Photochemical and Thermal Properties of Polysilane LB Films. Stabilization of Oriented Polysilane LB films by Cross-Linking

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ABSTRACT: Oriented polysilane LB films are cross-linked in order to increase their durability toward heat and deep UV lights. When oriented polysilane LB films without cross-linking are exposed to UV light polarized in the direction parallel to the silicon chains, the order parameter decreases because of scissions of the silicon chains. The order parameters also decrease when thin films are heated; this is a result of disorientation rather than thermal decomposition. The durability of the oriented polysilane LB films toward heat and UV irradiation increases considerably when they are cross-linked by exposure to HCl and HCHO vapor. The cross-linking of P2 (poly((3-hydroxyphenyl)hexylsilane)) is carried out without losing the polysilane orientation, however, in the case of P1 (poly(hydroxyhexyl)hexylsilane)), a decrease in the strength of the UV absorption was observed. Information on energy transfers within polysilane films is obtained by photolysis of oriented polysilane LB films.

Introduction

Ever since soluble polysilanes were first synthesized,[1,2] they have been extensively studied because of their unusual electronic and photochemical properties,[3–12] as well as potential applications in future electronic devices[13–24] such as in microlithography, photoconductivity, and nonlinear optics. These properties have been attributed to the extensive delocalization of σ electrons, which is strongly coupled with the polymer conformations.[11,12]

Since the σ electrons are delocalized along the silicon main chains, it would be useful to obtain thin films in which the silicon chains align in one direction in order to evaluate the polysilane properties. The Langmuir–Blodgett (LB) technique is an excellent method for preparing ultrathin films with well-defined molecular order.[25–30]

Such polysilane LB films have been prepared by employing either polysilanes with rigid structures or polymers with amphiphilic moieties. A representative example of the former is poly(bis(alkyloxyphenyl)silane) reported by Embs et al.[31] Polysilanes with hydroxyalkyl or hydroxyphenyl groups,[32–34] and those bearing ammonium groups,[35] have been reported to give LB films by us and by Seki et al. Some polysilanes have been found to align in the direction parallel to the dipping direction of the substrate when polysilane monolayers at the air–water interface are transferred to the substrate by dipping and withdrawing the substrates (Figure 1).[31–34]

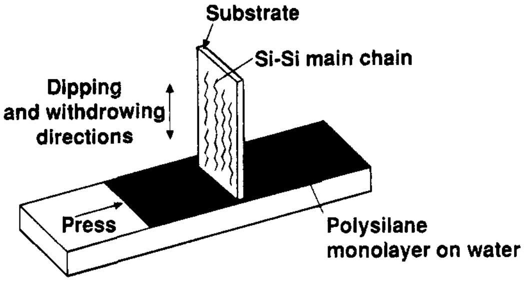

Figure 1. Schematic diagram of oriented polysilane LB films.

Orientation of the one-dimensional Si chains should be preferable when the polysilanes are employed in optoelectronic devices. However, polysilanes are commonly degraded by UV lights.[12] Moreover, the T_g or softening point of the polysilanes is usually low because of the one-dimensionality of the silicon chain. Miller et al. have proposed that some halogen compounds are useful in the stabilization of the polysilanes because they quench the excited polysilanes.[36,37] Two-dimensional polysilynes, whose backbones consist of networks of silicon atoms, have been shown to be more stable to UV light irradiation.[38–40] However, various advantageous optical properties, such as emission and nonlinear optical properties which are attributed largely to the one-dimensionality of the silicon chains, have been reported to disappear in the two-dimensional polysilyne random network backbone.[38–40] Some polysilanes, such as hydrosilylene polymers and cyclotetramethylenesilylenes, which can be crosslinked by reactions with oligomers bearing double bonds or oxidative reactions, respectively, have been reported.[41] However, these are not suitable for LB film cross-linking because it is difficult to make monolayers by applying these polysilanes or these mixtures.

We now report the cross-linking of highly oriented LB films of polysilanes without losing the one-dimensionality of the polymer backbone, which allows the polymer chains to keep their orientation even when the LB film is irradiated with UV light or heated at high temperature.

