

# Surface Photografting of Hydrophilic Vinyl Monomers onto Diethyldithiocarbamated Polydimethylsiloxane

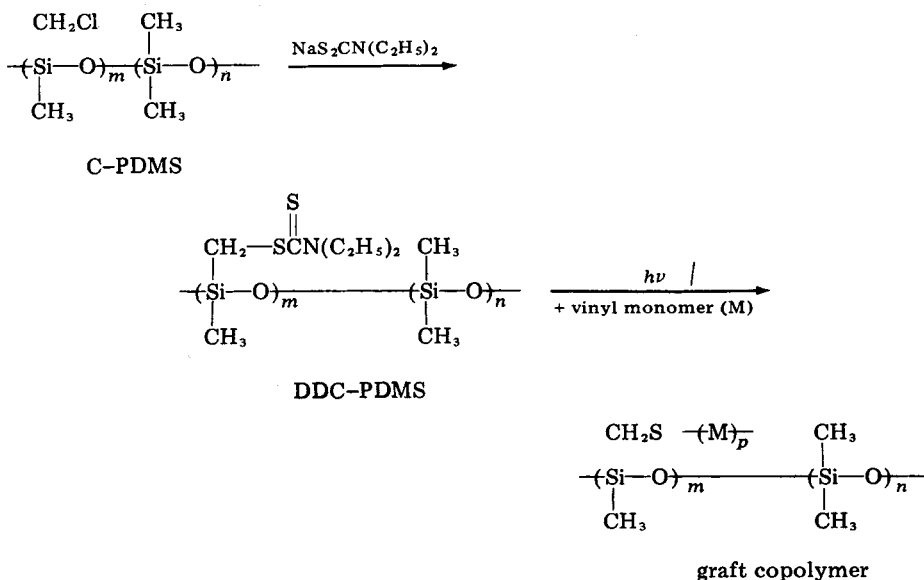
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## Synopsis

Photografting of vinyl monomers has been studied to make hydrophilic polydimethylsiloxane (PDMS) surfaces. A chlorine-containing polydimethylsiloxane (C-PDMS) prepared by polymerization of chloromethylheptamethylcyclotetrasiloxane was photocured on a glass plate. The crosslinked C-PDMS was subjected to a reaction with sodium diethyldithiocarbamate. The diethyldithiocarbamated PDMS was then photoirradiated in the presence of hydrophilic vinyl monomers such as 2-hydroxyethylmethacrylate and acrylamide to afford surface-grafted PDMS. Several vinyl monomers were found to graft onto the PDMS surface, as revealed by their attenuated total reflectance infrared and ESCA spectra. Hydrophilicity of the grafted PDMS surfaces was confirmed by the decrease in their water contact angle.

## INTRODUCTION

Surface modification of polydimethylsiloxane (abbreviated as PDMS, hereafter), typically, silicone rubbers, is of great interest, particularly, in medical application to endow biocompatibility and thromboresistance. It is certain that surface grafting of hydrophilic vinyl monomers is one of the most practical methods for surface modification.



Some literatures regarding surface grafting onto silicone rubbers by radiation technique have appeared.<sup>1-9</sup> The radiation grafting is of advantage to bind covalently hydrophilic monomers onto chemically inert surfaces without contamination by potentially hazardous catalyst fragments. However, a problem remains to use radiation machines. On the contrary, photografting was easy and convenient to modify a hydrophobic surface to hydrophilic one.<sup>10</sup>

In this work, surface photografting of hydrophilic vinyl monomers onto PDMS containing a photosensitive substituent, i.e., diethyldithiocarbamate (DDC), group has been studied. The DDC group was introduced into the PDMS side chain by a reaction of a chlorine-containing PDMS (C-PDMS), similar to the case of polyvinylchloride.<sup>11</sup> This was followed by photoirradiation of the diethyldithiocarbamated PDMS (DDC-PDMS) in the presence of vinyl monomers. Surface characterization of the grafted PDMS was also intensively studied.

## EXPERIMENTAL

### Materials

Chloromethylheptamethylcyclotetrasiloxane was prepared according to the procedure of Kribe and Elliott.<sup>12</sup> Sodium diethyldithiocarbamate trihydrate (special grade, Hayashi Pure Chemical Ind.) and triethylbenzylammonium chloride (Tokyo Chemical Ind.) were used as received. The following seven vinyl monomers were purified by distillation or recrystallization before use: acrylamide (Nakarai Chemicals), *N*-vinyl-2-pyrrolidone (Wako Pure Chemical Ind.), methacrylic acid (Nakarai Chemicals), sodium styrene sulfonate (Tokyo Chemical Ind.), 2-acrylamide-2-methylpropanesulfonic acid (Nitto Chemical Ind.), 2-hydroxyethyl methacrylate (Osaka Organic Chemical Ind.), 2-dimethylaminoethyl methacrylate (Tokyo Chemical Ind.). The solvents, methanol, acetone, and water, were also distilled.

