

# Preparation of Siloxane-Like Films by Glow Discharge Polymerization

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## Synopsis

Glow discharge polymerizations of tetramethoxysilane (TMOS), tetramethylsilane/oxygen mixture ( $\frac{1}{2}$  molar ratio) (TMS/O<sub>2</sub>), hexamethyldisiloxane (HMDSO), and tetramethyldisiloxane (TMDSO) were carried out for the preparation of thin, polymeric films with siloxane structures. The chemical composition of the formed polymers was examined by elemental analysis, infrared spectroscopy, and electron spectroscopy for chemical analysis (ESCA) in connection with polymerization conditions, especially, a level of the radiofrequency (rf) input power per mass of the monomers (*W/FM* value). The polymers prepared from HMDSO at fairly low *W/FM* values resembled in chemical composition the conventionally polymerized polydimethylsiloxane. The surface properties of the formed polymers also were evaluated by the measurement of surface energy.

## INTRODUCTION

Glow discharge polymerization is a unique polymer-forming process, whereby polymers can be obtained frequently as thin films from almost any organic compounds containing saturated hydrocarbons and organometallics. Reactions occurring in glow discharge are complex, and therefore the polymer-forming process has not been resolved completely. Recently, many investigators have taken interest in the reaction mechanism of the polymer-forming process, and proposed some tentative mechanisms, ionic<sup>1,2</sup> or radical.<sup>3,4</sup> One of these investigators, Yasuda,<sup>5</sup> has shown an aspect called atomic polymerization which is essentially different from those proposed by other investigators. Starting materials introduced into glow discharge are broken down into activated, small molecules, and in the extreme to atoms by the action of electrons, ions, and radicals. These fragments follow recombination with accompanying rearrangements, stepwise, to grow large molecules, and finally polymers deposit. Therefore, we believe that all the elements present in glow discharge could participate in the formation of polymers, and that the polymers would contain all these elements. Furthermore, chemical composition and physical properties of the polymers may be determined by the extent of the fragmentation of the starting materials, which is closely related to the level of the rf input power. If the fragmentation occurred vigorously, the formed polymers would be influenced by the kind of constituent atoms rather than the nature of the starting compounds; while, if mild, the formed polymers would be influenced by the nature of the starting compounds. Consequently, this aspect emphasizes the importance of the extent to which the starting molecules were broken down in a glow discharge state.

The aim of this study is to prepare thin films with siloxane structure by glow discharge polymerization technique. Monomers chosen for this aim are tetramethoxysilane (TMOS), tetramethylsilane/oxygen mixture ( $\frac{1}{2}$  molar ratio) (TMS/O<sub>2</sub>), hexamethyldisiloxane (HMDSO), and tetramethyldisiloxane (TMDSO). TMOS and TMS/O<sub>2</sub> are identical in atomic composition (C:H:O:Si = 4:12:4:1) but different in chemical nature. Both HMDSO and TMDSO have identical Si—O—Si structure but TMDSO contains Si—H bonds (71 kcal/mol) that is of weaker strength than Si—C bonds (104 kcal/mol). Glow discharge polymerizations of the four monomers are carried out, and the chemical composition of the formed polymers is discussed in connection with polymerization conditions, especially, a level of the rf input power.

## EXPERIMENTAL

### Chemicals

TMS (more than 98%), TMOS (more than 98%), HMDSO (more than 99%) (Tokyo Kasei Kogyo Co. Ltd.), and TMDSO (more than 98%) (Petrarch System Inc.) were used as monomers for the glow discharge polymerization without further purification.

### Glow Discharge Polymerization

The reaction system in this study was the reaction chamber (35 mm i.d., 400 mm long) made of Pyrex glass fitted with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for inductive coupling of a 13.56-MHz frequency source, of which the relative arrangement is illustrated (Fig. 1).

