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Energy Transfer and Electron Transfer Distances in Heteropolysilane Langmuir−Blodgett Films

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ABSTRACT: Energy transfer distances from polysilanes bearing alkyl groups to those bearing aromatic groups are estimated by employing heteropolysilane Langmuir−Blodgett (LB) films. In the heteropolysilane films, AL1-LB film (10 layers, poly((hydroxyhexyl)hexylsilane))/I1-LB film (*n* layers, insulator polymer, (isobutyl methacrylate))/AR1-LB film (10 layers, poly((hydroxyphenyl)butylsilane)), AL1 is selectively excited with 310 nm light and the fluorescence from AR1-LB film is observed, as the number of insulator layers, *n*, is changed. The results imply that energy does not transfer from AL1-LB film to AR1-LB film when two insulator LB layers (22 Å) are inserted between the two polysilane LB films. The electron transfer distances from polysilanes to (2,2′-(2-(cholan-24-yl)-2,5-cyclohexadiene-1,4-diylidene)-bis(propanedinitrile) (TCNQ1) are also estimated by employing a heteropolysilane LB film, AL1-LB film (10 layers)/I1-LB film (insulator, *n* layers)/TCNQ1-LB film (10 layers). The electron transfer distance from AL1-LB film to TCNQ1-LB film is determined by observing the decomposition of AL1 (the decrease in the UV absorption) when TCNQ1-LB film is selectively exposed to UV light. It is estimated that electron transfer from AL1-LB film to TCNQ1-LB film occurs through insulators of less than 22 Å thickness.

Introduction

Polysilanes have many interesting chemical and physical properties.[1,2] Photochemistry of polysilanes is particularly interesting,[3] with respect to various potential applications such as photoresists,[4−7] memories,[8] and optical wave guides.[9] Many studies have been done to clarify the relationship between polysilane structure and the photolysis mechanism.[3,10] Miller et al. have reported that certain additives are effective at increasing the photolysis rate,[10,13] which is brought by the electron transfer from photoexcited polysilanes to the additives. Another major energy transfer pathway is electronic energy transfer which occurs as a result of dipole−dipole interactions. Fluorescence polarization studies have suggested that in dilute polysilane solutions polysilane chains are composed of a distribution of chromophores of varying chain segment lengths and that energy transfer to the longer, low-energy segments occurs.[2] High quantum efficiencies of photoluminescence characterize the polysilanes, which is very useful for electroluminescence (EL) devices.[2]

In this paper, energy transfer distances from one polysilane layer to another polysilane layer, and electron transfer distances from polysilane to a tetracyanoquinodimethane derivative, are discussed by employing a Langmuir−Blodgett (LB) technique.

Experimental Section

Poly((hydroxyhexyl)hexylsilane) (AL1),[14] poly((hydroxyphenyl)butylsilane) (AR1),[15] poly(isobutyl methacrylate) (I1),[16] and (2,2′-(2-(cholan-24-yl)-2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile) (TCNQ1)[16] were synthesized by methods described in previous papers. Molecular weights of AL1, AR1, and I1 are 420 000, 500 000, and 230 000, respectively. Abbreviations of compounds used in this study are summarized in Figure 1.

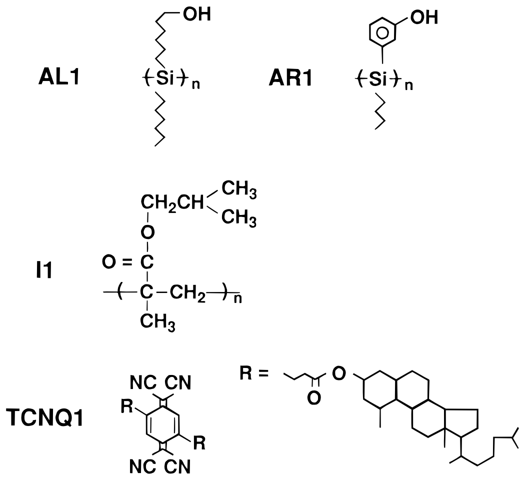

Figure 1. Abbreviations of compounds employed in LB film fabrication: AL1, MW 420 000; AR1, MW 500 000; I1, MW 230 000.

