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**CHEMICAL STRUCTURE OF PLASMA POLYMERIZED
FILM FORMED FROM PYRIDINE MONOMER**

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Translation of "Kai 10 Kai Purazuma Kagaku Kenkyukai, Koen
Yoshi," Kyoto University, November 28, 1980, pp. 1-6

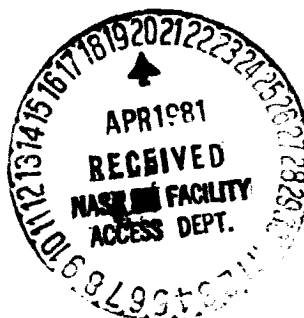
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16. Abstract This paper consists of three articles. The first gives the chemical structure of a film which was formed by plasma polymerization from pyridine monomer. The film has a hydrophilic chemical structure, its molecular weight is 900, and the molecular system is $C_{55}H_{50}N_{10}O_3$. The second article describes the electrical characteristics of a plasma polymerized film. The film has good insulating properties and was successfully applied as video disc coating. Etching resistance properties make it possible to use the film as a resist in etching. The third article concerns the characteristics of plasma polymer formed from monomer containing tetramethyltin. The polymer is in film form, displays good adhesiveness, is similar to UV film-UV-35 in light absorption and is highly insulating.			
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CHEMICAL STRUCTURE OF PLASMA POLYMERIZED FILM FORMED FROM PYRIDINE MONOMER

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1. Introduction

A film, plasma polymerized from monomer of a nitrogen containing /1/ compound, displayed the characteristics of hydrophilic semipermeable film when formed on a porous substrate. As a result the film was investigated for its value as film with reverse osmosis. The hydrophilic chemical structure of the film proved interesting.

In this experiment the nitrogen containing monomer was an aromatic compound with isomeric rings. The film was formed by low pressure glow discharge using pyridine. In addition to finding the chemical components and molecular weight, structural analysis was conducted focusing on the form of the nitrogen existing inside the molecules.

The means of analysis were elemental analysis, measurement of molecular weight by the vapor-pressure osmotic method, infrared absorption spectrum, the proton and carbon-13-NMR spectrum and high resolving power mass spectrum. The film substance was chemically modified as necessary for quantitative analysis of sulfur and halogen.

2. The Experiment

The film substance was formed inside a pyrex chamber (diameter 7 cm, length 30 cm). After eduction with acetone, the acetone was removed and the dried sample used for the structural analysis. The discharge system was a coil wound around the outside of a vertical chamber. The system was electrodeless, the frequency was 13.56 MHz and the output was 35 W.

*Numbers in the margin indicate pagination in the foreign text.

3. Results and Discussion

The mean molecular weight of the film substance by the vapor pressure osmosis method (standard mass: benzyl) was 900. This and the atomic components obtained by elemental analysis give the molecular system $C_{55}H_{50}N_{10}O_3$. This corresponds to 11 times the weight of the monomer. This is explained by the fact that one of the nitrogen atoms was eliminated. Also, existence of oxygen atoms which the monomer did not contain was noted.

Concerning the form of the nitrogen, there were pyridine rings, nitryl radicals, first and second order amine, and amide.

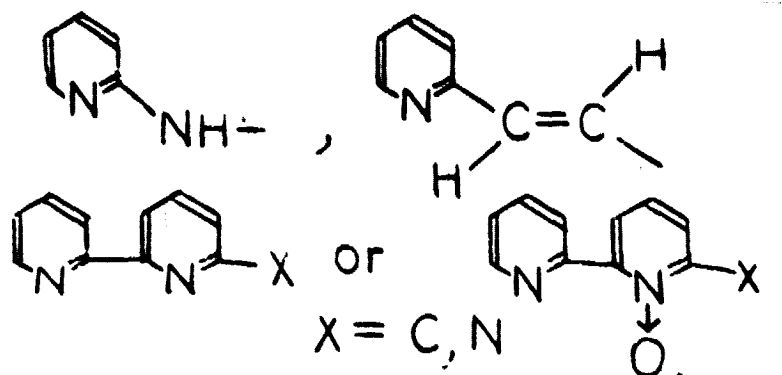
The following methods were used to measure the amounts of each of the above.

The pyridine rings were investigated from the integral ratio in the proton NMR spectrum. In the case of nitryl radicals and first order amide, methyl esterification was done and the number of methyl radicals introduced found by the proton NMR spectrum. For the amine, modification was done by acetylation and with carbon disulfide and the sulfur measured by potentiometric titration. Concerning the amide, its existence was confirmed and it was measured using the strong acylating agent N-methylbis (trifluoroacetoamide).

Concerning the substitution position of the pyridine rings, by using the IR spectrum and proton NMR spectrum, it was learned that two position monosubstitution bodies and 2.6 position bisubstitution bodies existed.

From the high resolving mass spectrum analysis, the structure of the pyridine rings was found to be as follows. (In the above measurements, the number of pyridine rings was found to be four for each molecule).

