

Silane Coupling Agent Having Dithiocarbamate Group for Photografting of Sodium Styrene Sulfonate on Glass Surface

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SYNOPSIS

For a photograft-polymerization of sodium styrene sulfonate onto a glass surface, glasses were treated with a photosensitive silane coupling agent (*N,N*-diethylamino)dithiocarbamoylpropyl(trimethoxy)silane (DATMS). The characteristics of the glass surfaces were examined by UV and IR spectroscopic methods and the contact-angle technique. The contact angles of air and *n*-octane in water were measured to estimate interfacial energy of the surfaces. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Silane coupling agents are useful materials for the modification of the surface of glass and some metal oxides.¹ The coupling reaction of the alkoxy silane group easily takes place under acidic conditions²: For example, the alkoxy silane group hydrolyzes to silanol and alcohol and the silanol couples with the OH group of the surfaces. If the coupling agent molecules have the photosensitive moiety to initiate photopolymerization of vinyl monomers, various properties could be introduced onto the surfaces.

The Dithiocarbamate group is a typical chromophore for the photopolymerization of vinyl monomers.³⁻⁵ We reported that poly(vinyl chloride) covalently bound with the dithiocarbamate group was very photosensitive and useful as a trunk polymer for photografting of vinyl monomers.⁶ The photosensitive polymer was applied to the preparation of a nonthrombogenic polymer⁷ and an immobilized enzyme matrix.⁸ Further, the kinetics of the photolysis of the polymer and the photograft polymerization of hydrophilic methacrylate monomers was studied in detail.⁹ Recently, we reported the preparation and the characteristics of a new type silane coupling agent having the dithiocarbamate group (abbreviated as DATMS) and the photograft polymerization of sodium styrene sulfonate (SSS) onto

a glass surface treated with DATMS, as an example of applications.¹⁰ In the present report, the properties of the glass surface treated with DATMS and photograft polymerization of SSS onto the surface were examined in detail.

EXPERIMENTAL

Materials

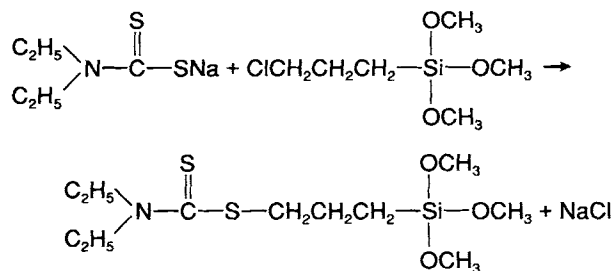
Chloropropyltrimethoxysilane (CPTMS) was supplied by Toshiba Silicone Co. and distilled under reduced pressure (0.3 mmHg) at 75°C before use. Sodium *N,N*-diethyldithiocarbamate (SDDC) was recrystallized from methanol. Acetone for the reaction solvent was distilled before use.

(*N,N*-Diethylamino)dithiocarbamoylpropyl-(trimethoxy)silane (DATMS) was prepared by the substitution reaction of CPTMS with SDDC (Scheme 1). Yellow liquid DATMS was obtained by distillation at 0.3 mmHg/178°C. The details of the preparation method were reported previously.¹⁰ Other reagents were used without further purification.

Measurements

IR spectra of DATMS were produced and ATR-IR spectra of the glass surfaces were measured using a Hitach IR260-10 spectrometer and Shimadzu FTIR

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Scheme 1 Reaction scheme for DATMS preparation.

8100 spectrophotometer, respectively. The FTIR spectra were taken at a 45° angle to the incident light. UV spectra of the glasses treated with DATMS were recorded on a Shimadzu UV-190 double-beam spectrophotometer. Contact angles between sample glasses and air or *n*-octane were measured in water with using Type CA-A produced by the Kyowa Kagaku Co.

According to previous methods,^{7,11} titrations of anionic fixed charges grafted SSS onto the surfaces were carried out in water using pH readings obtained on a Horiba H-7LD pH meter equipped with a Horiba combination electrode no. 6366.

