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Photodegradation and Electron-Beam-Induced Degradation of Poly[(pentamethyldisilyl)styrene sulfone]s

**Akira Watanabe,[†] Taro Sakakibara,[†] Seiki Ito,[‡] Hiroshi Ono,[‡]
Youichi Yoshida,[§] Seiichi Tagawa,[*,‖] and Minoru Matsuda[*,†]**

Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan, Yokohama Research Laboratory, Chisso Corporation, 2 Kamariya-cho, Kanazawa-ku, Yokohama 236, Japan, Nuclear Engineering Research Laboratory, Faculty of Engineering, University of Tokyo, Tokai-mura, Ibaraki 319-11, Japan, and Research Center for Nuclear Science and Technology, University of Tokyo, Tokai-mura, Ibaraki 319-11, Japan

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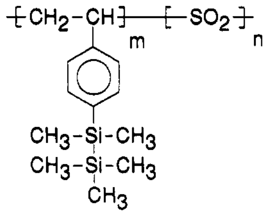
ABSTRACT: Photodegradation and electron-beam-induced degradation of poly[(pentamethyldisilyl)styrene sulfone]s were investigated by flash and pulse radiolysis techniques. The transient absorption spectra obtained by the flash photolysis for the solution of nonalternating poly[(pentamethyldisilyl)styrene sulfone]s in THF (tetrahydrofuran) showed the formation of benzyl radical as a transient intermediate. On the other hand, the transient absorption spectra for an alternating poly[(pentamethyldisilyl)styrene sulfone] did not show the absorption of benzyl radical but showed that of *p*-(pentamethyldisilyl)styrene monomer. The decay curve for an alternating poly[(pentamethyldisilyl)styrene sulfone] exhibited fast depropagation after the flash photolysis. The disilyl bond in the polymer dissociates easily by photolysis whereas the bond was stable under electron-beam irradiation. The transient absorption spectra of a radical anion of the sulfonyl group was observed by pulse radiolysis for the solution of poly[(pentamethyldisilyl)styrene sulfone]s in THF.

Introduction

Resist materials in microlithography must meet many requirements, excellent film-forming properties onto a semiconductor substrate, high resolution and sensitivity to irradiation, high resistivity to plasma treatments during substrate etching, and so on.[1] Poly[(pentamethyldisilyl)styrene sulfone]s which have a sulfonyl group in the main chain and a disilyl group in the side chain possess many characteristics to satisfy the requirements. The generic structure of poly[(pentamethyldisilyl)styrene sulfone]s is shown in Figure 1. First, they have high solubility which is needed to form good film on a substrate. Positive-tone polysulfone resists have been studied extensively because they have a weak C–S bond in the main chain upon UV light exposure.[1–4] The higher content of the weak C–S bond enhances the sensitivity to irradiation. However, alternating poly(styrene sulfone) is insoluble in the usual solvents. On the other hand, alternating poly[(pentamethyldisilyl)styrene sulfone] is highly soluble to the usual organic solvents by incorporation of a pentamethyldisilyl group. Second, poly[(pentamethyldisilyl)styrene sulfone]s have a high sensitivity to irradiation. Poly(olefin sulfone)s do not have a strong UV absorption whereas poly[(pentamethyldisilyl)styrene sulfone]s have a strong absorption in the deep-UV region and they are expected for a positive-tone deep-UV resist. Polysulfones are also positive-tone electron-beam resists owing to the high sensitivity of the C–S bond to the electron beam. O'Donnell et al.[5–9] and Bowden et al.[10–12] have investigated the radiation-induced degradation of poly(olefin sulfone)s extensively. Third, poly[(pentamethyldisilyl)styrene sulfone]s have a high resistivity to oxygen plasma etching owing to the high content of the Si atom. In bilayer lithography, consisting of a thick-base resist and a thin-imaging resist on top, the oxygen plasma etch resistance of the top layer is required to protect the thick-base resist. Organometallic polymers, primarily silicon-containing polymers, are significantly interested in bilayer lithography because of the high oxygen plasma etch resistance. Treatment of silicon-containing resists with oxygen plasma leads to the formation of silicon oxides, which generate a protective layer on the polymer surface.[1]



P2Si m/n

Figure 1. Generic structure of poly[(pentamethyldisilyl)styrene sulfone]s.