Also, it was noted from the elemental analysis that the film



took in oxygen atoms. From the results thus far, it is believed that the oxygen atoms in the film exist as acid amide and pyridine-N-oxide. It is believed that these and the partial structure described thus far which contains nitrogen contribute greatly to the hydrophilic chemical structure of the film.

CHARACTERISTICS OF PLASMA POLYMERIZED FILM AS ELECTRICAL MATERIAL

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When plasma polymerized film is considered as electrical material, dielectric characteristics, insulating characteristics and ion resistivity are involved. Here, for the most part, the characteristics of styrene polymer film are discussed. It is believed that this film can be used as a thin film insulating layer or as a resist in plasma etching.

1) Concerning Film Formation

When polymer film is grown by the direct method at a comparatively low frequency (1 - 100 KHz) on a substrate, factors causing film formation can be roughly divided into the bombardment effect in which polymerization takes place due to cations bombarding the adsorbed monomers and the transport effect in which polymerization takes place from the accumulation of free radicals formed inside the plasma or transported by the ions. The ratio of these is about 3:1.

In the case of styrene film, the effective cross section achieved by ion bombardment is polymerization by ion bombardment is about 200 \AA^2 . 5-6 styrene monomers are polymerized by one cation [1].

2) Electrical Characteristics of the Film

The merits and weaknesses of the electric characteristics of the film are expressed by resistivity ρ , dielectric tangency δ and dielectric breakdown voltage B.D.V.

1) $\tan \delta$: In general the $\tan \delta$ of the polymer membrane was inferior to that of scientifically manufactured polystyrene by about one unit. This is because there was bridging at the time of polymerization, divergence from three-dimensional regularity, and increase

in dipole moment due to bonding of residual radicals to oxygen.

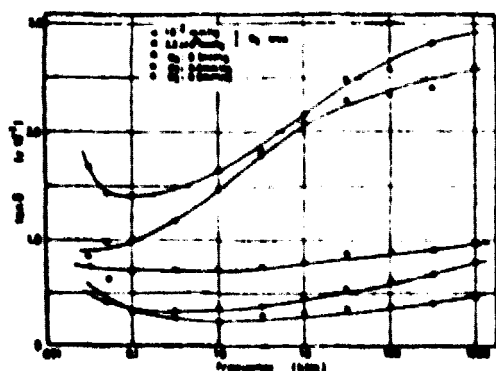


Fig. 1

Figure 1 shows the changes in $\tan \delta$ when the initial degree of vacuum was changed and oxygen was deliberately introduced during film formation.

Figure 2 shows the changes in $\tan \delta$ when the film was exposed to the air immediately after formation and when heat treatment was conducted at 200°C without breaking the vacuum.

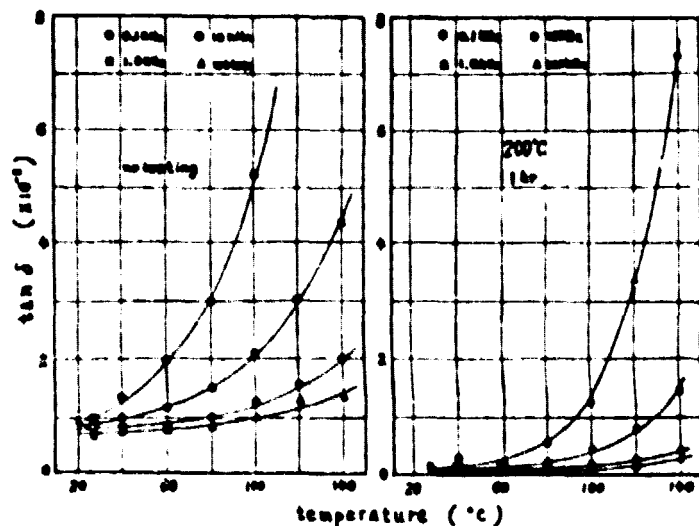


Fig. 2

In this case the residual radicals took in the oxygen, and carbonyl radicals were formed, and this is believed to have caused an increase in $\tan \delta$. The infrared spectrum also supports this.

Results showed that in making the same film layer, when the current density was reduced and the time increased, the $\tan \delta$ decreased more than when the reverse of this

was done. This thought to be the result of ion bombardment.

ii) ρ and B.D.V.

