

01 Jan 1981

GLOW DISCHARGE POLYMERIZATION.

H. Yasuda

Missouri University of Science and Technology, yasudah@mizzou.edu

Follow this and additional works at: https://scholarsmine.mst.edu/chem_facwork

 Part of the [Chemistry Commons](#)

Recommended Citation

H. Yasuda, "GLOW DISCHARGE POLYMERIZATION.," *Journal of Polymer Science, Macromolecular Reviews*, vol. 16, pp. 199 - 293, Wiley, Jan 1981.

The definitive version is available at <https://doi.org/10.1002/pol.1981.230160104>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Chemistry Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Glow Discharge Polymerization

H. YASUDA

Department of Chemical Engineering and Materials Research Center, University of Missouri-Rolla, Rolla, Missouri 65401

I. Introduction	200
II. Scope of Polymer Syntheses	201
A. Characteristic Form of Glow Discharge (Plasma) Polymers	201
B. Plasma-State Polymerization Versus Plasma-Induced Polymerization	202
C. Glow Discharge Polymerization Versus Graft Polymerization	203
D. Glow Discharge Polymerization Versus Radiation Polymerization	205
III. Processing Factors of Glow Discharge Polymerization	206
A. Modes of Electric Discharge	207
1. Types of Electric Discharge and Plasma Reactors	207
2. Volume and Intensity of Plasma	212
B. Monomer Flow Rate	220
C. System Pressure	223
D. Discharge Power	226
E. Geometrical Factor of Reactor	236
1. Bypass Ratio of Flow	236
2. Relative Position of Energy Input and Polymer Deposition	237
3. Relative Location of the Feed-In of the Starting Material and Flow Pattern	237
F. Nonpolymerizable Gas	238
G. Distribution of Polymer Deposition	241
H. Properties of Polymers	245
1. Polymers from Mixed Monomers	258
a. Mixture of Organic Compounds	258
b. Mixture of an Organic Compound and Nonpolymerizing Vapor	258
2. Substrate and Reactor Materials	260
IV. Mechanisms of Polymer Formation	264
A. Gas Phase Reaction Versus Surface Reaction	270
1. Energy Input Surface and Reaction Media	270
2. Fluid Mechanic Factors of Plasma	271
B. Polymerization Rates and Monomer Structure	275
C. Plasma-Induced and Plasma-State Polymerizations	280
D. Effect of Product Gas Plasma	281
E. Molecular Polymerization Versus Atomic Polymerization	284
1. Correlation between Polymer Deposition Rate and Chemical Structure of Monomer	284
2. Trapped Free Radicals in Polymers	286
F. Internal Stress in Glow Discharge Polymerization	287
G. Structural Difference of Monomer and Polymer	289
V. Concluding Remarks	290
References	291

I. INTRODUCTION

It has been known for many years that some organic compounds form polymers in plasma (ionized gas) generated by some kinds of electric discharge (de Wilde, 1874; Thenard, 1874; Schoepfle and Connell, 1929; Austin and Black, 1930; Linder and Davis, 1931; Harkins and Jackson, 1933; Koenig and Helwig, 1959; Otazai et al., 1954; Weisz, 1955). In most cases, however, the polymers were recognized as byproducts of phenomena associated with electric discharge; consequently, little attention had been paid either to properties of these polymers (undesirable byproducts) or to the process as a means of forming polymers.

Only in relatively recent years (about the 1960s) has glow discharge polymerization been practically utilized to make a special coating on metals (Goodman, 1960; Argnette, 1962; Coleman, 1962; Stuart, 1963; Bradley and Hammes, 1963). Once some of the advantageous features of glow discharge coating (e.g., flawless thin coatings, good adhesion to the substrate, and chemical inertness, and low dielectric constant) were recognized, much applied research concerning the use of the process was done.