Experimental Section

Synthesis. The polysilanes, poly((3-hydroxyphenyl)(*n*-hexyl)silane) (P1) and poly((6-hydroxyhexyl)(*n*-hexyl)silane) (P2) (Figure 2), were synthesized by a Wurtz-type coupling reaction starting from the corresponding dichlorosilanes, as described previously.[33,42]

Film Preparation. A quartz plate was treated for 10 min with a 3:1 (volume/volume) mixture of sulfuric acid and aqueous hydrogen peroxide solution and rinsed with deionized water. The plate was then washed with a 1% HF aqueous solution for 30 s and rinsed with deionized water. The procedure was repeated three times to remove organic contaminants. Finally, the plate was washed again with a 3:1 mixture of sulfuric acid and aqueous hydrogen peroxide solution and rinsed with deionized water. The plate was exposed to the vapor of hexamethyldisilazane at room temperature by suspending the plate over hexamethyldisilazane

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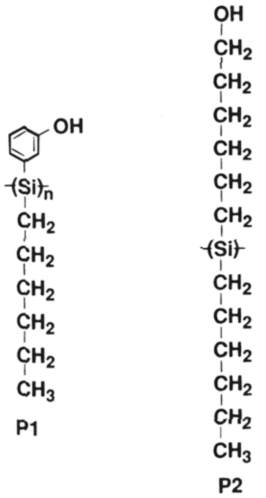

Figure 2. Structures of and abbreviations for the polysilanes used in this study.

for 12 h at room temperature in order to render the surface hydrophobic. LB films of polysilanes P1 and P2 were prepared by a vertical deposition method on a Kyowa Kaimen Kagaku Model HBM Langmuir trough. A solution of 0.4 g of polysilane in 1 L of cyclohexanone was spread at the air−water interface. The monolayers were compressed at 15 mN/m and transferred step by step onto a quartz plate at a compression rate of 20 mm/min and a dipping speed of 5 mm/min at 15 °C. The surface pressure−area isotherms were monitored with a Wilhelmy plate.

Spectroscopy. The absorption spectra of the LB films were recorded with a Shimadzu Model UV-260 visible recording spectrometer. All measurements were made in transmission geometry using quartz as the substrate. The incident beam was polarized with a Melles Griot Glan-Taylor polarizing prism or polarizing film (Polaroid technical filters 605215) to measure the anisotropy of the UV absorption. The dichroic ratio (R) was defined by the ratio of the UV absorption in the direction parallel to the dipping direction (A_a) to the UV absorption in the direction perpendicular to the dipping direction (A_e). The order parameter (S) was defined by $(A_a/A_e - 1)/(A_a/A_e + 2)$. Representative UV aborption dichroism spectra for polysilane LB films are shown in Figure 5. IR spectra were recorded with a Nippon Bunko Model IR Report 100 apparatus.

Photolysis. Photolysis of the LB films was carried out by using collimated UV light generated by a high-pressure mercury lamp. The light was polarized with Polaroid technical filters 605215. Lights of 280, 320, and 340 nm wavelength were selected with a Melles Griot band path filter, 03FIM018, 03FIU006, and 03FIU008, respectively. Photolysis was carried out by employing polarized light parallel or perpendicular to the polysilane chain direction. The UV absorption assigned to the $\sigma-\sigma^*$ transition of the silicon backbones of the LB films (300−400 nm) was monitored to determine the dichroic ratios.

Thermal Studies. LB films on quartz plates were placed in a UV cell equipped with a heater whose temperature was fixed by a temperature controller. The UV absorption assigned to the $\sigma-\sigma^*$ transition of the Si−Si chains (300−400 nm) was monitored with changes in temperature. The temperature of the films was raised at the rate of 5 °C/min and held for 10 min at each temperature before measuring the UV absorptions.