### Preparation of Graft Copolymers

**Polymerization of Chloromethylheptamethylcyclotetrasiloxane.** A mixture of 23.2 g (70 mmol) of chloromethylheptamethylcyclotetrasiloxane and 0.025 g (0.15 mmol) of hexamethyldisiloxane was introduced in a dried 200 mL conical flask with a stopcock. To the mixture, 0.51 g of ion exchange resin, Amberlyst 15, was added as a polymerization catalyst. The mixture was stirred by means of a magnetic stirring bar. The solution viscosity was increased with time to reach a stage of hard stirring. However, the reaction was further continued by allowing it to stand. After 96 h, the viscous solution was dissolved in benzene, and filtered through filter paper (no. 1) to separate the catalyst. The benzene solution was concentrated with a vacuum evaporator, and poured into a large amount of methanol containing a small amount of ammonia to precipitate poly(chloromethylheptamethylcyclotetrasiloxane) (C-PDMS). The C-PDMS was then dried under vacuum at 60°C to constant weight. Yield 20.1 g (86.4%), intrinsic viscosity (in toluene, at 25°C) 0.39 dL/g.

**Photocrosslinking of C-PDMS.** On a slide glass (JIS 1 st grade, 76 mm × 26 mm × 1 mm), about 0.2 g of the C-PDMS was coated (area ca. 7.5 cm<sup>2</sup>, thickness ca. 0.2 mm). The slide glass was placed horizontally in a 500 mL flask

for photochemical reaction (Eikosha PIH-100). A 100-W high-pressure mercury lamp was vertically mounted in the flask in the locus of 2.5 cm distance from the slide glass. A stream of dry nitrogen was introduced through a gas inlet to sweep the flask for 10 min or more. The slide glass was then irradiated at 25°C for 10 min in an atmosphere of nitrogen. The C-PDMS was almost cured with a decrease of weight in ca. 0.3%.

**Reaction of Crosslinked C-PDMS with Sodium Diethyldithiocarbamate.** In a 300 mL separable flask with a reflux condenser, 2.27 g (10 mmol) of sodium diethyldithiocarbamate trihydrate, and 1.14 g (5 mmol) of benzyltriethylammonium chloride were added to 250 mL of *N,N*-dimethylformamide-tetrahydrofuran (4:1 in vol), and were almost dissolved. The crosslinked C-PDMS/slide glass was immersed in the solution. The reaction was carried out with magnetic stirring at 60°C. After 3 h, the slide glass was dried under vacuum and stored in a dark desiccator. The surface-diethyldithiocarbamated PDMS (DDC-PDMS) was thus obtained with a weight loss of 1–3%.

**Photografting of Hydrophilic Vinyl Monomers onto DDC-PDMS.** In the 500 mL photochemical reaction flask mentioned above, the DDC-PDMS/slide glass was placed horizontally, and a solution comprising 3.0 g of vinyl monomer and 80 mL of solvent was added to immerse the slide glass. The solvents used here were as follows: methanol, methanol–acetone (1:1 in vol), and acetone for 2-hydroxyethyl methacrylate (HEMA); methanol–water (1:1 in vol) and water for acrylamide (AAm); methanol for 2-acrylamide-2-methylpropanesulfonic acid (AMPS); methanol for 2-dimethylaminoethyl methacrylate (DMAM); methanol–water (1:1 in vol) for sodium styrene sulfonate (SSS); methanol for *N*-vinyl-2-pyrrolidone (NVP); methanol for methacrylic acid (MAA). Dry nitrogen gas was bubbled through a gas inlet for 10 min. Then, a 100-W high-pressure mercury lamp was irradiated at a 2.5 cm distance from the slide glass at 25°C with bubbling nitrogen gas and stirring by a magnetic bar. After a given time, the slide glass was immersed in water or methanol over night to extract the homopolymers. The slide glass was finally dried in a desiccator with P<sub>2</sub>O<sub>5</sub> in vacuum to constant weight. The weight increase due to grafting was observed as small, usually, lower than 2 mg/cm<sup>2</sup>.

