

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

PLASMA-INITIATED POLYMERIZATION AND ITS APPLICATIONS

Y. Osada and E. Tsuchida

(NASA-TM-75848) PLASMA-INITIATED
POLYMERIZATION AND ITS APPLICATIONS

N81-19301

(National Aeronautics and Space
Administration) 19 p HC A02/MF A01 CSCL 07C

Unclas
G3/27 41758

Translation of "Purazuma Kaishi Jugo to Sono Oyo", Purazuma
to Kagaku, April, 1980, pp.68-76



STANDARD TITLE PAGE

1. Report No. NASA-TN-75848	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Plasma-Initiated Polymerization and Its Applications		5. Report Date JANUARY 1981	6. Performing Organization Code
		8. Performing Organization Report No.	
7. Author(s) Y. Osada, E. Tsuchida.		10. Work Unit No.	
		11. Contract or Grant No. NASW-3199	
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		13. Type of Report and Period Covered	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		15. Supplementary Notes Translation of "Purazuma Kaishi Jugo to Sono Oyo", Purazuma to Kagaku, April, 1980, pp. 68-76	
16. Abstract This text discusses plasma-initiated polymerization. This method of polymerization is divided into 3 categories: polymerization of a vinyl monomer, solid phase polymerization and inorganic ring compound polymers. These 3 areas are discussed and examples are given.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unlimited - Unclassified	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 18	22.

PLASMA-INITIATED POLYMERIZATION AND ITS APPLICATIONS

Y. Osada and E. Tsuchida¹

1. Introduction

On September 15 and 16, 1978, a special symposium on plasma polymerization was held by the ASC Polymer Promotion Committee in Miami Beach. This research report was carried in the ACS Symposium Series 108, "Plasma Polymerization," Ed. M. Shen and A. T. Bell (1979). The symposium participants were from Japan, Canada and Holland. /68

This chemical symposium differed from several others. Plasma chemistry has become of great interest to chemists of polymer, inorganic, organic and physical chemistry, electrical engineers, biologists, and physicists. The thesis was of importance to all of these groups because it was developed from each of their viewpoints. There is a deep interest in studying the characteristics of plasma chemistry, and accordingly, large prospects and development can be anticipated.

However, at the same time, this means that plasma chemistry techniques, such as the approach to plasma energy, plasma properties and reaction dynamics, are incomplete. From the viewpoint of developmental research tied to plasma chemistry, there are various problems and uncertainties.

At the Miami symposium, a total of 20 items concerning plasma polymerization and plasma-initiated polymerization related to hydrogen, fluorocarbons and silicon compounds were reported. The last 2 have been previously explained [1, 2]. As to plasma chemistry reaction, the results of recent years have been reviewed [3]. In this special

¹Mr. Osada is an assistant professor of education at the Ibaraki University. Mr. Tsuchida is a Dr. of Engineering at the Wasada University, Department of Physics and Engineering.

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

edition, detailed explanations are given from each analysis although, in this manuscript, due to the restrictions of the number of pages, the problems are limited to plasma-initiated polymerization, which the authors have considered and promoted.

2. What is Plasma-Initiated Polymerization?

Partial gas molecules are separated in low temperature plasma (unequal plasma). Electrons, ions, radicals, molecules, excited molecules and photons, which are separated, are included. Normal plasma chemical reactions are caused by these activated particles. Consequently, plasma chemical reactions are gas phase reactions. There are no exceptions to the application of polymers, even in plasma polymerization. In plasma polymerization, we use a bell jar or tube-shaped reaction chamber. Saturated and unsaturated hydrocarbons, fluorocarbons or vinyl compounds flow in the chamber as gases and become plasma. The polymer film of these compounds is formed on top of the substrate. This technique is the one generally used [1].

Through the activated components mentioned above, or by the extremely varied gas phase reaction between monomer gases, the thin film which is produced, makes an extremely high bridge building material and a net mesh composition that has 1 diverging composition for each 2 or 3 units of repetition. It is usually noncrystalloid [4]. The film itself is very durable and can be said to be pinhole free. Because it is chemically stable, its application as an insulating film, surface treating or modifying film, or a semifilm is common knowledge.

On the other hand, if we are discussing a fundamental reaction, which is also called a gas phase reaction, the fact that direct experimental conclusions concerning basic problems, such as the identification of the reaction components that carry the burden in polymerization reaction (radicals, ions and photons), is the actual state of affairs [5, 6]. With thin, insoluble films where the polymer deposits on the substrate, the polymer, which differs in chemical composition from the monomer, is difficult to analyze [4, 7].

From the viewpoint of polymerization chemistry, the authors have captured plasma as one energy source for producing polymerization reactions and they feel that techniques, resulting in various polymers that are not similar in chemical composition to the monomers, are established. Our polymerization methods differ from previous plasma polymerization. The polymerization reaction proceeds in the condensed phase of liquids and solids. As shown in Figure 1, the monomer is placed in the reaction chamber where the pressure is decreased between the parallel electrodes. The electrodes are connected to the plasma producing equipment where we have an aligned circuit. Next, plasma is produced using the monomer in a condensed phase at equilibrium. Of course, we are not concerned with outside inductive electrodes, etc., even though we use them.