Cross-Linking of the Polysilane LB Films. Cross-linking of the polysilane LB films was carried out by the method similar to that reported previously,[43] where poly(vinyl alcohol) LB films are cross-linked by HCl and HCHO vapors. Quartz plates bearing polysilane LB films were placed in a beaker in which small beakers containing 6 N HCl aqueous solution and 30% formaldehyde aqueous solution were put separately (Figure 3). The reaction was carried out by suspending the plate over the HCl and HCHO aqueous solutions for 6 and 20 h, respectively. After the reaction, residual HCl and unreacted HCHO in the films on the quartz plate were removed by exposing the films to vacuum for 5 h at room temperature.

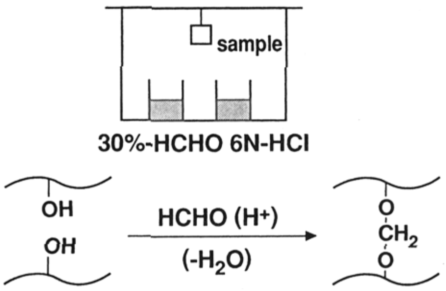

Figure 3. Schematic diagram of the reaction method and the reaction scheme of the polysilane cross-linking step.

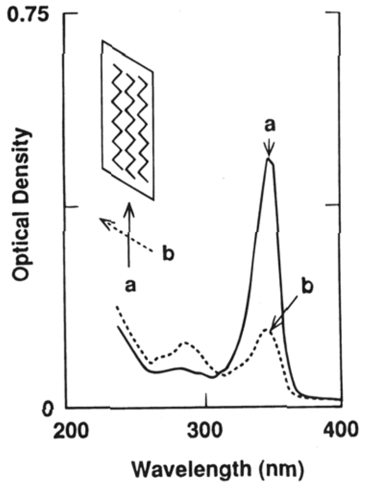

Figure 4. UV absorption anisotropy of un-cross-linked polysilane P1-LB film.

UV Absorption Changes in Temperature for a Spin-Coat Film. A spin-coat film of P2 was prepared on a quartz plate by using a 5% (weight/weight) solution of P2 in ethyl alcohol. The film was prebaked at 90 °C for 5 min. The thickness was 0.15 μm. The UV spectrum changes were monitored by changing the temperature in a UV cell.

Results and Discussion

Photolysis of Polysilane LB Films with Polarized UV Light. In this paper, polarized UV light parallel and perpendicular to the polysilane backbone chain direction is described as parallel light and perpendicular light, respectively, for convenience.

The P1-LB film displays a UV absorption maximum at λ_{max} = 350 nm, which is attributed to the $\sigma-\sigma^*$ transition of electrons in the silicon−silicon bonds, and another absorption at λ_{max} = 288 nm attributed to $\pi - \pi^*$ transitions in the substituent phenyl ring, as shown in Figure 4. The photolysis of the LB films was carried out by using polarized UV light of 340 or 280 nm. These photolysis results are summarized in Figure 5. When the P1-LB film was exposed to parallel light of 340 nm, the dichroic ratios decreased during irradiation. However, irradiation by perpendicular light of 340 nm results in an increase in the dichroic ratio. When the P1-LB film was irradiated with either parallel or perpendicular light of 280 nm, changes in the dichroic ratios were not observed, despite the fact that photodecomposition was actually observed because the optical density of the UV absorption at 340 nm assigned to Si−Si linkages decreased, accompanied by a blue shift of the absorption maximum to 335 nm. Experimental fluorescence depolarization results have been reported to suggest that energies in photoexcited polysilanes

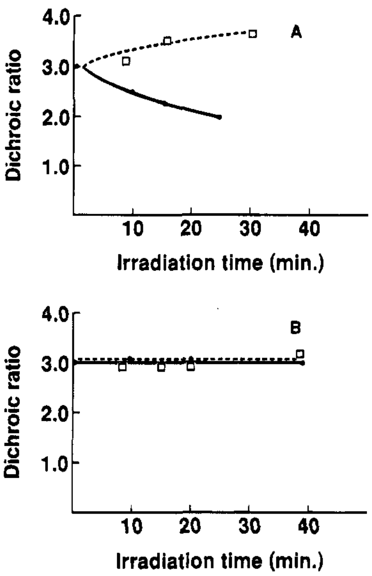

Figure 5. Photolysis of un-cross-linked P1-LB film with polarized light. The LB film is 10 layers thick. (A) Dotted line: photolysis by polarized light perpendicular to the Si chain at 320 nm. Solid line: photolysis by polarized light parallel to the Si chain at 320 nm. (B) Dotted line: photolysis by polarized light perpendicular to the Si chain at 280 nm. Solid line: photolysis by polarized light parallel to the Si chain at 280 nm.

