

Role of Unsaturated Groups in Glow Discharge Polymerization

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Synopsis

The role of unsaturated groups of the starting compounds in glow discharge polymerization was investigated by elemental analysis, infrared spectroscopy, and ESCA. Tetramethylsilane (TMS), trimethylvinylsilane (TMVS), and ethyltrimethylsilane (ETMS) were used as starting materials. Glow discharge conditions (W/FM value meaning the rf power input per mass of the monomers) as well as a degree of the unsaturation of the starting materials had strong influences upon the polymer deposition rate and the elemental composition of the formed polymers. The C_{1s} and the Si_{2p} spectra showed that the chemical composition of these polymers was distinguished by either presence or absence of the unsaturated groups in the starting compounds rather than kind of the unsaturated groups. The polymer formation, when the monomers containing double and triple bonds were served, is proceeded not only through these unsaturated bonds but also through the cleavage between Si and C atoms.

INTRODUCTION

Glow discharge polymerization is a unique polymer-forming process. Almost all organic compounds, even compounds with no functional groups, can be polymerized by this polymerization technique. Many investigators have endeavored to resolve the reaction mechanisms of this polymer-forming process. Two typical schemes for the polymer-forming process have been proposed by Kobayashi et al.¹ and Yasuda,² separately. One proposed by Kobayashi et al. involves the hypothesis that acetylene may be formed in the initial step when either of saturated and unsaturated hydrocarbons is in a glow discharge state, and, then, the formed acetylene may be polymerized to deposit polymers. The other proposed by Yasuda involves two independent reactions termed as plasma-induced polymerization and plasma-state polymerization. The plasma-induced polymerization is represented by chain propagation mechanism through unsaturated groups, which is essentially the same as conventional polymerizations such as radical. The plasma-state polymerization is represented by stepwise reactions. The starting materials introduced into a glow discharge state may undergo the fragmentation and rearrangement, and then two activated fragments may be recombined. By the repetition of the fragmentation and the recombination polymer chains grow, and finally polymers deposit. Therefore, the polymer-forming process in a glow discharge state consists of both plasma-induced polymerization and plasma-state polymerization. Either of these two polymerizations plays the predominant role in the polymer formation depends not only on the chemical nature of the starting materials but on the conditions of the discharge.

These two aspects proposed by Kobayashi et al. and by Yasuda, independently, are distinguished. When a series of methane, ethylene, and acetylene is used as the starting compounds, the three polymers from then should be identical in chemical structure if the polymerizations proceeded in the reaction scheme proposed by Kobayashi et al., and, if proceeded in the reaction scheme by Yasuda, there should be large differences in chemical structure among the three polymers. In other words, we believe that the Kobayashi's aspect shows less influence of the unsaturation of the starting materials upon the chemical composition of the polymers formed, and that the Yasuda's aspect shows strong influences of the unsaturation upon the chemical composition of the polymers formed.

This study focusses on the role of unsaturated groups of the starting materials in glow discharge polymerizations. TMS, TMVS, and ETMS which contain silicon atoms familiar to carbon chemical nature are used as starting compounds because more information on the chemical composition of the formed polymers are obtained in these systems than in the systems of pure hydrocarbons with no heteroatoms.

EXPERIMENTAL

Chemicals. Tetramethylsilane (TMS) (NMR grade), trimethylvinylsilane (TMVS) (more than 98%), and ethynyltrimethylsilane (ETMS) (more than 98%) were purchased from Petrarch System Inc., and used as monomers for the glow discharge polymerization without further purification.

Glow Discharge Polymerization. The reaction system used in this study was the reaction chamber (35 mm i.d., 400 mm long) made of Pyrex glass was 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 in Figure 1.