Although there are many papers reporting the resist characterization, few papers discuss the mechanism of degradation on the basis of direct observation of transient intermediates. One of the reasons is the complication of the degradation in solid state because the rapid reaction among the unstable intermediates easily occurs in the dense system and the proceeding complicated reaction prevents the observation of transient intermediates produced in the first stage of the degradation. However, the degradation in solution is somewhat different from that in solid state, since the solution reaction is less complex and affords useful information about the assignment of transient intermediates. In this paper we investigated the photodegradation of poly[(pentamethyldisilyl)styrene sulfone]s in solution by the flash photolysis technique and the electron-beam-induced degradation of these polymers by the pulse radiolysis technique.

Experimental Section

Materials. *p*-(Pentamethyldisilyl)styrene (2Si) was prepared from pentamethylchlorodisilane and *p*-chlorostyrene by Grignard reaction and purified by distillation under reduced pressure

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[†] Tohoku University.

[‡] Chisso Corp.

[§] Nuclear Engineering Research Laboratory, Faculty of Engineering, University of Tokyo.

[‖] Research Center for Nuclear Science and Technology, University of Tokyo.

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Table I
Molecular Weights and Compositions of Poly[(pentamethyldisilyl)styrene sulfone]s

abbrev	monomer/SO_2 ratio in copolym	mol wt (M_w/M_n)
P2Si	100/0	34.7×10^4 (2.59)
P2Si1/1	50/50	45.4×10^4 (2.42)
P2Si4/1	79/21	22.6×10^4 (1.54)
P2Si9/1	91/9	4.19×10^4 (1.83)

[104 °C (4 mmHg)].[13] Poly[(pentamethyldisilyl)styrene sulfone]s were prepared from *p*-(pentamethyldisilyl)styrene and SO_2 by radical copolymerization.[13] The composition of the copolymers was controlled by feed composition, total monomer concentration, and copolymerization temperature.[14,15] Alternating poly[(pentamethyldisilyl)styrene sulfone] was obtained by the copolymerization at low temperatures from −50 to −78 °C. The compositions of the copolymers were determined by elemental analysis. The molecular weight and the distribution were measured by GPC using monodispersed polystyrenes as standards. The characterization of poly[(pentamethyldisilyl)styrene sulfone]s and the abbreviations are summarized in Table I.

Measurements. The xenon flash photolysis was carried out using a 100-J lamp with a half-duration of ca. 10 μs. The decay curves of transient absorption were measured using a digital storage scope. The irradiation vessel was a cylindrical quartz cell (10 cm long and 1 cm in diameter). All measurements were carried out at 22 °C for a 1 mM (monomer unit) solution of poly[(pentamethyldilsilyl)styrene sulfone]s in degassed THF (tetrahydrofuran). The pulse radiolysis system has been described in a previous paper.[16,17] The electron pulse was of 2-ns duration from a 35-MV electron linear accelerator. The dose per pulse is evaluated from the absorbance of the hydrated electron in neat deaerated water, measured at 500 nm, and is 4–5 krad/2 ns pulse. The decay of the transient absorption obtained by the pulse radiolysis was monitored using a xenon flash lamp (EG&G FX279-U) as the monitor light and a PIN photodiode (HPK 1722-01) as the detector. All measurements were carried out for degassed poly[(pentamethyldisilyl)styrene sulfone] solutions.