### Surface Characterization

Attenuated total reflectance infrared (ATR-IR) spectra were measured with a Shimadzu Infrared Spectrophotometer IR-420 mounting an ATR equipment having a KRS-5 prism with both ends cut at 45°.

ESCA (electron spectroscopy for chemical analysis, or X-ray photoelectron spectroscopy) spectra were taken with a Shimadzu ESCA-750 using a magnesium anode (Mg K $\alpha$  radiation) connected with a data processor ESCAPAC-760 at room temperature and  $2 \times 10^{-7}$  Torr (6 kV, 30 mA). All aliphatic carbon 1s peaks were assigned a binding energy of 285.0 eV to correct for the energy shift resulting from electrification. Normalized ESCA peak intensity was obtained by dividing the integrated number of photoelectron counts in the peak area by a relative strength factor. The relative strength factors used here are carbon 1s 1.00, nitrogen 1s 1.50, oxygen 1s 2.90, and silicon 2s 0.86.<sup>13</sup>

Water contact angles of the graft copolymers were measured by sessile drop method at 23°C and 50 %RH, using an Erma contact anglemeter, Model II. All

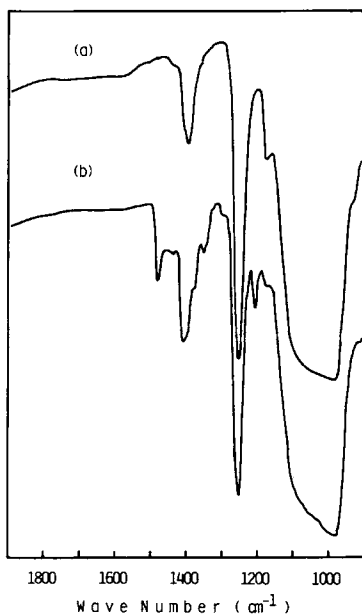


Fig. 1. ATR-IR spectra of crosslinked C-PDMS and DDC-PDMS: (a) crosslinked C-PDMS; (b) DDC-PDMS.

of the measurements were conducted within a few minutes after placing the drop on the graft copolymer/slide glass.

## RESULTS AND DISCUSSION

The DDC group is well known to be very photosensitive to dissociate homolytically to initiate radical polymerization.<sup>11,14</sup> Even for less reactive chlorine-containing polymers such as poly(vinyl chloride), the DDC group was readily introduced in the polymer as a dangling group, because of its high nucleophilicity. The chlorinated polydimethylsiloxane (C-PDMS) was also to react similarly with sodium diethyldithiocarbamate in an almost homogeneous state to form a photosensitive silicone.<sup>15</sup>

In the present work, the crosslinked C-PDMS film was first prepared on the slide glass by photoirradiation of poly(chloromethylheptamethyltetrasiloxane),<sup>16</sup> followed by the substitution reaction with sodium diethyldithiocarbamate in heterogeneous state. The DDC group was found to readily substitute for the chlorine to afford the DDC group-containing PDMS on the surface, although the chloromethyl group was less labile towards nucleophilic reagents.<sup>15</sup>

The photocrosslinking of C-PDMS was accompanied by homolytic scission of the C—Cl bond to implicitly lose the chlorine atom.<sup>16</sup> Therefore, the chlorine content of the crosslinked C-PDMS surface should be less than that of the starting C-PDMS. However, the existence of the surface chloromethyl group in the crosslinked C-PDMS was evidently confirmed by its ESCA spectra and its DDC substitution. When the crosslinking atmosphere was contaminated by air, the carbonyl group was formed as detected from its IR spectra. Conse-

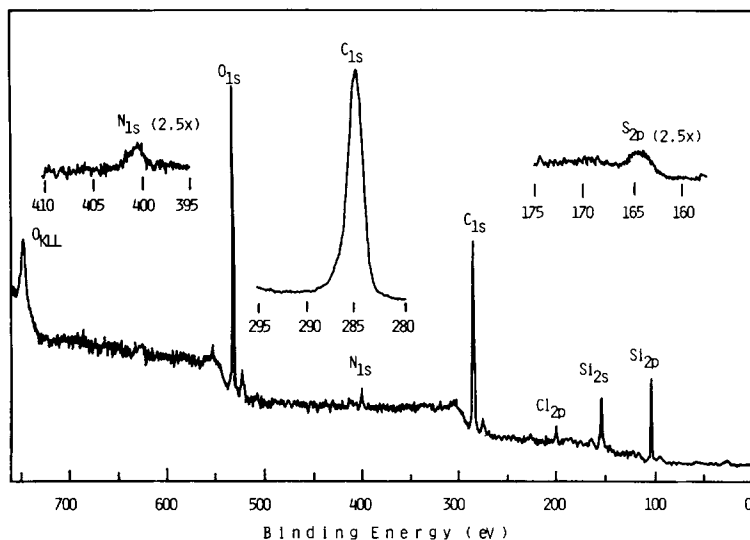


Fig. 2. ESCA spectra of DDC-PDMS.

quently, dry nitrogen gas was flowed in the flask before and during the reaction to avoid the surface oxidation.