The term "plasma" is used to describe the state of ionized gas (e.g., glow discharge) (Baddour and Timmins, 1967; McTaggart, 1967; Gould, 1969; Venugopalan, 1971). The ionized gas consists of positively charged (ionized) molecules or atoms (ions) and negatively charged electrons. The state of plasma can be created by a variety of means. In general, when a molecule is subjected to a severe condition, such as intense heat, ionization of the molecule occurs. At temperatures above 10,000 K, all molecules and atoms tend to become ionized. The sun and other stars of the universe have temperatures ranging from 5000 to 70,000 K or more, and they consist entirely of plasma. The space between the galaxies is also filled with plasma, though its density is much lower.

The classical definition limits the term plasma to an appreciably ionized gas or vapor that conducts electricity and is at the same time electrically neutral, fluid, "hot," and viscous. The modern definition is less restrictive, the term plasma simply denoting a more-or-less ionized gas. A gaseous complex that may be composed of electrons, ions of either polarity, gas atoms, and molecules in the ground or any higher state of any form of excitation, as well as of light quanta is referred to as "plasma." The plasma in this sense may be "cold." The plasma created by electric glow discharge is often called "low-temperature plasma" to distinguish it from "hot" plasma. In the laboratory, plasma has been generated by combustion, flames, electrical discharge, controlled nuclear reactions, shocks, etc. Since a plasma loses energy to its environment mainly by radiation and conduction to the walls, in order to maintain the plasma state continuously in a laboratory apparatus, energy must be supplied as fast as it is lost. Of the various means to maintain plasma state continuously for relatively long periods of time, the most obvious and common method is by means of an electrical discharge. For this reason, most experimental work, particularly in the study of polymerization, has been carried out using some kind of electric discharge.

The polymer formation in glow discharge or in plasma of organic vapors is

often referred to as “glow discharge polymerization” or “plasma polymerization.” In this review, glow discharge polymerization is used to describe the general process of polymer formation which occurs in glow discharge in order to distinguish specific polymerization mechanisms such as plasma-induced polymerization and plasma-state polymerization.

Polymer formation in glow discharge is a very complex phenomenon and the elucidation of reactions involved in the process is far behind the extent of technical exploitation of the process. Consequently, most research in this area is of empirical and correlation finding in nature. As far as “polymerization” is concerned, the mechanisms appearing in the literature are essentially hypothetical elucidations or speculations with numerous assumptions that explain empirical results.

The major efforts have been seen in finding correlations between ionization processes and the final polymer deposition, and the steps which increase the molecular weight of species involved have been dealt with by either the well-known process of “polymerization” or the mysterious and ill-defined process of “polymerization.” In this sense, in spite of numerous potential applications and the uniqueness of the polymer-formation process, the subject has not drawn much attention as a subject area of polymer science.

In this review, an attempt was made to present a critical review, to summarize some important aspects of “polymer formation” in the glow discharge polymerization or plasma polymerization, rather than present a bibliographical review of work. Accordingly, the review may reflect a highly biased view of the author more strongly than a consensus of opinions. It is believed that such a critical review will contribute to the deeper understanding of the phenomenon and to the correct applications of the process.

II. SCOPE OF POLYMER SYNTHESSES

A. Characteristic Form of Glow Discharge (Plasma) Polymers

Polymers formed by glow discharge polymerization are in most cases highly branched and highly crosslinked and adhere to solid surfaces (e.g., surface of electrode, surface of vessel, and moving substrate), though solvent-soluble polymers are also formed depending on the conditions of glow discharge.

Chemical reactions that occur under plasma conditions are generally very complex and nonspecific in nature. Consequently, a chemical reaction in plasma will not compete with other methods of a chemical reaction if such a chemical synthesis can be carried out by conventional methods. Chemical reactions in plasma have merit only for reactions that require special excited states of molecules as intermediate states and, consequently, cannot be carried out or can be obtained with only very poor yield by conventional means. Glow discharge polymerization, therefore, should be recognized as a special means of preparing special forms of polymers. Obviously, glow discharge polymerization acquires little merit for preparing ill-defined solvent-soluble polymers, which require

further steps of purification and fabrication before such polymers can be used as final products.

