The Plasma Polymerization of Vinyl Monomers. I. The Design, Construction, and Operation of an Inductively Coupled Plasma Generator and Preliminary Studies with Nine Monomers

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Synopsis

An apparatus was constructed which would allow vinyl-type monomers (and others) to polymerize at ambient temperatures in the presence of an inductively coupled RF field. The details of the construction of the system are reported along with preliminary results obtained from nine monomers: styrene, methylvinyldichlorosilane, vinyl acetate, acrylonitrile, vinyl fluoride, 1,1-difluoroethylene, vinyl chloride, ethylene, and 1,3-butadiene.

HISTORICAL

The phenomenon of plasma polymerization has been known since about 1900. However, until 1948 little attention was given to this method of obtaining a polymeric material. From 1948 until the present, work in the area of plasma polymerization was directed toward the formation of thin insulating films, with little or no attention given to fundamental considerations.

The first plasma polymerization studies were published by de Wilde¹ and Thenard² in 1874 when they simultaneously reported that acetylene reacted readily in a silent dc discharge to form a hard, brittle residue which was insoluble in common solvents. Investigations involving polymerplasma chemistry reported to date fall into two classifications: treatment of conventional polymer films in a plasma^{3,4} and actual polymerization of monomers using the plasma as an initiator.⁵⁻⁹ This comprehensive literature review will apply to all papers in this series.

Shaw¹⁰ polymerized a silicone oil on the surface of small electronic devices and produced an impermeable, insulating thin film. He used a medium-power, 4 megahertz, capacitively coupled plasma. The effect of the type of monomer and the bleed rate of the monomer on the final properties of the film was investigated. The chemical and physical properties of these polymers were not studied.

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Bazzarree and Lin¹¹ treated fiber glass filaments with various types of vinyl monomers (vinyltriacetoxysilane, vinyltriethoxysilane, and silane) in an attempt to increase their tensile strengths. The investigators studied the effect of three types of plasmas: (1) low-frequency radio frequency (RF), (2) high-frequency RF, and (3) direct current discharge, on the overall properties of these polymers. Ozawa¹² employed plasma polymerization techniques using styrene and tetrafluoroethylene to make thin-film insulators for microcapacitors. He used an alternating-current (lowfrequency) electrode-discharge plasma in a long glass tube.

Denaro, Owens, and Crawshaw¹³ investigated the glow-discharge polymerization of styrene. This is the most comprehensive study that has been reported to date. The investigators used a 500-watt, 2-megahertz alternating-current discharge to produce and sustain the plasma. The power was capacitively coupled to two parallel plates spaced 2.3 cm apart. The initial pressure of 10^{-5} torr was achieved with a forepump-oil diffusion pump couple. Two variables, time and pressure, were investigated. They found that the amount of polymer formed was a linear function of time at low power. The pressure-versus-rate plots show a linear dependence at low pressure, with the curves flattening out at higher pressures. The final operating pressure was achieved by adjusting the leak rate of the monomer, although the specific leak rate was unknown. The power at which the plates were operating was obtained using an inductively coupled radio frequency (RF) meter. This procedure makes any absolute calibrations very difficult. Williams and Hayes¹⁴ reported the glowdischarge polymerization of several common vinyl-type monomers: methyl methacrylate, vinyl acetate, styrene, α -methylstyrene, ethyl acrylate, methyl acrylate, isoprene, isobutene, and ethylene. Their reactor consisted of a bell jar containing parallel plate electrodes 50 cm² in area and spaced 2 cm apart. All connections to the system were made through the bottom plate of the bell jar. The power source was a lowfrequency (10 kilohertz), 1000-watt audio oscillator. The authors correlated the rate of polymerization of a given monomer to its adsorption rate on the electrodes. If the adsorption rate was the governing factor in the polymerization rates, then there could be no gas phase reactions of any consequence occurring in the capacitively coupled system. This fact has not been borne out in studies using an inductively coupled electrodeless system. The rate of polymerization was shown to be a linear function of power (current density); however, the limiting power was never reached. Their data show that for a given power level an increase in pressure results in an increase in rate of film deposition up to a critical pressure, beyond which no further rate increase is observed. If the pressure was regulated by adjusting the monomer input rate (as is suspected since no other means is evident from the description of their experimental apparatus), this rate increase would then be a result of increasing the monomer concentration. The authors attribute any increase in the rate of polymerization to an increase in the absoute pressure of the system. This statement is subject to interpretation, and their correlations with adsorption isotherms have not been proven. The same types of curves are obtained in systems where adsorption of the monomer on a surface is not the controlling factor.