Figure 1 shows ATR-IR spectra of the crosslinked C-PDMS and the DDC-PDMS. Characteristic but weak absorption bands attributable to the DDC group were observed at 1480, 1436, 1370, 1347, 1208, and 918  $\text{cm}^{-1}$  in the spectrum of DDC-PDMS. This suggests that the DDC substitution reaction on the C-PDMS surface readily proceeded in a DMF-THF mixture. This surface substitution was also demonstrated by the ESCA spectra for the DDC-PDMS shown in Figure 2.

Both the nitrogen 1s and the sulfur 2p peaks at 400.9 and 164.0 eV, respectively, were evidently attributed to those of the surface DDC group. The C<sub>1s</sub> peak was considered to be comprised of those of methyl (and ethyl), chloromethyl, and dithiocarbamate carbons around 285, 286 and 288 eV, respectively. This DDC group was very sensitive to photoirradiation to allow homolytic scission, probably, on both the S—C and C—N bonds, as shown by loss of the characteristic bands. The homolytic scission of this group also induced graft copolymerization onto the DDC-PDMS surface when in the presence of vinyl monomers, as anticipated. In this work, some vinyl monomers, particularly, hydrophilic ones, were examined for the graft copolymerization, in which the DDC-PDMS/glass slide immersed in a monomer-solvent mixture was photoirradiated in a nitrogen atmosphere. Only rarely, crack formation and/or peeling of the DDC-PDMS substrate from the slide glass were seen depending on the kind of solvents used.

After photoirradiation, their homopolymers were carefully removed by solvent extraction. Several graft copolymer/slide glasses were immersed in boiling water for 1 h and then subjected to the measurements again to confirm the surface grafting. Most of the ATR-IR absorbance, ESCA relative peak intensity, and water contact angle were varied much less after boiling water extraction than before, indicating progress of surface grafting. Degree of grafting was dependent on, mainly, light distance, surface concentration of the DDC group, monomer

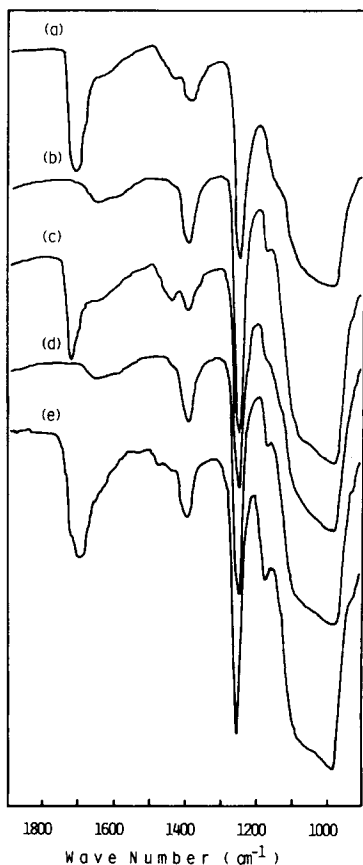


Fig. 3. ATR-IR spectra of surface-grafted C-PDMS: (a) polyHEMA; (b) polyAAm; (c) polyDMAM; (d) polyNVP; (e) polyMAA.

concentration, and kinds of monomers and solvents. In this work, however, most of the reaction conditions were fixed to study grafting activity of hydrophilic vinyl monomers onto the DDC-PDMS surface. In the present grafting conditions, usually, the degree of grafting was too low to estimate by weight, lower than 2 mg/cm<sup>2</sup>. Therefore, the ATR-IR, ESCA spectra, and water contact angle of the graft copolymers were employed to estimate it here.

Figure 3 shows ATR-IR spectra of surface-grafted C-PDMS.