Experimental procedures for the glow discharge polymerization are not essentially different from those reported elsewhere.³ 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 adsorbed 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

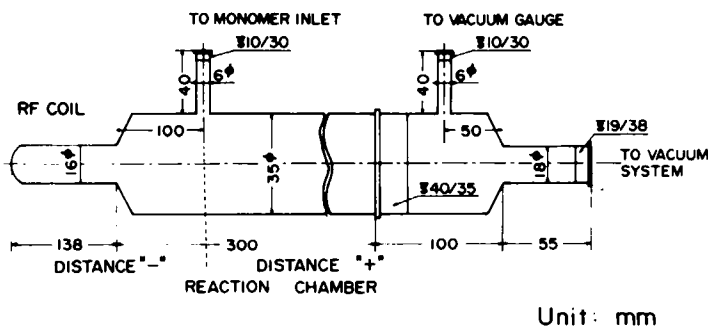


Fig. 1. Reaction chamber.

the reaction chamber at a given flow rate adjusted at a pressure of 1.3 Pa by a metering valve. The flow rate of the 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 plate 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 so that the sample weighed was made a combustion in oxygen atmosphere and further heated at 850°C until reaching a constant weight to be SiO₂.

Infrared Spectra. The polymers scraped off were provided for preparation of KBr disks. A Nihon Bunko Spectrometer A-3 was used.

ESCA Spectra. The polymer films (approximately 0.1 μm thick determined by interferometry) deposited on silicon wafers (5 × 5 mm) were provided for measurement of ESCA spectra. The spectra were recorded with a Shimadzu electron spectrometer ESCA 750 employing MgK_α exciting radiation. Typical operating conditions were: X-ray gun, 8 kV, 30 mA; the pressure in the sample chamber, 6.5 × 10⁻⁶ Pa. The Au core level at 84.0 eV was temporarily used for calibration of the energy scale.

The complex spectra of the C_{1s} and Si_{2p} 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.

RESULTS AND DISCUSSION

Glow discharge polymerizations of the three monomers yielded transparent and filmy polymers of which color varied from colorless to yellow with increasing the unsaturation of the monomer used, i.e., the polymers from TMS were colorless, the polymers from TMVS light yellow, and the polymers from ETMS yellow. All the formed polymers were insoluble in organic solvents such as alcohol, benzene, acetone, and carbontetrachloride. Figure 2 shows the polymer deposition rate deposited from the three monomers. The flow rate in Figure 2 is graduated in the units of mg/min to collect the different molecular weight among the used monomers (88 for TMS, 97 for TMVS, and 95 for ETMS). The flow rate in mg/min can be directly related to the W/FM value² because the glow discharge polymerizations were performed at a constant level of rf power (25 W). The W/FM value means apparent energy input per mass of the monomers to sustain glow discharge, where W , F , and M are the rf power, the monomer flow rate, and the molecular weight of the monomer, respectively.

The polymer deposition rate, as seen in Figure 2, were influenced mainly by two factors. First, the polymer deposition rate depended on nature of the monomers used. ETMS polymerized at the fastest rate, TMVS followed, and TMS did at the slowest rate, which indicates that the polymer-forming process may be closely related to the unsaturation of the monomers. Second, the poly-

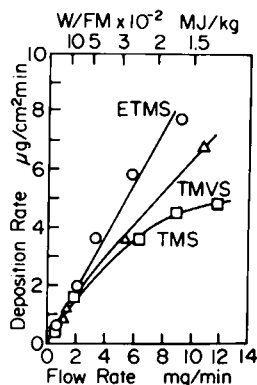


Fig. 2. Polymer deposition rate as functions of monomers and monomer flow rate.

mer deposition rate depended on the magnitude of the W/FM value. When the glow discharge polymerizations were performed at W/FM values below 1000 MJ/kg, there were fairly large differences in the polymer deposition rate among the three monomers. However, this difference became small when performed at W/FM values above 1000 MJ/kg. Therefore, we believe that the polymer-forming process may be influenced strongly by a level of the W/FM value as well as nature of the monomers.