Mearns¹⁵ published a review which includes the use of plasma polymerization in the production of thin insulating films. He reported two capacitively coupled systems which were used in film deposition; however, only general observations were outlined. In all of the papers presented in the above review, no attempts were made to study specific polymer properties, i.e., molecular weight, density, and infrared spectra as a function of the reaction parameters.

INTRODUCTION

In the investigations described in this series of papers, one of the most important parameters studied was absolute power input to the system. There are two criteria important when accurate values and precise control of radio frequency (RF) power is necessary. First, a system which can transfer the power efficiently (better than 85% efficiency) is advantageous. Second, a low-frequency (less than 50 megahertz) low-power (less than 100 watts output) system is easier to work with and regulate. There are two components necessary to couple a RF power source to a plasma reactor: a capacitive component and an inductive component. Either of these components could be arranged to transfer the power to the plasma with the other component serving to tune the circuit. When two parallel plates are used to transfer the power, these plates constitute an extremely large capacitor; and, hence, this system is known as a capacitively coupled or electrode discharge plasma. The other arrangement uses a coil usually consisting of several turns of 1/4-in. copper tubing wound around the reactor. A capacitor is then hooked in series with the hot end of the coil to complete the LC circuit. An optimum value of these components at 4 megahertz, to obtain the maximum efficiency, would be 0.04 henries for the coil and $0.05 \,\mu f$ for the capacitor. If either value vastly exceeds these, the efficiency of power transfer will be reduced. If a system is capacitively coupled, the plates are usually spaced 2 cm or more apart, which gives an extremely high value for the capacitance and no inductance value can be found to tune the circuit properly. For this reason, inductively coupled circuits are much more efficient than their capacitively coupled counterparts, and hence an inductively coupled system was designed and will be described in detail in this paper.

EXPERIMENTAL

In an inductively coupled system, the plasma is sustained by ionizing collisions of particles accelerated in the RF field. The initial particles are free electrons from the system. An inductively coupled plasma has a large magnetic field, while the capacitively coupled system has a large electrostatic field.

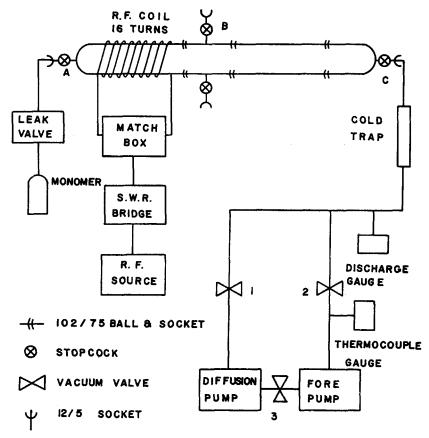


Fig. 1. Block diagram of plasma apparatus.

There were four parameters that needed to be controlled: temperature, pressure, bleed rate of the monomer, and power input to the system. The plasma polymerization system was designed for flexibility and control of those parameters which were directly related to polymerization rate and the properties of the polymers formed. The reactor was filled with gaseous monomer, and polymerization was started by applying an RF field to the inductor coil. The specific details of operation will be presented.

The purpose of this paper is to describe the system in detail. Specifically, the following systems will be discussed: (1) the reactor system, (2) the vacuum system, (3) the RF system and matching networks, and (4) the monomer inlet systems. A schematic drawing of the system is shown in Figure 1.

Construction of the Reactor

The type of reactor used in this study was a four-section, horizontal reactor, illustrated in Figure 2. The reactor was constructed of 70-mm Pyrex glass tubing. The horizontal reactor was constructed of four sections,

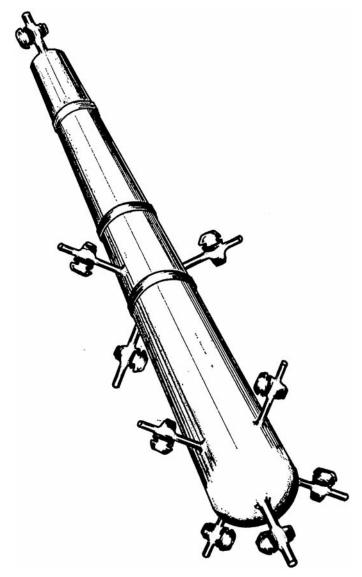


Fig. 2. Isometric sketch of plasma reactor showing position of stopcocks.