Several characteristic bands attributed to the grafts appeared in addition to those of the trunk polymer, i.e., C-PDMS. For five surface-grafted C-PDMS, typical additional characteristic bands were as follows: 3310 ( $\nu_{\text{OH}}$ ), 1716 ( $\nu_{\text{C=O}}$ ), 1435 ( $\delta_{\text{CH}}$ ) for polyHEMA graft; ca. 3600 ( $\nu_{\text{NH}}$ ), 1650 ( $\nu_{\text{C=O}}$ ) for polyAAm graft; 1718 ( $\nu_{\text{C=O}}$ ), 1460 ( $\delta_{\text{CH}}$ ) for polyDMAM; ca. 3300 ( $\nu_{\text{OH}}$ ), 1652 ( $\nu_{\text{C=O}}$ ) for polyNVP graft; ca. 3400 ( $\nu_{\text{OH}}$ ), 1698 ( $\nu_{\text{C=O}}$ ), 1470 cm<sup>-1</sup> ( $\delta_{\text{CH}}$ ) for polyMAA graft. In contrast, characteristic absorption bands of polyAMPS and polySSS grafts were little detected.

Figure 4 shows variation of carbonyl absorbance in the graft copolymers relative to  $\delta_{\text{Si-CH}_3}$  absorbance at 1250 cm<sup>-1</sup> against grafting time.

ATR-IR absorbance is regarded as a measure for total amount of the graft

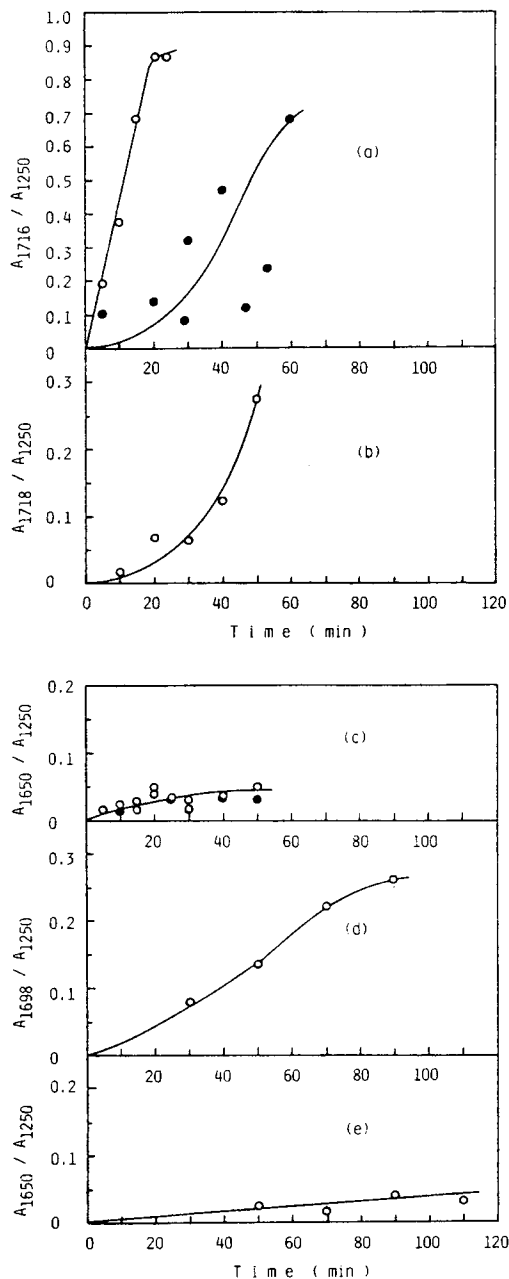


Fig. 4. Carbonyl absorbance of surface-grafted C-PDMS vs. grafting time: (a) polyHEMA, (O) in methanol-acetone, (●) in methanol; (b) polyDMAM; (c) polyAAm, (●) in methanol-water, (O) in water; (d) polyMAA; (e) polyNVP.

covering the C-PDMS substrate, while ESCA peak intensity can be taken as a measure for surface amount of the graft in a depth of less than 50 Å. Mostly, the relative carbonyl absorbance was found to increase with the grafting time. In the cases of polyAAm and polyMAA grafts, the grafting was accompanied by

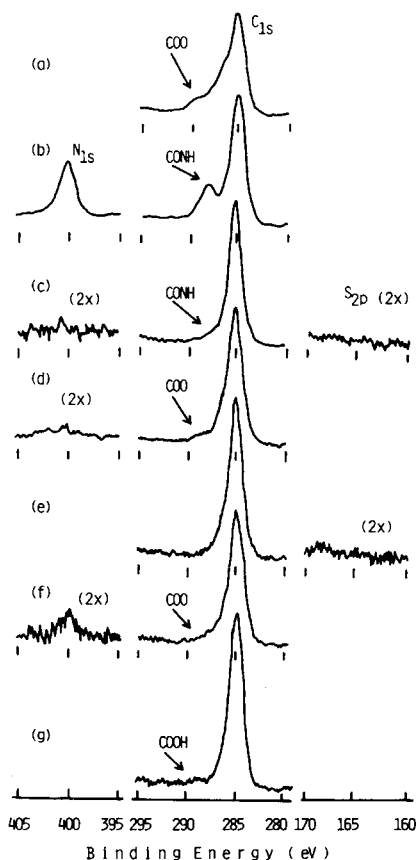


Fig. 5. ESCA spectra of surface-grafted C-PDMS: (a) polyHEMA; (b) polyAAm; (c) polyAMPS; (d) polyDMAM; (e) polySSS; (f) polyNVP; (g) polyMAA.