migrate, which occurs more frequently when the excitation wavelength is shorter.[44-46] Our results on polarized photolysis are consistent with those of the fluorescence depolarization. Namely, the photocleavage occurs at a site close to where UV absorption took place at 340 nm (longer wavelength). Therefore, when the film was irradiated with parallel light, the silicon chains parallel to the polarized light predominantly photodecomposed, resulting in a decrease in the dichroic ratios. In the case of 280 nm photolysis (shorter wavelength), photoexcited energy migrates to neighbors from the point where the UV absorption takes place. Accordingly, the photodecomposition takes place randomly and the dichroic ratios for both photolyses (perpendicular and parallel lights) do not change. The 280 nm light may be absorbed, not only by the polymer backbone but also by the phenyl substituents. Therefore, photoexcited energy may also migrate randomly from the phenyl substituent, so the random decomposition may be due to the different site where the absorption occurs. The P2-LB film, which does not have the phenyl group, was photodecomposed by perpendicular and parallel lights, respectively, in order to ascertain the explanation. The changes of dichroic ratio for the P2-LB film showed the same trend as those for the P1-LB film at the initial stage when these LB films were exposed by polarized 280 nm lights and 320 nm lights. Accordingly, we concluded that the energy migration takes place from the silicon main chain, not from the phenyl group.

Cross-Linking of Polysilane LB Films. One of the problems encountered when polysilanes are exposed to HCl gas is the instability of the silicon–silicon linkages toward acids.[47] Figure 6 shows the polarized UV absorption spectra of P2-LB films before and after the cross-linking reactions. Almost no change is the optical density was observed after the cross-linking. The dichroic ratio after the cross-linking was 2.6, which was the same as that before the cross-linking. These results suggest that serious cleavages did not take place and the orientation was preserved during the cross-linking reaction. In the IR spectrum of the P1-LB film after the cross-linking reaction, it was observed that the 3350 cm^{-1} peak assigned to OH stretching decreased and new peaks at 1040 and 1120 cm^{-1} assigned to C–O–C stretchings appeared. These changes in the IR spectrum also imply that the cross-linking was carried out according to the equation shown in Figure 3. The emission spectra of cross-linked P2 films excited at 320 nm displayed emission maxima at 343 nm, and no emissions were observed at wavelengths longer than 400 nm. It has been reported that if a one-dimensional polysilane contains branched Si chains, a broad emission at around 450 nm is observed.[48,49] Accordingly, the emission spectrum implies that the polysilane LB film cross-linked with HCl and HCHO has no branching of the Si main chains.

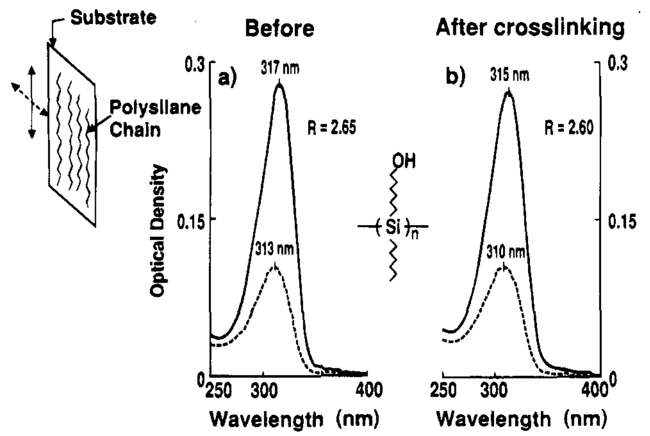

Figure 6. Polarized UV absorption spectra of a P2-LB film before and after cross-linking. The LB film is 10 layers thick. Time of cross-linking reaction: 20 h.