Historically, the formation of polymers under plasma conditions was recognized as a nonsoluble deposit that provided nothing but difficulty in cleaning the apparatus. This undesirable deposit that adheres tenaciously to the substrate and strongly resists chemical cleaning processes can be utilized in a desirable manner if a deposition of a polymer is placed on an appropriate substrate. This situation seems to provide an excellent illustration of the uniqueness of the form of glow discharge polymers.

In order to see the uniqueness of glow discharge polymerization, it may be worth comparing steps necessary to obtain such a good coating by a conventional coating process and by glow discharge polymerization. If one starts to coat a certain substrate with conventional polymers, it requires at least several steps: e.g., (i) synthesis of polymer or prepolymer, (ii) preparation of coating solution, (iii) cleaning of substrate surface, (iv) process of coating, (v) drying, and (vi) curing.

For such an application of polymers, the advantage of glow discharge polymerization is obvious, i.e., glow discharge polymerization accomplishes all these steps by essentially one-step polymerization starting from a monomer. Therefore, glow discharge polymerization provides a unique method of polymer synthesis if an ultrathin layer of polymer that is intimately bonded to an appropriate substrate is required.

B. Plasma-State Polymerization Versus Plasma-Induced Polymerization

Plasma can be utilized in the general "polymerization" of organic monomers in a number of ways. The formation of polymer film at the interface of monomer and vapor by a glow discharge created by a leak tester (Tesla coil) has been reported (Otazai et al., 1954; Kikuchi and Tsuda, 1961). As seen from this example, polymerization can be initiated by the action of plasma directly on the bulk phase of monomer solutions.

Osada, Bell, and Shen (1978) have recently applied this principle for polymerization of liquid vinyl monomers by inserting a sealed ampule between a pair of parallel-plate electrodes connected to a 13.5-MHz radio frequency generator.

Free radicals formed on the surface of polymers and other solid materials exposed to plasma can be utilized to initiate the graft polymerization (Bamford, Jenkins, and Ward, 1960; Bamford and Ward, 1961). Free radicals formed on polyethylene and polypropylene by plasma are utilized to obtain grafts of vinyl polymers on the surface of the substrates by (i) direct addition of degassed monomer and (ii) formation of peroxide followed by heating in the presence of degassed monomer.

Osada, Shen, and Bell (1978) have investigated plasma-initiated solid-state polymerization of trioxane and tetraoxane.

In all examples mentioned above, polymers are formed by plasma-induced

polymerization, and the essential chemical reaction is believed to be the conventional polymerization which can occur without influence of plasma. Although plasma is utilized in these polymerizations, they are distinguished from plasma-state polymerization, which occurs only under plasma conditions.

When conventional monomers such as vinyl compounds are used for glow discharge polymerization, both plasma-induced polymerization and plasma-state polymerization can occur simultaneously. The extent of both mechanisms in glow discharge polymerization is dependent on the conditions of glow discharge, particularly on flow rate and flow pattern in a reactor. The details of this aspect are discussed in a later section dealing with mechanisms of polymer formation.

C. Glow Discharge Polymerization Versus Graft Polymerization

Because glow discharge polymers are generally intimately bonded to substrate materials—particularly to organic polymer substrates—glow discharge polymerization may be viewed as a kind of graft polymerization. In this sense, glow discharge polymerization provides an extreme case of surface grafting in which the entire surface is covered by a new polymeric material and no macroscopic penetration of the polymer into the substrate polymer occurs. The comparison of glow discharge polymerization and conventional surface grafting may illustrate characteristic features of glow discharge polymerization.

In the approach of preparing a composite structure by grafting or by glow discharge polymerization, one must carefully examine the extent of compromise, i.e., how many of the bulk properties of a substrate polymer may be altered by the process of composite formation, and, conversely, to what extent the properties of the material to be grafted may be retained in the final form of the composite. The effect of surface grafting on the bulk properties of a substrate polymer and the effect of substrate polymer on the properties of the grafted surface layer may be worth examining using surface grafting as an example.