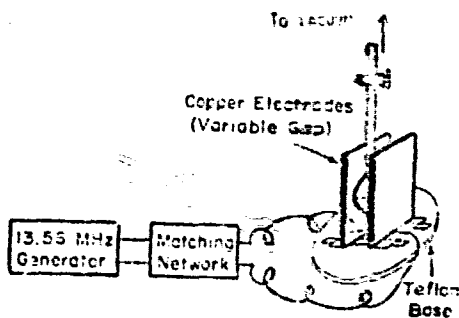


Figure 1. Plasma-Initiated Polymerization Equipment

The activated components that exist in gas plasma touch the liquids and solid surfaces and the polymerization growth reaction is induced. The polymerization reaction is in the gas phase and when there is a distinction between the plasma at the monomer condensed phase or the reaction is carried out by plasma absence, growth and suppression are characteristic. The initiation, growth, suppression reuniting and transferring reactions of polymerization differ from plasma polymerization (plasma-state polymerization) when there is contact with the plasma. We have called the process plasma-initiated or plasma induced polymerization.

According to this polymerization method, the authors have divided polymerization into 3 categories:

- A) plasma-initiated polymerization of a vinyl monomer (the formation of ultra-high molecular weight polymers),
- B) solid phase polymerization (single crystal polymers are formed),

C) inorganic ring compound polymers.

Research is proceeding on these three classifications, as described below.

3. Plasma-Initiated Polymerization of the Vinyl Monomer (Ultra-High Molecular Weight Polymer)

3.1 The Polymer of Methyl Methacrylic Acid (MMA)

The MMA is placed in an ampoule that is 0.8 cm in diameter and plasma irradiated for 60 seconds. When we leave it at 25°C, a polymer is obtained from postpolymerization [8]. The polymerization reaction gradually proceeds with the polymerization time, as shown in Figure 2.

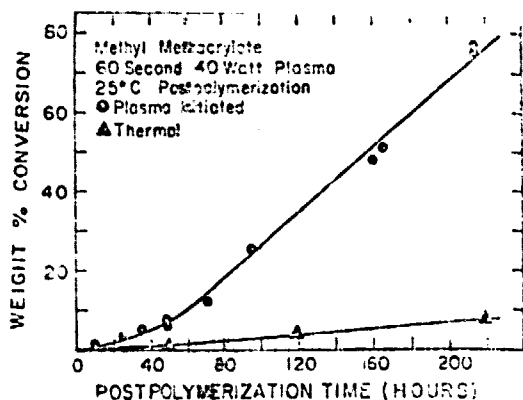
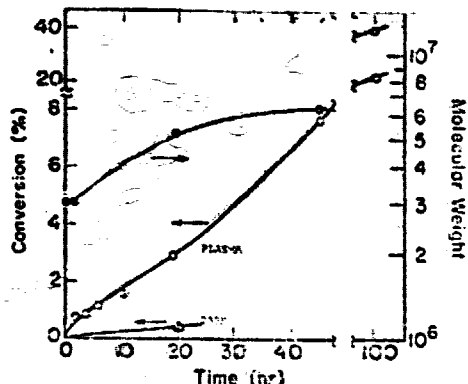


Figure 2
The Plasma-Initiated Polymerization of Methyl Methacrylic Acid

About 60% is polymerized in 1 week and 100% will be polymerized eventually. Post-polymerization is done at a lower temperature. For example it is possible at a temperature of -15°C. The polymethyl methacrylic acid (PMMA), which is obtained by plasma-initiated polymerization is different from that obtained by previous methods. There are [illegible] and good polymers in normal inorganic solutions. We obtain an ultra-high molecular weight polymer [9] (UHMWP) with a molecular weight of more than 10,000,000. /70

As shown in Figure 2, the plasma irradiation immediately after PMMA has a previous viscous equilibrium molecular weight of 3,000,000, which increases with the post-time and becomes several 10,000,000 four days later.³

³Since there is no viscosity formula that conforms to PMMA with a molecular weight of more than 10,000,000, the value is a [illegible] value estimated using the general viscosity formula.

According to Professor Fujita of the physics department of Osaka University, by a detailed light diffusion measurement in [term unknown]* and MEK solution, this polymer does not have any divergence or bridge building materials at equal molecular weights of 300,000,000 [10].

In Table 1, because we obtain this polymerization reaction and the same polymerization speed, the output of the necessary high energy irradiation polymerization (γ -ray, β -ray, high energy electron rays) must be compared. In these cases, we also obtained an ultra-high molecular weight polymer. When we compare the energy used and equipment treatment methods and stability, the advantages of plasma-initiated polymerization are clear.

