CHEMISTRY LETTERS, pp. 1321-1324, 1992.

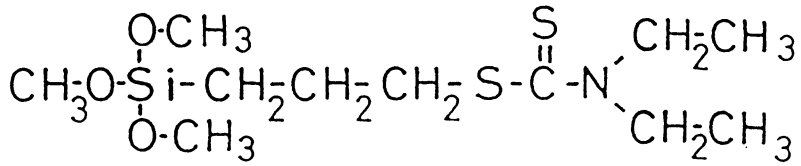
Silane Coupling Agents for Photografting of Vinyl Monomer. Preparation and Properties of (N, N-Diethylamino)-dithiocarbamoylpropyl(trimethoxy)silane

Takaomi KOBAYASHI,* Syun TAKAHASHI, Yoshio NOSAKA, and Nobuyuki FUJII
Department of Chemistry, Nagaoka University of Technology, Nagaoka, Niigata 940-21

A silane coupling agent having a photosensitive group for photograftpolymerization, (N, N-diethylamino)-dithiocarbamoylpropyl(trimethoxy)silane (DATMS), was prepared and its characteristics were examined. The application was as follows: a glass surface was treated with DATMS followed by the photografting of sodium styrenesulfonate (SSS).

Silane coupling agents are useful materials for modification of surfaces of glass and some metals.[1] Alkoxysilane group of coupling agents hydrolyzes to silanol and alcohol and then the silanol couples with OH group of the surfaces. If the coupling agent molecules have photosensitive moiety to initiate photopolymerization of vinyl monomers, various properties can be introduced to the surface because vinyl monomers provide multi-functional natures. In this communication, we report the preparation and applications of a new class of silane coupling agents, (N, N-diethylamino)dithiocarbamoylpropyl(trimethoxy)silane,[2] having a photosensitivity for photopolymerization.[3-7]

Utilizing a substitution reaction of chloropropyl(trimethoxy)silane (CPTMS) (supplied from Toshiba Silicone Co. LTD.) with sodium N, N-diethyldithiocarbamate (SDDC), DATMS was prepared as follows. A 50 mL acetone solution containing 23.89 g (12 mmol) of CPTMS and 9.02 g (40 mmol) of SDDC was stirred at 50 ℃ for 15 h. After cooling, the NaCl precipitated was filtrated, and then the solvent and unreacted CPTMS were



D A T M S

evaporated. The crude product remaining in the vessel was distilled under reduced pressure (0.3 mmHg/ 178 ℃). The yield of yellow liquid DATMS was 17.1 g (52%).

Figure 1 shows absorption spectra of DATMS in $CHCl_3$ solutions of various concentrations. The absorption peaks at 253 and 280 nm which can be assigned to N-C-S and S-C=S conjugations[4] have extinction coefficients ($dm^3mol^{-1}cm^{-1}$), ε =5430 and 6370, respectively. In addition, DATMS has another absorption peak at 335 nm (ε =50 $dm^3mol^{-1}cm^{-1}$).

Glass substrates were treated with DATMS according to the following procedure. The hydrolysis of the methoxy silane moiety of DATMS to silanol and methanol was carried out in acidic $CHCl_3$-methanol solution as follows: A glass substrate (18x18x0.1 mm^3) was immersed into various concentrations of DATMS in $CHCl_3$ solution containing 10 wt% of methanol and 1 wt% of HCl for 10 min. The wet glass was aged for 30 min at 70 ℃ . After the aging, the glass sample washed with $CHCl_3$ was used for characterization and photograftpolymerization.

Absorption spectra of the glass treated with DATMS solutions are shown in Fig. 2. The absorption peak at 335 nm increases with the increase in the DATMS concentration at the treatment, indicating the increase in the DATMS bound to the surface.