Experimental procedures for the glow discharge polymerization are not essentially different from those reported elsewhere.<sup>6</sup> A glass plate (35 × 240 × 1 mm) was positioned in the reaction chamber, and the system was evacuated to 0.13 Pa using a diffusion and a rotary pump. Argon gas was introduced into the reaction chamber, to eliminate water on surfaces of the glass plate. The surfaces were exposed to argon plasma for 15 min. Again the system was evacuated to 0.13 Pa, and the monomer gas stored in a reservoir was injected into the reaction chamber at a given flow rate adjusted by a metering valve at a pressure of 1.3 Pa. The flow rate of the

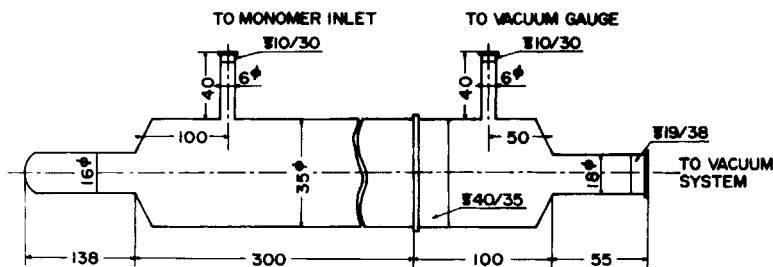


Fig. 1. Schematic presentation of reaction chamber; unit, mm.

monomer gas was determined from pressure increase according to the ideal gas equation when the outlet valve of the reaction chamber was closed. The rf power (13.56 MHz) was turned on, and the glow discharge polymerization was initiated and continued at a level of 25 W for 1 h. Polymer films deposited on the glass plate were provided for elemental analysis, infrared spectroscopy, and ESCA.

### Elemental Analysis

The polymers deposited on the glass plates and scraped off with a knife were provided for C, H, N, and Si analysis. The C, H, and N contents of the polymers deposited were determined using a CHN corder MT-2 (Yanagimoto Co.). The Si content was determined by gravimetry that the weighed sample was combusted in oxygen and further heated at 850°C until a constant weight of SiO<sub>2</sub> was obtained.

### Infrared Spectra

The polymers scraped off were analyzed as KBr disks. The spectrometer used was a Nihon Bunko spectrometer A-3.

### ESCA Spectra

The polymer films (approximately 0.1 μm thick determined by interferometry) deposited on silicon wafers (5 × 5 mm) were analyzed for ESCA spectra. The spectra were recorded with a Shimadzu electron spectrometer ESCA 750 using MgK<sub>α</sub> exciting radiation. Typical operating conditions were x-ray gun, 8 kV, 30 mA; the pressure in the sample chamber, 6.5 × 10<sup>-6</sup> Pa. The Au core level at 84.0 eV was temporarily used for calibration of the energy scale.

The complex spectra of the C<sub>1s</sub> core level were resolved into three Gaussian curves by variation of three parameters, i.e., the position and the height of the peak, and the full width at half-maximum (FWHM) using a Shimadzu data system ESCAPAC 760. The FWHM value of all the resolved curves was less than 1.8 eV.

### Surface Energy

Polymer films which were deposited on glass plates were used for contact angle measurements against water, glycerol, formamide, diiodomethane, and tricresyl phosphate. A Kyowa Kagaku contact angle meter CA-1 was used. The contact angle data were analyzed to estimate a dispersive contribution,  $\gamma_s^d$ , and a polar contribution,  $\gamma_s^p$ , according to Kaelble's method.<sup>7</sup>

## RESULTS AND DISCUSSION

Glow discharge polymerizations of TMOS, TMS/O<sub>2</sub>, HMDSO, and TMDSO yielded colorless, transparent polymer films, which were insoluble in common organic solvents such as alcohols, carbon tetrachloride, and acetone.