labeled I-IV in Figure 2, joined with 105/75 standard ball-and-socket joints. Sections II and III can be interchanged to obtain different reactor geometries. A variety of monomer inlet and vacuum outlet combinations can be used without changing the geometry of the reactor. The dimensions of the sections were: I, 35 cm; II, 18 cm; III, 31 cm; IV, 13 cm. The gas inlets are standard ball-and-socket joints joined to the system through a vacuum stopcock. Electrical feed-through connections can be made through the stopcock by sealing a smooth copper conductor in a ball

joint with a high-vapor-pressure epoxy. The reactor was equipped with a series of 4-in. sleeves which were secured inside the primary reactor to form a liner. The sleeves were used to obtain kinetic data since this arrangement allowed quantitative recovery of the polymer. A similar vertical reactor was also constructed.

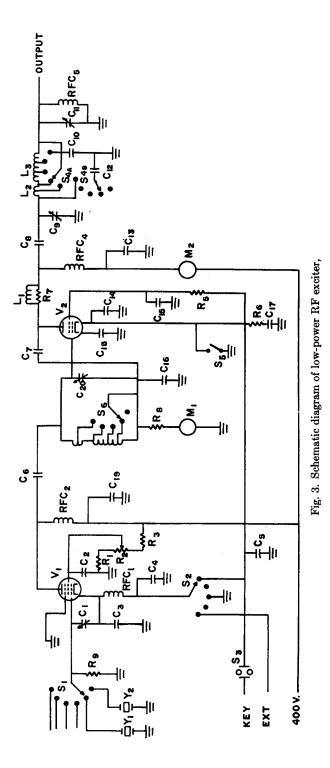
Construction of the Vacuum System

The vacuum system was constructed entirely of copper and brass with all solder joints. The Welch two-stage duo-seal forepump served as both the backing pump for the 4-in. oil diffusion pump and as the preevacuation pump for the reactor. The forepump was switched between the two modes of operation with 1-in. brass Granville Phillips-type vacuum valves.

The vacuum was monitored using two thermocouple gauges and one discharge gauge located as illustrated in Figure 1. The thermocouple gauges were National Research Corporation Type 701 and were accurate to a vacuum of about 25 microns. The discharge gauge was a Phillips Gauge Type PHG-1 and was accurate to a vacuum of 10^{-4} microns. It should be noted that these guages are sensitive to the type of gas in the system. They are precise for a given gas; however, if absolute accuracy is a criteria, a capacitance-monometer type of gauge is recommended. An efficient cold trap on the foreline is important to prevent contaminating the pump oil with monomer. The cold trap should operate at liquid nitrogen temperature.

Construction of the RF System

The radio frequency (RF) oscillator and amplifiers are the most important part of the system. The radio frequency generator was designed to supply a variable-frequency (4-30 megahertz), variable-power (5-50 watts) output and consisted of a low-power exciter capable of an output of 50 watts, Figure 3. The low-power exciter was a Hartley oscillator coupled to a 6DQ5 operating as a class B amplifier. The output was increased by increasing the capacitance of C9 and resonating, the output LC (inductance-capacitance) circuit with C11. The exciter had a nominal 50 ohm output. The impedance of the inductor-capacitor network on the plasma reactor had a nominal impedance of 250 ohms; hence, some type of matching network was required. A Johnson "matchbox" type of coupler, Figure 4, was used to optimize the match between the RF generator and the load. The standing wave ratio (SWR) is a measure of the ratio of maximum current to minimum current along a transmission line. It is a measure of the mismatch between the load and the line and is equal to 1 when the load, line, and source are perfectly matched. Hence, with a SWRbridge, Figure 5, the matching network was adjusted for minimum SWR. An SWR of 1.1 was achieved which corresponds to an efficiency of better than 95%. This correction has been applied to all of the power data reported in this work. With this system, very precise control of power input was achieved.



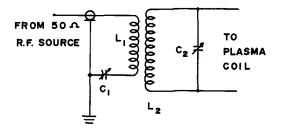


Fig. 4. Schematic diagram of matching network.