In the case of the P1-LB film, if the cross-linking reaction proceeds, it is reasonable to assume that a phenol moiety reacts with HCHO to provide a phenol–formaldehyde resin type cross-linking structure, where, the ortho position of the phenol group is linked with methylene groups to form (HO)Ph–CH$_2$–Ph(OH),[50] rather than that shown in Figure 3. Exposure of the P1-LB film to HCl and HCHO gases resulted in a decrease in the optical density of the 350 nm peak, as well as the 280 nm peak assigned to the phenyl group absorption. Cleavage of Si–Ph bonds by acids, especially by HCl, has been reported by West et al.[41] However, the IR spectrum of the P1-LB film before cross-linking treatment was the same as that after the cross-linking treatment. There was no apparent decrease in IR peaks assigned to the phenyl rings. Further, the ratios of intensities between the 350 nm peak and 280 nm peak in UV absorption were almost the same, and blue shifts of these peaks were not observed. The scissions of Ph–Si bonds whose amounts are not detected by the IR spectra, rather than cross-linking, may have occurred by the exposure to HCl.

Thermal Studies of Cross-Linked Polysilane LB Films. Oriented polysilane films usually lose the orientation when the films are heated because of the large molecular motions caused by the heat, especially for one-dimensional polymers. Figure 7 shows a decrease in the order parameter determined by the UV absorption anisotropy of the P2 films when the temperature increases. The order parameter of the P2-LB film before cross-linking starts to decrease at around 140 °C. The temperature at which a decrease in the order parameter is observed increased to 170 °C after 6 h of cross-linking and to 190 °C after 20 h of cross-linking. The experiment clearly shows that thermally-induced

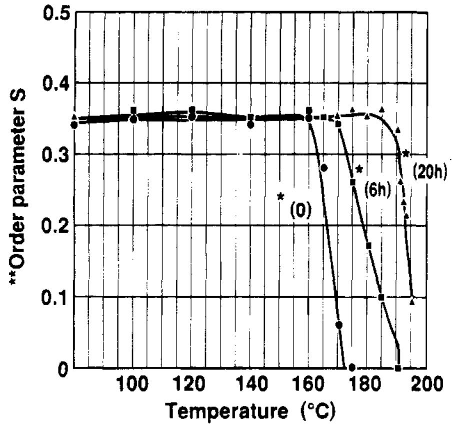

Figure 7. Relation between the order parameter of a P2 polysilane LB film (10 layers thick) and temperature after various cross-linking reaction times.

Table 1. Dichroic Ratios during Photolysis[a]

	irradiation time[b] (min)			23 h after 30 min photolysis[c]
	0	10	30	
cross-linked P2-LB film	1.99	1.94	1.90	1.90
P2-LB film	1.99	1.85	1.72	1.25

[a] Initial dichroic ratio: 1.99. The figures in this table show dichroic ratios. [b] The P2-LB film was irradiated with parallel light of 320 nm. [c] The P2-LB film was stored in the dark for 23 h after the 30 min photolysis.

loss of orientation in the polymer films decreases upon cross-linking. From the fact that the UV absorption of a P2 spin-coated film did not change up to 200 °C, the decrease in the order parameter at high temperatures is considered to result from disordering of the silicon chains and not from thermal decomposition of the chains.

Stability of Cross-Linked Polysilane LB Films toward UV Photolysis. Table 1 shows the decrease in the order parameter which occurs when the P2-LB film was irradiated with parallel light of 320 nm. After the irradiation, the LB film was held in the dark for 23 h. Before cross-linking, the dichroic ratio of the P2-LB film decreased from 1.99 to 1.70 after 30 min of irradiation by parallel UV light (320 nm) and continued to decrease even in the dark to 1.25. For the cross-linked P2-LB film, the decrease in the dichroic ratio was only about 0.1 (from 1.99 to 1.90) after 30 min of irradiation. The dichroic ratio did not decrease in the dark. The increased resistance toward photolysis provided by cross-linking the LB films during the photolysis may arise from the recombination of silyl radicals such as $-SiR_2$ formed during the photolysis. The decrease in the dichroic ratio of P2-LB films in the dark may be caused by diffusion of low-molecular-weight oily products produced by the photolysis of the P2-LB film. The fact that the dichroic ratio was constant for the cross-linked LB film in the dark proved that cross-linking of the LB films is effective for preserving their orientation even after photolysis.