Elemental Composition of the Polymers

Table I shows the elemental composition of the polymers prepared from TMS, TMVS, and ETMS as a function of the W/FM value. All the polymers consisted of C, H, N, O, and Si atoms. The origin of oxygen and nitrogen atoms, which are never contained in the starting compounds, is air remaining still in the reaction chamber. The relative composition represented as atomic ratio in Table I was varied by the used monomers and the W/FM value both. The polymers from ETMS possessed the highest C/Si and H/Si ratios, the polymers from TMVS followed, and the polymers from TMS possessed the lowest C/Si and H/Si ratios. There was not large a difference in the N/Si and the O/Si ratio among the three polymers. Drastic changes in the C/Si and the H/Si ratio could be

TABLE I
Elemental Composition of Polymers Prepared from ETMS, TMVS, and TMS

Monomer	W/FM (MJ/kg)	Elemental composition ^a (wt %)					Empirical formula of polymers
		C	H	N	O	Si	
ETMS	170	53.2	8.7	0.6	18.8	18.7	$C_{6.6}H_{13}N_{0.06}O_{1.8}Si$
	300	54.0	8.7	0.5	16.1	20.7	$C_{6.1}H_{12}N_{0.04}O_{1.4}Si$
	1000	43.0	7.5	1.7	21.0	26.8	$C_{3.7}H_{7.7}N_{0.13}O_{1.4}Si$
TMVS	140	52.6	9.4	0.2	18.4	19.4	$C_{6.3}H_{14}N_{0.02}O_{1.7}Si$
	290	53.6	8.7	0.4	15.8	21.5	$C_{5.8}H_{11}N_{0.03}O_{1.3}Si$
	1300	52.3	7.6	1.2	13.3	25.6	$C_{4.8}H_{8.3}N_{0.09}O_{0.91}Si$
TMS	290	43.6	8.5	0.6	19.5	27.8	$C_{3.7}H_{8.6}N_{0.04}O_{1.2}Si$
	1400	44.2	8.2	2.6	17.3	27.7	$C_{3.7}H_{8.2}N_{0.19}O_{1.1}Si$

^a Average of five samples.

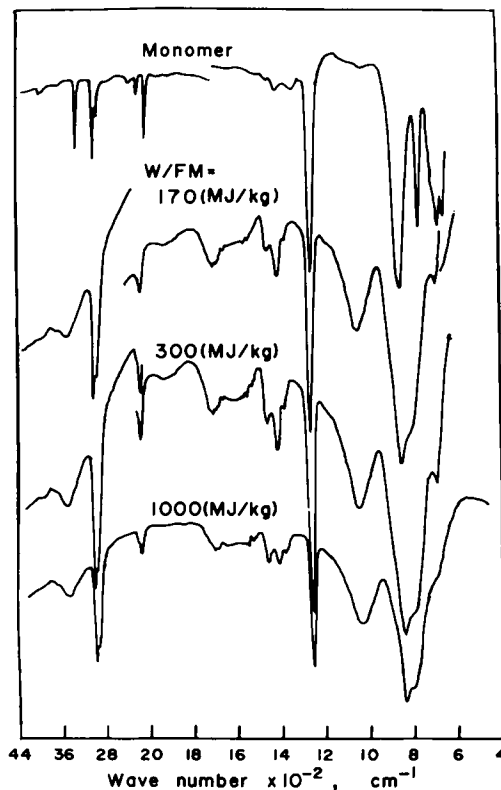


Fig. 3. IR spectra of polymers prepared from ETMS at W/FM values of 170, 300, and 1000 MJ/kg.

observed also by varying the magnitude of the W/FM value even when ETMS or TMVS was served for the glow discharge polymerizations. In the system of TMS, however, the C/Si and the H/Si ratio were changeless even when the W/FM value was magnified from 290 to 1400 MJ/kg. The different dependence of the C/Si and the H/Si ratio on the W/FM value among the three monomers might rise from the unsaturation of the monomers used.

Such results seem to provide important information concerning the polymer-forming process occurring in glow discharge. When the glow discharge polymerizations in the systems of ETMS and TMVS were performed at low W/FM values, e.g., at 140 MJ/kg for ETMS and at 170 for TMVS the polymers with C/Si ratios of more than 6 were formed. Increasing the W/FM value, the C/Si ratio decreased, and at W/FM values of more than 1000 MJ/kg the ratio reached approximately 4, where there was not a large difference in the C/Si ratio among the three polymers. Such high C/Si ratio in operation at low W/FM values and the W/FM dependence cannot be explained only by the chain reactions through triple or double bonds of the monomers.