Treatment with DATMS onto the Glass Surface

The coupling reaction of DATMS with the glass surface (Scheme 2) was carried out as follows: A glass substrate (18 × 18 × 0.1 mm³) was immersed into various concentrations of DATMS in CHCl₃ solution containing 10 wt % of methanol and 1 wt % of HCl. The wet glasses were aged for 30 min at 70°C. After the aging, the glass washed with CHCl₃ was used for characterization and photopolymerization.

Photograft Polymerization

Photografting of SSS onto the glasses was performed as follows: The substrate glasses treated with the acidic solution containing various DATMS concentrations were put into the 5 wt % of SSS aqueous solution degassed with N₂ and then photoirradiated by 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 a photometer (TPM-316, Gentec). After the irradiation, the sample glass was washed with a large quantity of water and then dried *in vacuo* at room temperature.

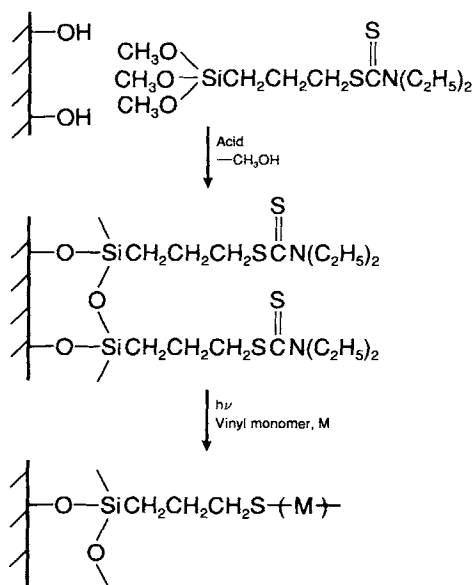
RESULTS AND DISCUSSION

Characterization of Glasses Treated with DATMS

The DATMS prepared was soluble in CHCl₃, CCl₄, acetone, THF, DMSO, DMF, and benzene but not in water, methanol, ethanol, and propanol. In general, the hydrolysis of the alkoxy groups was carried out in the acidic alcohol solution.^{1,2,12} In the present work, the hydrolysis reaction of the —Si—O—CH₃ groups was carried out in a CHCl₃-methanol solution.

As reported previously,^{3,6} the dithiocarbamate group has characteristic absorption peaks at about 250 and 280 nm in the ultraviolet region. The absorption spectrum of DATMS in CHCl₃ have characteristic peaks at 253, 280, and 335 nm having extinction coefficients of $\epsilon = 5430, 6370, \text{ and } 50 \text{ M}^{-1} \text{ cm}^{-1}$, respectively.¹⁰ The absorption peaks were assigned to N—C—S and S—C=S conjugations.¹³ Figure 1 shows the absorption spectra of quartz glass treated with (a) 0.2 wt % and (b) 10 wt % of the acidic DATMS solution. From the spectra, it was indicated that the chromophore group of DATMS bonds to the surfaces.

The absorbance at 335 nm for the glasses aged at 70°C after the treatment of DATMS solutions increased with an increase in the DATMS concentration used. The increase is shown in Figure 2. The



Scheme 2 Schematic illustrations of glass treatment of DATMS and photograft polymerization on to the glass surfaces. The vinyl monomer is abbreviated as M.

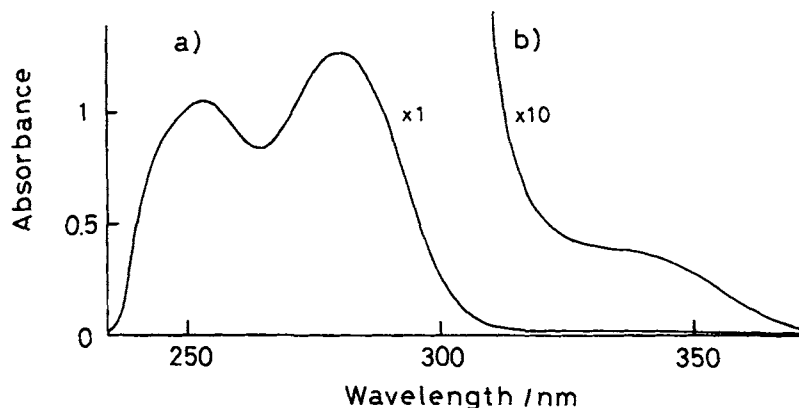


Figure 1 Absorption spectra of quartz glass treated with (a) 0.2 and (b) 10 wt % of DATMS solutions.

absorption peaks of the dithiocarbamate group, however, were not observed in the nonaged glasses. This difference suggests that the coupling reaction of DATMS with the surface influences the aging condition.