Table 1. THE POLYMERIZATION OF METHYL METHACRYLIC ACID BY VARIOUS IRRADIATION POLYMERIZATION TECHNIQUES

SOURCE	ENERGY	R_p (MOLE/L-SEC)	MOL. WT.
PLASMA	50 W, 60 SEC	4×10^{-6} (25°C)	30×10^6
γ -RAY	2×10^{-2} RAD/SEC	" (20°C)	0.5×10^{10}
β -RAY	2.2 MeV. 5×10^{-6} cal/sec	" (30°C)	1×10^{10}
High Energy Electron	3 MeV, 1.5×10^5 REP	" (20°C)	$1.8 - 3 \times 10^6$

This type of ultra-high molecular weight polymer is valuable scientifically, not only as a research object, but also as a raw material. Figure 3 shows the stress-relaxation curve of PMMA with equal molecular weights of 300,000,000 [11]. Even at a high temperature of 213°C, dynamic strength is maintained for a long time. However, conversion after the termination of the test is small, only about 5%. The curved line also shows that the low polymer portion is not entirely included when the dynamic strength decreases.

As shown above, it is thought that PMMA, which is obtained by this method, shows improved anticrazing properties. Because the chemical examples of polymerized substances, solvents and stable substances are not included, the procedure became progressively stable.

*[Translator's note: possibly typographical error for "acetone."]

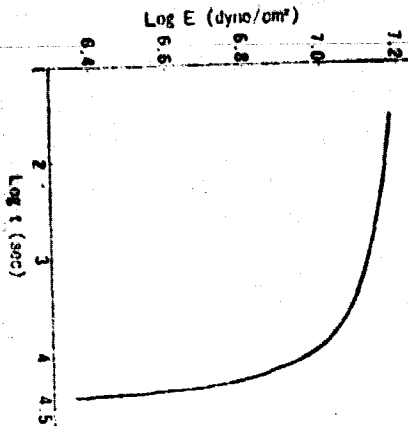


Figure 3
The stress-relaxation curve of methyl methacrylate from polymerization.

The use of PMMA in artificial limbs and false teeth is anticipated.

Next, we would like to discuss the mechanism of this polymer reaction system. The presence of radicals and ions in plasma polymerization has been explained. Thus, in order to determine the reaction components (in particular, the growth activation components), which are found in this reaction, the detailed composition of PMMA with a molecular weight of 30,000,000 is analyzed using 180 MHz of high power NMR immediately following plasma irradiation [12].

The results show a triad distribution of 7% iso, 27% hetero, and 66% syndio. This conforms to the plasma polymerization products [8]. From the activated energy of the polymerization reaction (about 6 Kcal/mole), the activated growth component confirms the presence of a radical in the polymerization results explained previously. Next, this radical is formed in some way by plasma irradiation. We don't have room to explain the details here, but we can disregard initiation by light (ultraviolet rays). A direct attack on the MMA molecules in the gas phase by electrons that are separated is essential [11, 12]. As a matter of fact, even when hydrogen or nitrogen plasma is irradiated in MMA, polymerization does not occur. It does not occur in a large organic substance with steam pressure (solution polymerization) from MMA [11]. Therefore, how a radical, which was produced in the gas phase, can be polymerized at the liquid phase, which it has been in for a long time, is an unsolved question.

3.2 The Polymerization of Other Vinyl Monomers

Plasma-initiated polymerization is carried out on other vinyl

monomers. These results are given in Table 2 [12, 12]. Plasma-initiated polymerization is classified in 3 categories:

- 1) polymer by the plasma-initiated method,
- 2) formation of only thin film polymers and
- 3) a completely inactive plasma-initiated polymer.

1) contains the aqueous solvents of methacrylic acid, acrylic acid, acrylamide and methacrylamide. 2) is styrene and methylstyrene. 3) includes each type of acrylic acid ester. Other than MMA, methacrylic acid esters are polymerized immediately after irradiation, but they are not postpolymerized.

Table 2. PLASMA-INITIATED POLYMERIZATION OF VINYL MONOMERS [13]

Monomer	Polym. Medium	Plasma Duration (Sec)	Post-Polym. Condition	Yield (%)
Methyl Methacrylate	Bulk Liq.	60	100 hr., 25°C	40
Methacrylic Acid	Bulk Liq.	30	168 hr., 5°C	3
	75% Aq. Soln.	15	90 hr., 5°C	80
Acrylic Acid	Bulk Liq.	30	168 hr., 5°C	3
	75% Aq. Soln.	15	90 hr., 5°C	50
Methacrylamide	Bulk Solid	120	45 hr., 20°C	Trace
	30% Aq. Soln.	12	45 hr., 20°C	80
Acrylamide	Bulk Solid	40	45 hr., 20°C	Trace
	50% Aq. Soln.	15	45 hr., 20°C	60
Ethyl Methacrylate	Bulk Liq.	60	168 hr., 5°C	1
n-Butyl Methacrylate	Bulk Liq.	30	168 hr., 5°C	1-2
Methyl Acrylate	Bulk Liq.	180	200 hr., 20°C	0
	Bulk Liq.	900	168 hr., 5°C	0
n-Butyl Acrylate	Bulk Liq.	20	168 hr., 5°C	0
Styrene	Bulk Liq.	60	168 hr., 5°C	0
	94% CCl ₄ Soln.	60	66 hr., -15°C	0
	50% CCl ₄ Soln.	15	66 hr., -15°C	0
α -Methylstyrene	Bulk Liq.	30	168 hr., 5°C	0