gel formation, partly allowing scattering of grafting yield. On the other hand, the grafting yield in the case of polyHEMA graft was relatively scattered with time, although gel was not visually observed in the liquid phase. It is almost certain that both SSS and AMPS were also able to graft onto the DDC-PDMS, as shown by ESCA spectra and water contact angles.

In Figure 5, ESCA spectra are illustrated for N<sub>1s</sub>, C<sub>1s</sub>, and S<sub>2p</sub> peaks of those graft copolymers. The carbonyl carbon C<sub>1s</sub> peaks for polyHEMA, polyAAm, polyDMAM, polyNVP, and polyMAA were detected, mostly, as shoulders at higher energies than those of the main aliphatic carbon peaks at 285 eV. The N<sub>1s</sub> peaks were also observed for the polyAAm, polyAMPS, polyDMAM, and polyNVP grafts. Furthermore, very weak S<sub>2p</sub> peaks of both polySSS and polyAMPS grafts could be detected. Relative peak intensities of C<sub>1s</sub>, N<sub>1s</sub>, and S<sub>2p</sub> were used as a measure for degree of surface grafting and plotted against grafting time. The surface of the trunk polymer, C-PDMS, was gradually covered by the graft with the loss of the DDC group. Accordingly, the Si<sub>2s</sub> peak intensity of C-PDMS, which decreased with the progress of grafting, was used here as a reference.

Figure 6 shows plots of ESCA relative peak intensity versus grafting time.



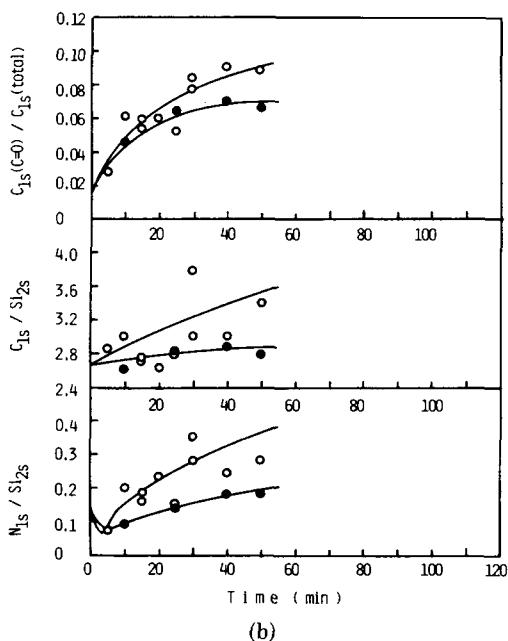
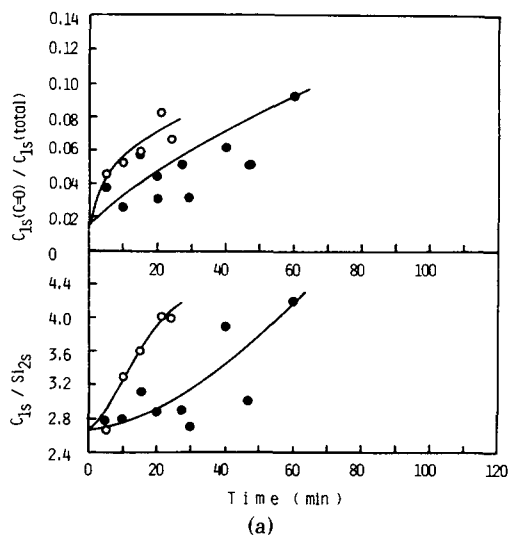
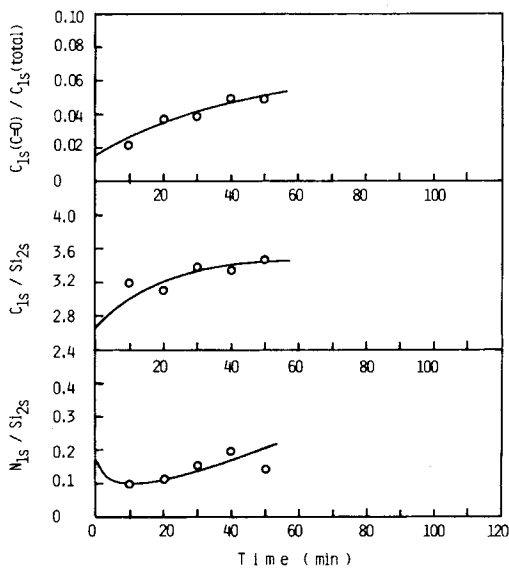
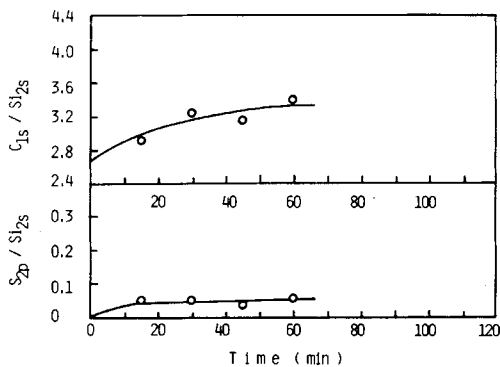