Results and Discussion

Flash Photolysis. The absorption spectra of *p*-(pentamethyldisilyl)styrene (2Si) and alternating poly[(pentamethyldisilyl)styrene sulfone] copolymer (P2Si1/1) are shown in Figure 2. P2Si1/1 should be an excellent deep-UV resist since its absorption maximum at 247 nm (with a tail to 290 nm) is well matched with the Xe–Hg lamp's UV emission at 254 nm. The transient absorption spectra obtained by flash photolysis for poly[(pentamethyldisilyl)styrene sulfone]s with various compositions are shown in Figure 3. These are absorption spectra at 500 μs after the flash. The transient absorption spectrum of a 4:1 copolymer (P2Si4/1; Figure 3b) shows an absorption shoulder at about 320 nm and a weak absorption maximum at about 455 nm. This spectrum can be resonably assigned to benzyl radical. It is known that the benzyl radical has two absorption maxima, the allowed transition at 318 nm and the forbidden transition at 453 nm.[18] The formation of the sulfonyl radical is also expected properly as a transient intermediate by the main-chain fission of poly[(pentamethyldisilyl)styrene sulfone]s. In our experiments, however, the sulfonyl radical could not be detected by xenon flash photolysis. The measurements of the absolute rate were tried by laser flash photolysis.[19,20] In the case of the benzylsulfonyl radical, the rate for cleavage of the S–C bond and formation of the stable benzyl radical is so fast that the sulfonyl radical cannot be detected even with 20 ns of the laser pulse.

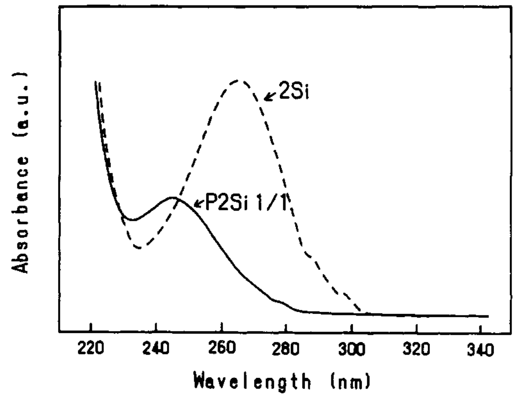


Figure 2. Electronic absorption spectra of *p*-(pentamethyldisilyl)styrene (2Si) and poly[(pentamethyldisilyl)styrene sulfone] (P2Si1/1) in 1,2-dichloroethane.

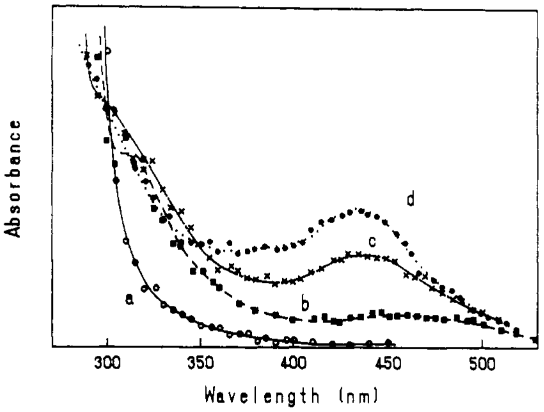


Figure 3. Transient absorption spectra obtained by flash photolysis for a 1 mM THF solution of poly[(pentamethyldisilyl)styrene sulfone]s and poly[(pentamethyldisilyl)styrene] at 500 μs after the flash: (a) P2Si1/1, (b) P2Si4/1, (c) P2Si9/1, and (d) P2Si.

With an increase in the (pentamethyldisilyl)styrene content of the copolymer, the absorption shoulder at 320 nm decreased and a wavelength shift appeared for the 400–500-nm peak as shown in Figure 3. The absorption maxima are 455 nm for spectrum b of P2Si4/1, 437 nm for spectrum c of P2Si9/1, and 434 nm for spectrum d of the P2Si homopolymer. Such a wavelength shift may be due to the overlapping of different transient species formed by photodegradation of the disilyl side chain. Shizuka et al. have reported the photolysis of pentamethylphenyldisilane, and they assigned the absorption at 420 nm to silene which is produced by intramolecular rearrangement, a 1,3 shift of the silyl group to an ortho carbon in the benzene ring.[21] The absorption maximum at 434 nm of spectrum d can be assigned to such a silene produced by photolysis of the disilyl side chain. Flash photolysis of a monosilyl-substituted polymer, poly[(trimethylsilyl)styrene] homopolymer (P1Si) which does not have C–S and Si–Si bonds, was carried out to compare with P2Si and poly[(pentamethyldisilyl)styrene sulfone]s. P1Si did not show any transient absorption in the region from 300 to 600 nm. This suggests that the transient intermediates observed for poly[(pentamethyldisilyl)styrene sulfone]s are not formed by CH_3–Si fracture photodegradation of the solvent, but they are formed by the cleavage of the C–S bond in the main chain or the Si–Si bond in the side chain.