Figure 2 shows the polymer deposition rate as functions of the monomers and their flow rate. The flow rate in this figure is graduated in units of

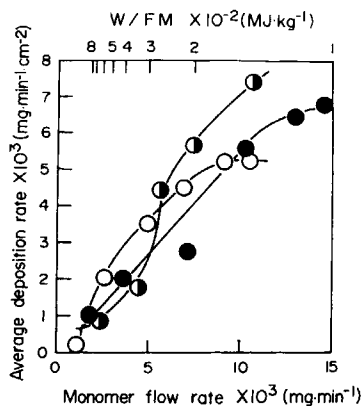


Fig. 2. Deposition rate as functions of monomers and their flow rate. (○) TMOS, (●) HMDSO, (◐) TMDSO.

mg/min to collect differences in molecular weight among the used monomers. The flow rate (mg/min), when the glow discharge polymerizations were performed at a constant level of rf power, can be directly related to the  $W/FM$  value that means apparent rf energy input per mass of the monomer,<sup>5</sup> where  $W$  is the rf power,  $F$  and  $M$  are the flow rate and the molecular weight of the monomer, respectively. All the polymer deposition rates (Fig. 2), increased with increasing flow rate; in other words, with decreasing  $W/FM$  value, and then at fairly low  $W/FM$  values there appeared substantial differences in the deposition rate among the three monomer systems. In polymerizations of  $W/FM$  values of less than approximately 250 MJ/kg TMDSO deposited polymer at a faster rate than did TMOS and HMDSO. Such difference in the deposition rate may be due to weakness in the bond strength of Si—H bonds of TMDSO. The TMS/ $O_2$  mixture (½ molar ratio) deposited polymers at very slow deposition rate, for example, the deposition rate was 2.73  $\mu\text{g}/\text{cm}^2$  at a  $W/FM$  value of 140 MJ/kg compared with the rate of 5.2  $\mu\text{g}/\text{cm}^2$  at 140 MJ/kg in the TMOS system. This large difference in the polymer deposition rate between the four monomers, which became predominant at fairly low  $W/FM$  values seems to suggest variation in the chemical composition of the formed polymers.

TABLE I  
Elemental Composition of Polymers

Monomer	$W/FM$ (MJ/kg)	Elemental composition <sup>a</sup> (wt %)					Empirical formula of polymers
		C	H	N	O	Si	
TMOS	140	19.7	4.6	0	47.0	28.7	$C_{1.6}H_{4.4}O_{3.0}Si$
	550	24.8	4.3	0.8	44.8	25.3	$C_{2.3}H_{4.8}N_{0.07}O_{3.1}Si$
TMS/ $O_2$	140	0.9	0.7	0.1	56.3	42.0	$C_{0.05}H_{0.5}O_{2.4}Si$
HMDSO	120	33.2	8.8	0	32.8	25.2	$C_{3.1}H_{9.8}O_{2.3}Si$
	830	36.3	6.8	0.5	23.7	32.7	$C_{2.6}H_{5.9}O_{1.3}Si$
TMDSO	140	24.7	6.9	0.4	33.2	34.8	$C_{1.7}H_{5.6}O_{1.7}Si$
	690	30.5	6.4	3.3	19.8	40.0	$C_{1.8}H_{4.5}N_{0.2}O_{0.9}Si$

<sup>a</sup> Average of five samples.

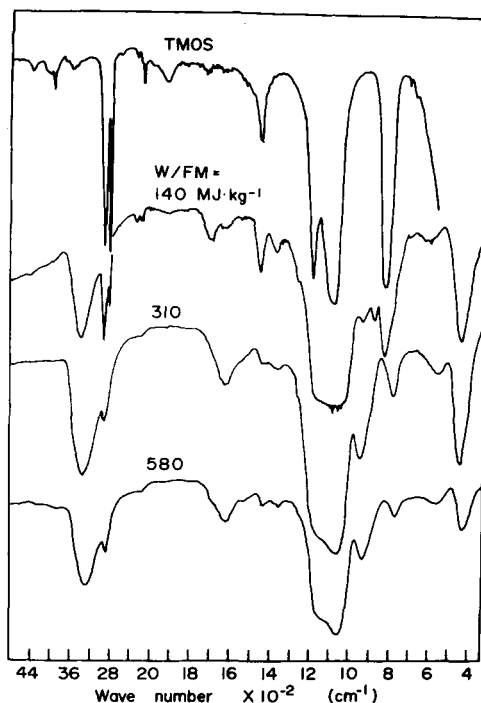


Fig. 3. Infrared spectra of polymers prepared from TMOS as a function of the  $W/FM$  values.