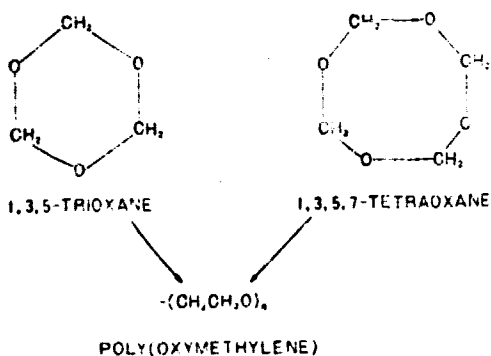
The results show the special characteristics of the polymerization method. It differs from the usual activated radical polymerization.

It is possible to use the same polymerization technique with MMA and styrene or methacrylic acid [13]. In both cases, we get the usual radical polymerization and the same polymerization constitution, as well as the same sequence distribution. In the case of styrene, there is a plasma-initiated polymerization inactive monomer, as previously

explained. Together with the increase in its density, the amount of both polymers obtained decreases.

4. The Solid Phase Polymerization of Trioxane and Tetraoxane (The Formation of a Single Crystal Polymer)

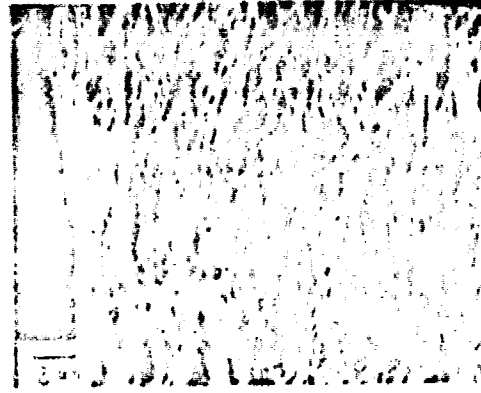
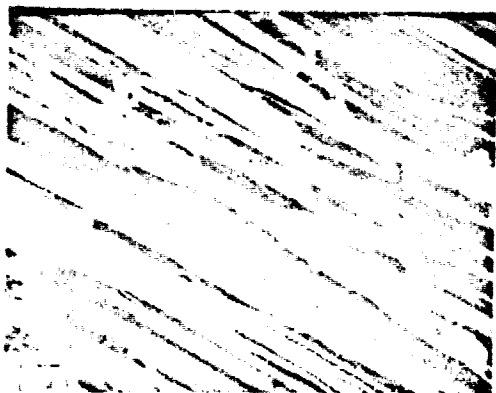
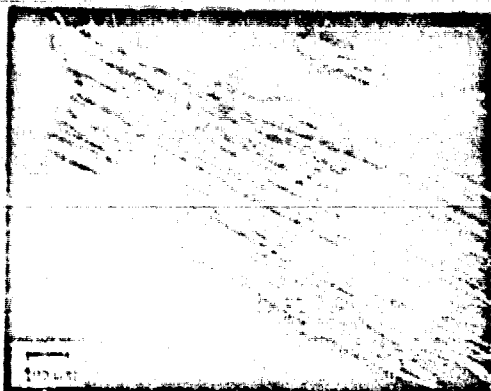
We used the same method as that used in Section 3. When plasma is irradiated for a short time in single crystals of 1,3,5-trioxane (TOX) and 1,3,5,7 tetraoxane (TEOX), strands of polyoxymethane (POM), which was oriented to a high degree, are obtained [14]. For example, when we irradiate plasma for 10 to 60 seconds in single TOX crystals at an output of 40 W, a POM crystal forms immediately on the TOX surface. However, after this, when we carry out postpolymerization at an appropriate temperature, polymerization progresses inside the crystal and the efficiency of the polymerization shows a remarkable increase. In these procedures, there is no change observed on the outside of the monomer crystal. As the monomer crystal is maintained, polymerization is completed. Polymerization does not occur fully in solvents of cyclohexanes, etc.



Reaction formula 1

In Table 3, the plasma irradiation conditions and the results of the amount of POM obtained and its composition are given. The significance of the POM, which is obtained by this polymerization method, is that it has a crystal composition and morphology. In Figure 4 (a), the scanning electron microphotograph (SEM) of the polytrioxane (PTOX) is shown. It has a fiber composition, which is oriented at mutually fixed

sides. This conforms to the axis of the monomer crystal. Each fiber does not have a divergence at the smooth cylindrical surface. A wide angle X-ray diffraction photograph of the PTOX fibers is shown in Figure 5 (a). There is a strong dispersion in 6 spots. Except for the main crystal on the (110) surface, we know that sub-crystals (twin crystals) also exist. It is thought that the 3-dimensional highly



(a) プラズマ: 50w, 60秒, 後重合 45°C, 66時間

(b) プラズマ: 70w, 30秒, 後重合 85°C, 66時間

Figure 4. Scanning Electron Microphotographs of Polytrioxane (Figure (a)) and polytetraoxane (Figure (b)) Obtained from Plasma-Initiated Polymerization.

