

Glow Discharge Polymerization of Trimethylvinylsilane and Tetramethylsilane

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Synopsis

Glow discharge polymerizations of trimethylvinylsilane (TMVS) and tetramethylsilane (TMS) were compared. Vinyl groups in TMVS slightly contribute the polymer-formation process only when glow discharge polymerization was performed at the *W/FM* parameter less than 500 MJ/kg. Elemental compositions of the polymers prepared from TMVS, which are rich in carbon content, shows strong dependence on operational conditions, the *W/FM* parameter; but the polymers from TMVS consist of the almost same chemical structures as those from TMS. Slight differences between the starting materials in chemical structure does not reflect on bulk properties of the formed polymers but on surface properties such as surface energy and adhesion.

INTRODUCTION

Organic molecules injected into a discharge state are activated by interactions of electron, ions, and radicals which are present in a discharge to form polymeric materials. Although the process of the polymer formation is complex and has not yet been resolved completely, at least two major types of the polymerization have been considered to understand the polymer formation in a glow discharge state. One is plasma-induced polymerization, and the other is plasma polymerization.¹

Plasma-induced polymerization is essentially identical to conventional polymerization, and the polymerization is initiated by activated species such as radicals and electron created in a discharge, and is propagated by chain mechanism. The plasma-induced polymerization, therefore, requires that starting materials contain functional groups such as double bonds and cyclic structures.

Plasma polymerization is a unique polymerization that occurs only in a discharge state. Evidence that nonfunctional groups containing materials such as methane and ethane can be polymerized in a discharge state is a good example.² The starting materials injected into a discharge state are broken into fragments by the action of electron, ions, radicals, etc., and the reactive fragments are rebonded to form larger molecules. These processes are repeated to form polymeric materials. This polymerization, therefore, proceeds stepwise, and the formed polymers are highly crosslinked.

Polymerization in a glow discharge essentially involves two distinct processes mentioned above. Which process occurs predominantly depends primarily on the conditions of glow discharge, and to a lesser extent on the nature of starting materials, and the change of the polymerization process may be reflected on physical properties of the formed polymers.

In this study glow discharge polymerizations of tetramethylsilane that contains

no functional groups and trimethylvinylsilane that contains vinyl groups as a functional group are compared, and some physical properties of the formed polymers are examined.

EXPERIMENTAL

Materials

Chemicals used for glow discharge polymerization in this study were trimethylvinylsilane (TMVS) (provided from Petrarch Systems Inc.) and tetramethylsilane (TMS) (provided from Ventron Co.). Polymer substrates provided for the measurement of adhesion between plasma films and polymer substrates were high-density polyethylene (PE) and polycarbonate (PC) (provided from Mitsubishi Chemical Industries) and polypropylene (PP) (from Chisso Co.); and their dimensions were $34 \times 24 \times 2-3$ mm. The surface of their substrates was washed with acetone, or methanol, further detergent, rinsed with distilled water, and then stored in a desiccator over silica gel.

Glow Discharge Polymerization

The apparatus and experimental procedures for glow discharge polymerization are essentially the same as those reported elsewhere.³ The reaction chamber is a tubular reactor (35 mm inner diameter, 400 mm long) made of Pyrex glass, and is constructed with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for inductive coupling of a 13.56 MHz radio frequency source.

Substrates were horizontally placed in the reaction chamber, and the system was evacuated to approximately 0.1 mTorr using a diffusion and a rotary pump. Argon gas was introduced into the reaction chamber, and to eliminate water adsorbed on surfaces of the substrates, the surfaces were exposed to argon plasma for 10 min. Again the system was evacuated to 0.1 mTorr, and the monomer gas which was adjusted at a given flow rate was injected into the reaction chamber. The rf power was turned on, and glow discharge polymerization was initiated and continued at an rf power level of 25 W. The operational conditions employed for the glow discharge polymerization were as follows: the flow rate of the monomer gas, 0.26–3.4 cm³ (STP)/min; the pressure in the reaction chamber before initiating a glow discharge, 10 mTorr; the rf power level, 25 W.

The polymer deposition rate was calculated from weight increase of aluminum foils (5×22 mm, 0.007 mm thickness), which were horizontally placed in the reaction chamber. The aluminum foils were lined with a cover glass (5×22 mm, 0.13 mm thickness) and were mounted on a glass plate (35×250 mm) at the regular interval of 10 mm with a double Scotch tape. An average weight increase of 11 aluminum foils placed at locations from -8 to $+12$ cm was taken as the polymer deposition rate. The distance was taken from the monomer inlet.