### Elemental Composition and Infrared Spectra of Polymers

Table I shows the elemental composition of polymers formed from TMOS, TMS/O<sub>2</sub>, HMDSO, and TMDSO at high and low  $W/FM$  values. The elemental composition represented as atomic ratio in Table I strongly depended on both the nature of the used monomers and the magnitude of the  $W/FM$  values. The polymers from HMDSO possessed the highest C/Si and H/Si ratios; the polymers from TMOS and TMDSO possessed the middle C/Si ratio; and the polymers from TMS/O<sub>2</sub> possessed the lowest C/Si and H/Si ratios. The magnitude of the  $W/FM$  values also showed influences on the elemental compositions of the formed polymers. For TMOS the increase in the  $W/FM$  values resulted in increasing the carbon and the hydrogen content of polymers formed. And in contrast, for HMDSO and TMDSO the

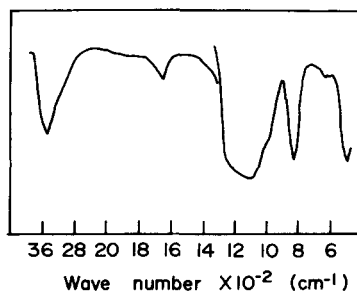


Fig. 4. Infrared spectra of polymers prepared from TMS/O<sub>2</sub> mixture at a  $W/FM$  value of 140 MJ/kg.

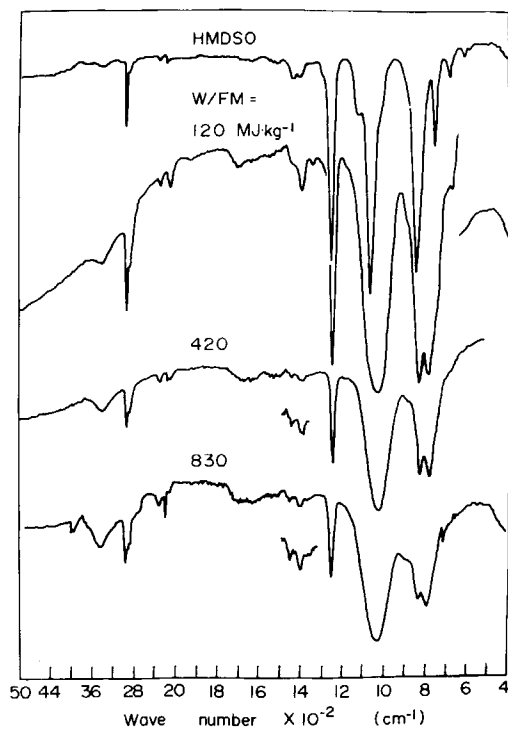


Fig. 5. Infrared spectra of polymers prepared from HMDSO as a function of the  $W/FM$  values.

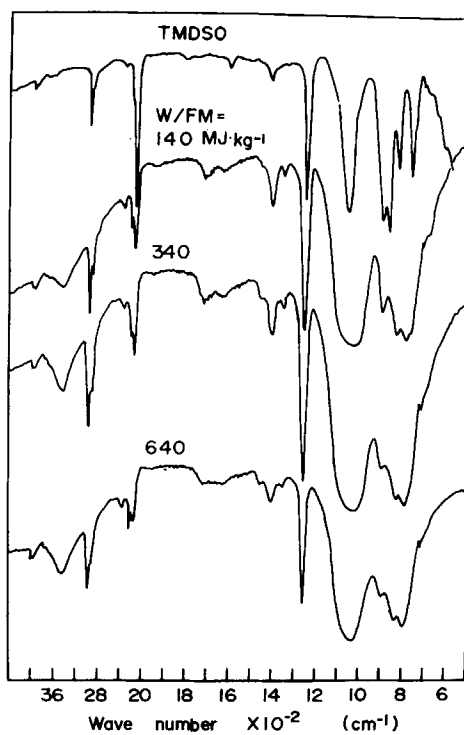


Fig. 6. Infrared spectra of polymers prepared from TMDSO as a function of the  $W/FM$  values.