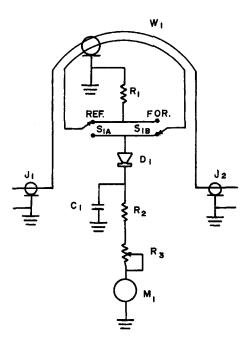


Fig. 5. Schematic diagram of SWR bridge.

Construction of Monomer Inlet System

Two states of monomer were used in this study: those which were liquids and those which were normally gaseous monomers at room temperature. The normally gaseous monomers were bled into the system through a Granville Phillips leak valve. The liquid monomers were vaporized in an all-Pyrex glass system prior to being sent through the leak valve, Figure 6. The leak valve was wrapped with heating tape, and the temperature was adjusted by means of a Variac to prevent condensation of the monomer in the valve. The vapors in the leak valve were distilled from the inhibitor, and thus care was taken to prevent overheating and subsequent polymerization. Modifications for special experiments will be described under the specific experiment.

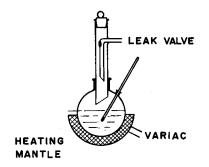


Fig. 6. Liquid monomer inlet system.

Polymerization Procedures

The first experiments were designed to study various monomers and their products. The following experimental procedure was found to give the best results. In order to obtain reproducible data, previous experience showed that two experimental details were of particular importance. First, the system had to be thoroughly cleaned after each run and all of the Pyrex joints lubricated with Apiezon N grease. Secondly, the system had to be thoroughly purged with monomer prior to the initiation of the plasma. If the system was not clean, a satisfactory, initial vauum was not attained. The Pyrex joints were cleaned with petroleum ether immediately after the reactor was disassembled. The reactor was assembled using a minimum amount of Apiezon N grease.

The vacuum system was started with valves 1 and 2 (Fig. 1) closed and valve 3 open to the diffusion pump with the diffusion pump on. The reactor was preevacuated by closing V3 and opening V2. When the system had pumped to a vacuum of 100 microns or less (not leaving the forepump off of the diffusion pump for more than 10 min), V2 was closed; V1 and V3 were opened. The system was allowed to pump until a vacuum of 10^{-2} microns When this pressure was reached, V1 was closed and the was achieved. reactor was bled to atmospheric pressure with dry argon and evacuated as before. When a vacuum of 10^{-2} microns was reached, the monomer was bled into the system through the leak valve until the system reached 25 microns (a vacuum of 25 microns gave an optimum plasma). V1 and V3 were closed; the diffusion pump was shut off and V2 was opened. The experiments were run with the forepump on and liquid nitrogen in the cold trap. The cold trap was kept filled all of the time the forepump was on in order to condense unreacted monomer and to prevent contamination of the The monomer was allowed to purge through the system for 1 hr prior oil. to starting and adjusting the plasma.

The procedure for starting the RF generator was as follows: the plate current was turned on and the driver adjusted for a maximum driver grid current with C20 (Fig. 3). The drive current was adjusted to 0.8 milliamperes with R2. The plate current (M2) was adjusted with C11 for a minimum (dip) valve. C9 was used to increase the load and retuned with C11 for a minimum plate current. These steps were repeated until the desired power output was achieved. The matching network was then adjusted for the minimum SWR. An initial vacuum of 25 microns was employed. Gaseous samples were introduced directly through the leak valve. However, liquid samples were vaporized in a liquid monomer inlet system as shown in Figure 6.

Reactor Configuration Studies

It was found that the low-power, inductively coupled 4 MHz radio frequency (RF) plasma provides a low temperature and unique method for the gas phase polymerization of a wide variety of monomers. This is one of the few methods that may be utilized to carry out a vapor phase polymerization. Initial experiments were carried out using nine monomers: styrene, methylvinyldichlorosilane, vinyl acetate, acrylonitrile, vinyl fluoride, 1,1difluoroethylene, vinyl chloride, ethylene, and 1,3-butadiene. The structures of these monomers are presented in Table I for comparison.

There are three interrelated parameters associated with the plasma reactor: power input, bleed rate, and pressure. The reactor system was operated at an absolute power input in the range 8-50 watts. Between the power levels of 8 and 50 watts, the temperature generated was less than 1.5°C above ambient (25°C). In the power level range of 50-500 watts, noticeable temperature rises were observed which would introduce additional complexities into the reaction studies. A power input range of 8-50 watts was therefore selected for this investigation. Bleed rates between 0.03 and 0.15 g/hr were investigated, and a value of approximately 0.06 g/hr was found to give the most stable plasma over the power range of 8-50 watts. This bleed rate resulted in a pressure of 25 microns when the initial pressure was 0.08 microns. The above conditions were found to be consistent for all of the monomers utilized when a molecular weight correction was applied. A series of tests was performed using vinvl chloride in order to determine the optimum reactor geometry for subsequent studies.