In Figure 3, the transient absorption spectrum of alternating P2Si1/1 does not show the transient absorption of the benzyl radical, an absorption shoulder at about 320 nm and an absorption maximum at about 450 nm. This result is particularly surprising in view of the fact that P2Si1/1 has the highest content of weak C–S bond. In contrast, P2Si4/1 and P2Si9/1 showed larger absorptions assigned to benzyl radicals which are produced by C–S

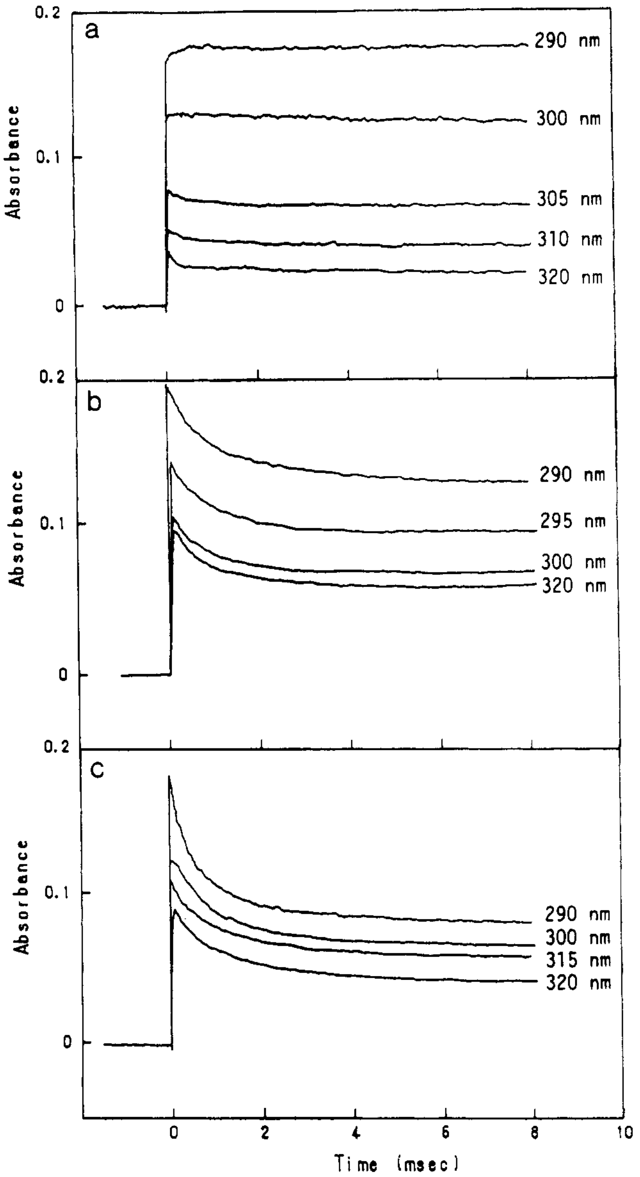


Figure 4. Decay curves of transient absorption following flash photolysis for a 1 mM THF solution of (a) P2Si1/1, (b) PSi4/1, and (c) PSi9/1. Inserted numbers are the wavelengths at which the decay curves were monitored.