Infrared Spectra of the Polymers

Figures 3–5 show infrared spectra of the polymers formed from ETMS, TMVS, and TMS as a function of the W/FM value. These polymers gave similar infrared

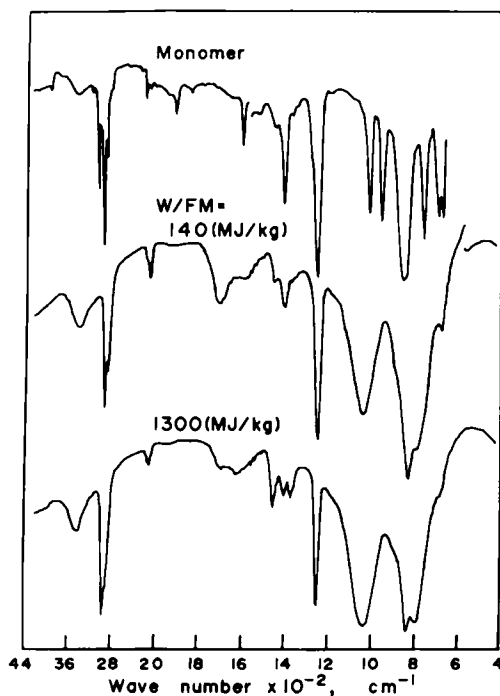


Fig. 4. IR spectra of polymers prepared from TMVS at W/FM values of 140 and 1300 MJ/kg.

spectra although there were large differences in the elemental composition among them. The polymers formed from ETMS, as seen in Figure 3, gave infrared spectra containing absorptions at 2950 (CH_3), 2900 (CH_2), 2130 (Si-H), 1700 (C=O), 1460 (CH_3), 1410, 1370, 1250 (Si-CH_3), 1045 (Si-O-C , Si-O-Si), 835 (CH), 800 (Si-CH_3 , Si-CH_2), and 685 cm^{-1} (unknown); and had no ab-

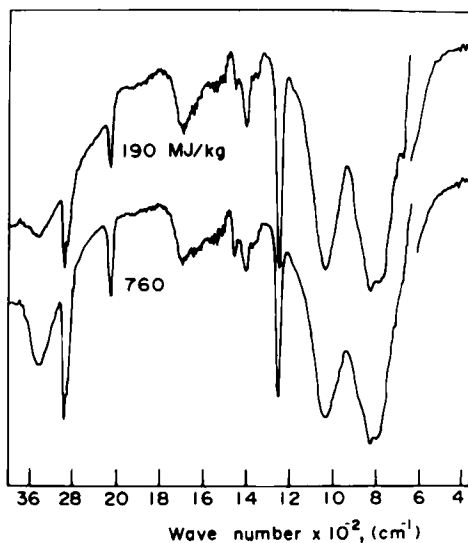


Fig. 5. IR spectra of polymers prepared from TMS at W/FM values of 190 and 760 MJ/kg.

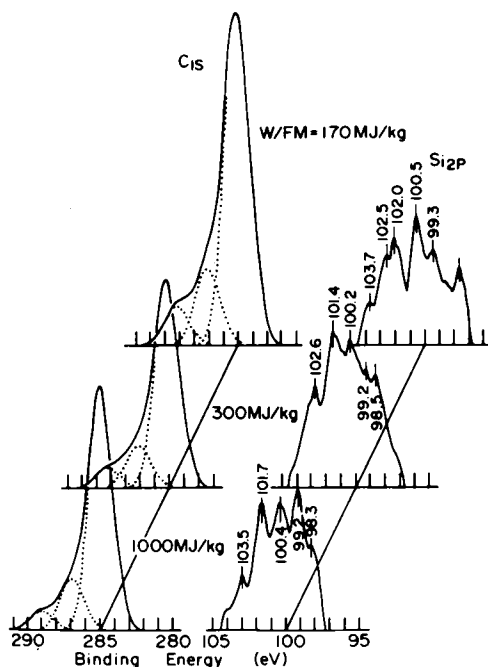


Fig. 6. ESCA (C_{1s} and Si_{2p}) spectra of polymers prepared from ETMS at W/FM values of 170, 300, and 1000 MJ/kg.

sorptions at 3270 and 2030 cm^{-1} due to ethynyl groups of ETMS used as the monomer. No substantial change in the infrared spectra appeared among the polymers formed at different three W/FM values of 170, 300, and 1000 MJ/kg.