Conclusion

Photochemical and thermal properties of polysilane LB films were examined. The photolysis of oriented LB films by polarized light of longer wavelengths suggests that scission occurs at sites close to where UV absorption takes place. On the contrary, when the LB film was excited by light of shorter wavelengths, the energy of the excited polysilanes migrated much more widely. The reactions undergone by polysilane P2-LB films with HCl and HCHO vapors were found to be excellent methods of cross-linking the polysilane chains without disturbing their orientation or cleaving the Si–Si backbone linkages. The cross-linking effectively increases resistance of polysilane P2-LB films toward loss of chain orientation by heat and photolysis.

References and Notes

(1) West, R.; David, L. D.; Djurovitch, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1352.
(2) Trujillo, R. E. *J. Organomet. Chem.* **1980**, *198*, C27.
(3) Wreber, P.; Guillon, D.; Skoulios, A.; Miller, R. D. *J. Phys. Fr.* **1989**, *50*, 793.
(4) Wreber, P.; Guillon, D.; Skoulios, A. *Liq. Cryst.* **1990**, *8*, 825.
(5) Asuke, T.; West, R. *Macromolecules* **1991**, *24*, 343.
(6) Trefonas, P., III; Damewood, J. R., Jr.; West, R. *Organometallics* **1985**, *4*, 1318.
(7) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209.
(8) Miller, R. D.; Hofer, D.; Rabolt, J. *J. Am. Chem. Soc.* **1985**, *107*, 2172.
(9) Schilling, F. C.; Bovey, F. A.; Davis, D. D.; Lovinger, A. J.; Macgregor, R. B.; Walsh, C. A.; Zeigler, J. M. *Macromolecules* **1989**, *22*, 4645.
(10) Song, K.; Miller, R. D.; Wallraff, G. M.; Rabolt, J. F. *Macromolecules* **1991**, *24*, 4084.
(11) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; p 1207.
(12) Miller, R. D. *Chem. Rev.* **1989**. *89*, 1359.
(13) Kepler, R.; Zeigler, J. M.; Harrar L. A.; Kurtz, S. R. *Phys. Rev. B* **1987**, *35*, 2818.
(14) Fujino, M. *Chem. Phys. Lett.* **1987**, *136*, 451.
(15) Stolka, M.; Yuh, H. J.; McGrane, K.; Pai, D. M. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 8243.
(16) Abkowitz, M.; Knier, F. E.; Yuh, H. J.; Weagley, R. J.; Stolka, M. *Solid State Commun.* **1987**, *62*, 547.
(17) Samuel, L. M.; Sanda, P. N.; Miller, R. D. *Chem. Phys. Lett.* **1989**, *159*, 227.
(18) Yokoyama, K.; Yokoyama, M. *Chem. Lett.* **1989**, 1005.
(19) Kajzar, F.; Messier, J.; Rosillo, C. *J. Appl. Phys.* **1986**, *60*, 3040.
(20) Baumert, J. C.; Bjorklund, G. C.; Jundt, D. H.; Jurich, M. C.; Looser, H.; Miller, R. D.; Rabort, J.; Sooriyakumaran, R.; Swalen, J. D.; Twieg, R. *J. Appl. Phys. Lett.* **1988**, *53*, 1147.
(21) Miller, R. D.; Sooriyakumaran, R.; Rabort, J. F. *Bull. Am. Chem. Soc.* **1987**, *32*, 886.
(22) Miller, R. D.; Hofer, D.; Mckean, D. R.; Willson, C. G.; West, R.; Trefonas, P. T., III. *ACS Symp. Ser.* **1984**, *266*, 299.
(23) Wallraff, G. M.; Miller, R. D.; Clecak, N.; Baier, M. *Advances in Resist Technology and Processing VIII*; SPIE Vol. 1146; SPIE: Bellingham, WA, 1991; p 211.
(24) Kuna, R. R.; Bianconi, P. A.; Horn, M. W.; Paladuge, R. R.; Shaver, D. S.; Smith, D. A.; Freed, C. A. *Advances in Resist Technology and Processing VIII*; SPIE Vol. 1146; SPIE: Bellingham, WA, 1991; p 218.
(25) Good, R. D.; Stromberg, R. R.; Patrick, R. L. *Technique of surface and colloid chemistry and physics*; Marcel Dekker: New York, 1972; Vol. 11.
(26) Nishikata, Y.; Morikawa, Y.; Takiguchi, Y.; Kanemoto, M.; Kakimoto, M.; Imai, Y. *Jpn. J. Appl. Phys.* **1988**, *27*, L1163.
(27) Nishikata, Y.; Morikawa, Y.; Takiguchi, Y.; Kanemoto, M.; Kakimoto, M.; Imai, Y. *Nippon Kagaku Kaishi* **1987**, 2174.
(28) Duda, G.; Schouten, A. J.; Arndt, T.; Lieser, G.; Schmidt, G. F.; Bubeck, C.; Wegner, G. *Thin Solid Films* **1988**, *195*, 221.
(29) Duda, G.; Wegner, G. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 495.
(30) Orthmann, E.; Wegner, G. *Angew. Chem.* **1986**, *98*, 114.
(31) Embs, F. W.; Wegner, G.; Neher, D.; Albouy, P.; Miller, R. D.; Willson, C. G.; Schrepp, W. *Macromolecules* **1991**, *24*, 5068.
(32) Nakano, Y.; Murai, S.; Kani, R.; Hayase, S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3361.
(33) Kani, R.; Nakano, Y.; Majima, Y.; Hayase, S.; Chien-hua Yuan, West, R. *Macromolecules* **1994**, *27*, 1911.
(34) Yoshida, H.; Kani, R.; Hayase, S.; Horie, K. *J. Phys. Chem.* **1993**, *97*, 5370.