Figure 3 shows the IR spectrum of DATMS and the ATR-IR spectra of the glasses treated with 0.2 and 10 wt % of DATMS solution. DATMS has weak characteristic peaks,¹³ assigned to the dithiocarbamate group, at 918, 995, 1208, 1270, 1350, 1420, and 1492 cm^{-1} . The strong peaks of the $\text{CH}_3\text{—O—Si}$ group attributed to asymmetric Si—O—C stretching^{14,15} are observed at 820 and 1095 cm^{-1} . The other asymmetric CH stretch falls at 2945 cm^{-1} . Also, the weak peak for the Si—C bond is observed

at 1200 cm^{-1} as a result of the substituent reaction of SDDC with CPTMS (Scheme 1). For CPTMS, a strong peak at 1200 cm^{-1} , assigned to a CH_2 wagging vibration for the $\text{CH}_2\text{—Cl}$ group, disappeared after the reaction and then the weak peak of Si—C bonds appeared.

In the spectrum of the glasses treated with DATMS, weak characteristic peaks of the dithiocarbamate group were observed in the range between 1200 and 1500 cm^{-1} . It is noted that the strong peaks of DATMS at 820 and 1095 cm^{-1} disappeared after the coupling reaction of DATMS with the glass surface (Scheme 2). In the glasses treated, strong peaks at 650–700 and 1000–1150 cm^{-1} regions were observed. The band of the former region is due to a symmetric Si—O—Si stretching vibration and that of the latter is due to an asymmetric Si—O—Si stretching vibration. The appearance of Si—O—Si groups in the spectra of the glass surfaces implies that the coupling reaction proceeds on the surfaces by forming a siloxane chain, as shown in Scheme 2.

Figure 3 also compares the ATR-IR spectra of the glasses treated with (b) 0.2 wt % and (c) 10 wt % of DATMS solution. According to the model experiments for the IR analysis of siloxane oligomers reported by Alvic and Dale,^{16,17} the maximum band at about 1000 cm^{-1} of the glass treated with the 10 wt % solution are assigned to the monosubstituted siloxane chain. Also, the bands in the 1030–1100 cm^{-1} region were assigned to highly structured siloxane such as di-, tri-, and polysubstituted siloxane chains. Especially, the highly cross-linked ladder polymer has absorption at about 1130 cm^{-1} . In addition, for the glasses treated with the 10 wt % solution, the broadening in the range of the wavenum-

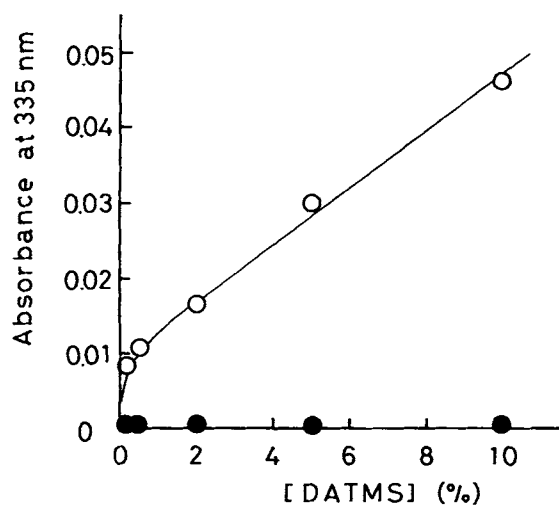


Figure 2 Absorbance at 335 nm for glasses treated with various DATMS concentrations: (O) aging at 70°C; (●) nonaging.