Film Preparation for Energy Transfer (LB1-*n* Structure). The structures of hetero-LB films are shown in Figure 2. The quartz plate was treated with a mixture of sulfuric acid and a hydrogen peroxide aqueous solution and rinsed with deionized water. The process was repeated three times. After 1 h of baking at 150 °C, the plate was treated with hexamethyldisilazane for 12 h at room temperature in order to render the surface hydrophobic. LB films were prepared by a vertical deposition method on a Kyowa Kaimen Kagaku Model HBM Langmuir trough. Surface pressure−area isotherms were monitored with a Wilhelmy plate. A solution of 0.4 g of polysilane AR1 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 (10 layers) onto a quartz plate at a compression rate of 20 mm/min and a dipping speed of 55 mm/min at 15 °C. Then, a solution of 0.45 g of insulator polymer I1 in 1 L of toluene was spread at the air−water interface. The monolayers were compressed at 12.5 mN/m and transferred step by step (*n* layers) onto the AR1-LB film on the quartz plate at a compression rate of 20 mm/min and a dipping speed of 0.5 mm/min at 15 °C. The abbreviation *n* of LB1-*n*, stands for the number of the insulator layers (I1). The value of *n* was varied from 0 to 20. Finally a solution of 0.4 g of polysilane AL1 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 (10 layers) onto the above

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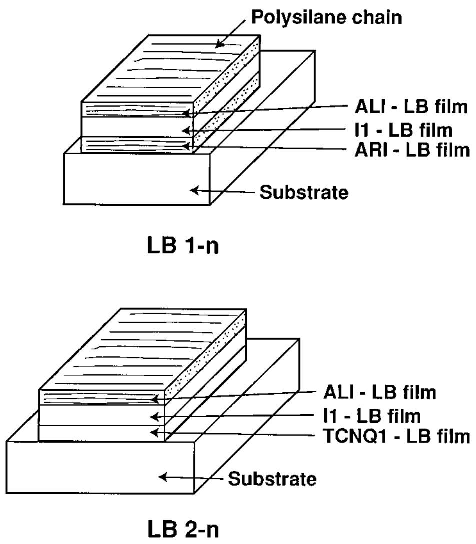


Figure 2. LB1 and LB2 structures: LB1-*n*, AL1-LB film (10 layers)/I1-LB film (*n* layers)/AR1-LB film (10 layers); LB2-*n*, AL1-LB film (10 layers)/I1-LB film (*n* layers)/TCNQ1-LB film (10 layers). In this abbreviation, *n* stands for the number of I1 layers.

hetero-LB film at a compression rate of 20 mm/min and a dipping speed of 5 mm/min at 15 °C.

Film Preparation for Electron Transfer (LB2-*n* Structure). A solution of 0.6 g of TCNQ1 in 1 L of toluene was spread at the air–water interface. The monolayers were compressed at 30 mN/m and transferred step by step (10 layers) onto a quartz plate at a compression rate of 20 mm/min and a dipping speed of 5 mm/min at 15 °C.[16] Then, a solution of 0.45 g of insulator polymer I1 in 1 L of toluene was spread at the air–water interface. The monolayers were compressed at 12.5 mN/m and transferred step by step onto the TCNQ1-LB film on the quartz plate at a compression rate of 20 mm/min and a dipping speed of 5 mm/min at 15 °C. The value of *n* was varied from 0 to 3. Finally, a solution of 0.4 g of polysilane AL1 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 (10 layers) onto the above hetero-LB film at a compression rate of 20 mm/min and a dipping speed of 5 mm/min at 15 °C.

Energy Transfer. Energy transfer was monitored by observing the fluorescence spectra of LB1-*n*. The fluorescence intensity of the AL1-LB film was compared with that of the AR1-LB film when the AL1-LB film was selectively excited (310 nm excitation).

UV Irradiation for Electron Transfer Study. Photolysis was carried out by using collimated UV light generated by Ushio Model UI-501C photolysis assembly equipped with a high-pressure mercury lamp. The light below 400 nm was cut with a Melles Griot cut off filter GG 395 in order to irradiate the TCNQ1 selectively.

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 fluorescence spectra were monitored by a Hitachi M-850 spectrometer.