increase in the  $W/FM$  value resulted in decreasing the carbon and the hydrogen content of formed polymers.

Figures 3–6 show infrared spectra of the polymers formed from the four monomers. These spectra were similar but different in detailed absorptions. Polymers formed from TMOS (Fig. 3) showed sharp absorptions at 2950 ( $\text{CH}_3$ ), 2850 ( $\text{CH}_3\text{O}$ ), 1700 ( $\text{C—O}$ ), 1640 (adsorbed  $\text{H}_2\text{O}$ ), 1460, 1380 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 1270 ( $\text{Si—CH}_3$ ), 950, 890 ( $\text{Si—CH}_3$ ,  $\text{Si—CH}_2$ ), 840 ( $\text{Si—OCH}_3$ ), and  $460\text{ cm}^{-1}$  ( $\text{Si—O—Si}$ ,  $\text{Si—O—C}$ ); and a large but broad absorption at  $1200\text{--}1050\text{ cm}^{-1}$  ( $\text{Si—O—Si}$ ,  $\text{Si—O—C}$ ). The absorptions due to  $\text{CH}_3$  and  $\text{CH}_2$  groups, especially  $\text{CH}_3\text{O}$  groups, became dull with increasing the  $W/FM$  values. Compared with that of TMOS, monomer absorptions at 2850, 1200, and  $840\text{ cm}^{-1}$ , due to  $\text{CH}_3\text{O}$  groups, were weaker for the polymers, which indicates that the predominant degradation of  $\text{CH}_3\text{O}$  groups occurred to form the polymers.

The polymers formed from  $\text{TMS/O}_2$  showed spectra different from those of the former (Fig. 4). The spectra can be characterized by strong absorptions due to  $\text{Si—O—C}$  and  $\text{Si—O—Si}$  groups and weak absorptions due to  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{Si—CH}_3$  groups, which indicates that predominant degradation of  $\text{CH}_3$  groups occurred to form the polymers. These differences in the chemical composition between the two polymers prepared from TMOS and  $\text{TMS/O}_2$ , which are composed of the identical atomic ratios ( $\text{C:H:O:Si} = 4:12:4:1$ ), may be differences in the nature of the used starting materials.

The polymers from HMDSO showed simple spectra on which absorptions appeared at 2960, 2900 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 1400 ( $\text{CH}$ ), 1260 ( $\text{Si—CH}_3$ ), 1040 ( $\text{Si—O—Si}$ ), 840, 790 ( $\text{Si—C}$ ), and  $680\text{ cm}^{-1}$  ( $\text{Si—CH}_3$ ) (Fig. 5). The absorptions at 2960, 2900, and  $1400\text{ cm}^{-1}$ , due to  $\text{CH}_3$  and  $\text{CH}_2$  groups became weak at high  $W/FM$  values. These spectra are similar to that for polydimethylsiloxane polymerized conventionally.<sup>8</sup>