The term “surface grafting” is generally used in contrast to “through grafting” in which grafting extends all the way through the bulk of the original polymer sample. Through grafting may be referred to as homogeneous grafting in comparison with the heterogeneous surface grafting; however, grafting in many cases occurs in a quite heterogeneous manner in the submicroscopic sense. Surface grafting and through grafting may be schematically represented as in Figures 1(b) and 1(c), using heterogeneous phases to distinguish substrate polymer and grafted polymer.

In through grafting, the grafted polymer penetrates all the way through the substrate. If the grafted polymer is water-soluble and the substrate polymer is hydrophobic, the grafted polymer would swell considerably in water as indicated in Figure 1(c). In surface grafting, the penetration of grafting is limited to the vicinity of the surface, and, consequently, the change of properties, such as swelling in the solvent for the grafted polymer, is restricted to the vicinity of the surface as indicated in Figure 1(b).

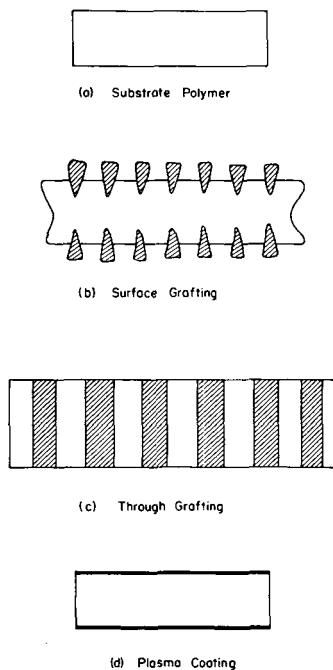


Fig. 1. Schematic representation of grafting and plasma polymerization (surface coating). Illustrations represent the situations of grafting and plasma polymerization of a hydrophilic polymer onto a hydrophilic polymer substrate and polymers are kept in water (solvent of the grafted polymer): (a) substrate, (b) surface grafting, (c) through grafting, (d) plasma polymerization.

The extent of penetration and the concentration of the grafted polymer at the surface are dependent on the condition of the grafting reaction; however, the general characteristic features of grafting can be visualized by the schematic representation shown in Figure 1.

Examination of grafting procedures (schematically represented in Fig. 1) makes it clear that a certain degree of change in the bulk properties of the substrate polymer is expected even with surface grafting and the extent of change is more or less proportional to the degree of surface grafting. Conversely, the surface properties of the grafted polymer are also affected by grafting. The degree of compromise is thus an inherent problem of grafting. An increase in the degree of grafting may change surface properties; however, this may be obtained with considerable deterioration of the bulk properties of the substrate polymer.

Characteristic features of glow discharge polymerization to form a composite structure or a coating are quite clear from the comparison. Glow discharge polymerization (on polymeric substrates) provides modification of the surface with least alteration of bulk properties of substrate polymers, whereas surface grafting by conventional means tends to alter the bulk properties of substrate due to partial penetration of grafting into the bulk substrate.

Another important difference between conventional surface grafting and glow discharge polymerization is the dependence of the efficiency of the processes on the nature of the substrate polymer and on the reactivity of the monomers. In conventional grafting, the efficiency of graft copolymerization is greatly dependent on the nature of the substrate polymers and of the monomers to be polymerized. A particular monomer may graft well onto a particular polymer but the same monomer may not graft at all onto other polymers. This is particularly true for grafting initiated by chemical means. Even with less specific radiation-induced graft copolymerization, the efficiency depends on the free radical yield (G values) of polymers and monomers.

In glow discharge polymerization, the polymer deposition is not greatly affected by the nature of the substrate polymers. A polymer deposits similarly onto the surfaces of glass, organic polymers, and metals. Therefore, the use of glow discharge polymers is less restricted by the choice of the substrate material.

D. Glow Discharge Polymerization Versus Radiation Polymerization

Glow discharge polymerization of organic compounds seems to proceed by the free radical mechanism. The first stage of forming a free radical from an organic molecule has not been well elucidated; however, the subsequent process of polymerization can be explained by the free radical mechanism by analogy with radiation-induced polymerization.

