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Performance

Effects of Functional Groups in Glow Discharge Polymerization

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SUMMARY

Glow discharge polymerizations of allyltrimethylsilane (ATMS) and trimethylvinyloxysilane (TMVOS) were investigated by elemental analysis and infrared spectroscopy. The formed polymers were far different in elemental composition from the starting materials, and possessed high carbon and hydrogen contents. There was less difference in an infrared-spectral sense between the two polymers from ATMS and TMVOS. A polymer-forming process in a discharge state is discussed.

INTRODUCTION

Concerning the polymer formation in glow discharge polymerization two processes are assumed (YASUDA, 1981). These are an chain reaction and a stepwise reaction which are essentially different from each other in the sense of chemistry. The former process is familiar to conventional polymerization such as radical. Functional groups such as vinyl are activated by plasma, then follow to successive addition of other molecules, and finally macrochains are generated. On the other hand, the latter process is unique and can be observed only in glow discharge state. Molecules introduced into plasma are broken down into activated small molecules or frequently into atoms by action of plasma, and these fragments are recombinated stepwise to grow larger molecules. This continum of the fragmentation and the recombination leads the polymer formation. From this conception, therefore, it can be believed that the chemical composition and properties of the formed polymers may be dependent on the chemical structure of the monomers used if proceeded predominantly in the chain reaction mechanism, and that the chemical composition and properties may be dependent on the elemental composition rather than chemical structure of the monomers used if the stepwise reaction is predominant. Consequently, we believe that the polymer formation proceeds by either chain or stepwise reaction is an important subject in the practical utilization of glow discharge polymerization.

This study focusses on comparison of glow discharge polymerization of two vinyl groups-containing compounds. One of them is trimethylvinyloxysilane (TMVOS) that involves vinyl groups being polymerizable and ether links being susceptible to fragmentation by plasma exposure. The other is allyltrimethylsilane (ATMS) that contains allyl groups being polymerizable and no susceptible component.

EXPERIMENTAL

Chemicals: ATMS (Tokyo Kasei Kogyo Co.) and TMVOS (Shin-Etsu Chemicals Co.) of which the purity was more than 98% were used as monomers in glow discharge polymerization without further purification.

Glow Discharge Polymerization: The pyrex tubular reaction chamber (35 innerdiameter, 400 mm long) was fitted with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for teh inductive coupling of a 13.56 MHz radio frequency source. The relative arrangement of these components has been illustrated schematically in an earlier paper (INAGAKI, et al., 1981). The electric power to sustain a glow discharge was supplied by the inductive coupling of the radio frequency source with a coil (9turn) placed outside the chamber.

The experimental procedure for glow discharge polymerization have been also detailed in an earlier paper (INAGAKI and KISHI, 1983). Substrates were placed horizontally in the reaction chamber, and the system was evacuated to approximately 0.14 Pa by combination of a diffusion and a rotary pump. Argon gas was introduced into the reaction chamber, and to eliminated water adsorbed on surfaces of the substrates the surfaces were exposed to argon plasma for 10 min. Once again the system was evacuated to 0.13 Pa. Monomer gas adjusted at a fixed flow rate at a pressure of 1.3 Pa was injected into the reaction chamber, and the rf power was turned on. The glow discharge polymerization was then initiated and continued at a level of 25 W for a suitable period.

Elemental Analysis: Polymers deposited on a glass plate and scraped off with a knife were provided for C, H, N, and Si analysis. The C, H, and N contents in the polymers were determined with a CHN corder MT-2 (Yanagimoto Co.). The Si content was determined by gravimetry. The weighed polymers were heated in an oxygen atmosphere at 850°C until residual products became a constant weight. And the residual products were assumed to be SiO_2.

Infrared Spectra: Polymers deposited on a glass plate were scraped off with a knife in preparation for a KBr disk. A Nihon-Bunko spectrometer A-3 was used.

RESULTS AND DISCUSSION

Colorless and transparent polymer films were formed from ATMS and TMVOS by glow discharge polymerization. These polymers were insoluble in ordinary organic solvents, acids, and bases. The polymer deposition rate, as shown in Fig. 1, increased gradually with increase in the monomer flow rate. The monomer flow rate in the figure was graduated in mg/min to collect the different molecular weight between the two monomers. The flow rate in mg/min can be related to the W/FM parameter meaning the apparent rf input energy per mass of the monomer, where W, F, and M are the rf power, the flow rate, and the molecular weight of the monomer, respectively (YASUDA, 1981). In operation at high W/FM values there is less difference in the polymer deposition rate between the two monomer systems; but at low W/FM values below 200 MJ/kg fairly large differences can be observed, i.e., ATMS deposited polymers faster than TMVOS did. Therefore, the differences in chemical structure between the two starting materials reflect the polymer formation at relatively low W/FM values.