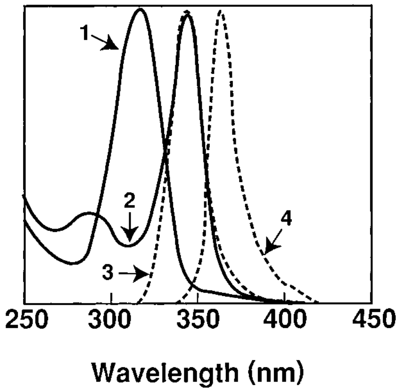


Figure 3. UV absorptions and fluorescence spectra of AL1 and AR1: (1) UV absorption spectrum of AL1; (2) UV absorption spectrum of AR1; (3) fluorescence spectrum of AL1; (4) fluorescence spectrum of AR1.

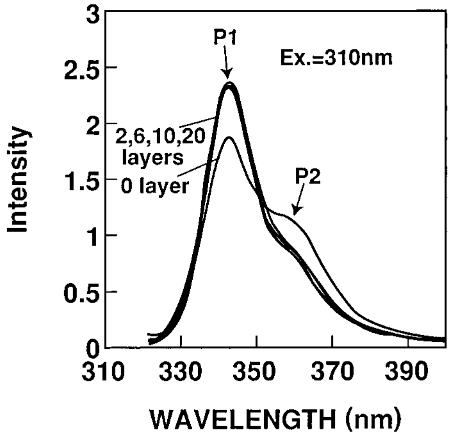


Figure 4. Fluorescence spectra of LB1-*n*, with an excitation of 310 nm. P1 and P2 stand for fluorescences from AL1-LB and AR1-LB films respectively; 0, 1, 2, 6, 10, and 20 stand for the number of I1-LB films inserted.

Results and Discussion

Energy Transfer. Figure 3 shows UV absorption and fluorescence spectra for AL1-LB and AR1-LB films, respectively. The silicon chains of AL1-LB and AR1-LB films align with each other in the direction parallel to the dipping direction, and the dichroic ratios were 2.0 and 2.8, respectively.[14,15] LB1-*n* was fabricated so that the silicon chain orientation in AL1-LB film was parallel to that in the AR1-LB film, because energy transfer should occur more efficiently when the dipole–dipole interactions between the polysilane chains become large.[17,18] AL1-LB and AR1-LB films have $\lambda_{\max}$ at 316 and 345 nm, respectively. The fluorescence of the AR1-LB film is distinguishable from that of the AL1-LB film because the fluorescence spectrum of AL1-LB film (343 nm) is blue-shifted by 21 nm compared to that of AR1-LB film. The quantum yields of AL1-LB and AR1-LB films were 20% (310 nm excitation) and 5% (350 nm excitation), respectively. The AR1-LB film also emitted fluorescence by 310 nm light excitation because the AR1-LB film has small UV absorption at 310 nm. However, the fluorescence itself was much weaker than that for AL1-LB film when the LB films were excited with 310 nm light. The superposition of fluorescence from the AL1-LB film itself and from the AR1-LB film itself gives the same fluorescence from LB1-20 in which 20 insulator layers were inserted between the AL1-LB and AR1-LB films, and the insulator is thick enough to ignore the energy transfer between the two polysilane LB films. It was difficult to excite the AL1-LB film only selectively with 310 nm light. However, the selectivity was good enough to judge the energy transfer. The I1-LB film itself did not quench the fluorescence from the AL1-LB film. If AL1-LB film is excited and the energy transferred from the AL1-LB film to AR1-LB film fabricated in LB1-*n*, fluorescence of the AR1-LB film should be observed.

When LB1-0 was excited by 310 nm light, both 345 and 364 nm fluorescences were observed, as shown in Figure 4, indicating that a part of the energy was transferred from the photoexcited AL1-LB to AR1-LB film. When two layers of I1 were inserted between AL1-LB and AR1-LB films (LB1-2), the 345 nm fluorescence increased and the 364 nm fluorescence decreased. The fluorescence spectra did not change even when *n* increased from 2 to 20. The shoulder at around 360 nm seen in Figure 4 did not decrease to zero because the AR1-LB film itself is slightly excited with the 310 nm light as mentioned above. The result suggests that the energy of the photoexcited AL1-LB film is not transferred to AR1-LB film when the two LB films are separated by I1-LB films with more than two layers.