Key: (a) Plasma: 50 W, 60 seconds, postpolymerization, 45°C, 66 hours. (b) Plasma: 70 W, 30 seconds, polypolymerization, 85°C, 66 hours.

crystallized PTOX, which was oriented to a high degree, is that in which polymerization advances in conditions where there is an analogy to a "topochemical" reaction. We know that the TOX and TEOX are obtained by α -ray and γ -ray irradiation.

Thus, PTOX, which is obtained by γ -ray and plasma-initiated polymerization was tested for detailed microtextures using X-ray narrow angle diffusion (Figure 5 (b)), DXC, etc. There is no room here to give a detailed explanation. However, in Table 3 the results obtained by Professor Odajima of the Hokudai Engineering Department are shown. The PTOX obtained by both polymerization methods is given with an analogy between both. The sub-crystal content in the plasma-initiated polymerization is higher and the crystal size is larger [15].

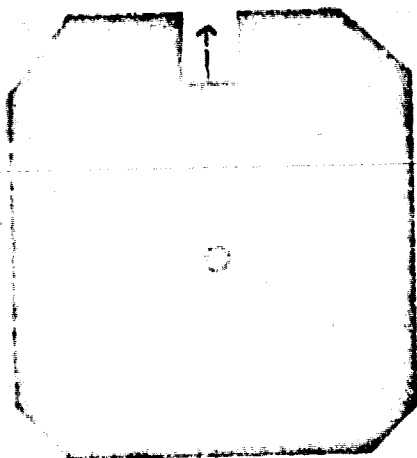
The fibers of the polytetraoxane (PTEOX) obtained by γ -ray irradiation are observed by SEM. The PTEOX is oriented on the same side side as PTOX was. The wide angle X-ray microphotograph also shows a

Table 3. THE SOLID POLYMERIZATION OF TRIOXANE AND TETRAOXANE BY γ -RAYS OR PLASMA-INITIATED POLYMERIZATION [14, 15]

Sample	Post-Polymerization Temperature (°C)	Post-Polymerization Duration (hrs)	Yield (wt %)	M.P. (°C)	M. W. (Mn) $\times 10^{-3}$	Sub-crystal Fraction (vol %)	Crystal Size along Chain Axis (Å)	Lattice Distortion (%)
RADIATION INITIATION								
PTOX-80	55	20	80	187	36~39	450	0.7
PTOX-12	62	25	12	173				
PTOX-25	81	25	25	181				
PTOX-40	105	6	40	179				
PTOX-39	105	6	80	174				
PLASMA INITIATION								
PTOX-20-1P	45	16	20	189				
PTOX-20-2P	45	46	20	185				
PTOX-30P	45	65	40	186	27~31	650	1.25
PTOX-41	110	21	4	183				
PTOX-5P	110	24	5	...				
PTOX-63P	110	3	83	182				
PTOX-A	40	20 (in air)	25		253			

radiation: 1 MRad, room temp. plasma: 40~100 w, 30~50 sec, room temp.

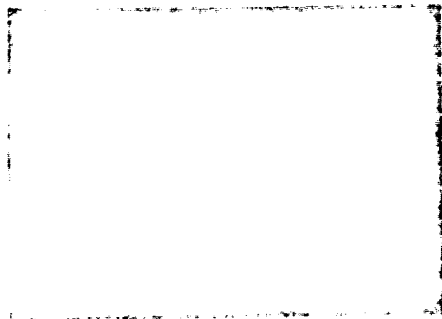
ORIGINAL PAGE IS
OF POOR QUALITY



(a)



PION plasma induced. Polymer Yield = 40%



PFOX γ -ray induced. Polymer Yield = 40%

(b)

Figure 5.
Wide angle (a) and narrow angle (b) X-ray photographs of polytrioxane obtained from plasma-initiated polymerization. (For comparison, look at the narrow angle X-ray diffraction photo of polytrioxane obtained from γ -ray irradiation.)
Plasma: 50 W, 60 seconds, post polymerization, 45°C, 66 hours.
 γ -ray: 1 megarad post polymerization, 55°C, 20 hours.

mechanical expansion orientation, this type of high orientation and high

high orientation [15]. However, the PTEOX obtained by plasma-initiated polymerization is completely different [16]. As shown in Figure 4 (b), both the size and direction are formed from strands of irregular waves and have wide distribution. Lowering is observed in the wide angle X-ray photograph and there is no orientation. However, the small angle diffusion shows no diffusion in the center. It is the same with PTOX.

A polymer with this type of composition can be obtained by plasma-initiated polymerization. However, the γ -ray permeates even in the TOX and TEOX crystal lattice. In contrast to being able to polymerize between the crystals, in the case of plasma, there are, at the very most, several microns between the crystal surface and, moreover, the monomer steam or plasma reaction products, which directly sublime from the crystal surface, are plasma-initiated polymerization components. This type of manifestation is also possibly connected to the facts mentioned above.