As shown in Figure 2, there were several combinations of vacuum outlet and monomer inlet positions possible with both the vertical and horizontal reactors. In studying the basic operating parameters of the reactor, the distribution of polymer along the reactor was of major importance. One of the parameters which was felt would affect the distribution was the position of the monomer inlet coupled with the vacuum outlet. This study was carried out for both the vertical and horizontal systems. The vacuum outlet, and monomer input geometries were chosen for each run as shown in Figures 7 and 8, and the geometries are listed in their respective Tables. The results of the horizontal reactor configuration studies are presented in Figure 9. These results show several characteristics for this type of reactor. All of these results are for 10 hr of operating time, 22 watts power input, 25 microns pressure, 25°C, and using a constant bleed rate. The distribution of polymer along the reactor length and the mass of polymer formed are

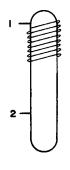
Name	Structure	Boiling point, °C	Molec- ular weight
	H		
Styrene	C=CH2	145	104
	•		
	Ç CH₃		
Methylvinyldichlorosilane	$Cl - Si - C = CH_2$	57	141
Methylvinyldichlorosnane		57	141
A		50	50
Acrylonitrile	$CH_2 = CHC = N$ O H	78	53
	ii i		
Vinyl acetate	$CH_3 - C - O - C = CH_2$	72	86
Methyl methacrylate	$CH_2 = C - CH_3$	100	100
	CĤ₃ H		
	}		
Vinyl fluoride	$\mathbf{CH}_2 = \mathbf{C}_1$	-51	46
	\mathbf{F}		
	H		
Vinyl chloride	$CH_2 = C$	-14	62
•	d		
Ethylene	$CH_2 = CH_2$	-103	28
	н н	100	
1.9 Date Bare	1	0	E 1
1,3-Butadiene	$CH_2 = C - C = CH_2$	-3	51
1,1-Difluoroethene	$CH_2 = CF_2$	-84	64

 TABLE I

 A List of the Monomers Used in this Study

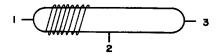
dependent upon the position of the monomer inlet and vacuum outlet. The configuration used for run I (vacuum inlet at RF end and vacuum outlet at opposite end) was selected as the one to be used for the principle part of this investigation. Under these conditions the plasma can be sustained over the entire length of the reactor, and the highest polymer yield having a uniform distribution is obtained.

Several attempts were made to explain the differences shown by the curves in Figure 9. All paths led to the realization that a knowledge of the flow patterns for the various configurations and a pressure gradient profile must be available before feasible explanations can be offered. It is important to note that polymer is formed throughout the reactor length (volume) regardless of the position of the monomer inlet and the vacuum outlet.



RUN NO.	MONOMER INLET	VACUUM OUTLET
	1	2
н	2	t

Fig. 7. Inlet-outlet positions for vertical reactor.



RUN NO.	MONOMER	VACUUM
I	I	3
11	3	I.
14	2	T
IV	3	2
v	1	2
VI	2	3

Fig. 8. Inlet-outlet positions for horizontal reactors.

The vertical reactor was constructed for a series of experiments which was designed to allow polymer formed in the bulk phase to fall and be collected outside of the plasma field. These experiments were not successful.

Figure 10 shows the distribution and mass of polymer formed under the conditions presented in Figure 8. The vertical reactor presented handling

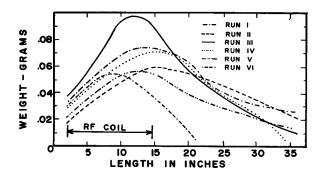


Fig. 9. Polymer distribution from horizontal reactor experiments.

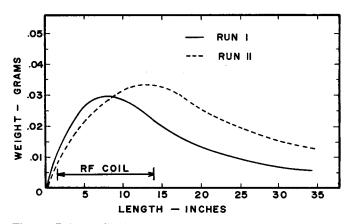


Fig. 10. Polymer distribution from vertical reactor experiments.

and experimental difficulties not encountered with the horizontal system and the magnitudes of the weight of polymer formed could not be related to the results presented in Figure 9. However, the shapes of the distribution curves are presented for comparison. The vertical reactor was not used to obtain any of the data presented in this discussion.