Elemental Analysis

Polymers which were deposited on a glass plate and which were scraped with a knife were provided for C, H, N, and Si analyses. The C, H, and N contents in the deposited polymers were determined using CHN corder MT-2 (Yanagimoto Co.), and the Si content was determined by gravimetric analysis.

Infrared Spectra

KBr powder ground to approximately 150 mesh was thinly sprinkled on the glass plate, and glow discharge polymerization was performed according to the same procedures as mentioned above. The KBr powder coated with polymer films prepared by the glow discharge polymerization was provided for preparation of KBr disk. The spectrometer used was a Nihon Bunko spectrometer A-3.

Surface Energy

The contact angles of polymer films which were deposited on glass plate against water, glycerol, formamide, diiodomethane, and tricresyl phosphate were measured by a drop-on-plate method using a Kyowa Kagaku contact angle meter CA-1. The contact angle data were analyzed to estimate a dispersive contribution γ_s^d and a polar contribution γ_s^p , according to Kaelble's method.⁴

Evaluation of Adhesion between Plasma Films and Polymer Substrates

For evaluation of adhesion between polymer substrates and plasma films, a Scotch tape test was designed. The Scotch tape test was carried out according to ASTM D-3354-76.

RESULTS AND DISCUSSION

Glow discharge polymerization of TMVS as well as TMS yielded light-yellow polymers, which deposited as films on surfaces of substrates placed in the reaction chamber. To distinguish between the polymerizations of TMVS and TMS in a discharge, polymer deposition rates were first compared.

Figure 1 shows the polymer deposition rate in the TMVS and the TMS systems as a function of the flow rate of the monomer gases. In this figure the flow rate is graduated in the unit of mg/min to correct the different molecular weight be-

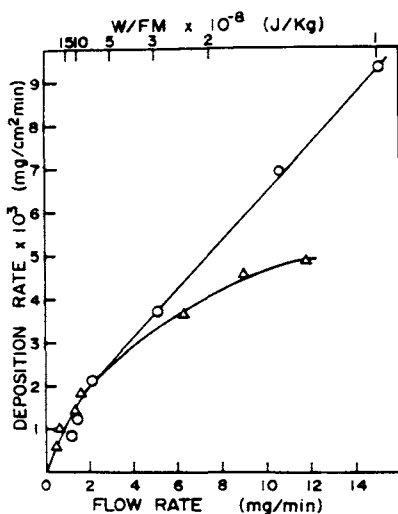


Fig. 1. Deposition rate of polymers prepared from TMVS and TMS by glow discharge polymerization as a function of a flow rate of monomer: (O) TMVS; (Δ) TMS.

tween the monomer gases used (the molecular weight of TMVS is 100, and that of TMS, 88). The flow rate (mg/min) can be directly related to the W/FM value,⁵ and the abscissa in Figure 1 is also represented in J/kg by the W/FM parameter. The W/FM value means the energy input for glow discharge polymerization per mass of monomer, and W , F , and M denote the input of rf power, the flow rate of monomer gas, and the molecular weight of the monomer, respectively. TMVS, as seen in Figure 1, showed the polymer deposition rate as fast as TMS when the flow rate was lower than 3 mg/min (when the W/FM value was more than 500 MJ/kg); but when the flow rate increased (when the W/FM value was less than 500 MJ/kg), there appeared differences in the polymer deposition rate between the TMVS and the TMS systems. The discrepancy in the polymer deposition rate became great as the flow rate of the monomer gases increased (as the W/FM value decreased). This comparison indicates that TMVS is favored to form polymers when a glow discharge is operated at a low W/FM value, and the contribution of vinyl groups in TMVS to the formation of polymers can be recognized.

Successively, chemical structures and physical properties of the polymers formed from TMVS were compared with those of the polymers prepared from TMS, which contains no vinyl groups.

Chemical Structures of the Formed Polymers

Elemental compositions of polymers prepared from TMVS and TMS by glow discharge polymerization were determined as a function of the W/FM parameter. Specimens for the analyses are polymers prepared at the W/FM parameters more and less than 500 MJ/kg, where there appeared differences in the polymer deposition rate between TMVS and TMS. Results are listed in Table I. Polymers prepared from TMVS and TMS consist of mainly carbon, hydrogen, oxygen, and silicon with a small amount of nitrogen. It is worthwhile noticing that there are differences in elemental composition between polymers from TMVS and TMS: (1) In the TMVS system the relative ratios of carbon and hydrogen to silicon are strongly dependent on the magnitude of the W/FM parameter; and in the TMS system the ratios are independent. (2) In operation at the W/FM parameter less than the threshold value (500 MJ/kg), the polymers formed from TMVS contain more carbon and hydrogen than the polymers from TMS. (3) As the W/FM parameter increases, the relative ratios of carbon and hydrogen to silicon in polymers formed from TMVS decrease, and above the threshold value of the W/FM parameter the differences in the ratios between polymers from TMVS and TMS become subtle.

