

structures or compact, colloidal particles, respectively.^{9,10} During deposition of the zeolite/silicate suspensions by dip-coating, the solvent is evaporated, and the silicate films gel, "freezing in" the incorporated zeolite crystals (Figure 2). Final consolidation of the porous matrix structure to a nonporous film occurs by viscous sintering.^{11,12}

The molecular sieving behavior of zeolite Y¹³ (Y, crystal size, 0.2 μm ; pore size, 7.5 \AA), chabazite¹⁴ (CHA, crystal size, 1-3 μm ; pore size, 3.7 \AA), ZSM-5¹⁵ (crystal size, 0.5 μm ; pore size, 5.4 \times 5.6 \AA), and zeolite A (LTA, crystal size, 3 μm ; pore size, 4.1 \AA) crystals is maintained when they are embedded in TEOS sol-gel derived glassy thin films.^{16,17} For example, the acid form of zeolite Y¹⁸ embedded in a silicate-based film adsorbs pyridine (5.9 \AA kinetic diameter) as shown by consumption of the intrazeolite bridged hydroxyl groups (at 3540 and 3640 cm^{-1}) and the formation of pyridinium ions (band at 1545 cm^{-1} ; Figure 1B). However, exposure of a similar film to perfluorotributylamine (10.2 \AA) does not indicate any reaction with the internal bridged hydroxyls. Similarly, acidic chabazite-based films (pore size 3.7 \AA) react with ammonia (2.6 \AA) but not with tributylamine (8.1 \AA).

The selectivity of zeolite films is maintained even in aqueous systems. For example, pyridine or NH_3 diffused into Cu(II)-containing faujasite-silica thin films¹⁹ from aqueous solution co-ordinate to intrazeolite Cu(II) to form $[\text{CuL}_4]^{2+}$ complexes as shown by the appearance of corresponding ligand vibrations, e.g., at 1610, 1543, 1487, and 1450 cm^{-1} for $[\text{Cu}(\text{py})_4]^{2+}$. When CHA (3.7 \AA) or LTA (4.1 \AA) are incorporated in the glassy matrix, pyridine is completely excluded from the pores. In aqueous phase, the pyridine molecules bind selectively to Cu-FAU films but not to the corresponding Na or NH_4 forms.

Having demonstrated the chemical and size-based molecular selectivity of zeolite-silica films, we present the first application of these films as coatings on SAW devices. We note that thin silica films alone, processed similarly, have extremely low porosity (<2%) and surface areas (1 cm^2/cm^2).⁸ A glassy silica matrix of ca. 150 nm thickness, embedding crystals of ZSM-5 (pore size 5.4 \times 5.6 \AA), was coated on the active surface of a SAW device. A striking difference in frequency response to different probe molecules was observed. While vapors of MeOH (ca. 3.8 \AA kinetic diameter) and PrOH (ca. 4.7 \AA) adsorb at levels of 500-800 ng/ cm^2 in the film, the response to isooctane (2,2,4-trimethylpentane; 6.2 \AA) is minimal (below 5 ng/ cm^2). This dramatic difference can be understood if the kinetic diameters of these molecules are compared to the pore size of the zeolite film. The amount of vapor adsorbed in the film is in reasonable agreement with that calculated from crystal area densities observed in electron micrographs.

We have established that (i) zeolite-silica thin films with molecular sieving properties can be prepared, (ii) the films can be modified such that different chemical selectivities result, and (iii) these zeolite films can be utilized to introduce chemical selectivity to highly sensitive surface acoustic wave devices. Other zeolite thin film coatings with modified chemical selectivities are presently being explored.

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Novel Anionic Polymerization of Masked Disilenes to Polysilylene High Polymers and Block Copolymers¹

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Polysilylenes, the linear silicon-silicon bonded polymers, have several interesting properties and are a subject of current intense investigations.² Polysilylenes are prepared mostly by the Wurtz-type coupling reactions of dichlorodialkylsilanes which, however, have several difficulties such as the poor control of structure, molecular weight, and polydispersity. The yields of polymers are also usually low.⁷ In this paper, we will describe an entirely novel method of preparing polysilylenes based on anionic polymerization of masked disilenes.⁹

After examination of several possibilities, we have found that 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes (**1b-1d**) can be used for anionic polymerization.¹³ Alkylolithiums such as *n*- and

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(13) Synthesized according to U.S. Patent 4,175,059, 1979, example 3.

(14) Synthesized according to ref 1, p 288.