RESULTS AND DISCUSSION

Prior to each run, the sleeve liners were washed with a hot detergent solution, rinsed with distilled water, rinsed with methanol and acetone, and dried and weighed. After each polymerization, the sleeves were removed from the reactor and were weighed to give the total weight of polymer plus sleeve. Care was exercised not to contaminate the sleeves with vacuum grease from the reactor ball joints. The polymer was removed by the most suitable means (scrapping, peeling, loosening in warm solvents, etc.). The sleeves were then cleaned as before, weighed, and the amount of polymer taken as the difference between the weights of the coated sleeves and the cleaned sleeves. This technique gave results which were reproducible to within 3%.

The polymers that were produced by plasma polymerization consisted of two distinct phases, a soluble phase and an insoluble phase. The soluble polymer was present in very small quantities (usually less than 2%), and because of this limiting factor the types of characterizations were limited. The soluble portion was extracted from the insoluble film and recovered by freeze drying from the benzene. The insoluble material was filtered from the benzene using Whatman 541 filter paper. The polymer was removed from the paper and dried in a vacuum oven at room temperature. Infrared spectra of the insoluble material were obtained with some difficulty. Both the KBr pellet and the nujol mull techniques were employed, with both procedures giving spectra with less than desirable results. The KBr spectra were used as they were slightly better resolved. The pellets were made employing standard techniques. Following are general comments concerning the initial nine monomers tested, along with their IR spectra.

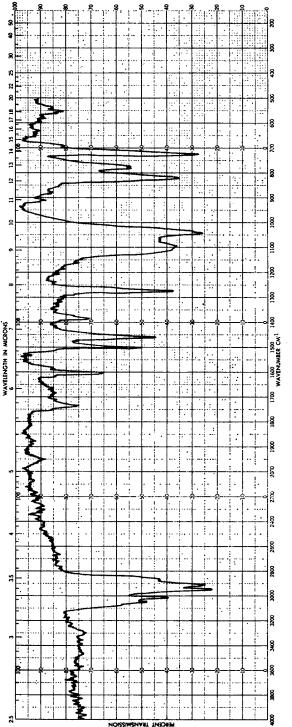
Styrene. The styrene yielded a "snow" and film which was almost white at a wide variety of bleed rates; however, it did not form as rapidly as the polymer formed from vinyl chloride. Both the film and the snow were partially soluble in benzene. The infrared spectrum of the soluble portion was a clean polystyrene spectrum (Fig. 11). The spectrum of the insoluble portion (Fig. 12) was clearly polystyrene; however, it indicated that unsaturation was present.

Methylvinyldichlorosilane. This monomer would not yield "snow" polymer even at high bleed rates. The product formed as an intensely yellow film which was insoluble in methyl ethyl ketone, methylene dichloride, and cyclohexane. The film was very tough and difficult to strip from the glass. The infrared spectrum indicated an unsaturated silane polymer. The infrared spectrum (Fig. 13) is characteristic of a chlorinated polysiloxane.

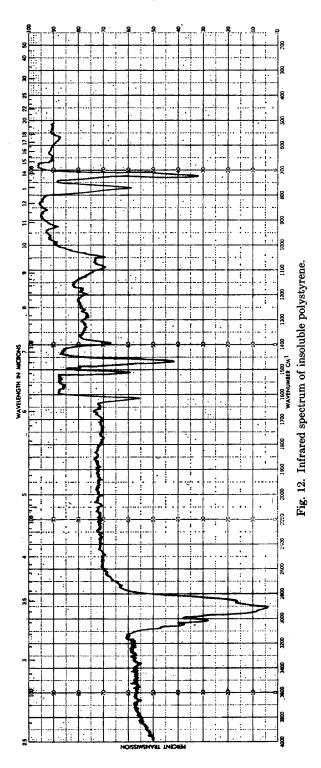
Vinyl Acetate. The polymer formed from vinyl acetate was either "snow" or a film, depending on bleed rate. Methyl ethyl ketone stripped the film from the glass, swelled it, and partially dissolved it. The undissolved film is clear and only very slightly colored as compared to the usually dark-brown residue. The spectrum of the polymer (Fig. 14) indicated the material was poly(vinyl acetate) and contained very little unsaturation. The conversion of this monomer to polymer was lower than either the vinyl chloride or styrene.