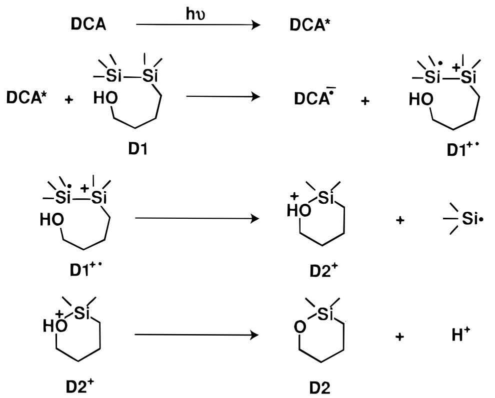
As the thickness of one I1-LB film is determined to be 11 Å,[16] it is concluded that the energy transfer occurred within a distance of 11 × 2 Å plus $(d_1 + d_2)/2$, where d_1 and d_2 stand for the thickness of one layer for the AL1-LB film and the AR1-LB film, respectively. The distance between the two polysilane chains in the oriented poly(dihexylsilane) film has been reported to be 12 Å,[19] which was taken as d_1. The d_2 value has been determined to be 13 Å.[20] Therefore, it turns out that the energy does not transfer from the AL1-LB film to the AR1-LB film when the Si chains are separated by about 35 Å.

Energy transfer in LB films has been studied by employing oxacyanine (host) and thiacyanine (guest), where the guest was packed in the monolayer adjacent to the host−aggregate monolayer. The efficiency of the energy transfer depends on the average distance of the acceptor chromophores in the acceptor layer. In this report, the energy transfer distance reaches 500 Å, where the LB film containing guest molecules contacts the LB film containing host molecules.[21] In case of hetero-LB films in which, for example, oxycyanine LB film is separated from thiacyanine LB film by fatty acid LB films, the energy transfers up to about 80 Å.[22−25] Recently, the energy transfer distance of 400−500 Å has been reported by use of surface plasmon.[26]

The result that the limit of the energy transfer for polysilane LB film is shorter than that for the aromatic compounds would be explained as follows. The longest UV absorption of polysilanes is associated with Wannier-like excitons.[27] Kepler et al. have reported that the excitons are highly mobile in solid films, but not in solution. They explained this phenomena by the fact that energy transfer can occur to neighboring, parallel chain segments through dipole−dipole interactions.[28]

In AL1-LB and AR1-LB films, the polysilane chains, indeed, align each other. However, the conformation of the chain is not all-trans, but random-coil-like.[20] Excitons for the disordered polysilane have been reported to be Frenkel type.[29] Therefore, the dipole−dipole interaction between the two silicon chains in this LB film is not very large along the chain because of the random conformation. This is one explanation of why the energy transfer distance between the two polysilane LB films is shorter than that of the aromatic dye compounds. Another possible explanation is that the electronic coupling between polysilane chains through the overlap of the molecular wave function is less than that for organic dye LB films because the Wannier- or Frenkel-like exciton in the polysilane backbone exists along the chains, and extended tails of the molecular wave functions should be small in the direction perpendicular to the Si−Si back bone. Sawodny et al. have reported that the photoexcited poly(bis(*m*-butoxyphenyl)silane)-LB film transferred the energy through about seven cadmium−arachidate layers to aluminum metal which was observed by fluorescence life time measurement.[30] The seven layers correspond to a thickness of 150−200 Å. They have also reported that the photoexcited energy transferred to Al metal by 150−200 Å through a polyglutamate LB film insulator.[30] The longer energy transfer distance, compared with our results, may be explained by the fact that the energy transfers from polysilane to Al metal, not polysilane to polysilane, and that the polysilane employed by Sawodny et al. has an all-trans conformation which should have a large dipole−dipole interaction.[31]

Scheme 1. Electron Transfer Reaction from Disilane to DCA[a]



[a] See ref 38.