(15) Synthesized according to van Santen, R. A.; Keijsper, J.; Ooms, G.; Kortbeek, A. G. T. G. In *New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, A., Ward, J. W., Eds.; Kodansha: Tokyo, Japan, 1986; p 169.

(16) Silica sols were prepared from a stock solution of 61.0 mL of TEOS (tetraethylorthosilicate), 61.0 mL of EtOH, and 5.0 mL of 0.04 M HCl. For the preparation of A2 sol, 10 mL of the stock solution was combined with 0.12 mL of 1.0 M HCl and 0.4 mL of H₂O. B2 sol was obtained by adding 1.0 mL of 0.05 M NH_4OH to 10 mL of the stock solution. See: Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Assink, R. A.; Kay, B. D.; Ashley, C. S. *J. Non-Cryst. Solids* **1984**, *63*, 45.

(17) Dip-coated composites were made from suspensions of 0.5-2.5 g zeolite in 2.5 mL of silica sol which was diluted with 5 mL of EtOH and coated on Si wafers at 50 mm/min vertical pulling rate. All wafers were dried in air at 360 K.

(18) Obtained by degassing the NH_4 -exchanged form at 670 K in vacuo.

(19) Zeolites were 50% ion-exchanged with 0.1 M $\text{Cu}(\text{NO}_3)_2$ prior to dispersion in the sol.

(1) Chemistry of Organosilicon Compounds 257.

(2) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) West, R. *Organopolysilanes*. In *Comprehensive Organometallic Chemistry*; Abel, E., Ed.; Pergamon: Oxford, England, 1982; Chapter 9.4, pp 365. Recent applications of polysilylenes as SiC precursors,³ in microlithography,⁴ as photoinitiators,⁵ and in reprography⁶ are noteworthy.

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(4) (a) Gobbi, G. C.; Fleming, W. W.; Sooriyakumaran, R.; Miller, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 5624. (b) West, R.; Wolff, A. R.; Peterson, D. J. *Radiation Curing* **1986**, *13*, 35.

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(7) A few other routes are indicated for the preparation of polysilylenes such as catalyzed dehydrogenative coupling of primary organosilanes, but at this moment the method is limited to the preparation of low molecular weight oligomers of arylsilanes.⁸

(8) (a) Aitkin, C. T.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11. (b) Aitkin, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4095. (c) Aitkin, C. T.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986**, *64*, 1677.

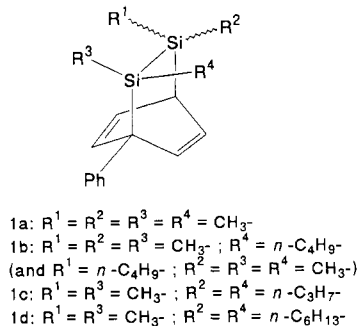
(9) Conceptually, polymerization of disilenes, the silicon-silicon double bonded species, may be a straightforward route to linear polysilylenes. It is not possible in practice though, because disilenes are not stable enough to be isolated except for those with very bulky substituents.¹⁰ Incidentally, 7,8-disilabicyclo[2.2.2]octa-2,5-dienes have been known as precursors of disilenes; Roark and Peddie¹¹ reported generation of disilenes by thermolysis of **1a**. We have also reported that a 2,3-benzo-7,8-disilabicyclo[2.2.2]octa-2,5-diene system afforded *cis*- and *trans*-1,2-diphenyl-1,2-dimethyldisilenes by thermolysis.¹² Therefore, we have expected that these 7,8-disilabicyclo[2.2.2]octa-2,5-diene systems could behave as masked disilenes even in ionic reactions.

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Table I. Anionic Polymerization of 1-Phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes (**1**) in THF

monomer (M)	initiator (I)	I/M	temp, ^c °C	time, h	yield, ^a %	$\bar{M}_n^b \times 10^{-4}$	\bar{M}_w/\bar{M}_n^b	λ_{\max} , nm
1b	MeLi	0.04	-110 → rt ^c	6	72	3.4	1.9	
1b	<i>sec</i> -BuLi	0.03	-110 → rt ^c	9	60	5.3	1.5	306 (<i>n</i> -hexane)
1b	<i>n</i> -BuLi	0.03	-110 → rt ^c	18	79	11.0	1.5	305 (THF)
1b	<i>n</i> -BuLi	0.03	-110 → rt ^c	6	62	11.0	1.5	
1b	<i>n</i> -BuLi	0.03	rt	11	52	9.5	1.5	306 (THF)
1b	<i>n</i> -BuLi	0.04	rt	3	54	8.9	1.6	
1c	<i>n</i> -BuLi	0.02	-110 → rt ^c	2	33 ^d	7.2	1.5	307 (THF)
1c	PhLi	0.13	-78 → rt ^c	1	63	4.7	1.3	
1d	<i>n</i> -BuLi	0.02	-110 → rt ^c	15	68	14.0	1.3	307 (<i>i</i> -octane)