The polymers formed from TMVS, as shown in Figure 4, gave similar infrared spectra to the former polymers. On the spectra absorptions appeared at 2960 (CH_3), 2900 (CH_2), 2120 ($Si-H$), 1700 ($C=O$), 1460 (CH_3), 1410, 1370, 1250 ($Si-CH_3$), 1050 ($Si-O-C$, $Si-O-Si$), 835 (CH), 800 ($Si-CH_3$, $Si-CH_2$), and 690 cm^{-1} (unknown). Characteristic absorptions due to vinyl groups of TMVS at 3070 and 1590 cm^{-1} could not be observed on these spectra. There was no dependence of these absorptions on the W/FM values.

The polymers formed from TMS showed infrared spectra resembling those of the two polymers from ETMS and TMVS, and absorptions appeared at 2950 (CH_3), 2900 (CH_2), 2120 ($Si-H$), 1700 ($C=O$), 1455 (CH_3), 1410, 1370, 1250 ($Si-CH_3$), 1040 ($Si-O-C$, $Si-O-Si$), 830 (CH), and 800 cm^{-1} ($Si-CH_3$, $Si-CH_2$).

These spectral comparisons indicate following important informations concerning the polymer-forming process in glow discharge.

(i) The polymers formed from ETMS, TMVS, and TMS showed the almost identical infrared spectra, which were constructed with characteristic groups such as CH_3 , CH_2 , $C=O$, $Si-H$, $Si-CH_3$, $Si-CH_2$, $Si-O-C$, and $Si-O-Si$ groups.

(ii) The formation of $Si-H$, $Si-O-C$, and $Si-O-Si$ groups suggests that the polymer-forming process involves cleavage between Si atoms and ethynyl, vinyl, or methyl groups.

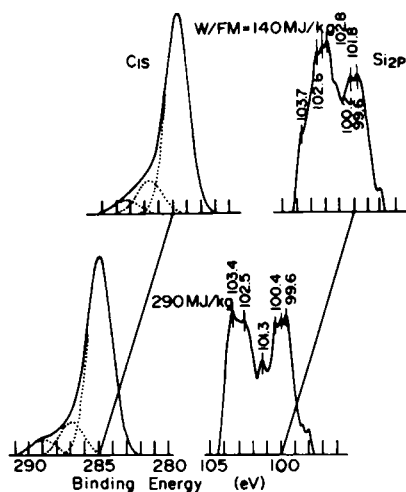


Fig. 7. ESCA (C_{1s} and Si_{2p}) spectra of polymers prepared from TMVS at W/FM values of 140 and 290 MJ/kg.

ESCA Spectra

Figures 6–8 show typical ESCA (C_{1s} and Si_{2p}) spectra of the three polymers formed from ETMS, TMVS, and TMS, respectively. The C_{1s} spectra for the polymers formed from ETMS, as seen in Figure 6, expanded over ca. 10 eV, and consisted of a peak at ca. 285 eV and a shoulder at ca. 289 eV. It is obvious that these spectra are superpositions of more than two C_{1s} features having different binding energy. These spectra could be fitted with three Gaussian curves as illustrated in dotted lines in Figure 6. The third curve was determined from the difference between the observed curve and the sum of the first and the second