Electron Transfer from Polysilane to TCNQ Derivatives. Electron transfer reactions have been found to promote polysilane photolysis.[2] For example, trichloromethyltriazine increases the photolysis rate of poly(phenylmethylsilane).[2] Miller et al. have reported that electron transfer from the photoexcited polysilane to triazines is the cause of the increase in the photolysis, and the resulting polysilane radical cations decompose rapidly.[2] They have determined the quenching volume to be 2300 Å (radius = 8 Å) from the quenching studies of poly(methylphenylsilane) with various quenchers in solution.[12,13] They have reported that photodecomposition via electron transfer occurs more swiftly than that via homolytic cleavage.[10−13,32,33]

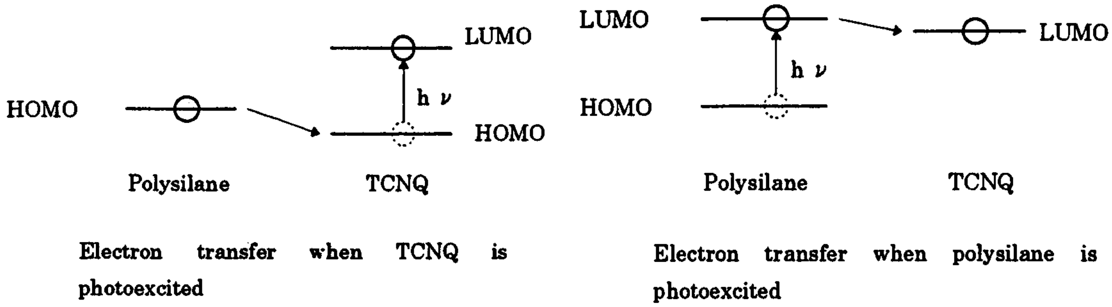
It has been also reported that oligosilanes or cyclic silanes provide charge transfer complexes with acceptors such as tetracyanoethylene (TCNE).[34−37] The polysilanes do not make CT complexes with 9,10-dicyanoanthracene (DCA) in the dark; however, the electrons transfer from the polysilanes to the photoexcited DCA when the DCA is selectively excited by UV irradiation.[38−40]

$$(\mathrm{Me_2Si})_6 \rightarrow \mathrm{Cl(SiMe_2)_6Cl} + \mathrm{Cl_3CCCl_3}$$
$$(\text{in DCA/CCl}_4\text{−CH}_2\text{Cl}_2)$$
$$h\nu\ (\lambda > 300\ \mathrm{nm})$$

Nakadaira et al. have reported that for a disilane bearing a hydroxy group photodecompositions due to photoinduced electron transfer were observed, as shown in Scheme 1.[38]

In this reaction, an electron shifts from the disilane D1 to the photoexcited DCA to form the DCA radical anion and the disilane radical cation. The disilane radical cation is attacked by the OH group intramolecularly, resulting in the formation of a silyl radical and a cyclic silyl ether D2. This photoreaction is different from those reported by Miller et al. because, in the former case, DCA is photoexcited in the first

Scheme 2. Electron Transfer Reactions



Electron transfer when TCNQ is photoexcited

Electron transfer when polysilane is photoexcited

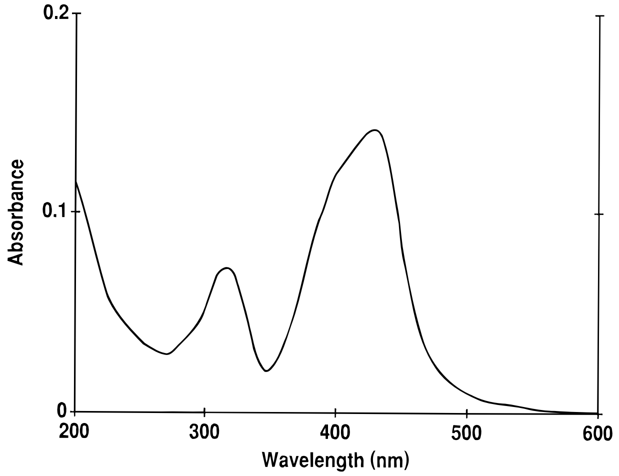


Figure 5. UV absorption of LB2-20. See the Experimental Section for details.

place, followed by electron transfer from polysilanes to the DCA, but in the latter case, polysilanes are photoexcited in the first place and then the electron shifts from the photoexcited polysilane to the additives.[10−13,32,33] The difference is shown in Scheme 2. The former is industrially important because polysilanes could be photodecomposed by UV light with lower energies.