Contact angles of air and n-octane in water for the glasses treated with various DATMS solutions were measured. The treatment increases the

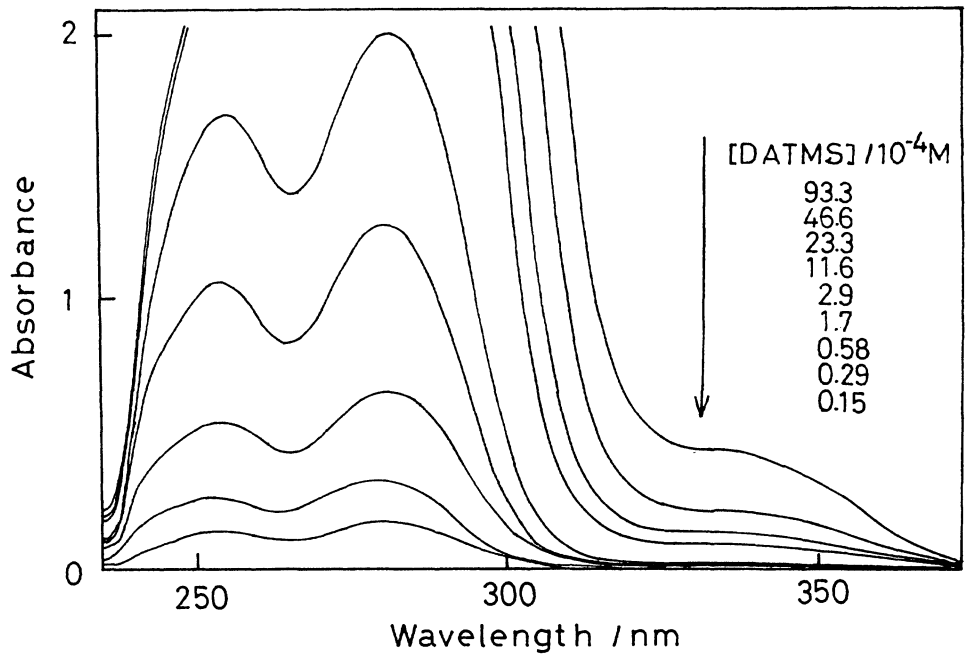


Fig. 1. Absorption spectra of DATMS in $CHCl_3$ at various concentrations.

contact angle, while the value was independent on the DATMS concentration as shown in Table 1. This observation indicates that the treatment with DATMS enhances the degrees of hydrophilic nature of the glass surface, perhaps owing to diethylaminodithiocarbamate groups bound to the surface.

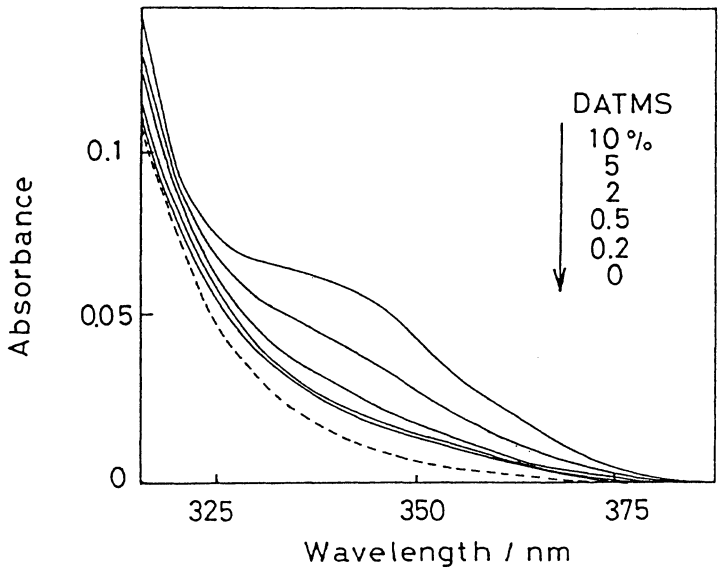


Fig. 2. Absorption spectra of glass plate treated with various DATMS solutions.
Dashed line, without treatment.

Photografting of SSS onto the glasses was performed as follows. The glasses treated with DATMS were put into 5 wt% of SSS monomer solution and photo-irradiated for 6 h using a 100 W high pressure mercury lamp, where the distance between the light source and the glass plate was about 10 cm. The light power was measured by photometer and checked through the photoirradiation. After the irradiation the sample glass was washed with a large amount of water and dried in vacuo at room temperature.

Figure 3 shows FT-IR spectra of the glasses photoirradiated in the SSS monomer solution. In the spectrum (a), the peaks at 670, 770, 830, and 1000-1200 cm^{-1} are assigned to SSS group, indicating that photopolymerization of SSS proceeds on the glass surface treated with DATMS. Further study on photografting is now under progress and the details will be reported elsewhere.