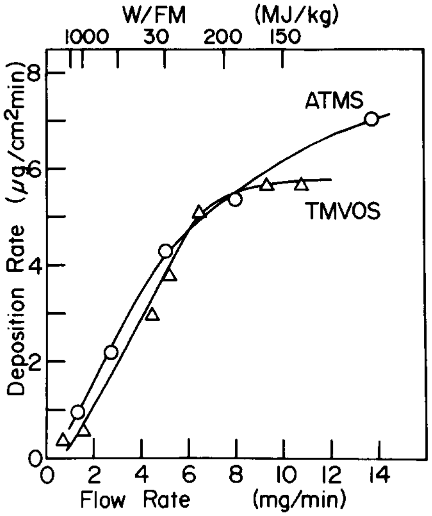

Fig. 1. Polymer Deposition Rate as a function of the Flow Rate.

Elemental Composition of formed Polymers

Table 1 shows elemental composition of the polymers formed from ATMS and TMVOS at various W/FM values. These polymers consisted mainly of C, H, O, and Si atoms. The incorporation of oxygen atoms into the polymers formed from ATMS which never contains oxygen atoms itself may be related to residual air remaining still in the reaction chamber. The incorporation of nitrogen atoms also is due to residual air. Their elemental composition were surprisingly different from those expected from the assumption that the polymers would be formed in chain reactions through double bonds of the monomers. If polymers were generated by the chain propagation mechanism through double bonds the C/Si and H/Si ratios of the formed polymers should be equal to those of the monomers, i. e., the C/Si ratio should be 6 and 5 for ATMS and TMVOS, respectively. Actually, the C/Si and H/Si ratios determined by elemental analysis, as shown in TABLE 1, showed a great disparity. For example, the C/Si ratio for the polymers formed from ATMS was more than 8, and the ratio for the polymers from TMVOS was more than 10. The disparity in the C/Si and H/Si ratios between the polymers and the monomers used was greater in the TMVOS system than in the ATMS system, which seems to be due to effects of ether links of TMVOS. Furthermore, the elemental composition of the formed polymers depended strongly on the W/FM value. Especially in the TMVOS system the C/Si and H/Si ratios diminished to approximately halves when operated at W/FM values from 190 to 580 MJ/kg. Such dependences of the elemental composition on the W/FM value are never expected if proceeded in the chain reaction mechanism.

TABLE 1
Elemental Composition of Polymers prepared from ATMS and TMVOS

Monomer	W/FM MJ/kg	Empirical Formula of Polymers
ATMS	110	$C_{8.9}H_{18.9}O_{2.4}Si$
($C_6H_{14}Si$)	210	$C_{8.1}H_{16.8}O_{2.1}Si$
	1100	$C_{9.8}H_{20.8}O_{4.3}Si$
TMVOS	190	$C_{11.6}H_{26.8}O_{8.1}Si$
($C_5H_{12}OSi$)	240	$C_{10.4}H_{23.5}N_{0.1}O_{6.1}Si$
	580	$C_{6.3}H_{13.1}N_{0.1}O_{3.2}Si$

These notable evidences indicate that the polymer-forming process in the ATMS and TMVOS systems can be never interpreted only by the conventional chain propagation mechanism through double bonds, and that another process should be taken into consideration.

Infrared Spectra of formed Polymers

Figure 2 and 3 show infrared spectra of the polymers prepared from ATMS and TMVOS at different levels of the W/FM parameter. The two polymers from ATMS and TMVOS showed analogous infrared spectra although these polymers possessed different elemental composition tabulated in TABLE 1. The polymers from ATMS showed strong absorptions at 2950 (CH3), 2900 (CH_2), 2100 (Si-H), 1700 (C=O), 1450, 1410, 1250 ($Si-CH_3$), 1045 (Si-O-Si, Si-O-C), 830 (CH), 790 ($Si-CH_3$, Si-CH2), and 680 cm^{-1} (unknown). Characteristic absorptions at 3080, 1630, 1150, 990, 925, and 910 cm^{-1} due to allyl groups of ATMS could not be observed on these spectra. Absorptions related to CH_3, CH_2, and Si-H groups became weak with increasing the W/FM value, which indicates the decrease in the carbon and hydrogen contents of the formed polymers. No other influence of the W/FM value could be observed.

