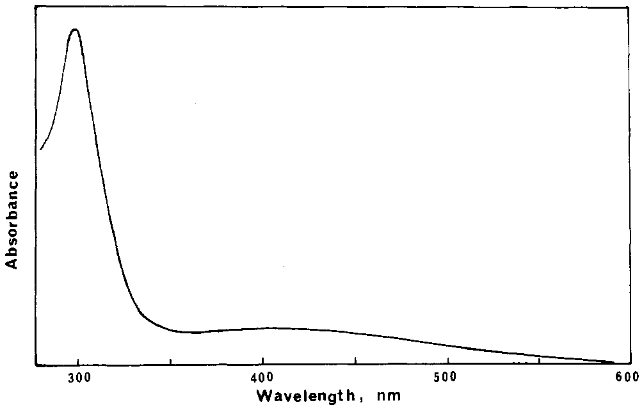

Figure 2. Absorption spectrum of MTHF solution containing 2×10^{-2} M dimethylphenylchlorosilane irradiated with a dose of 3×10^{19} eV/g at 77 K.

anion, a dramatic spectral shift was observed in the infrared band of the radical cation. The band shifted from 2000 to 1700 nm. The absence of the spectral change in the radical anion state is due to the weak intramolecular interaction force between the radical anion and the adjacent neutral pendant groups. We have previously reported a similar spectral shift in the infrared bands of radical cations of polystyrene and poly(2-vinylnaphthalene).[6] The shift was assigned to the geometrical reorientation of the pendant phenyl or naphthyl groups. A similar interpretation can be applied to the shift observed in polysilastyrene. The pendant phenyl groups change the conformation from the unrelaxed to relaxed dimer radical cation state about the connecting silylene chains.

Although we assigned the absorption bands in the UV region observed in MTHF and *n*-BuCl to the radical anion and cation of polysilastyrene, respectively, a silyl radical bearing a phenyl group is also expected to have an absorption band in a similar region.[13] In order to eliminate the ambiguousness of the assignment, we also measured the absorption spectrum of dimethylphenylsilyl radical. The radical was produced by the dissociative electron attachment reaction of dimethylphenylchlorosilane. Alkyl or aryl halides(RX) are well-known to dissociate into R$^\bullet$ and X$^-$ by reaction with an electron.[10]

$$RX + e \rightarrow R^\bullet + X^-$$

Figure 2 shows the absorption band of an MTHF solution containing 2×10^{-2} M dimethylphenylchlorosilane irradiated by a dose of 3×10^{19} eV/g and measured at 77 K. The spectrum is ascribable to the dimethylphenyl silyl radical. The radical has two bands at 300 and 420 nm. The absorption maximum and the band structure are very similar to those of the benzyl radical.[13] The spectra observed in MTHF and *n*-BuCl solutions containing polysilastyrene are quite different from the radical spectrum.

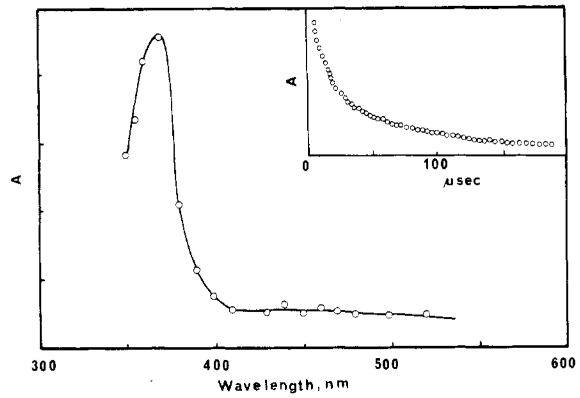

Figure 3. Transient absorption spectrum of MTHF solution containing 1×10^{-2} polysilastyrene. Insert is the absorption profile recorded at 370 nm representing the decay of the transient.

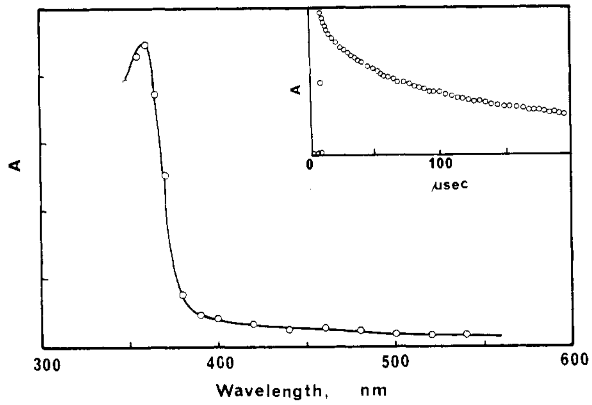

Figure 4. Transient absorption spectrum of an *n*-BuCl solution containing 1×10^{-2} M polysilastyrene. Insert is the absorption profile recorded at 360 nm representing the decay of the transient.