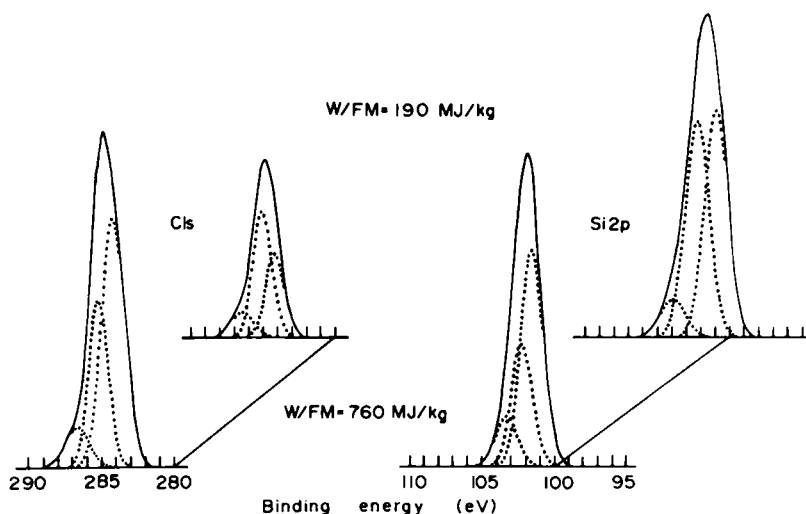


Fig. 8. ESCA (C_{1s} and Si_{2p}) spectra of polymers prepared from TMS at W/FM values of 190 and 760 MJ/kg.

component. The peak position and the relative peak area for the each component resolved are listed in Table II. The three components resolved, as seen in Table II, centered at 284.9, 287.0, and 289.1 eV, at 285.0, 287.0, and 289.1 eV, and at 284.9, 286.9, and 289.0 eV for the polymers polymerized at W/FM values of 170, 300, and 1000 MJ/kg, respectively. These components can be assigned as aliphatic carbon and C—Si, C—O, and C=O groups in the order of increasing in the binding energy.⁴⁻⁹ The relative concentrations of the each component which were independent of the magnitude of the W/FM value were approximately 76%, 16%, and 8% for aliphatic carbon and C—Si, C—O, and C=O groups, respectively, which indicates that the polymers are constructed with C—C, C—Si, and C—O sequences.

By similar curve-fitting procedures the C_{1s} spectra for the polymers formed from TMVS and TMS could correspond with three Gaussian curves as illustrated with dotted line in Figures 7 and 8. Results of these curve fittings are summarized in Table II. The three components divided from the C_{1s} spectra for the polymers from TMVS can be assigned as aliphatic carbon and C—Si, C—O, and C=O groups,⁴⁻⁹ which were the same components as observed on the C_{1s} spectra for the former polymers. The relative concentrations of the each component were changeless when the polymerizations were performed at different W/FM values, and were approximately 80%, 14%, and 6% for aliphatic carbon and C—Si, C—O, and C=O groups, respectively. The comparison between the C_{1s} spectra for the two polymers indicates similarity between the two polymers from TMVS and ETMS in the carbon feature.

The C_{1s} spectra for the polymers formed from TMS at W/FM values of 190 and 760 MJ/kg could be also fitted with three Gaussian curves centered at 284.1, 284.9, and 286.3 and at 284.1, 285.2, and 286.6, respectively. These components could be assigned as carbonized carbon, aliphatic carbon and C—Si, and C—O groups,⁴⁻⁹ which indicates that the polymers from TMS are drastically different in carbon feature from the two former polymers (from TMVS and ETMS). The polymers from TMS are characterized to be somewhat carbonized polymers, which is supported by the weak infrared absorption of CH_3 and CH_2 groups.

Furthermore, the Si_{2p} spectra were compared among the three polymers. The Si_{2p} spectra for the polymers formed from ETMS and TMVS, as seen in Figures 6 and 7, showed many peaks that were too complex to be resolved. These peaks could be grouped into five categories (Table II). The first category is the peak appearing at 99.2–99.6 eV, the second is the peak at 100.2–100.5, the third is the peak at 101.3–102.0, the fourth is the peak at 102.5, and the fifth is the peak at 103.4–103.7 eV, which can be assigned as Si—Si, Si—C, Si—(O—C)_x, $x = 1 - 2$, Si—O—C(O), and SiO₂ groups,^{10,11} respectively. In addition to the five peaks the Si_{2p} spectra in Figure 6 showed an unknown peak at ca. 98 eV, while the polymers formed from TMS showed simple Si_{2p} spectra which could correspond to three Gaussian curves centered at 100.9 (Si—C), 102.2 [Si—(O—C)_x], and 103.8 eV (SiO₂) for the polymers performed at a W/FM value of 190 MJ/kg and at 101.4, 102.2, and 103.3 eV for the polymers performed at a W/FM value of 760 MJ/kg. The assumption induced from the C_{1s} spectra, i.e., that the polymers formed from TMS may be different in chemical composition from those from ETMS and TMVS, can be recognized also by these Si_{2p} spectra.