One of the features of plasma polymerized film is the small quantity of pin holes. Because of this it is easy to make film of $\rho > 10^M$ ($\Omega\text{ cm}$) and $\text{B.D.V.} > 10^6$. Figure 3 is an example showing the changes in V-I characteristics due to the introduction of oxygen. Taking advantage of the good insulating properties the film was tried as video

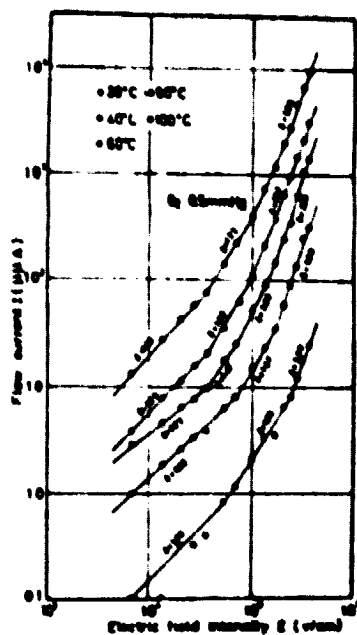
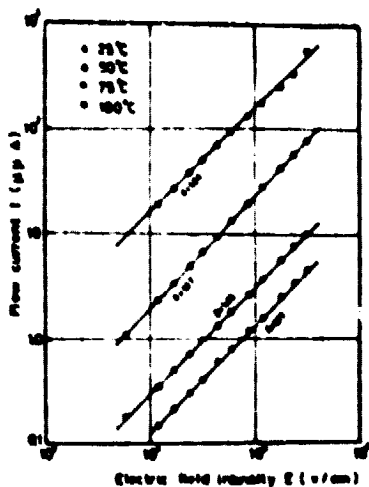


Fig. 3

disk coating with tentative success.

3) Ion Resistance Properties (Etching Characteristics)

An interesting fact was discovered when the plasma polymerized film was exposed a second time to the plasma. The styrene film obtained by plasma polymerization was easily etched in oxygen plasma, but when it was exposed beforehand to CF_4 gas discharge, the etching resistant properties increased so that it is possible to use the film as a resist.

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CHARACTERISTICS OF PLASMA POLYMERIZED TETRAMETHYLTIN

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1. Introduction

Glow discharge polymerization has many peculiarities compared to regular methods of polymerization. One of these is that polymer can

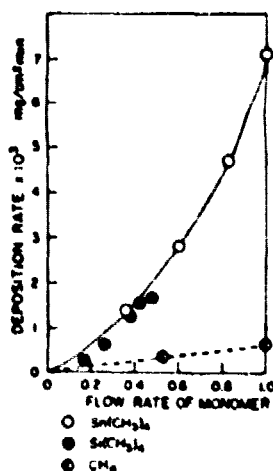


Fig. 1. Polymer Deposition Rate as a Function of Flow Rate of Monomers

be obtained from monomer not containing a functional group. Making use of this characteristic, polymer containing metal or semimetal can be easily produced. Such polymer can be expected to have characteristics not seen in polymer of the past. In the present experiment tetramethyltin was used as the monomer and several characteristics of the polymer formed from this were studied.

2. Experiment

A tube type reaction vessel was used and polymerization conducted under the conditions of 13.56 MHz and 25 W.

3. Results

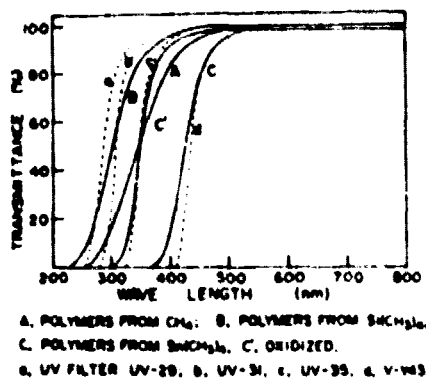


Fig. 2. Transmission Curves for Polymer Films Prepared by Glow Discharge Polymerization

The polymer obtained under the experimental conditions was all in film form. The polymer deposition rate was fast. Compared with methane containing no tin, it was exceedingly fast. (Figure 1). When

oxygen or methane was added the polymer deposition rate dropped. It is very unlikely that copolymerization occurred.

The polymer formed was not soluble in ordinary organic solvent. The polymer contained Sn, C and O and the composition was approximately C/Sn = 6.9, O/Sn = 3.1. Infrared absorption was noted for Sn-C, Sn-O-Sn and CH_2 radicals. The tin was not simply taken in by the polymer, but the polymer is one which contains tin.

The adhesiveness of the polymer to the substrate was good and with the exception of polypropylene, it displayed good adhesiveness to other polymer.

TABLE 1. Absorption Characteristics of Polymer Films Prepared by Glow Discharge Polymerization

Monomer	Thickness (μ)	λ_{150} (nm)	λ_{175} (nm)	$\lambda_{150} - \lambda_{175}$ (nm)
CH_4	1.15	346	377	31
$\text{Si}(\text{CH}_3)_4$	1.15	309	332	23
$\text{Sn}(\text{CH}_3)_4$	7.0	427	440	13
(oxidized)	7.0	351	366	15
UV-31		310	320	10
UV-35		350	365	15
V-V43		430	450	20

Concerning light transmittance, absorption was at less than 450 nm (Figure 2). When the polymer was oxidized, the absorption band differed from the short wave length and the rise in absorption was sharp. This is similar to the commercial UV film--UV-35.

The polymer shows no electrical conductivity and is highly insulating.