It is well known that, in comparison to fibers obtained by

crystal PTOX fiber is mechanically and thermally superior (for example, after polymerization by the Derlin chemically initiated method). The activated polymer, which leads to the release of polymerization, uses inactive gases, such as nitrogen and argon. When the plasma initiation of plasma treatment is carried out, it is possible to end-cap easily. In comparison to the radioactive irradiation method, practical application is anticipated from the viewpoint of simplicity, stability and equipment.

5. The Polymerization of Inorganic Ring Compounds

Research connected with inorganic polymers as insulation and antidotes has developed in the United States. The authors have noticed the high energy of plasma and developed plasma-initiated polymerization of inorganic compounds, such as various phosphazene compounds, inorganic silicon compounds and carboranes using solid phase polymerization. We would like to introduce one of these here.

5.1 Polymerization of Phosphazene Compounds

Inorganic gum has been known for over 100 years. According to H. R. Allcock, ever since the success of fiber polymer formation, research connected with the polymer of hexachlorocyclotriphosphazene (chemical reaction formula 2, abbreviated as PNC below) and its inorganic displacement polymer, has been developed [17]. Usually, PNC, as shown in chemical reaction formula 2, becomes a polymer (polycyclophosphazene) by 1 or 2 days of fusion heating at about 250-300°C under vacuum pressure. When the existence of air and polymer percentage is high, a bridge-building reaction is produced. At a temperature of less than 200°C, the polymerization rate is a few %/day. This percentage is very small.

Related to the solid phase polymerization of PNC, several tests have been done. For example, using γ -rays, a high amount of radiation of 10^6 - 10^8 rads is added and a polymer is barely obtained [18]. Using 4 MeV high energy electron rays, 10^9 rads absorption rays are added at temperatures of -70, 25, and 120°C in the PNC crystal. In spite of

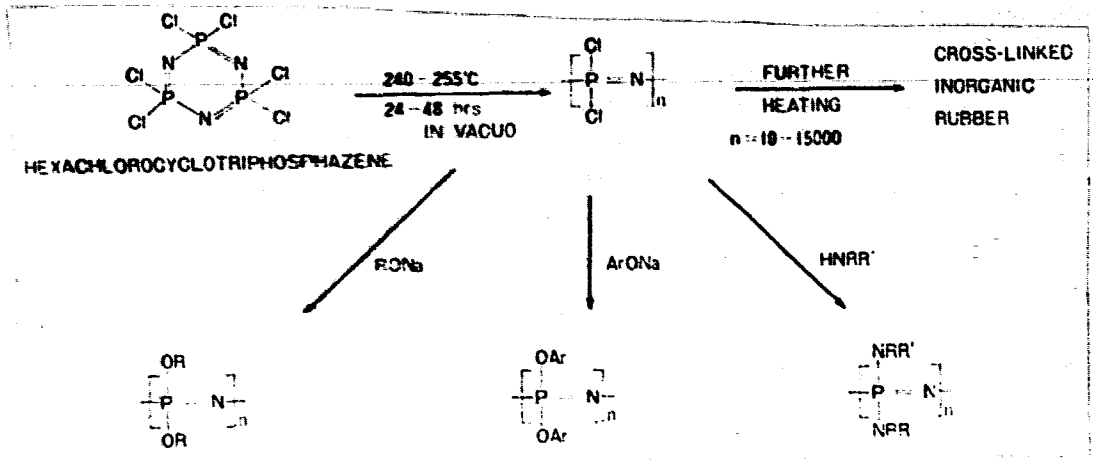
the high energy, only 1 or 2% of inactive products are obtained [19]. Finally, in 1962, we used a 50KV X-ray. We irradiated by 1 or 2 rads rays at 100°C and only 9% of the polymer was obtained [20].

When we irradiate the high frequency plasma in the PNC crystal at an output of 50-110 W, we observe that a polymer can be obtained very efficiently. For example, at an output of 100 W, when plasma is irradiated in the PNC crystal, a polymer is initiated immediately and 15 minutes later about 41% of the polymer is obtained. The polymer is a white elastomer. In short, while plasma is irradiated for 5 minutes, a "polymerization activated component" is produced. After that polymerization progresses rapidly and a phosphazene polymer is easily obtained (Table 4). Plasma differs from other high energy irradiation methods. How to carry out the heat polymerization reaction efficiently is a significant question. The reaction organization is presently being tested.