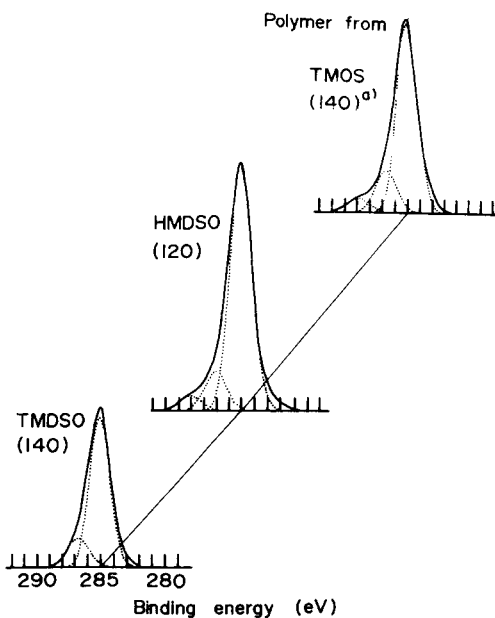


Fig. 7. ESCA ( $\text{C}_{1s}$ ) spectra of polymers prepared from TMOS (at a  $W/FM$  value of 140 MJ/kg), HMDSO (at a  $W/FM$  value of 120 MJ/kg) and TMDSO (at a  $W/FM$  value of 140 MJ/kg).

TABLE II  
C<sub>1s</sub> and Si<sub>2p</sub> Core Level Spectra of Polymers Prepared from TMOS, TMS/O<sub>2</sub>, HMDSO, and TMDSO

Monomer	W/FM (MJ/ kg)	Core Level	Component No. 1 centered at(eV)	Component No. 2 centered at(eV)	Component No. 3 centered at(eV)	Component No. 4 centered at(eV)	Component No. 5 centered at(eV)
TMOS	140	C <sub>1s</sub>	285.0 (76%) <sup>a</sup>	286.7 (17%)	289.0 (7%)		
HMDSO	120	C <sub>1s</sub>	285.0 (82%)	287.0 (13%)	288.9 (5%)		
TMDSO	140	C <sub>1s</sub>	285.0 (82%)	286.6 (28%)			
TMOS	140	Si <sub>2p</sub>					103.3
HMDSO	120	Si <sub>2p</sub>			101.8		
TMDSO	140	Si <sub>2p</sub>	99.5	100.9	101.4	102.1	103.3

<sup>a</sup> Relative peak area.



The polymers from TMDSO showed similar spectra to those from HMDSO (Fig. 6). On the spectra there appeared absorptions at 2960, 2900 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 2130 ( $\text{Si-H}$ ), 1410 ( $\text{CH}$ ), 1355 ( $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ ),<sup>9</sup> 1260 ( $\text{Si-CH}_3$ ), 1040 ( $\text{Si-O-Si}$ ), 900 ( $\text{Si-H}$ ), 840, 790 ( $\text{Si-C}$ ), and  $720\text{ cm}^{-1}$ . These polymers are distinguished from those prepared from HMDSO by the presence of  $\text{Si-H}$  and  $\text{Si-CH}_2\text{-CH}_2\text{-Si}$  groups.

### ESCA Spectra

Although qualitative differences in the chemical composition among the four polymers could be elucidated by infrared spectroscopy, detailed chemical compositions were examined by ESCA. Specimens chosen for the examination were the polymers prepared from HMDSO, TMDSO, and TMOS at lower  $W/FM$  values of less than 150 MJ/Kg. Figure 7 shows the  $\text{C}_{1s}$  core level spectra for the three polymers. All the  $\text{C}_{1s}$  spectra, (Fig. 7), were a single peak in the range from 282 to 292 eV, and their FWHM values were more than 2 eV. The necessity for at least two curves is obvious to deconvolute these spectra. The third curve was determined from the difference between the observed curve and the sum of the first and the second component. According to this curve-fitting procedure, each of the  $\text{C}_{1s}$  spectra could be fitted by two or three Gaussian curves (dotted line, Fig. 7). The peak position and the relative peak area for each component are listed (Table II). For the polymers from HMDSO the three resolved components centered at 285.0, 287.0, and 288.9 eV could be assigned to aliphatic carbon and  $\text{C-Si}$ ,  $\text{C-O}$ , and  $\text{C=O}$  groups,<sup>10-14</sup> respectively. Likewise, the two components for the polymers from TMDSO could be assigned to aliphatic carbon and  $\text{C-Si}$  and  $\text{C-O}$  groups. And the three components for the polymers from TMOS corresponded to aliphatic carbon and  $\text{C-Si}$ ,  $\text{C-O}$ , and  $\text{C=O}$  groups. These  $\text{C}_{1s}$  features show all the polymers were oxidized, and the concentration of the oxidized carbon atoms reached approximately 20 mol %. Such oxidation indicates that the bond rupture between  $\text{C-H}$  bonds of HMDSO, TMDSO, and TMOS may accompany the polymer-forming process.