The authors wish to express their thanks to Hiroaki Syudo and Yasuji

Table 1. Contact angles of glass surface treated with various DATMS solutions

	Contact angles in water	
DATMS (%)	θ_{air}/degree	θ_{octane}/degree
0	44	50
0.5	73	128
2	77	116
10	76	125

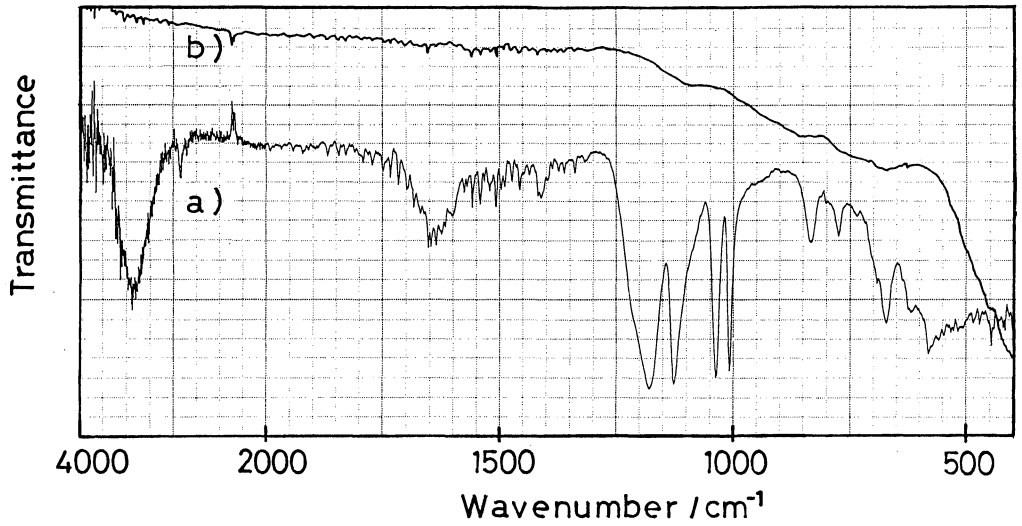


Fig. 3. FT-IR spectra of glasses photoirradiated in SSS solution for 6 h. (a) pretreated with DATMS and (b) without pretreatment.

Matsumoto of Toshiba Silicone Co. LTD., for supplying chloropropyl-(trimethoxy)silane and for variable suggestions.

References

1)E. P. Plueddemann, "Silane Coupling Agents," Plenum Press, New York (1982), pp.75-108.

2)IR(cm^{-1}) 820, 1095 (-Si-O-CH_3), 1200 (-Si-CH_2-), 1208, 1270, 1420, 1492 (-S-C=S), 2945 (CH). ^{1}H-NMR 60 MHz ($CDCl_3$) δ 0.5-1.0 (t,2 H, Si-$\underline{CH_2}$), 1.2-1.6 (t, 6H, $\underline{CH_3}$-CH_2-), 1.7-2.3 (t, 2H, -$\underline{CH_2}$-), 2.9-3.7 (t, 4H, -N-$\underline{CH_2}$-), 3.2 (s, 9H, O-$\underline{CH_3}$), 3.8-4.3 (t, 2H, -$\underline{CH_2}$-S-). Anal. Found: C, 42.89; H, 8.01; N, 4.56%. Calcd for $C_{11}H_{25}NO_3S_2Si$: C, 42.41, H, 8.09, N, 4.50%.

3)S. Ogawara, H. Yamashina, K. Ishiyama, and E. Imoto, Kougyo Kagakukaishi, 66, 1369(1963).

4)H. Miyama, N. Fujii, Y. Shimazaki, and K. Ikeda, Polymer Photochem., 3, 445(1983).

5)N. Fujii, Y. Shimazaki, I. Ikeda, and H. Miyama, Kagaku Kougaku Ronbunshu, 9, 427(1983).

6)A. Kuriyama and T. Otsu, Polymer J., 16, 511(1984).

7)H. Inoue and S. Kohama, J. Appl. Polym. Sci., 29, 877(1984).

(Received April 24, 1992)