Fig. 6. ESCA relative peak intensity of surface-grafted C-PDMS vs. grafting time: (a) polyHEMA, (O) in methanol-acetone, (●) in methanol; (b) polyAAm, (●) in methanol-water, (O) in water; (c) polyDMAM; (d) polySSS; (e) polyNVP; (f) polyMAA.

All of the grafts contained more carbon than the trunk polymer, C-PDMS, therefore increasing the surface abundance of carbon in the graft copolymer, represented by  $C_{1s}/Si_{2s}$ , with grafting. Interestingly, the surface abundance of nitrogen atoms for polyAAm, polyDMAM, and polyNVP grafts were found to first decrease and then increase gradually with grafting time, indicating simultaneous occurrence of the DDC group loss and surface covering of graft. In



(c)

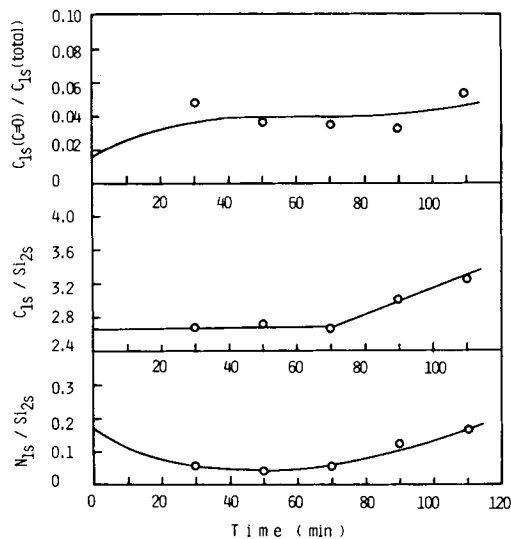


(d)

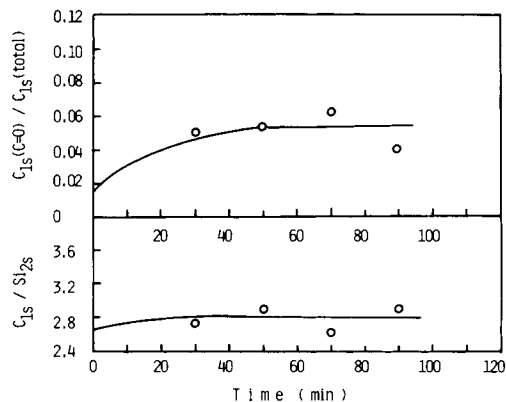
Fig. 6. (Continued from the previous page.)

the case of AMPS, the grafting proceeded very slowly, as revealed by increase of the relative intensity,  $C_{1s}/Si_{2s}$ , and a little appearance of  $N_{1s}$  and  $S_{2p}$  peaks.