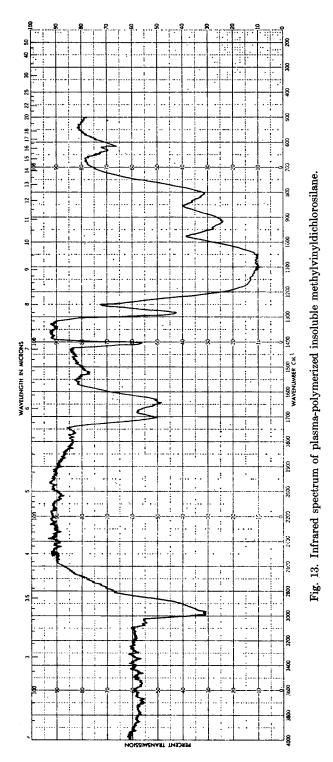
Acrylonitrile. Acrylonitrile formed a polymer very rapidly which was a yellow film. At high bleed rates, snow polymer formed. With this monomer the plasma is sustained at high bleed rates so the rate of monomer introduction can be higher. The snow is partially soluble in DMF, although most of the material was insoluble. The film had very poor adhesion to the sleeves. Although the insoluble portion gave a very diffuse infrared spectrum (Fig. 15), it was very similar to a pure polyacrylonitrile spectrum.

Vinyl Fluoride. This normally gaseous monomer yielded a brown film which had poor adhesion to the glass. The film was flexible, tough, and could be removed in whole, large pieces. Only a small amount of insoluble