bond cleavage. Therefore, the degradation mechanism for alternating copolymer is apparently different from that for the nonalternating copolymers. Such differences appear remarkably in the decay curves of the transient absorption. The decay curves of transient absorptions for P2Si1/1, P2Si4/1, and P2Si9/1 are shown in Figure 4. P2Si4/1 and P2Si9/1 show the decay of the transient absorption which is assigned to the benzyl radical. On the other hand, P2Si1/1 shows the formation of an undecayed component immediately after flash photolysis. A possible explanation for the undecayed component is the formation of the monomer *p*-(pentamethyldisilyl)styrene which is produced by the extrusion of SO_2 from both sides of the *p*-(pentamethyldisilyl)styrene unit in the alternating copolymer chain. *p*-(Pentamethyldisilyl)styrene has absorption extending to about 310 nm as shown Figure 2. Increase of the absorption near 300 nm may be due to depropagation by the C–S bond scission. Taking into account the formation of two components, the benzyl radical and the undecayed component, decay curve fitting was carried out. As the decay reaction of the benzyl radical, the second-order coupling reaction between benzyl radicals was considered. The obtained second-order rate constants were on the order of 10^5 (M^{-1} s^{-1}). Figure 5 shows the relationship between the mole fraction of poly[(pentamethyldisilyl)styrene sulfone]s and the initial absorbance calculated by the curve fitting. With an increase in the SO_2 fraction, the absorbance of the benzyl radical decreases and the undecayed component increases. The sequence information of the copolymers may be valuable in explaining the apparently different degradation mechanism of the different copolymers. The sequence structure of poly(styrene sulfone) has been studied by NMR spectroscopy.[14,22] The styrene distribution depends only upon the copolymer composition irrespective of the copolymerization condition; in the distribution, the major styrene sequence for each copolymer changed with the copolymer composition. The styrene monoad is the main component in a 1:1 (styrene/SO_2) copolymer, and the styrene triad is the main component in a 3:1 (styrene/SO_2) copolymer, for example. The mechanism of the photodegradation of poly[(pentamethyldisilyl)styrene sulfone]s is summarized in Scheme I. In the case of alternating P2Si1/1, *p*-(pentamethyldisilyl)styrene is produced by extrusion of SO_2 by photolysis owing to the fast decomposition of the benzylsulfonyl radical. In the case of nonalternating copolymers, photodegradation occurs via the benzyl radical.

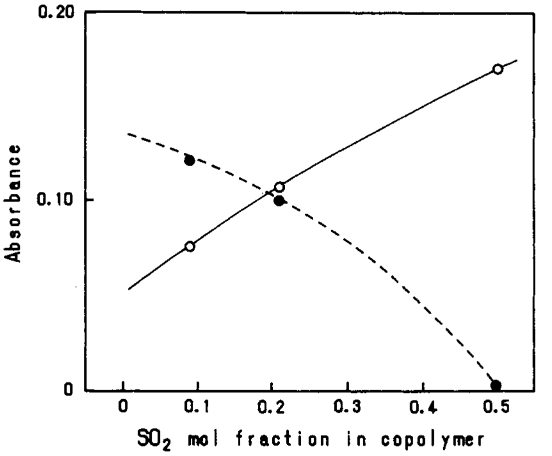
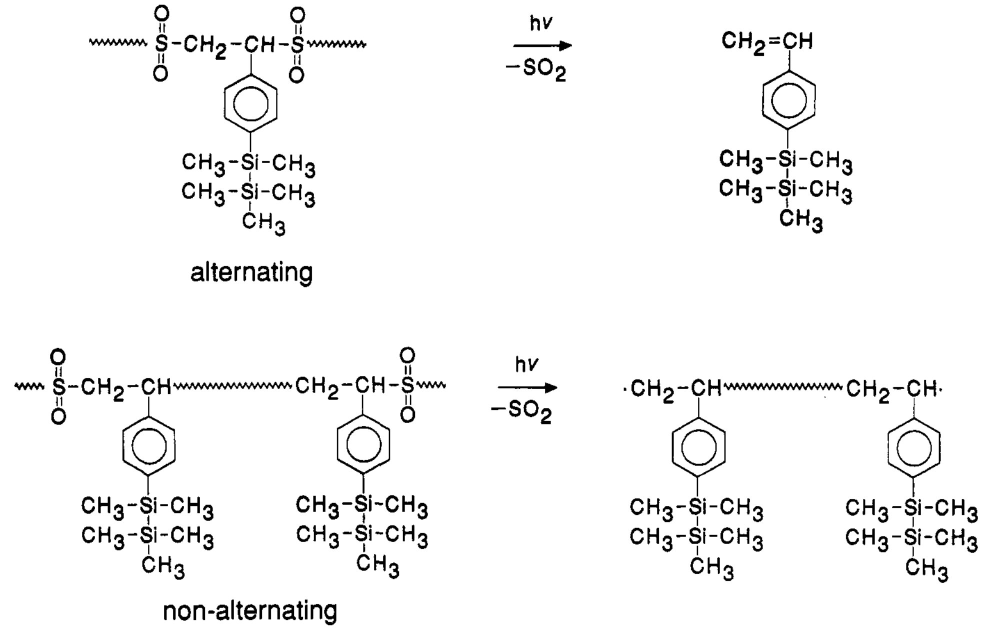