^a After reprecipitation and freeze-drying. ^b From GPC elution volume relative to polystyrene. ^c Both monomer and initiator solutions were cooled and kept at the temperature indicated. Two solutions were then mixed at the temperature where the solution had just started to melt. ^d At 59% conversion. * Room temperature is abbreviated as rt.

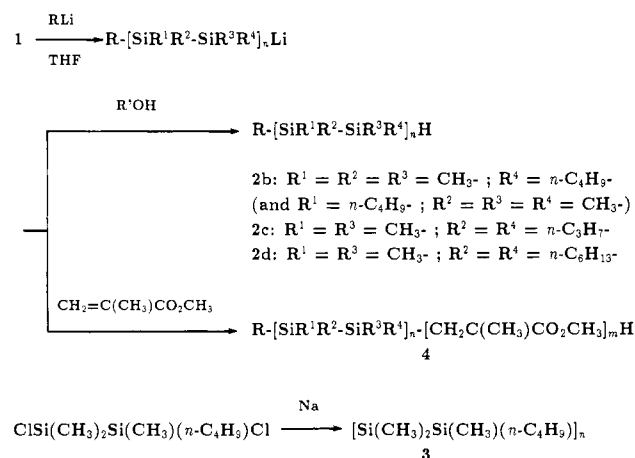
Chart I

sec-butyllithium and phenyllithium serve as initiators.

The monomer **1b–1d** was synthesized by the method of Roark and Peddle.¹¹ The reaction of dichlorodisilanes with lithium biphenylide in THF at -78°C gave the monomers in 60–70% yields. These monomers were purified by distillation and used for polymerization. Anionic polymerization was carried out by using a break-seal method under high vacuum conditions ($<10^{-5}$ mmHg). A typical example of the polymerization is as follows. A THF solution of the monomer **1b** was degassed by freeze–thaw cycles, and then a toluene solution of an initiator (alkyllithium) was added to the THF solution of the monomer at the temperature when the solution had just started to melt. The temperature of the mixture was then gradually raised.¹⁴ The mixture was stirred at room temperature for several hours. The solution was colorless at first but then became orange-red later. A terminator (ethanol) was then added to the solution, and the mixture became colorless again. In addition to the expected byproduct, biphenyl, the only product was a polymeric material. The polymer was purified by precipitation from a benzene solution with methanol, followed by freeze-drying. The product was identified as a polysilylene polymer (**2b**) with its ^1H , ^{13}C , and ^{29}Si NMR, IR, and UV spectra.^{2a} For comparison, a polysilylene of similar composition (**3**) was prepared by sodium coupling of $\text{ClSiMe}_2\text{SiMe}(n\text{-Bu})\text{Cl}$. Table I summarizes the results.

The molecular weight distributions of these polysilylene polymers were determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent. The molecular weight distribution of the polymer synthesized by the present method (**2a**, $\bar{M}_n = 5.3 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.5$) is much narrower than that prepared by the conventional condensation method (**3**, $\bar{M}_n = 0.97 \times 10^4$, $\bar{M}_w/\bar{M}_n = 2.6$).

The mechanism of the polymerization should involve repetitive attack of the polysilylenyl anions to a silicon atom of the monomer resulting in the formation of the new propagating polymer anion

Scheme I

and biphenyl. The reaction is rapid, and polysilylenyl anions may be involved as key intermediates in the process. Although the polymerization is not perfectly living under these conditions,¹⁵ after the polymerization, the polymer end is still reactive enough to initiate the second polymerization with a conventional vinyl monomer. Thus instead of a terminator, a THF solution of methyl methacrylate (MMA) was added at 0°C to a reddish solution of polysilylenyl anions prepared from **1b** with *n*-butyllithium.¹⁶ The color of the solution changed to yellow. Addition of a small amount of ethanol resulted in the formation of a colorless solution. GPC analysis of the solution indicates the presence of a single polymer in addition to biphenyl. The elution profiles of **4**, detected by both UV (305 nm) and RI, show the same molecular weight distribution curves which should be taken as a strong support for the formation of a block copolymer.¹⁷ The block copolymer, *block*-[SiMe(*n*-Bu)SiMe₂]_{*n*}-*co*-[CH₂CMe(CO₂Me)]_{*m*} (**4**), is soluble in benzene but gave only suspensions in both cyclohexane and acetone. The copolymer **4** shows a slightly broader molecular weight distribution ($\bar{M}_n = 1.8 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.9\text{--}1.6$) than polysilylene homopolymers. The *n*/*m* ratios were determined by ^1H NMR for two samples with different monomer ratios to be 1.5 (theory 1.1) and 0.30 (theory 0.33). IR spectra indicates the