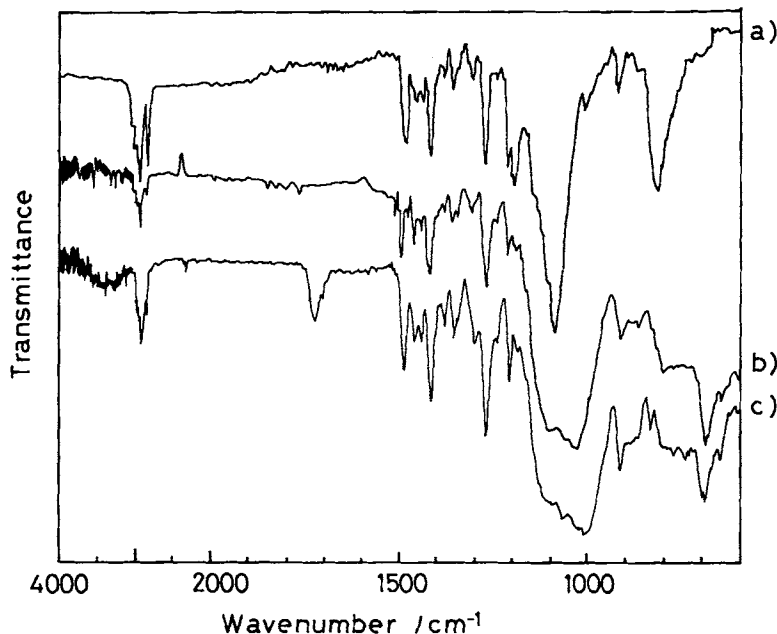


Figure 3 (a) IR spectrum of DATMS, and ATR spectra for glasses treated with (b) 0.2 wt % and (c) 10 wt % of DATMS solutions.

ber is somewhat larger than that for the 0.2 wt % solution. Therefore, in the high DATMS concentration used for the pretreatment of the glass surface, it appears that many siloxane chains were formed on the surfaces.

To evaluate the surface properties, the contact-angle method in water was adopted as presented in Figure 4. The contact angles of air (θ_{air}) and *n*-octane (θ_{octane}) and interfacial free energy (γ) for both glass surfaces untreated and treated with DATMS are shown in Figure 4. Here, the values of γ were calculated according to the method of Andrade et al.¹⁸ Before the measurements of the contact angles, the sample glasses were fully soaked in distilled water. As shown in Figure 4(a), the DATMS treatment obviously increases the values of θ_{air} and θ_{octane} , whereas the values obtained are constant regardless of the changes of DATMS concentration.

Figure 4(b) shows the relationship between the interfacial free energy (γ) and the DATMS concentration. Here, γ for solid–vapor (γ_{sv}), water–vapor (γ_{wv}), and solid–water (γ_{sw}) interfaces are presented as

$$\gamma_{\text{sv}} - \gamma_{\text{sw}} = \gamma_{\text{wv}} \cos(180 - \theta_{\text{air}})$$

where $\gamma_{\text{wv}} = 72.1 \text{ erg/cm}^2$ for the water–air interface. The term ($\gamma_{\text{sv}} - \gamma_{\text{sw}}$) is called the adhesion tension.

Also, γ_{sv} involves two contributions, $\gamma_{\text{sv}}^{\text{d}}$ and $\gamma_{\text{sv}}^{\text{p}}$, for a van der Waals (dispersion) contribution and polar (nondispersion) contribution, respectively, as follows:

$$\gamma_{\text{sv}} = \gamma_{\text{sv}}^{\text{d}} + \gamma_{\text{sv}}^{\text{p}}$$

In the surfaces treated with DATMS, the values of the adhesion tension are smaller than 0 because $\theta_{\text{air}} \leq 90^\circ$, as shown in Figure 4(a). This results in $\gamma_{\text{sv}} \leq \gamma_{\text{sw}}$ for the glass surfaces treated with DATMS. In γ_{sv} , for the *n*-octane–glass (solid) interface, the values calculated for the treated glasses are larger than those for the untreated one. As shown in the figures, the surfaces treated with DATMS give a larger polar component than they do a dispersion one, i.e., $\gamma_{\text{sv}}^{\text{p}} \geq \gamma_{\text{sv}}^{\text{d}}$. This results from the increase of the dithiocarbamate group on the surface by the DATMS treatments.