Although experimental evidence of free radicals does not preclude other possible reaction mechanisms, there is ample evidence of (i) free radicals in glow discharge polymers (Bamford, Jenkins, and Ward, 1960; Bamford and Ward, 1961; Jesch, Bloor, and Kronick, 1966; Denaro, Owens, and Crawshaw, 1968; Millard, Windle, and Pavlath, 1973; Morosoff et al., 1976; Morita, 1976; Yasuda et al., 1976; Yasuda and Hsu, 1977a, 1977b) and (ii) organic radicals in plasma detected by emission spectroscopy (Havens, Mayhan, and James, 1978). Therefore, it seems quite reasonable to assume that the glow discharge polymerization proceeds by a mechanism which involves free radicals.

Since plasma polymerization deals with vapor phase monomer whereas radiation-induced polymerization is more or less confined to the condensed phase reaction, the direct comparison of these two polymerizations is not possible. Perhaps the most significant difference between glow discharge polymerization and radiation-induced polymerization is the rate of initiation or the dose rate of the processes. The concentration of free radicals in plasma is much higher than that in the media where radiation polymerization takes place. Westwood (1971) has estimated from G values of polymer formation that the dose rate in plasma is 10^6 times higher than the dose rate commonly used in radiation polymerization. Therefore, plasma-induced polymerization that occurs in glow discharge polymerization is analogous to radiation-induced polymerization in which an extremely high dose rate is employed.

Because of the very high dose rate, the concentration of free radicals increases and the recombination of free radicals (termination) is favored over the prop-

agation reaction by addition reaction onto reactive double bonds, which comprises the main step of polymer formation in conventional free radical addition polymerization. The continuous reinitiation of oligomers formed by the recombination of free radicals followed by the repeat of the cycle leads to the formation of high-molecular-weight compounds (plasma-state polymerization). Consequently, organic compounds, which do not polymerize by radiation, polymerize in plasma just as easily as double-bond-containing monomers, which polymerize by radiation.

Because of this unique mechanism, nearly all organic compounds can be polymerized in plasma, though some elements and groups tend to be absent in the resulting polymers. Due to the fragmentation of organic compounds (monomer) in plasma, the polymer formed in plasma is not always what one would expect from the chemical structure of the monomer. Details of this aspect are presented in a later section where polymerization mechanism is discussed.

III. PROCESSING FACTORS OF GLOW DISCHARGE POLYMERIZATION

It is extremely important to recognize the difference between polymer-forming plasmas and nonpolymer-forming plasmas in order to understand the true meaning of the processing factors of glow discharge polymerization. Not all glow discharges yield polymer deposition. For instance, plasmas of Ar, Ne, O₂, N₂, and air are typical nonpolymer-forming plasma. The significance of polymer-forming plasmas, such as glow discharges of acetylene, ethylene, styrene, benzene, etc., is that a considerable portion or the majority of molecules of starting material leave the gas (plasma) phase and deposit as a solid polymer.

In contrast to polymer-forming plasmas, the total number of gas phase molecules in nonpolymer-forming plasmas do not change. Only a portion of gas molecules repeat the process of being ionized, excited, and quenched. However, the total number of gas molecules remains constant. This situation can be visualized by the pressure change that occurs before, during, and after the glow discharge. In the case of a nonpolymer-forming plasma, no pressure change is observed unless a material which reacts with excited species of plasma is placed in the discharge system (Yasuda et al., 1975). The system pressure of a polymer-forming plasma changes as soon as discharge is initiated. The pressure change is dependent on the characteristic nature of the starting material, which is related to the product gas formation. With starting materials that yield very little product gas (e.g., acetylene, benzene, styrene, etc.) the system pressure drops to nearly zero when a high polymerization yield is obtained. In other words, an efficient plasma polymerization is an excellent vacuum pump, whereas a nonpolymer-forming plasma has no characteristic of this nature (Yasuda and Hirotsu, 1978).