TABLE I
Elemental Composition of Polymers Prepared from TMVS and TMS by Glow Discharge Polymerization

Polymers from	W/FM (MJ/kg)	Elemental Composition (wt %)					Empirical formula of polymers
		C	H	N	O	Si	
TMVS	140	52.6	9.4	0.2	18.4	19.4	$C_{6.33}H_{13.5}N_{0.02}O_{1.66}Si$
	290	53.6	8.7	0.4	15.8	21.5	$C_{5.83}H_{11.3}N_{0.03}O_{1.28}Si$
	1300	52.3	7.6	1.2	13.3	25.6	$C_{4.78}H_{8.29}N_{0.09}O_{0.91}Si$
TMS	290	43.6	8.5	0.6	19.5	27.8	$C_{3.67}H_{8.59}N_{0.04}O_{1.23}Si$
	1400	44.2	8.2	2.6	17.3	27.7	$C_{3.72}H_{8.23}N_{0.19}O_{1.09}Si$

Consequently, the main differences in chemical composition between polymers prepared from TMVS and TMS appear only in operation of the glow discharge polymerization at the W/FM parameter less than 500 MJ/kg.

Infrared spectra of the polymers prepared from TMVS and TMS are compared (Fig. 2). Four polymers prepared from each monomer at the W/FM parameter more and less than 500 MJ/kg were provided for the measurements. Two polymers prepared from TMVS at different W/FM parameters (140 and 1300 MJ/kg) show essentially the same spectra, although there are differences in absorption intensity. These spectra consist of main absorptions at 2960, 2900 (CH_3 , CH), 2300 ($\text{C}\equiv\text{C}$), 2120 (Si—H), 1710 ($\text{C}=\text{O}$), 1460, 1410 (CH_2), 1250 (Si— CH_3), 1050 (Si—O—Si, Si—O—C), 835, 800 (Si— CH_3 , Si— CH_2 — CH_2 —Si), and 685 cm^{-1} (Si—C). On the spectrum of the polymers prepared at the high W/FM parameter, absorptions due to CH_3 , CH_2 , and CH groups become weak. Essentially the same absorptions can be detected on the spectra of the polymers prepared from TMS. In the TMS system absorptions due to CH_3 , CH_2 , and CH groups, when the polymerization was operated at the high W/FM parameter, become surprisingly less intense. This indicates that TMS is subjected more vigorously to fragmentation to form polymers, especially at the high W/FM parameter, than TMVS. The strong absorption due to vinyl groups in TMVS, which will appear at 1590 cm^{-1} ,⁶ can scarcely be detected on the spectra of the two polymers, but the absorption appears as weak as a shoulder on the spectrum of the polymers only when polymerized at the W/FM parameter of 140 MJ/kg. From these spectral results it can be concluded that the polymers from TMVS are essentially identical to those from TMS, and their polymers consist of groups such as CH_2 , CH, Si—O—Si, Si—O—C, Si— CH_3 , Si— CH_2 — CH_2 —Si, and $\text{C}=\text{O}$ groups. The polymers prepared from TMVS, only when the polymer-

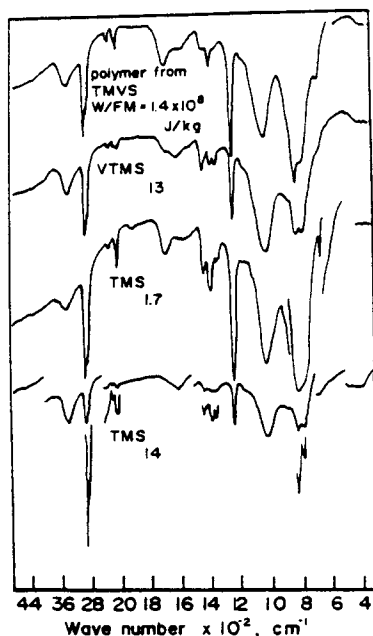


Fig. 2. Infrared spectra of polymers prepared from TMVS and TMS by glow discharge polymerization.

ization was operated at the W/FM parameter less than 500 MJ/kg, possess a very small amount of vinyl groups in the polymer chains. This is a subtle difference between the polymers from TMVS and TMS.