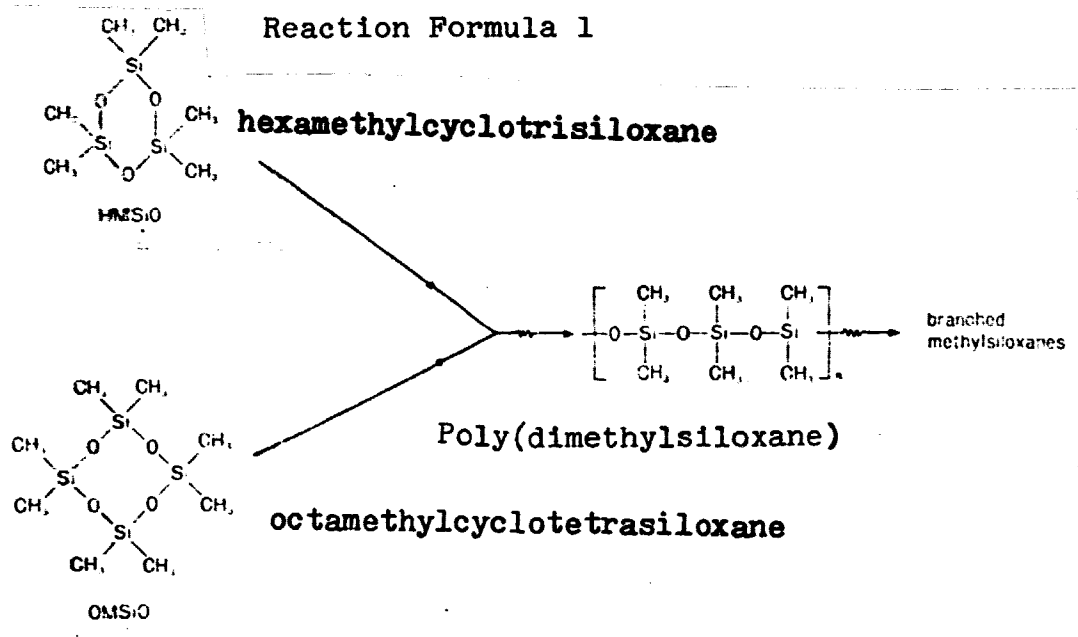
5.2 The Polymerization of Inorganic Silicon Compounds

The silicon polymer, which is a representative inorganic polymer (polymethylsiloxane), usually starts out as dimethyl cyclo-silane. It is manufactured by hydrolysis and equilibrium polymerization. Oligomer rings, which are obtained as intermediate products, for example, hexamethylcyclotrisiloxane (HMSiO) or octamethylcyclotrisiloxane (OMSiO), are immediately polymerized and have deep significance from the viewpoint of coating that is superior to high induced electrical film insulation and optics. Even here the polymerization has been tested by γ -ray and electron ray irradiation.

For example, S. Lawton [21], uses high energy electron ray equipment of 800 KV. With regard to HMSiO near the melting point (65°C), after 2.3×10^6 roentgen irradiation, a bridge building polymer is obtained at about 20%. However, in the case of OMSiO, only 2 polymers are obtained [22]. With γ -rays, there is 10% of HMSiO at rays of 5×10^5 rads and with a dose of rays of 1.2×10^5 /hr, 100 hours later, 5% of the bridge building polymer is obtained [24].



Reaction Formula 1



Reaction Formula 2

Table 4. 1 EXAMPLE OF PLASMA-INITIATED POLYMERIZATION OF HEXACHLOROCYCLOTRIPHOSPHAZENE

POWER (W)	PLASMA-DURATION (MIN.)	POSTPOLYMERIZATION	CONVERSION (%)
110	5	NONE	18
110	15	NONE	41
70	15	NONE	26
110	5	180°C 2 hrs	61
110	1	180°C 2 hrs	17

OTHER METHODS OF SOLID STATE POLYMERIZATION OF HEXACHLOROCYCLOTRIPHOSPHAZENE

METHOD	DOSE	TEMPERATURE	CONVERSION
γ-RAY	$10^6 - 10^7 \text{ rad}$	-10°C	NO POLYMERIZATION
HIGH ENERGY ELECTRON	$4 \text{ MeV}, 10^7 \text{ rad}$	25°C	1%
		120°C	SOLUBLE
X-RAY	$50 \text{ KV}, 1.2 \times 10^6 \text{ rad}$	100°C	9%/10hrs

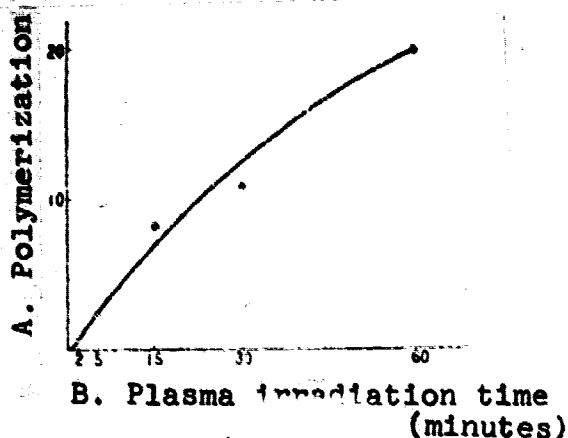


Figure 6

The plasma irradiation time and polymerization efficiency of the plasma-initiated polymerization of A. Polymerization; B. Plasma irradiation time (minutes)