Unfortunately, most fundamental work on the plasma state was done with nonpolymer-forming plasmas, and the concept of the operational parameters

used in such studies cannot be applied directly to polymer-forming plasmas.

Characteristic polymer deposition by glow discharge polymerization occurs onto surfaces exposed to (directly contacting) the glow. Some deposition of polymer occurs on surfaces in nonglow regions (but the deposition rate is orders of magnitude smaller). The surface on which a polymer deposits could be an electrode surface, a wall surface, or a substrate surface suspended in the glow region. Another important factor that must be considered in dealing with operational factors of glow discharge polymerization is that it is system dependent. Consequently, polymer deposition rates are dependent on the ratio of surface to volume of glow. Therefore, other operational parameters such as flow rate, system pressure, and discharge power are insufficient parameters for the complete description of glow discharge polymerization. Such parameters serve as empirical means of describing operational conditions of glow discharge polymerization in a particular system, but they should not be taken beyond this limitation.

The following operational factors are important; however, all factors influence glow discharge polymerization in an interrelated manner. Therefore, any single factor should not be taken as an independent variable of the process.

A. Modes of Electric Discharge

Although a number of methods can be used to generate plasma, the methods utilized in plasma polymerization of organic compounds are more or less limited to some kind of electric discharge. This is perhaps due to the fact that organic compounds decompose at high temperatures and "hot plasma" cannot be used for polymer synthesis. Another factor is that electric discharge is the most practical means for creating and maintaining "low-temperature plasma" in a laboratory.

1. Types of Electric Discharge and Plasma Reactors

Electric discharge can be obtained in a number of ways, and numerous combinations of factors involved in the design of a reaction vessel are given in the literature. Basically, however, the combination of two major factors (i.e., type of electric power source and mode of coupling) will cover nearly all practical cases. For glow discharge polymerization, the location of the surface on which plasma polymer is deposited also plays an important role. These factors are tabulated in Table I. Combinations Nos. 1–6 may be characterized by discharge with internal electrodes, Nos. 7 and 8 may be characterized by discharge with external electrodes. All inductively coupled discharges are called "electrodeless" glow discharge, since electrodes are not employed. Principles of reactor design are illustrated with typical examples as follows.

In Figures 2 and 3, examples of reactors (Westwood, 1971) that use capacitive coupling and an electrode surface as the polymer deposition surface (Nos. 1, 3, and 5 in Table I) are shown. Bell-jar-type reactors (Fig. 2) can be used in static

TABLE I
Factors of Plasma Polymerization Reactor

	Power source	Mode of coupling	Location of substrate surface
1.	dc	Capacitive	On an electrode surface (Cathode)
2.	dc	Capacitive	In between electrodes
3.	ac	Capacitive	On an electrode surface
4.	ac	Capacitive	In between electrodes
5.	rf	Capacitive	On an electrode surface
6.	rf	Capacitive	In between electrodes
7.	ac and rf	Capacitive, external electrodes	In between electrodes
8.	ac and rf	Capacitive, external electrodes	In tail flame
9.	rf	Inductive	Inside rf coil
10.	rf	Inductive	In tail flame
11.	Microwave	Inductive	In the coupling region
12.	Microwave	Inductive	In tail flame