The values of γ_{sw} for the surfaces treated decreased with the DATMS concentrations and was constant regardless of the increase of DATMS concentration. The results indicate that, in the water–solid interface, the adhesion of water molecules to the polar sites, such as $(\text{C}_2\text{H}_5)_2\text{N}-$ and $\text{S}-\text{C}=\text{S}$ groups of DATMS, on the surfaces decreases the surface energy. We also measured contact angles of water (θ_{water}) in air. The values for the glasses un-

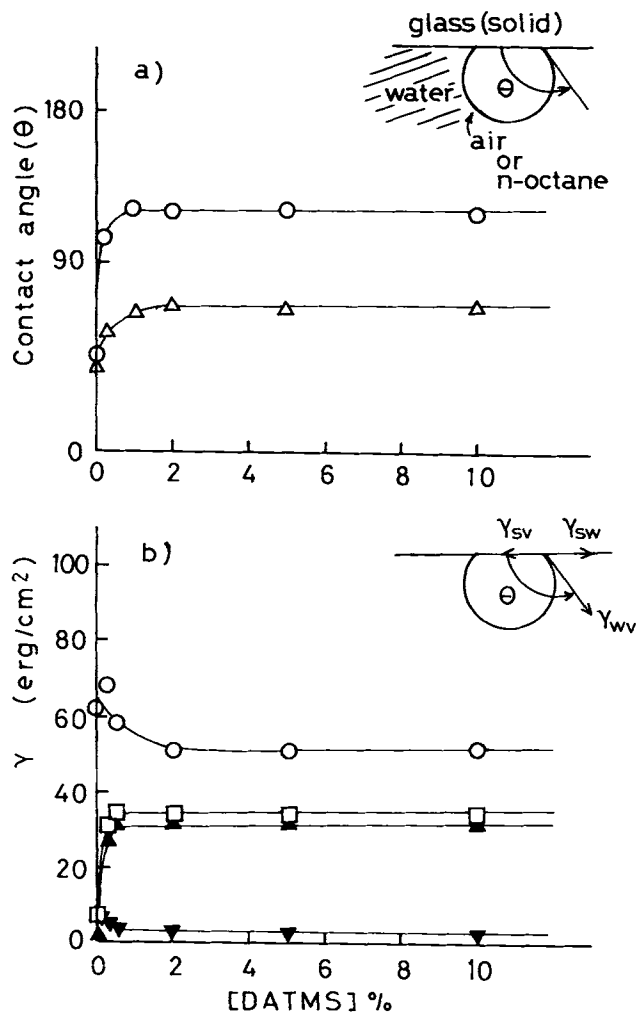


Figure 4 Contact angles of air and n -octane in water and interfacial free energy (γ) for glasses treated with various DATMS concentrations. (a) contact angles of (○) n -octane and (△) air; (b) (○) γ_{sw} ; (□) γ_{sv} ; (▼) γ_{sv}^d ; (▲) γ_{sv}^p .

treated and treated with DATMS are 50 and 74, respectively. In air, the latter large value suggests that the surface repels the water droplets, because the hydrophobic propyl group and Si—O—Si chains may be exposed on the air–solid interface. But, subsequently, the value of the water droplet in air decreased with time and was finally reached at $\theta_{\text{water}} \sim 60^\circ$. This change of θ_{water} indicates that the wettability of the surfaces across water–glass interface increases.