(15) The polymerization might involve living anions, but the livingness is not provided yet in a rigorous manner. If the polymerization is a well-behaved living system, the degree of polymerization (at 100% conversion) should equal $[\text{M}]/[\text{I}]$. However, polymers shown in Table I have molecular weights about 10 times too high. This indicates that initiation is incomplete due to some deactivation (killing) reactions for the initiators and/or that propagation is much faster than initiation.

(16) The polysilylenyl anions are not stable at 0°C : after standing in the solution for more than 30 min, addition of a solution of MMA resulted in the formation of only polysilylene polymers.

(17) Styrene failed to be block-copolymerized with polysilylenyl anions. Presumably, an electron transfer from the silyl anion to aromatics¹⁸ occurred to give a mixture of polysilylene and polystyrene homopolymers. Since only polysilylenes have UV absorption at 305 nm, GPC profiles detected by UV (305 nm) and RI differ from each other in this case.

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(12) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Am. Chem. Soc.* **1979**, *101*, 487.

(13) Another system, for example, 2,3-benzo-7,8-disilabicyclo[2.2.2]octa-2,5-diene generates the hitherto unknown disilanyl anion which gave disilane-carboxylic acid from the reaction with carbon dioxide. Details will be reported in a forthcoming paper.

(14) Low reaction temperature is not always required. See Table I.

presence of C=O and SiMe but no Si-O-Si groups. UV maxima was found at 305 nm.

The present new method of preparing polysilylenes is quite versatile in designing new polymers. The work is supported in part by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, No. 63106003).

Time-Resolved Study of the Photooxygenation of 3-Hydroxyflavone

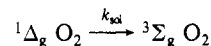
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3-Hydroxyflavones (Scheme I) are prototype molecules¹ for studying the dynamics of the proton-transfer reaction in the excited state as well as in the ground state. Their lasing action has been reported with a high efficiency of laser gain.²⁻⁴ Unfortunately, a major obstruction to the practical application of 3-hydroxyflavones as laser dyes is due to a photochemical reaction possibly involving molecular oxygen. In this communication we report a direct time-resolved study of the photooxygenation of 3-hydroxyflavone (3HF) in the normal state as well as in the tautomer state. Our results not only provide a detailed mechanism of the photooxygenation reaction but also give indirect evidence to support the role of the triplet state in the reverse proton-transfer reaction.

(i) **In the Normal State.** Studies of the 3HF (normal form) + $^1\Delta_g$ O₂ reaction have been reported by Matsuura and co-workers.^{5,6} By analyzing the photosensitization products, they proposed that 3HF undergoes the ene-ol type concerted reaction⁷ with $^1\Delta_g$ O₂ (mechanism a, Scheme I) to form the ketohydroperoxide intermediate i. In this course of study, the dynamics of the 3HF + $^1\Delta_g$ O₂ reaction was monitored by a time-resolved $^1\Delta_g$ O₂ emission (1.27 μ) detected by a near-infrared detection system.¹⁹ The sensitizer, either rose bengal, tetraphenylporphine, or tetrakis(4-sulfatophenyl)porphine, was excited at 532 nm in aerated 3HF solution. The dynamics of the quenching of $^1\Delta_g$ O₂ in the presence of 3HF can be expressed by