Consequently, there is not a significant difference in the  $\text{C}_{1s}$  feature among the three polymers, although the polymers from TMDSO contained no  $\text{C=O}$  groups and the polymers from TMOS possessed the oxidized component in slightly higher concentration than the other polymers.

The  $\text{Si}_{2p}$  core level spectra, (Fig. 8), were significantly different among the three polymers. For the two polymers from TMOS and HMDSO, the  $\text{Si}_{2p}$  spectra were composed of a monotone peak positioned at 103.3 and 101.8, respectively, which could be assigned to  $\text{SiO}_2$  for the polymers from TMOS and  $\text{Si-(O-C)}_x$  or  $\text{Si-(O-Si)}_x$ ,  $x = 1$  or 2 for those from HMDSO.<sup>15,16</sup> The  $\text{Si}_{2p}$  spectrum for the polymers from TMDSO was too complex to be resolved, but many peaks could be observed at 99.5 ( $\text{Si-Si}$ ), 100.9 ( $\text{Si-C}$ ), and 101.4 [ $\text{Si-(O-C)}_x$  or  $\text{Si-(O-Si)}_x$ ,  $x = 1$  or 2]. This  $\text{Si}_{2p}$  feature shows the polymers from TMDSO were composed not only of  $(\text{CH}_3)_2\text{Si-O}$  units, but also of  $\text{Si-Si}$  and  $\text{Si-C}$  units. Therefore, it can be concluded that the polymers from HMDSO have chemical compositions resembling polydimethylsiloxane.

Finally, the surface energies were determined to compare surface properties of polymers prepared by glow discharge polymerization with conven-

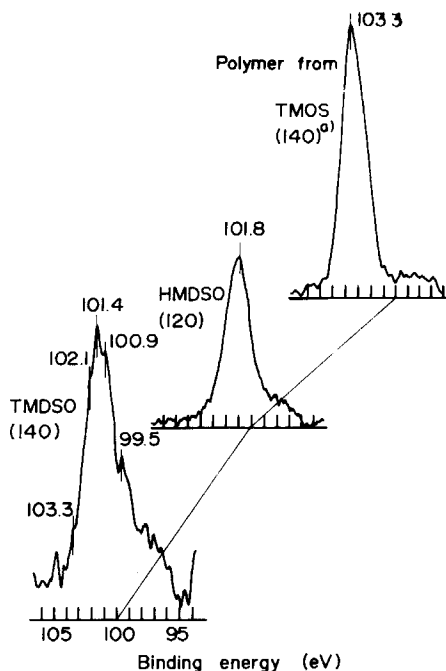


Fig. 8. ESCA ( $\text{Si}_{2p}$ ) spectra of polymers prepared from TMOS (at a  $W/FM$  value of 140 MJ/kg), HMDSO (at a  $W/FM$  value of 120 MJ/kg) and TMDSO (at a  $W/FM$  value of 140 MJ/kg).

tionally polymerized polydimethylsiloxanes (Table III). The polymers polymerized at a  $W/FM$  value of 120 MJ/kg showed a surface energy of 19.0 dyn/cm which corresponds to that of conventionally polymerized polydimethylsiloxane (19.8 dyn/cm).<sup>17</sup> The other polymers from TMOS and TMDSO showed higher surface energies. This evidence supports our conclusion that the polymers prepared from HMDSO are analogous to conventionally polymerized polydimethylsiloxane. The tendency of the surface energies in all the monomer systems to become large as the  $W/FM$  values