Photografting of Vinyl Monomer

The dithiocarbamate group is known to initiate photopolymerization of vinyl monomers.^{3–9} We re-

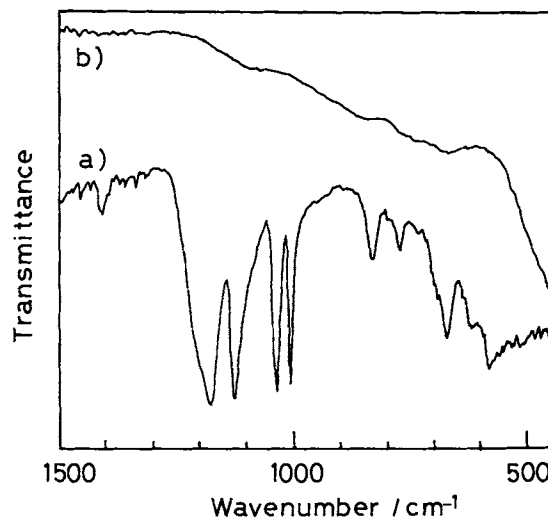


Figure 5 ATR spectra of glasses photoirradiated in SSS solution at 6 h: (a) treatment with 10 wt % of DATMS solution; (b) without treatment.

ported that the chromophore bound to the glass surface can initiate the photograft-polymerization of vinyl monomers (abbreviated as M in Scheme 2).¹⁰

Figure 5 shows the ATR–IR spectra of the glasses photoirradiated in the SSS aqueous solution. As reference, an untreated glass was photoirradiated under the same conditions as those of the treated glasses. Spectrum (b) of the glass untreated did not change before and after 6 h irradiation. For the glass treated with DATMS, however, spectrum (a) of the glass photoirradiated at 6 h has the typical char-

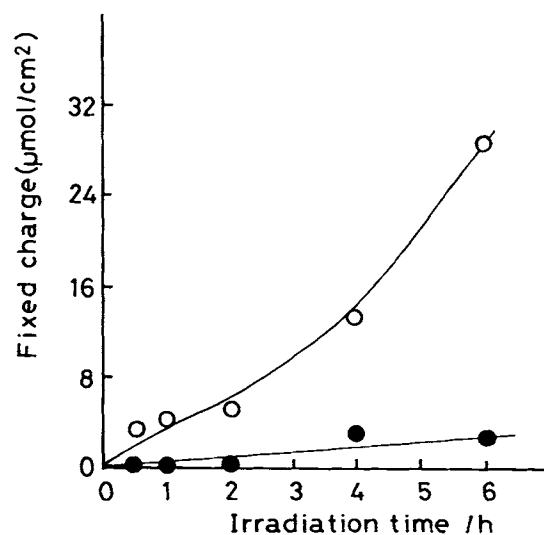


Figure 6 Plots of fixed charges against irradiation times: (○) aging at 70°C; (●) nonaging. The glass used was treated with 10 wt % of DATMS solution before the aging.