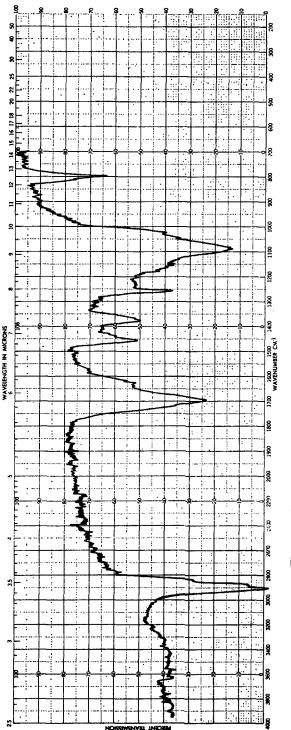




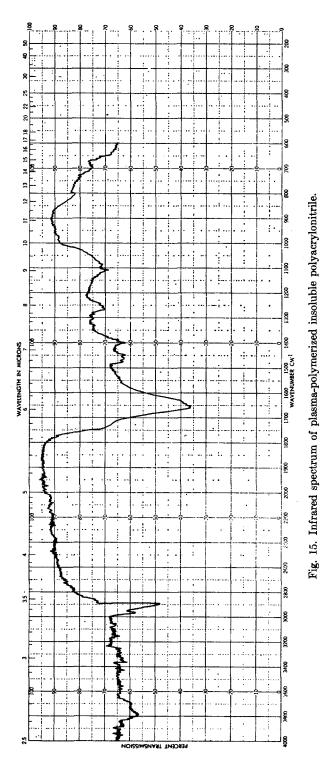


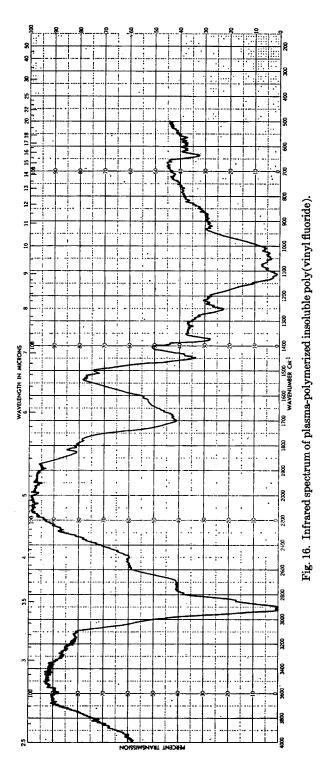


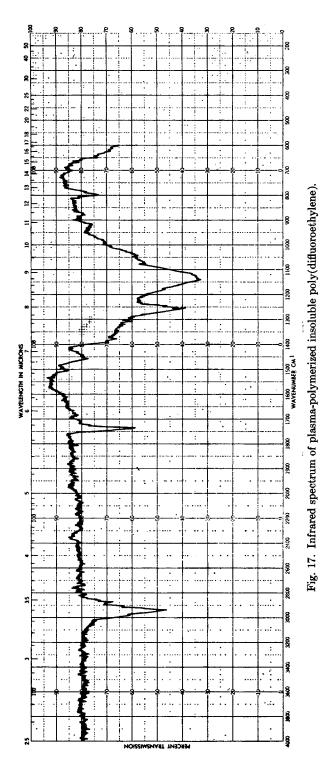


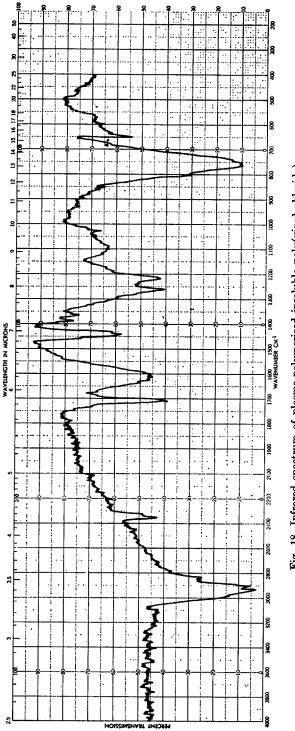














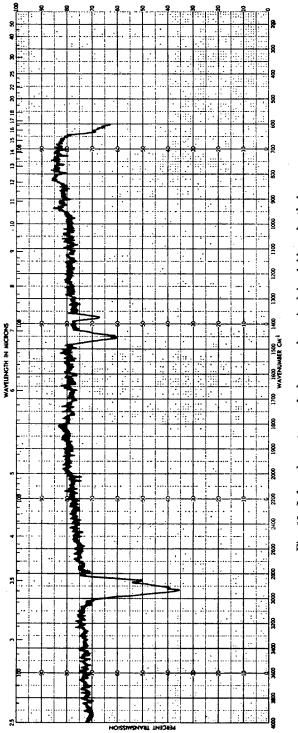
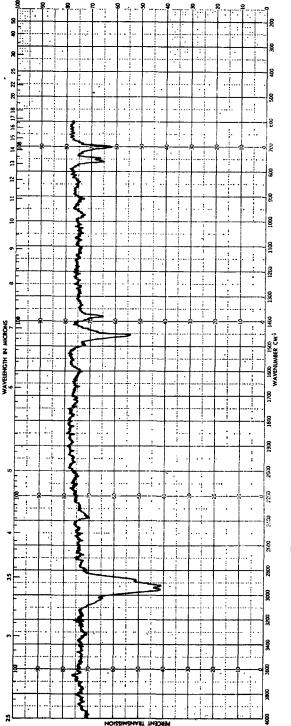


Fig. 19. Infrared spectrum of plasma-polymerized insoluble polyethylene.





snow could ever be formed. The film was insoluble in hot 1,1,1-trichloroethylene. The IR spectrum (Fig. 16) obtained from the film indicated the material was poly(vinyl fluoride) which contained some unsaturation.

1,1-Difluoroethylene. This monomer formed a brown, totally insoluble film which did not adhere well to the glass reactor. Figure 17 is a diffuse infrared spectrum of the film and indicates that some unsaturation is present in the polymer.

Vinyl Chloride. The plasma polymerization of vinyl chloride yielded a tough insoluble film with excellent adhesion to the glass. The yield was high with this monomer. The infrared spectrum (Fig. 18) is typical of a slightly unsaturated poly(vinyl chloride).

Ethylene. When ethylene was employed as the monomer, both film and snow polymer could be produced easily. Both forms were totally insoluble in common organic solvents. The products were almost white or clear, and the infrared spectrum (Fig. 19) indicated there was no unsaturation present.

1,3-Butadiene. The results using this monomer were the same as obtained with the ethylene, and the infrared spectrum is given in Figure 20.

The reactor showed the same general operating characteristics with all of the monomers studied.

CONCLUSIONS

The low-power, inductively coupled radio frequency plasma reactor described in this paper produced stable polymer films with a low power output from the RF generator. It was found that the parameters power and pressure were easily regulated and reproduced.

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