TABLE III  
Surface Energy of Polymers Prepared from TMOS, TMS/ $\text{O}_2$ , HMDSO, and TMDSO

Monomer	$W/FM$ (MJ/kg)	Surface energy (dyn/cm)		
		$\gamma_s$	$\gamma_s^d$ <sup>a</sup>	$\gamma_s^p$ <sup>b</sup>
TMOS	140	31.8	25.0	6.8
	220	33.8	26.0	7.8
	560	45.6	29.0	16.4
TMS/ $\text{O}_2$	140	54.8	27.9	26.9
	HMDSO	120	19.0	19.0
TMDSO	206	20.7	20.7	0
	825	28.0	26.6	1.4
	140	22.1	22.0	0.1
	270	24.7	24.6	0.1
Polydimethylsiloxane	690	27.3	26.8	0.5
		19.8		

<sup>a</sup> Dispersive contribution.

<sup>b</sup> Polar contribution.

increased may be explained by changes in chemical composition of the formed polymers as described in former sections.

### CONCLUSION

The preparation of polysiloxane-like polymer films by glow discharge polymerization was investigated using TMOS, TMS/O<sub>2</sub>, HMDSO, and TMDSO as monomers.

(i) The operating conditions for glow discharge strongly influenced the chemical composition of the formed polymers. The operation at fairly low  $W/FM$  values is preferable for the preparation of polymer films.

(ii) The nature of the monomer influenced the chemical composition of the polymer. Oxygen must be excluded because heavy degradation occurs during polymerization.

(iii) HMDSO is the most suitable monomer of the four studied. The polymers formed from HMDSO are analogous to polydimethylsiloxane and show low surface energies comparable to polydimethylsiloxane.

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### References

1. A. R. Denaro, P. A. Owens, and A. Crawshaw, *Eur. Polym. J.*, **4**, 93 (1968).
2. A. R. Westwood, *Eur. Polym. J.*, **7**, 363 (1971).
3. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.*, **16**, 2317 (1972).
4. H. Kobayashi, A. T. Bell, and M. Shen, *Macromolecules*, **7**, 277 (1974).
5. H. Yasuda, *Thin Film Process*, J. L. Vossen and W. Kern, Ed., Academic, New York (1978), p. 361.
6. N. Inagaki and A. Kishi, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 1847 (1983).
7. D. H. Kaelble, *Physical Chemistry of Adhesion*, Wiley-Interscience, New York, 1971.
8. D. O. Hummel, *Infrared Spectra of Polymers in the Medium and Long Wavelength Regions*, Wiley-Interscience, New York, 1966, p. 70.
9. A. M. Wrobel, J. E. Klemberg, M. R. Wertheimer, and H. P. Schreiber, *J. Macromol. Sci. Chem.*, **15**, 197 (1981).
10. U. Gelis, P. F. Heden, J. Hedman, B. J. Lindberg, R. Mann, R. Nordberg, C. Nording, and K. Seigbalm, *Phys. Scr.*, **2**, 70 (1970).
11. W. B. Perry and W. L. Jolly, *Inorg. Chem.*, **13**, 1211 (1974).
12. J. E. Drake and C. Riddle, *Can. J. Chem.*, **53**, 3602 (1975).
13. D. T. Clark, B. J. Cromarty, and A. Dilk, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 3173 (1978).
14. K. Miyoshi and D. H. Buckley, *Appl. Surf. Sci.*, **10**, 357 (1982).
15. R. Nordberg, H. Brecht, R. G. Albridge, A. Fahlman, and J. R. Van Wazer, *Inorg. Chem.*, **9**, 2469 (1970).
16. R. C. Gray, J. C. Carver, and D. M. Hercules, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 343 (1967).
17. D. W. Van Krevelen and P. J. Hoftyzer, *Properties of Polymers*, Elsevier, Amsterdam 1976, p. 170.

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