In order to determine the photoexcited electron transfer distance in LB films, we made the polysilane hetero-LB films (LB2-n) shown in Figure 2. Considering the results of Nakadaira et al., the electron transfer should be detectable by observing the change of the UV absorption of polysilanes bearing OH groups in the presence of acceptors. The UV absorption of the LB2-10 is shown in Figure 5. UV absorptions observed at 316 and 428 nm are assigned to AL1 and TCNQ1, respectively. When the LB2-10 was exposed to 400 nm light in order to excite the TCNQ1-LB films selectively, the UV absorption of the AL1-LB film did not change. However, for LB2-0 and LB2-1, decreases in the UV absorptions were observed, as shown in Figure 6. A small decrease in the UV absorption was also seen for LB2-2.

The decrease in the UV absorption of the AL1-LB film when n is 0, 1, and 2 is explained by the decrease in the molecular weight of the AL1-LB film caused by photoinduced electron transfer, which are the same as in the reaction reported by Nakadaira et al.[38] These results suggest that electron transfer from the AL1-LB film to the photoexcited TCNQ1-LB film does not occur when the insulator thickness is more than two layers. As the thickness of one I1-LB film is determined to be 11 Å,[16] it is concluded that the electron transfer from the AL1-LB film to the TCNQ1-LB film occurs through insulators within a 22 Å thickness. TCNQ1-LB film was fabricated by starting with the dipping mode on the hydrophobic substrate. Therefore, cholanyl of TCNQ1 should be contacting the I1. The thickness of TCNQ1-LB film is reported to be 18 Å.[41] Assuming that turnover of the TCNQ1-LB film does not occur when the LB film is transferred from the air−water interface to the substrate, the limit of the electron transfer distance should be from around $11 + 18 + 12/2 = 35$ Å (one insulator) to $22 + 18 + 12/2 = 46$ Å (two insulator). In electron transfer, the electronic coupling between donor and acceptor through the overlap of the molecular wave function is needed. The photoinduced electron transfer distance from thiacyanine to the ferrocene layer is about 30 Å.[42] A similar result has been reported for the electron transfer from an oxycyanine derivative to AgBr[43] and from photoexcited pyrene to bipyridinium cation.[44] The electron transfer distance in polysilane LB films is in the range reported above.

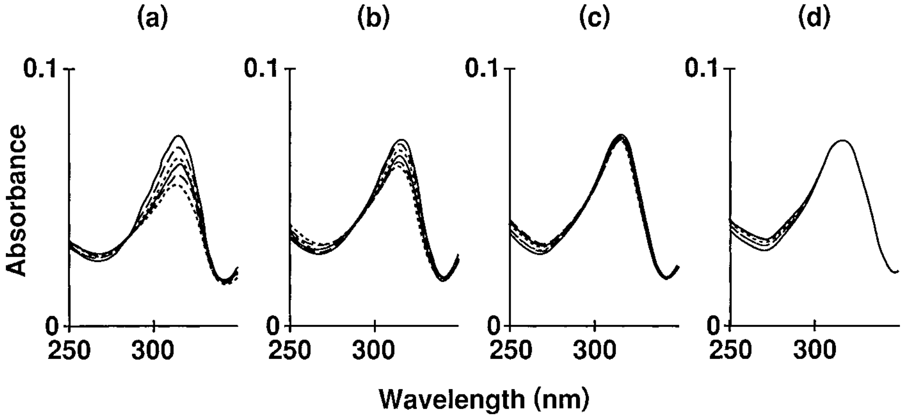


Figure 6. Decrease in UV absorption after photolysis: (a) LB2-0, AL1-LB (10 layers)/TCNQ1-LB (10 layers); (b) LB2-1, AL1-LB (10 layers)/I1-LB (1 layer)/TCNQ1-LB (10 layers); (c) LB2-2, AL1-LB (10 layers)/I1-LB (2 layers)/TCNQ1-LB (10 layers); (d) LB2-3, AL1-LB (10 layers)/I1-LB (3 layers)/TCNQ1-LB (10 layers). See the Experimental Section for details.