Figure 5. Relationship between P2Si copolymer composition and transient absorbance at the end pulse of flash photolysis: (●) absorption of the benzyl radical at 290 nm; (○) absorbance of the undecayed component at 290 nm. These values were determined by decay curve fitting considering the second-order decay of the benzyl radical and the undecayed components produced immediately after flash photolysis.

Product analysis was carried out for poly[(pentamethyldisilyl)styrene sulfone]s after long-time irradiation by a 500-W Xe lamp. After irradiation of a 6 mM THF solution of P2Si1/1 (M_w = 87.9 × 10^4, M_w/M_n = 1.90) for 10 min, the GPC elution curve showed three main peaks, 85% of the polymer component (M_w = 66.8 × 10^4, M_w/M_n = 7.01), 7% of the oligomer component (M_w = 580, M_w/M_n = 1.98), and 8% of the monomer component, whereas only the monomer component is expected by Scheme I. The oligomer component may be produced by a photochemical reaction of the monomer component. For example, formation of the oligomer by photopolymerization of the monomer or reaction between the monomer and the transient intermediate produced by photolysis of the disilyl group is presumed. ^1H NMR spectra showed the existence of a vinyl group. ESR measurements were also carried out during irradiation of poly[(pentamethyldisilyl)styrene sulfone]s. A broad and weak ESR signal increased with irradiation time. Such radicals were fairly stable after irradiation. They are not assigned to benzyl radicals because the lifetimes of benzyl radicals are not so

Scheme I
Photodegradation of Poly[(pentamethyldisilyl)styrene sulfone]s



long. Transient techniques are necessary to detect the transient intermediates with short lifetimes.

The energy-transfer reaction in the polymer chain should play an important role in the photodegradation of polymers.[23] The degree of the energy transfer can be estimated by measuring the fluorescence depolarization.[24] The polarized fluorescence spectra of P2Si were measured in rigid glasses of 2-methyltetrahydrofuran (2MTHF) at 77 K to exclude the affect of depolarization by normal molecular motion. P2Si showed two emission maxima at 310 and 420 nm in glass (2MTHF) at 77 K. Such dual fluorescence of the aryldisilanes has been reported by Sakurai et al.[25] The excited state for shorter wavelength emission was assigned to $^1(\pi,\pi^*)$, and that for longer wavelength emission was assigned to the $^1(\sigma,\pi^*)$, intramolecular charge-transfer state in which the disilyl group is a donor and the aryl group is an acceptor. The degrees of polarization of P2Si were determined to be 0.33 at 310 nm and nearly 0 at 420 nm of the CT fluorescence. This suggests effective energy transfer to the disilyl side chain. Cleavage of the Si–Si bond may occur via such an intramolecular charge-transfer state.