Ratner et al.<sup>7</sup> reported that the surface composition of radiation-grafted silicone rubbers differed in the dry state from that in the hydrated one, and the surface abundance of both polyHEMA and polyAAm grafts was significantly decreased upon dehydration, as evidenced by their ESCA spectra. They explained this phenomena in terms of graft migration effect. In our ESCA measurements, the dry grafted C-PDMS samples were used after being stored in a desiccator for more than 2 days. There was also a possibility of graft migration or penetration into the C-PDMS substrate. It probably depends mainly on the permeability of monomers and solvents to the C-PDMS. However, argon ion etching of the HEMA-grafted C-PDMS to a depth of about 500 Å resulted in a monotonous decrease in the relative peak intensity of ester carbon  $C_{1s}$ . Furthermore, a relationship between ATR-IR absorbance and ESCA  $C_{1s}$  relative



(e)



(f)

Fig. 6. (Continued from the previous page.)

peak intensity of the amide group for the AAm-grafted C-PDMS significantly differed from those of the other graft copolymers. Namely, the polyAAm graft was localized on the C-PDMS surface, because the ESCA carbonyl  $C_{1s}$  relative peak intensity was appreciably high in spite of ATR-IR carbonyl absorbance. This data might lead to a conclusion opposite to those of Ratner et al. However, more detailed measurements is undoubtedly necessary to afford any other comment on the graft migration.

Water contact angle of the grafted C-PDMS surface is regarded as a useful measure of hydrophilicity. Both the DDC-PDMS and C-PDMS had contact angle above  $90^\circ$  toward water. Figure 7 shows variation of water contact angles for the grafted C-PDMS during grafting. It was seen that the water contact angles decreased with surface-grafting of hydrophilic monomers. The rate of contact angle lowering depended on the monomers and solvents. The graft copolymers prepared from HEMA in acetone, AAm in water, SSS in metha-

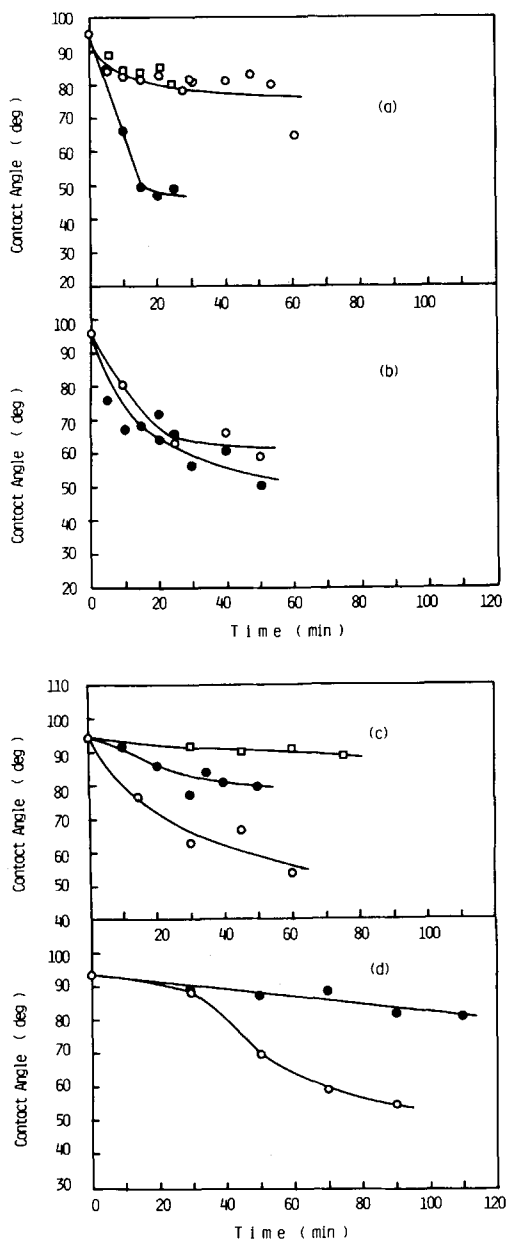


Fig. 7. Water contact angle vs. grafting time: (a) polyHEMA, (O) in methanol; ( $\square$ ) in methanol-acetone; ( $\bullet$ ) in acetone; (b) polyAAM, (O) in methanol-water; ( $\bullet$ ) in water; (c) ( $\square$ ) polyAMPS, ( $\bullet$ ) polyDMAM, (O) polySSS; (d) ( $\bullet$ ) polyNVP, (O) polyMAA.

nol-water, and MAA in methanol exhibited significant decrease in the contact angles. Especially, in the case of the SSS graft, the contact angles decreased to a much lower degree because of ionic character of  $\text{SO}_3\text{Na}$  group, in spite of lower surface abundance. It was also noted that the solvents with higher solubility to the C-PDMS caused higher degree of grafting.

Thus, the C-PDMS was readily converted to the DDC-PDMS, followed by the surface grafting of hydrophilic vinyl monomers. Several C-PDMS grafted with HEMA, AAm, SSS, and MAA were found to have hydrophilicity, necessary for medical application.

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