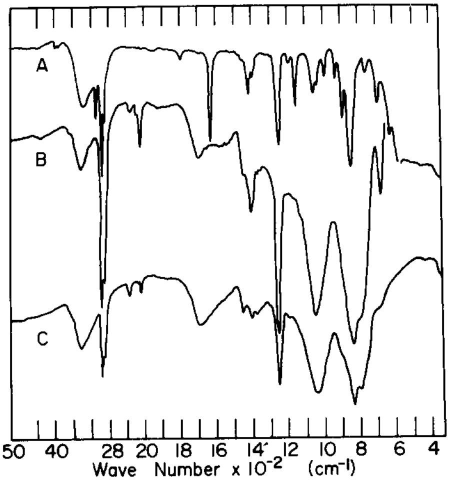

Fig. 2. Ir Spectra of Polymers prepared from ATMS; A, Monomer; B, at W/FM Value of 145 MJ/kg; C, at 517 MJ/kg.

The polymers from TMVOS showed not identical but similar to the former (Figure 3). Strong absorptions appeared at 2950 (CH_3), 2900 (CH_2), 1450, 1410, 1375, 1255 ($Si-CH_3$), 1040 (Si-O-Si, Si-O-C), 840 (CH), 790 ($Si-CH_3$, $Si-CH_2$), and 685 cm^{-1} (unknown). On the spectra from TMVOS, compared with those from ATMS, less absorption at 2100 and 1700 cm^{-1} which were due to Si-H and C=O groups, respectively, appeared; and the absorption at 1410 cm^{-1} was weak. Influences of the W/FM value also could be observed on these spectra.

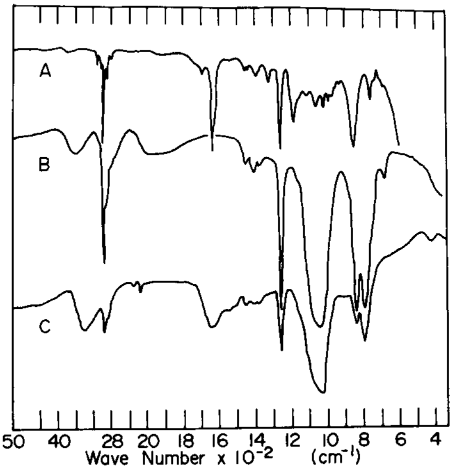

Fig. 3. Ir Spectra of Polymers prepared from TMVOS; A, Monomer; B, at W/FM Value of 144 MJ/kg; C, at 740 MJ/kg.

From these spectral results following common features can be pointed out. (i) Functional groups such as allyl and vinyloxy groupss of the starting materials can be never found in all the formed polymers.

(ii) New sequences including Si-O-Si, Si-O-C, and Si-H groups which the starting materials never contain can be found in the formed polymer chains. (iii) Absorptions related to CH_3, CH_2, and Si-H groups become weak with increasing the W/FM value. The feature (ii) indicates that the bond scission between C and Si atoms or Si and O atoms occured in a discharge state. This conception is not unreasonable because the fission of the Si-C bonds and the elimination of methoxy groups occur easily when organosilicon compounds are bonbarded with electrons at 25 eV (NAKADAIRA, at al., 1976). For example, on mass spectra of 1,2-dimethoxytetramethyldisilane [Me_2(MeO)SiSi(OMe)Me_2] the mass 163 $[M-15]^+$ and 133 $[M-15-30]^+$ ion peaks are major. If we assume Si-C and Si-O bond scissions in perior to the polymer formation singuralities observed in this study, that is extremely high C and H contents of the formed polymers and the W/FM dependence of their elemental composition, can be interpreted well. For example, in glow discharge polymerization of ATMS firstly the monomer introduced into a discharge state is broken down into allyl, methyl, and silyl fragments; and then each of these fragments are recombinated to larger molecules. Say in other wards, the polymer-forming process is competitive polymerization of some fragments broken down from the monomer. The formed polymers are results of ease of the fragmentation and of the recombination. The W/FM level may be closely related to fragmentation. This conception does not exclude the chain process through double bonds.

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