Pulse Radiolysis. In the case of the electron-beam-induced reaction in solutions, most of the electron beams are absorbed by solvent and ionic species of the solvent are produced. The characteristics of the solution influence the reaction mechanism. When solvent is THF, THF-solvated electrons are produced and some of them are transferred to the solute, polysulfones. On the other hand, cationic species are produced by electron-beam irradiation to chlorinated hydrocarbons, and electron abstraction from the solute by the cationic species forms a radical cation of the solute.[26-28]

Transient absorption spectra obtained by pulse radiolysis for a 20 mM THF solution of the P2Si homopolymer are shown in Figure 6. The broad absorption extending to the near-IR region at the pulse end is assigned to the tail part of the absorption of the solvated electron. The absorption at about 320 nm must be assigned to the benzyl radical.[18] In Figure 6, an absorption maximum appears near 430 nm. The wavelength is similar to that of silene produced by the photolysis as shown in Figure 3. However, they show quite different decay rates. The intermediates produced by radiolysis decay within 100 ns whereas silene produced by photolysis was observed even at 500 μs after the flash. Therefore, the absorption at about 430 nm obtained by pulse radiolysis may be assigned to some kind of radical anion stabilized by the phenyl group of P2Si. The radical anions of polystyrene[29] and poly[(trimethylsilyl)styrene][30] have absorption maxima around 400 nm. It is interesting that photolysis of P2Si and radiolysis of P2Si gave quite different intermediates. It is noteworthy that the disilyl group shows significant resistance to electron-beam irradiation. Degradation of the disilyl group in the polymer side chain may induce a side reaction such as cross-linking which is undesirable for the positive-tone resist.

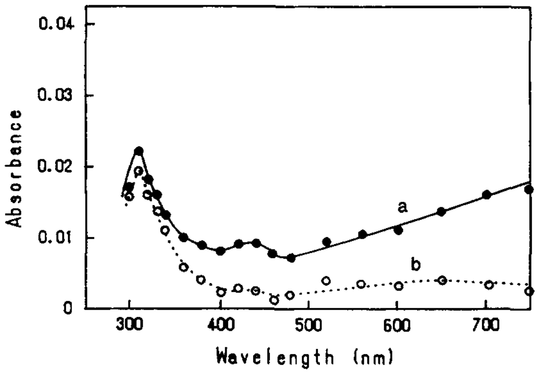


Figure 6. Transient absorption spectra obtained by pulse radiolysis for a 20 mM THF solution of the P2Si homopolymer (a) at the pulse end and (b) at 60 ns after the pulse.

Figure 7 shows transient absorption spectra obtained by pulse radiolysis for a 100 mM THF solution of alternating P2Si1/1 in THF. Transient absorption spectra at the pulse end and 10 ns after the pulse exhibit two absorption maxima at 400 and 620 nm. Figure 8 shows the difference spectrum calculated from transient absorption at 10 ns and that at 60 ns. Two absorption maxima at about 400 nm and at about 630 nm are exhibited more clearly. Quenching experiments were carried out to assign the intermediate using CCl_4 as a quencher for the radical anion. The absorbance was decreased significantly by addition of the radical-anion quencher CCl_4 as shown in

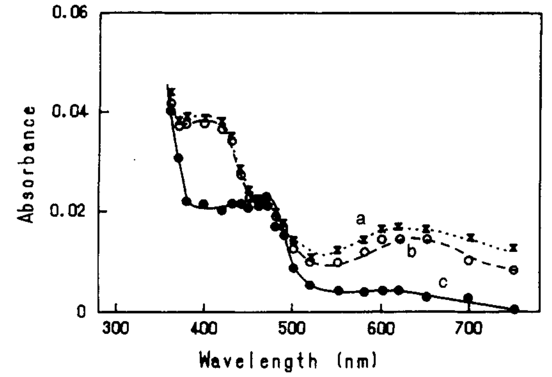


Figure 7. Transient absorption spectra obtained by pulse radiolysis for a 100 mM THF solution of P2Sil/1 (a) at the pulse end, (b) at 10 ns, and (c) at 60 ns after the pulse.