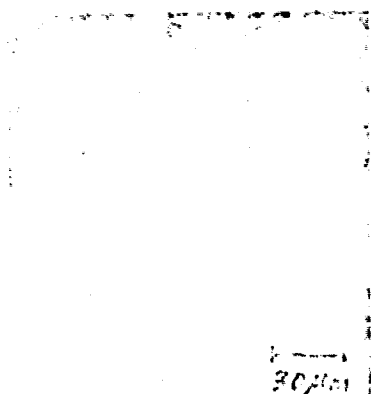


Figure 7

A scanning electron microphotograph of plasma-initiated polymerized poly(dimethylsiloxane)

As shown above, it is clear that a polymerization reaction occurs immediately in the [illegible] phase by using plasma-initiated polymerization. The products we obtained were not the thin films found earlier. We obtained "resins" with high molecular weights or crystal characteristics. This polymerization method differs in reaction discussions from other high energy irradiation polymerization methods. In contrast to the fact that γ -ray angular high speed electron rays, that have an enormous output, cannot polymerize a small PNC crystal,

The authors note that when plasma irradiation is done in HMSiO we can very efficiently carry out polymerization. The irradiation time-polymerization percentage curve of HMSiO is shown in Figure 6. The polymer is formed as a milky white film. The white film peels off the walls with the polymerization reaction. The thick film is determined by the density of the HMSiO. In Figure 7, a SEM photograph of the film surface obtained in this way is shown. From the results of IR, element analysis, etc., HMSiO is polymerized. The existence of a diverging composition becomes clear. At the time of polymerization, as well as film, oil oligomers and a fiber polymer with a relatively low molecular weight are also formed. As shown above, OMSiO is difficult to polymerize using irradiation. When we use plasma, HMSiO is easily polymerized.

6. Conclusion

the occurrence of an efficient polymerization reaction in a short time with plasma of about 100 W is interesting.

As for the analysis of a detailed reaction stage, there are no radicals and ion polymerization must be considered. From the explanation in this text, it is thought that this polymerization reaction is useful from the viewpoint of equipment and management methods, maintenance cost and stability. Scientific samples were not mixed among the products of the polymerization induced reaction. This was not just a basic reaction analysis. We tried to test the polymerization reactions from broad viewpoints. We hope that these tests will be further developed.

REFERENCES

1. Kobayashi, H., "Plasma Polymerized Thin Films," 111.
2. Shen, M., Editor, Plasma Chemistry of Polymers, Marcel Dekker Inc., 1976.
3. "Chemical Reactions in Electrical Discharges," Advances in Chemistry Series 80, ACS, 1969.
4. Shen, M. and A. Bell, "A Review of Recent Advances in Plasma Polymerization," Plasma Polymerization, ACS Symposium Series 108, 1979.
5. Morita, S., M. Shen and Ieda, J. Polym. Sci., Polym. Phys. Ed. 15, 981 (1979).
6. Morita, S., A. Bell and M. Shen., J. Polym. Sci., Polym Chem. Ed., 17, 2775 (1979).
7. Yasuda, H., Polymers, 26, 783 (1977).
8. Osada, Y., A. Bell and M. Shen., J. Polym. Sci. Polym. Letters Ed., 16, 309 (1978).
9. Fetter, L. J. et al., Science 176/104 (1972).
Micurasova, D., K. Horie, et al., Makromol. Chem. 175, 2091 (1974).
10. Fujita, H. et al., Polymer. J.
11. Nagada, Tsuchida, M. Shen and A. Bell, Polymer Association Bulletin, 27, 1162 (1978).
12. Osada, Y., A. Bell and M. Shen., Polymer Preprints, 19, 482 (1978).
13. Osada, Y., A. Bell and M. Shen, "Plasma Polymerization," 253, ACS Symposium Series 108, 1979.
14. Osada, Y., M. Shen and A. Bell, J. Polymer, Sci., 16, 669 (1978).
15. Odajima, A., Y. Nakase, A. Bell and M. Shen, "Plasma Polymerization," 263, ACS Symposium Series 108, 1979.
16. Nagada, Tsuchida, M. Shen and A. Bell, Polymer Committee Bulletin 27, 1166 (1978).
17. Allcock, H. R. and R. L. Kugel, J. Am. Chem. Soc., 87, 4216 (1965).
18. Manley, T. R., Nature 184, 809 (1959).
19. Spindler, M. W. and R. L. Vale, Makromol. Chem., 43, 237 (1961).

20. Caglioti, V., D. Cordiaschi and A. Mele, Nature, 195, 492 (1962).
21. Lawton, E. J., W. T. Grubb and J. S. Balwit, J. Polym. Sci., 19, 455 (1956).
22. Kantor, S. W., U.S. Patent 2766220 (1956) Chem. Abstr., 51, 3181, 1957.
23. Burlant, W. and C. Taylor, J. Polym. Sci., XLI/138, 547 (1959).
24. Tabata, K., M. Kimura and T. Sobue, Manufacturing Reports 67, 1274 (1964).