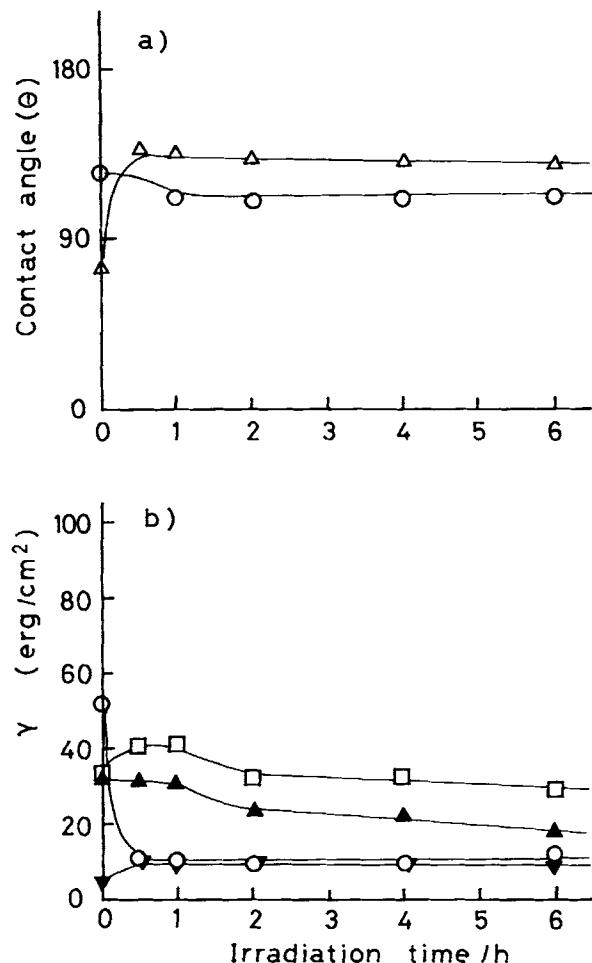


Figure 7 Plots of contact angles of air and *n*-octane in water and interfacial free energy (γ) against irradiation times for glasses photografted with SSS: (a) contact angles of (\circ) *n*-octane and (Δ) air; (b) (\circ) γ_{sv} ; (\square) $\gamma_{\text{sv}}^{\text{p}}$; (\blacktriangledown) $\gamma_{\text{sv}}^{\text{d}}$; (\blacktriangle) γ_{sw} .

acteristic peaks at 560, 670, 770, 830 ($\nu_{\text{benzene ring}}$), and 1000–1250 ($\nu_{\text{SO}_3\text{Na}}$), assigned to the SSS group.¹⁹ Also, the CH bending of the polymer chains formed is shown at about 1420 cm⁻¹. These indicate that the photopolymerization of SSS proceeds on the glass surfaces treated with DATMS as shown in Scheme 2.

Figure 6 shows amounts of fixed charges of SO_3^- ($\mu\text{mol}/\text{cm}^2$) per whole glass area (cm^2) at various irradiation times. The values of the fixed charges for glasses treated with 10 wt % of DATMS increased with the irradiation time. It is shown that the grafting of the monomer occurs effectively by the photoirradiation. On the other hand, in the glasses without the pretreatment, amounts of the

fixed charges grafted are remarkably lower than those in the treated glasses.

Figure 7(a) exhibits plots of θ_{air} and θ_{octane} against the irradiation times for the glasses photografted with SSS. The values of θ_{air} increased with the grafting of SSS as compared with that of the DATMS treatment, whereas those of θ_{octane} are almost constant in the irradiation time. We reported the dependence of the contact angles on the photoirradiation time for the surface grafted with SSS on photosensitive polyacrylonitrile membranes.²⁰ The values obtained in this work agree with those for polyacrylonitrile membranes photografted with SSS. It is clear that the photografting of SSS enhances the degree of the hydrophilic nature of the surface because of the graft of SO_3 groups onto the surface.

The values of interfacial free energy γ (γ_{sv} and γ_{sw}) of the glasses photoirradiated at various irradiation times are shown in Figure 7(b). The values of γ_{sv} increased by the grafting of SSS and then was independent of the irradiation time. It appears that γ_{sv} for the *n*-octane–glass interface contributes to the polar component of SSS grafted onto the surfaces: $\gamma_{\text{sv}}^{\text{p}} > \gamma_{\text{sv}}^{\text{d}}$. On the other hand, the values of γ_{sw} remarkably decreased by the photografting of SSS and then become constant at about 8–10 erg/cm² regardless of the increase of the graft of SSS with irradiation time. In the water–solid interface, the low interfacial free energy of the surface grafted results from adhesion of the water to hydrophilic sites of the SSS group.

As reported by Andrade et al.,¹⁸ the values of γ_{sw} for hydrophilic polymeric gels decreased with an increase in the water fraction in the gel. Also, γ_{sw} approached zero for the value of water, especially at the high water fraction. In the present work, the values of γ_{sw} for the surfaces grafted with SSS approached zero, while those are slightly greater than zero. This may be due to the hydrophobicity of the benzene ring of the SSS group grafted onto the surface.

CONCLUSION

The treatment of the silane coupling agent having the dithiocarbamate group was carried out. From the results for contact angles of air and *n*-octane in water, the surface free energy of the glass treated with DATMS was estimated. Also, the photograft-polymerization of SSS onto the glass surface was examined. The degree of the photografting increased

with photoirradiation time. The surface free energy of the glass, however, was constant regardless of the increase of the irradiation time. The results suggest that the photografting of SSS enhanced the degree of the hydrophilic nature of the surface.

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