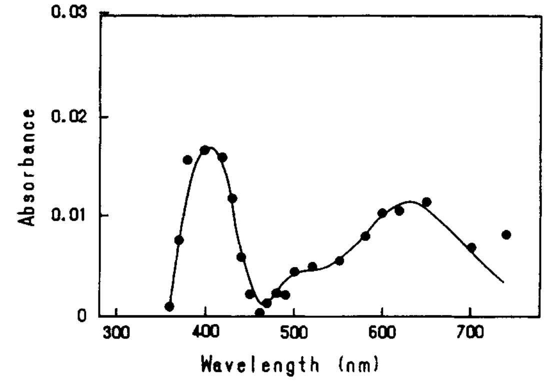


Figure 8. Difference transient absorption spectrum calculated from transient absorption at 10 ns and that at 60 ns for P2Sil/1 in THF.

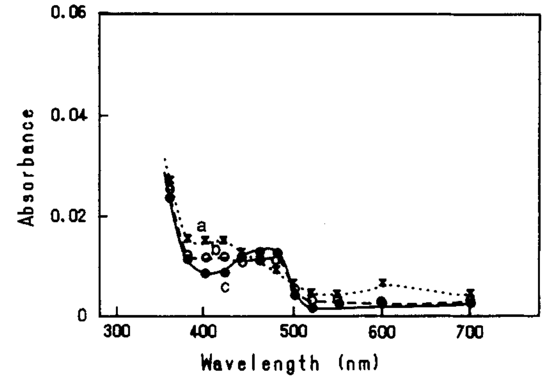


Figure 9. Transient absorption spectra obtained by pulse radiolysis for a 100 mM THF solution of P2Sil/1 containing 20 mM CCl_4 as a radical-anion quencher (a) at the pulse end, (b) at 10 ns, and (c) at 60 ns after the pulse.

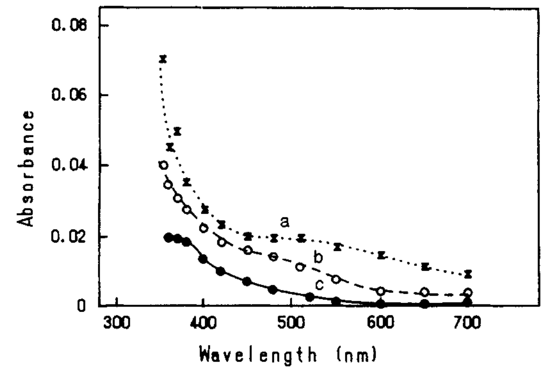


Figure 10. Transient absorption spectra obtained by pulse radiolysis for a 100 mM CH_2Cl_2 solution of P2Sil/1 (a) at the pulse end, (b) at 10 ns, and (c) at 60 ns after the pulse.

Figure 9. These absorption maxima are similar to the radical anion of the sulfonyl group which is produced by γ-irradiation to sulfones in 2-methyltetrahydrofuran at 77 K.[31-33] Formation of the radical anion is due to the electron affinity of the sulfonyl group in the polymer main chain.

Figure 10 shows the transient absorption spectrum obtained by pulse radiolysis for a 100 mM CH_2Cl_2 solution of P2Sil/1. It has been reported that cationic species produced by electron-beam irradiation to chlorinated hydrocarbon and the electron abstraction from the solute by the cationic species form a radical cation of the solute.[26-28] The radical cations of polystyrenes show absorption maxima near 500 nm. Figure 10 does not show a distinct absorption maximum. The absorption below 400 nm may be assigned to a benzyl-type cation which was produced by the extremely fast decomposition of the radical cation of P2Sil/1 in CH_2Cl_2. This result is coincident with the mechanism for the electron-beam resist reactions of poly(olefin sulfone)s. It has been reported that degradation begins with generation of a radical cation and leads to expulsion of SO_2.[5-9,12] The electron-beam-induced degradation is due to the instability of the radical cation of polysulfones.

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