The decrease in the molecular weight of polysilanes is usually accompanied by the decrease in the UV absorbance as well as a blue-shift of the UV absorption.[1] However, as shown in Figure 6, the blue-shift was not observed for the AL1-LB film. If photoexcited energies transfer intra- or intermolecularly from where UV light was absorbed to the place having lower energies, polysilane chains having lower energies should preferentially be photodecomposed and blue-shifts should be observed for the duration of the photolysis. Electron transfers from donors to acceptors located spatially close to the donors, may explain the photolysis not accompanied by the blue-shift. In this photoinduced electron transfer, TCNQ1 is excited and electron shifts from polysilane to TCNQ1 molecules. The photoexcited TCNQ1 should accept the electron from the polysilane close to the TCNQ1. The resultant polysilane radical cation would decompose at the place where the polysilane released the electron. Therefore, the polysilane photolysis products contain mixtures of long-chain polymers and photodecomposed short-chain polymers. For the polysilane photolysis, there is no selectivity seen that longer chains photodecompose preferentially. Even if the long chain polysilane decomposed, the λ_{max} of the UV absorption should not move unless the molecular weight decreases to a certain value.[1] Moreover, photodecomposed low molecular weight polysilane may release the electrons again because the TCNQ1 is still there or because the oligomers may be easy to diffuse to the TCNQ1. The fact that λ_{max} of the polysilane does not blue-shift at the beginning of the photoinduced photodecomposition is reported by Karatsu et al., where poly(methylphenylsilane) and poly(dihexylsilane) are photodecomposed in the presence of acceptors such as 9,10-dicyanoanthracene.[44] The same bleaching profiles have been also reported by Miller et al., when the poly(methylphenylsilane) is photodecomposed in the presence of phthalimidotosylate by 254 and 336 nm light.[12,13,32,33]

Conclusion

Energy transfer distances from a polysilane LB film to another polysilane LB film bearing different excitation energies and electron transfer distances from a polysilane LB film to a TCNQ derivative were estimated by observing the increase in fluorescence and the decrease in the UV absorption of polysilanes in hetero-LB films, respectively. It was concluded that both energy and electron transfers occur through insulators within a 22 Å thickness.