The assignment was further confirmed by using a mixed matrix of MTHF and *n*-BuCl. In the mixed matrix electrons ejected by radiation are stabilized as Cl$^-$ and positive holes, counterpart of the ejected electrons, are trapped in the protonated form of MTHF, as described before. Therefore, both electrons and positive holes generated as a consequence of ionization of the solvent by radiation are considered to be captured immediately by surrounding solvent molecules in the mixed solution and neither radical anions nor cations are expected to be formed.[14] The spectrum of the irradiated mixed solution containing polysilastyrene had no absorption band in the wavelength region longer than 350 nm. Both bands in the UV and infrared regions disappeared. This result confirms our assignment of the band observed at 365 nm in MTHF solution to the radical anion of polysilastyrene and the bands at 358 and 2000 nm in *n*-BuCl to the radical cation.

Absorption Spectra of Radical Ions at Room Temperature. On the basis of knowledge of the spectra of the radical ions of polysilastyrene at low temperature, we carried out a pulse radiolysis study at room temperature in MTHF and *n*-BuCl solutions. Figure 3 shows the transient absorption spectra of MTHF solution containing 1×10^{-2} M polysilastyrene, observed immediately after the pulse. The inset shows the time dependence of the absorption band at 370 nm. The absorption band at 370 nm is ascribable to the radical anion of polysilastyrene on the basis of the spectra at low temperature. The half-life of the radical anion was obtained to be 30 μs. By the addition

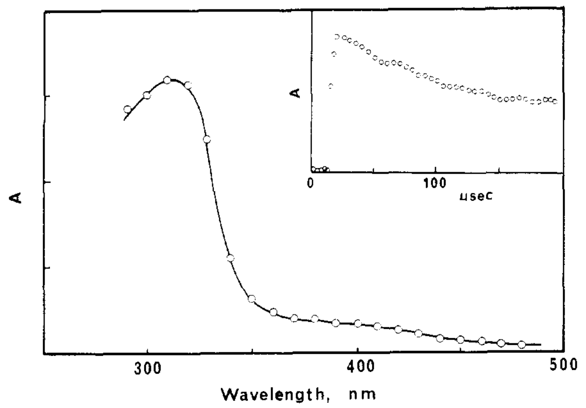

Figure 5. Transient absorption spectrum of MTHF solution containing 1×10^{-2} M dimethylphenylchlorosilane. Insert is the absorption profile recorded at 360 nm representing the decay of the transient.

of electron scavenger, *n*-BuCl, the band at 370 nm disappeared. This result confirms that the band is due to the radical anion.

Figure 4 shows the transient absorption spectrum of an *n*-BuCl solution containing polysilastyrene at the end of electron pulse. The inset shows the time dependence of the absorption band at 360 nm. The band at 360 nm is assigned to the radical cation of polysilastyrene on the basis of the spectra at low temperature. The half-life was obtained to be 85 μs. The absorption band at 360 nm also disappeared by the addition of a positive hole scavenger, MTHF.

The absorption spectrum of dimethylphenylsilyl radical was also measured in MTHF solution containing dimethylphenylchlorosilane as shown in Figure 5. As described in the previous section, the radical is produced by the reaction of dimethylphenylchlorosilane with electrons ejected by radiation. The radical has the absorption band at 310 nm. The decay fits well to a reciprocal plot. This means the radicals disappear by a bimolecular reaction.

Registry No. (Dimethyldichlorosilane)(methylphenyldichlorosilane) (copolymer), 70158-17-7.

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Association Behavior in End-Functionalized Polymers. 1. Dilute Solution Properties of Polyisoprenes with Amine and Zwitterion End Groups

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ABSTRACT: The dilute solution properties of linear polyisoprenes with a highly polar sulfo-zwitterion group on one end of the chain were examined in several solvents by osmometry, light scattering, and viscometry. The polymers were prepared by anionic polymerization with initiation by (3-(dimethylamino)propyl)lithium. The terminal tertiary amine groups were converted to zwitterions by treatment with cyclopropane sultone. A few linear and star materials with all ends functionalized were also prepared. The zwitterion-capped polymers were found to associate strongly in aliphatic hydrocarbons. Solutions of monofunctional zwitterion polymers were highly aggregated in cyclohexane. The multifunctional versions (two or more zwitterions per molecule) formed gels which, however, readily dissolved when small amounts of alcohol were added. Considerably less association of the zwitterion-capped chains was found in aromatic or more highly polar solvents. The number of molecules per zwitterion aggregate in cyclohexane decreased with increasing chain length, a characteristic that we have attributed to excluded volume repulsions of the polymeric tails. The aggregates were found to resemble star polymers in behavior. Some tentative conclusions are drawn about aggregate lifetimes, polar core geometry, and the concentration dependence of aggregation in these systems.

Introduction

The dilute solution properties of flexible chain polymers are reasonably well-understood when the interactions between chain units are weak.[2] Progressive dilution below the coil overlap concentration c^* separates the individual chains, and their influence upon one another diminishes rapidly. Extrapolation of osmotic pressure or small angle scattering measurements to infinite dilution provides absolute values of the molecular weight, and similar extrapolation of viscosity or diffusion measurements provides information about the chain dimensions. Initial departures from these various limits yield data about the thermodynamic and hydrodynamic interactions of the chains. The influence of chain length and chain branching on dimen-

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