It is difficult for TMVS to form polymers by a radical polymerization technique because the Q and the e values for TMVS are 0.029 and 0.04, respectively,⁷ and generally an anionic polymerization technique using butyl lithium as a catalyst is employed to form polymers that are noncrystalline and that are soluble in organic solvents such as THF, toluene, chloroform, etc.⁸ The polymers even when formed from TMVS by glow discharge polymerization at the W/FM parameter as small as 140 MJ/kg was insoluble in these solvents, and properties of the polymers formed are considered to be different from those polymerized from TMVS by conventional method.

Physical Properties

Thermal Stabilities

Thermal stabilities of the polymers prepared from TMVS and TMS were evaluated by thermogravimetric analysis, and typical results are listed in Table II. The polymers prepared from TMVS at the W/FM parameter of 140 MJ/kg initiated weight loss at a temperature near 240°C and remained residual products of approximately 70 wt % when heated at 500°C, indicating that the polymers possess better thermal stabilities than conventionally polymerized polysiloxanes such as polydiphenylsiloxane.⁹ These stabilities of polymers from TMVS, if polymerized at the higher W/FM value of 1300 MJ/kg, rise up. Such thermal stabilities of these polymers from TMVS, as seen in Table II, are comparable to those of polymers from TMS. There is less difference in thermal stabilities between polymers from TMVS and TMS.

Surface Energies, and Adhesion between Plasma Films and Plastic Substrates

Surface energies of the polymers from TMVS as well as TMS, as seen in Table III, showed the W/FM parameter dependence that the energies raised up by increasing the W/FM parameter. If two polymers are compared from TMVS and TMS at approximately the same level of the W/FM parameter (1300 and 1400 MJ/kg), the polymers prepared from TMVS possess surface energies as low as those from TMS, but there is a difference between the two polymers in a magnitude of components constructing the surface energies. Table III shows

TABLE II
Thermal Stabilities of Polymers Prepared from TMVS and TMS by Glow Discharge Polymerization

Polymers from	W/FM (MJ/kg)	Threshold temperature for weight loss (°C)	Residual products (wt %)	
			At 500°C	At 850°C
TMVS	140	237	70.0	41.5
	1300	245	78.5	55.4
TMS	170	240	63.5	
	1400	270	79.5	59.3

TABLE III
Surface Energies of Polymers Prepared from TMVS and TMS by Glow Discharge Polymerization, and Adhesion between Their Plasma Films and Polymer Substrates

Polymers from	W/FM (MJ/kg)	Surface energy (dyn/cm)				Adhesion ^a		
		γ_s	γ_s^d	γ_s^p	γ_s^d/γ_s^p	PC	PE	PP
TMVS	140	24.4	24.1	0.3	0.01	±	+	--
	290	29.6	29.2	0.4	0.01			
	1300	32.5	31.4	1.1	0.04	±	+	--
TMS	870	24.2	23.6	0.6	0.03	-	+	--
	1400	33.7	27.9	5.6	0.2	-	+	--

^a Evaluated by Scotch tape test: (+) not peeled off; (±) partially peeled off; (-) completely peeled off.

that surface energies of the polymers prepared from TMVS rise mainly from a dispersive contribution composing surface energy, and the a polar contribution is low. A ratio of the polar and the dispersive contribution is almost independent of a magnitude of the *W/FM* parameter, although surface energies (a sum of the polar and the dispersive contribution) are altered by a magnitude of the *W/FM* parameter. This is a remarkable difference between the polymers prepared from TMVS and TMS.

To distinguish surface properties of polymers prepared from TMVS and TMS, adhesion between polymer films prepared by glow discharge polymerization and polymer substrates such as polycarbonate (PC), polyethylene (PE), and polypropylene (PP) was semiquantitatively examined by Scotch tape test (Table III). Adhesion between polymer films formed from TMVS and polymer substrates including PC and PE was good, but adhesion with PP was poor, while adhesion between plasma films prepared from TMS and the polymer substrates was inferior to that of the former plasma films. This discrepancy may be raised from differences in surface energies between the polymers prepared from TMVS and those from TMS.

This study points out important aspects on application of glow discharge polymerization. Slight differences in chemical structure between the starting materials scarcely reflect on the polymer-forming process, and polymers having almost the same chemical structures are formed. Alterations of the formed polymers in chemical structure are enhanced by changing the *W/FM* parameter. The importance of operational conditions for glow discharge polymerization is recognized. However, slight differences between the starting materials reflect on surface properties such as surface energy and adhesion.

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