On the O_{1s} spectra of the three polymers a monotonous peak appeared at approximately 533 eV (FWHM value was more than 2.5 eV). There was no sig-

TABLE II
ESCA (C_{1s} and Si_{2p}) Spectra of Polymers prepared from ETMS, TMVS, and TMS

Monomer	W/FM (MJ/kg)	Core level	Deconvoluted component #1 centered at (eV)	Deconvoluted component #2 centered at (eV)	Deconvoluted component #3 centered at (eV)	Deconvoluted component #4 centered at (eV)
ETMS	170	C_{1s}	284.9 (74%) ^a	287.0 (17%)	289.1 (8%)	289.1 (8%)
	300		285.0 (76%)	287.0 (16%)	289.1 (8%)	289.1 (8%)
	1000		284.9 (77%)	286.9 (17%)	289.0 (6%)	289.0 (6%)
TMVS	140		284.6 (79%)	286.6 (15%)	288.3 (6%)	288.3 (6%)
	290		284.8 (80%)	286.9 (13%)	288.9 (7%)	288.9 (7%)
TMS	190		284.1 (35%)	284.9 (52%)	286.3 (13%)	286.3 (13%)
	760		284.1 (58%)	285.2 (32%)	286.6 (10%)	286.6 (10%)

Monomer	W/FM (MJ/kg)	Core Level	Group #1 centered at (eV)	Group #2 centered at (eV)	Group #3 centered at (eV)	Group #4 centered at (eV)	Group #5 centered at (eV)	Group #6 centered at (eV)
ETMS	170	Si_{2p}	99.3	100.5	101.4	102.0	102.5	103.7
	300		99.2	100.2	101.7	102.6	102.6	103.5
	1000		99.2	100.4	101.8	102.2	102.6	103.7
TMVS	140		99.6	100.2	101.3	102.2	102.5	103.4
	290		99.6	100.4	101.3	102.2	102.5	103.8
TMS	190		100.9	(46%) ^a	101.4	(45%)	102.2	(9%)
	760		100.9	(46%) ^a	101.4	(57%)	102.2	(30%)

^a Relative peak area.

nificant change in the spectra among the three polymers, so these spectra are not dealt with here for the sake of brevity.

These investigations by elemental analysis and infrared and ESCA spectroscopy seem to provide important aspects concerning glow discharge polymerization:

(i) The unsaturation of the monomers used in glow discharge polymerization makes the polymer deposition rate fast, and the enhancement in the polymer deposition rate becomes significant when polymerized at low W/FM values.

(ii) The polymers, essentially, are constructed with C—C, C—Si, Si—O—C, and Si—O—Si sequences. The chemical composition, however, is strongly influenced by whether the monomers possessed unsaturated groups or not. The unsaturated groups bring about the formation of polymers rich in the carbon and hydrogen contents, and the saturated groups bring about dehydration to yield carbonized polymers.

(iii) The polymer-forming process, when the monomers containing double or triple bonds were served, occurs not only through these unsaturated bonds but also through the cleavage between Si and C atoms. By such assumption the high C/Si ratio of the polymers prepared from ETMS and TMVS can be interpreted well. First, ETMS and TMVS undergo fragmentation to yield activated ethynyl and vinyl, and trimethylsilyl fragments. These fragments individually form polymers. Therefore, the formed polymers may be mixtures of hydrocarbon polymers and Si-containing polymers. At low W/FM values the polymer formation from the ethynyl and vinyl fragments is believed to be fairly faster than that from trimethylsilyl fragments, which results in the formation of polymers rich in carbon. As increasing the W/FM value the rate of the polymer formation from trimethylsilyl fragments becomes fast, and this enhancement may contribute the decrease in carbon content of the formed polymers. However, this assumption never exclude the polymer-forming process through triple or double bonds.

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