$$[^1\Delta_g \text{ O}_2] = [^1\Delta_g \text{ O}_2]_0 e^{-k_{\text{obs}} t}$$

$$k_{\text{obs}} = k_{\text{sol}} + k_q[3\text{HF}]$$

In the above equations, k_{sol} is the rate constant for solvent deactivation, k_q is the rate constant for the chemical quenching, and $[^1\Delta_g \text{ O}_2]_0$ is the initial concentration of $^1\Delta_g$ O₂. In a pseudo-first-order approximation, k_q is obtained by a Stern-Volmer plot of k_{obs} versus [3HF]. The results in Table I clearly demonstrate that the rate of quenching of $^1\Delta_g$ O₂ by 3HF is highly dependent on the chosen solvent. The bimolecular quenching rate constants in the nonpolar solvents, which vary from 1.6×10^4 to $1.87 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, are indicative of theoretical physical quenching rate constants of $^1\Delta_g$ O₂. This point is illustrated by observing the bimolecular quenching rate constant to be 1.5×10^4 and $1.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for 3-methoxyflavone (3MeOF) in C₆D₆ and CCl₄, respectively. 3MeOF is a compound which is chemically inert to $^1\Delta_g$ O₂ in nonpolar solvent due to the lack of the hydroxyl proton.⁹ These results are consistent with the negligible yield of products in the steady-state photolysis experiment of 3HF performed in our laboratory.¹⁰ We therefore conclude that 3HF (normal form) is chemically inert to $^1\Delta_g$ O₂ in nonpolar solvent.

Realizing that the solvents used in our experiments are different from those used by Matsuura et al., a photosensitization experiment was carried out in pyridine. The value of k_q in pyridine was observed to be $7.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is ~ 4 orders of magnitude larger than that in nonpolar hydrocarbon solvents. However, the absorption spectrum of 3HF in pyridine, unlike that in hydrocarbon solvent, has a long wavelength absorption band with a maximum at 450 nm. Upon excitation at 450 nm, an emission spectrum shows a maximum at 512 nm. These spectral features suggest that the anion species is present in pyridine. Hence, the anion form of 3HF in pyridine may be responsible for the anomalous increase of reactivity toward $^1\Delta_g$ O₂. In order to verify this proposal, the study of the 3HF + $^1\Delta_g$ O₂ reaction was performed in aqueous solution. In basic H₂O (pH = 12.0) and D₂O solution (pD = 12.0) in which the anion form of 3HF (or 3DF) predominates, k_q was observed to be 2.2×10^8 and $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. However, k_q was observed to be $2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in acidic D₂O solution (pD = 3),¹¹ which is the same order of magnitude as that in CH₃OH.

We now propose a 3HF + $^1\Delta_g$ O₂ reaction mechanism which encompasses the experimental results for a broad range of solvents. A photodynamic study of 3HF by Standjord and Barbara^{11j} indicates that the intramolecular hydrogen bond remains intact even in strong hydrogen bonding solvents such as MeOH. In other words, the enol proton forms a planar five-membered ring, a position in which abstraction of this proton by $^1\Delta_g$ O₂ is not facile. Hence, we suggest an alternative reaction pathway (mechanism b, Scheme I) to that proposed by Matsuura et al. (mechanism a). We propose that addition of $^1\Delta_g$ O₂ at carbons 2 and 4 of the γ -pyrone ring may take place (mechanism b) with concomitant proton transfer between the hydroxyl proton and carbonyl oxygen to form the five-membered cyclic peroxide ii. The increase of chemical reactivity of 3HF toward $^1\Delta_g$ O₂ in polar solvents can be rationalized by solvent stabilization of the transition state which presumably has a large dipole moment. It is noteworthy that there is an ~ 2.5 -fold increase of k_q in CH₃OH in comparison with

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(7) An alternative mechanism involving a four-membered cyclic peroxide was also proposed by Matsuura et al. to explain the liberation of carbon dioxide upon UV irradiation. However, irradiation at $\lambda > 455 \text{ nm}$ shows no significant CO₂ production. Thus, in this communication only the mechanism shown in Scheme I is discussed.

(8) In order to minimize the error in the curve fitting procedure due to a small k_q in comparison to k_{sol} , deuterium isotopes were used for some solvents. (9) Although it is stable in nonpolar solvents, our results show that 3MeOF is extremely photosensitive in protic solvents. This type of photoreaction has been reported in ref 13 and 15.

(10) In the course of a steady-state photolysis experiment of 3HF in which $^1\Delta_g$ O₂ was sensitized by either rose bengal (RB) or tetraphenylporphyrin (TPP) dye excited at $\lambda > 455 \text{ nm}$ (150 W Xe lamp coupled with CuSO₄ 5H₂O and SG455 filters), the starting material (3HF) was quantitatively recovered after prolonged irradiation ($\sim 4 \text{ h}$) in various nonpolar solvents.

(11) Since the solubility of 3HF in acidified D₂O is low, 15% of CH₃OD was added to increase the solubility.