(35) Seki, T.; Tamaki, T.; Ueno, K. *Macromolecules* **1992**, *25*, 3825.
(36) Wallraff, G. M.; Miller, R. D.; Clecak, N.; Baier, M. *Proc. SPIE* **1991**, *1145*, 211.
(37) Miller, R. D.; Baier, M.; Diaz, A. F.; Ginsburg, E. J.; Wallraff, G. M. *Pure Appl. Chem.* **1992**, *64*, 1291.
(38) Bianconi, P. A.; Weidman, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 2341.
(39) Bianconi, P. A.; Schilling, F. C.; Weidman, T. W. *Macromolecules* **1989**, *22*, 1697.
(40) Furukawa, K.; Fujino, M.; Matumoto, N. *Macromolecules* **1990**, *23*, 3423.
(41) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
(42) Horiguchi, R.; Onishi, Y.; Hayase, S. *Macromolecules* **1988**, *21*, 304.
(43) Ito, S.; Ueno, T.; Yamamoto, M. *Thin Solid Films* **1992**, *210/211*, 614.
(44) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7438.
(45) Michl, J.; Downing, J. W.; Karatsu, T.; McKinley, A. J.; Poggi, G.; Wallraff, G. M.; Sooriyakumaran, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959.
(46) Michl, J.; Downing, J. W.; Karatsu, T.; Kingensmith, K. A.; Wallraff, G. M.; Miller, R. D. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 5, p 61.
(47) Bazant, V.; Chvalovsky, V.; Rathousky, J. *Organosilicon Compounds 1*; Publishing House of the Czechoslovak Academy of Sciences and Academic Press: Prague, New York, and London, 1965, p 160.
(48) Watanabe, A.; Miike, H.; Tsutsumi, Y.; Matsuda, M. *Macromolecules* **1993**, *26*, 2111.
(49) Wilson, W. L.; Weidman, T. W. *J. Phys. Chem.* **1991**, *95*, 4568.
(50) Cram, D. J.; Hammond, G. S. *Organic Chemistry*; McGraw-Hill Book Co., Inc.: New York, Toronto, London; p 385.

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