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References and Notes

(1) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; p 1207.
(2) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
(3) Trefonas, P., III; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737.
(4) Hofer, D. C.; Miller, R. D.; Willson, C. G. *Proc.* SPIE—*Int. Soc. Opt. Eng.* **1984**, *469*, 16.
(5) Miller, R. D.; Willson, C. G.; Wallraff, G. M.; Clecak, N.; Sooriyakumaran, R.; Michl, J.; Karatsu, T.; McKinley, A. J.; Klingensmith, K. A.; Downing, J. *Polym. Eng. Sci.* **1989**, *29*, 882.
(6) Miller, R. D.; Willson, C. G.; Wallraff, G. M.; Clecak, N.; Sooriyakumaran, R.; Michl, J.; Karatsu, T.; McKinley, A. J.; Klingensmith, K. A.; Downing, J. In *Polymers In Microlithography: Materials and Processes*; ACS Symposium Series 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington, DC, 1989, p 115.
(7) 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.
(8) Yamaguchi, Y.; Hiroshige, Y.; Kakui, M.; Yokoyama, M. *J. Imaging Technol.* **1992**, *36*, 256.
(9) Hirnak, L. A.; Weidman, T. W.; Kwock, E. W. *J. Appl. Phys.* **1990**, *67*, 2235.
(10) Wallraff, G. M.; Miller, R. D.; Clecak, N.; Baier, M. *Advances in Resist Technology and Processing VIII*; SPIE: Bellingham, WA, 1991; Vol. 1466, p 211.
(11) Wallraff, G. M.; Miller, R. D.; Baier, M.; Ginsburg, E. J.; Kunz, R. R. *J. Photopolym. Sci. Technol.* **1992**, *5*, 111.
(12) Miller, R. D.; Baier, M.; Diaz, A. F.; Ginsburg, E. J.; Wallraff, G. M. *Pure Appl. Chem.* **1992**, *64*, 1291.
(13) Wallraff, G. M.; Baier, M.; Diaz, A.; Miller, R. D. *J. Inorg. Organomet. Polym.* **1992**, *2*, 87.
(14) Kani, R.; Nakano, Y.; Majima, Y.; Hayase, S.; Yuan, C. H.; West, R. *Macromolecules* **1994**, *27*, 1911.
(15) Nakano, Y.; Murai, S.; Kani, R.; Hayase, S. *J. Polym. Sci., Part A, Polym. Chem. Ed.* **1993**, *31*, 3361.
(16) Naito, K. *J. Colloid Interface Sci.* **1989**, *131*, 218.
(17) Wilkinson, F. *Photoinduced electron transfer, Part A*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; Chapter 1.5, p 207.
(18) Formherz, P.; Reinbold, G. *Thin Solid Films* **1998**, *160*, 347.
(19) Lovinger, A. J.; Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2657.
(20) Yoshida, H.; Nakano, Y.; Hayase, S. *Macromolecules* **1995**, *28*, 2389.
(21) Mobius, D. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 848.
(22) Kuhn, H. *Verh. Schweiz. Naturforsch. Ges.* **1965**, 245.
(23) Kuhn, H. *J. Photochem.* **1979**, *10*, 111.
(24) Butcher, H.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 183.
(25) Bucher, H.; Kuhn, H.; Mann, B.; Mobius, D.; Szentpaly, L. V.; Tillmann, P. *Photogr. Sci. Eng.* **1967**, *11*, 233.
(26) Knobloch, H.; Brunner, H.; Leitner, A.; Aussenegg, F.; Knoll, W. *J. Chem. Phys.* **1993**, *98*, 10093.
(27) Hasegawa, T.; Iwasa, Y.; Sunamura, H.; Koda, T.; Tokura, Y.; Tachibana, H.; Matsumoto, M. *Phys. Rev. Lett.* **1992**, *69*, 668.
(28) Kepler, G. R.; Soos, Z. G. *Mater. Res. Soc. Symp. Proc.* **1994**, *328*, 679.
(29) Tilgner, A.; Trommsdorff, H. P.; Zeiglar, J. M.; Hochstrasser, R. M. In *Large-Scale Molecular Systems*; Gans, W., et al., Eds.; Plenum Press, New York, 1991; p 403.
(30) Sawodny, M.; Embs, F.; Miller, R. D.; Aussenegg, F.; Stumpe, J.; Wegner, G.; Knoll, W. *Makromol. Chem., Macromol. Symp.* **1991**, *235*, 46.
(31) Embs, F. W.; Wegner, G.; Neher, D.; Albouy, P.; Miller, R. D.; Willson, C. G.; Schrepp, W. *Macromolecules* **1991**, *24*, 5068.
(32) Wallraff, C. M.; Miller, R. D.; Clecak, N.; Baier, M. *Proc. SPIE—Int. Soc. Opt. Eng.* **1992**, *1466*, 211.
(33) Michl, J.; Downing, J. W.; Karatsu, T.; Mckinley, A. T.; Poggi, G.; Wallraff, G. M.; Sooriyakumaran, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959.
(34) West, R.; Traven, V. F. *J. Am. Chem. Soc.* **1973**, *95*, 6824.
(35) Sakurai, H.; Kira, M.; Uchida, T. *J. Am. Chem. Soc.* **1973**, *95*, 6826.
(36) Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1213.
(37) Kyushin, S.; Izumi, Y.; Tsunakawa, S.; Matsumoto, H. *Chem. Lett.* **1992**, 1393.
(38) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.* **1985**, 1781.
(39) Watanabe, H.; Kato, M.; Tabei, E.; Kuwabara, H.; Hirai, N.; Sato, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1662.
(40) Nakadaira, N.; Sekiguchi, A.; Funada, Y.; Sakurai, H. *Chem. Lett.* **1991**, 327.
(41) Naito, K.; Miura, A.; Azuma, M. *Langmuir* **1991**, *7*, 627.
(42) Hsu, Y.; Penner, T. L.; Whitten, D. G. *J. Phys. Chem.* **1992**, *96*, 2790.
(43) Bucher, H.; Kuhn, H.; Mann, B.; Mobius, D.; Szentpaly, L. V.; Tillmann, P. *Photogr. Sci. Eng.* **1967**, *11*, 233.
(44) Hsu, Y.; Penner, T. L.; Whitten, D. G. *J. Phys. Chem.* **1992**, *96*, 2790.
(45) Kararsu, T.; Kobayashi, H.; Shinkai, E.; Kitamura, A. *Chem. Lett.* **1992**, 2131.

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