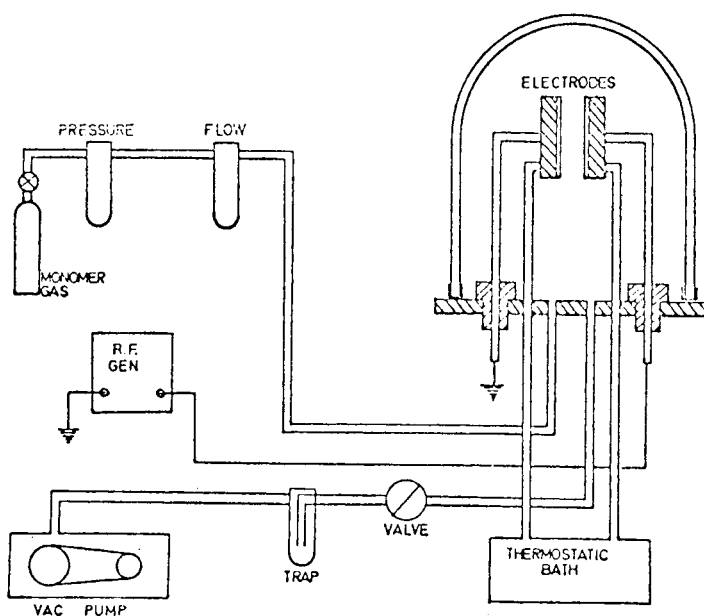


Fig. 2. Schematic representation of a glow discharge reactor with internal electrodes. [Reproduced from Westwood (1971), p. 364, courtesy of Pergamon Press.]

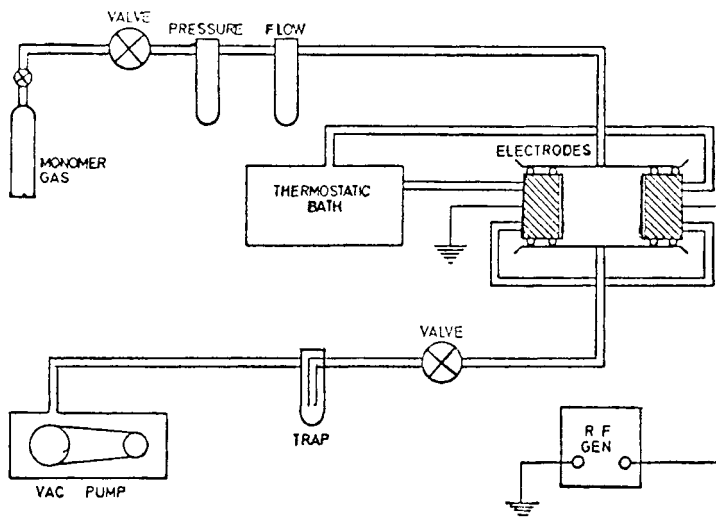


Fig. 3. Schematic representation of a glow discharge reactor with internal electrodes for a flow system. [Reproduced from Westwood (1971), p. 364, courtesy of Pergamon Press.]

or flow systems; however, a reactor such as the one shown in Figure 3 is more suited for reactions in a flow system.

In Figure 4, an example of a reactor (Stancell and Spencer, 1972) in which the polymer deposition surface is placed between electrodes (Nos. 2, 4, and 6 in Table I) is shown. Figure 5 shows an example of a plasma reactor (Hollahan and Wydeven, 1973) with external electrodes (No. 8 in Table I). The external electrodes can be parallel or curved plated and placed parallel to the axis of a glass tube. The external electrodes can be placed in a radial direction as shown in Figures 6 (Ranney and O'Connor, 1969) and 7 (Blais, Carlsson, and Wiles, 1971). When the radius of an electrode surface is small, the discharge occurs at higher pressure (even at atmospheric pressure). This type of discharge is often called "corona" discharge. In the reactor shown in Figure 6, a threaded rod (threaded surface acting as the surface with small radius) is used as an electrode for a corona discharge reactor. In external electrode discharge, the substrate

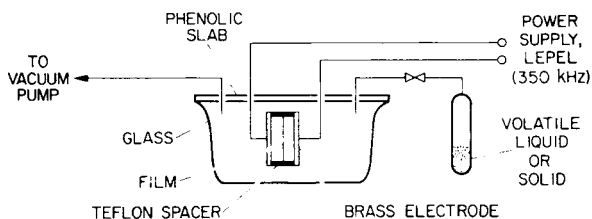


Fig. 4. Schematic representation of a glow discharge reactor with internal electrodes. A polymer substrate is placed in between the electrodes. [Reproduced from Stancell and Spencer (1972).]

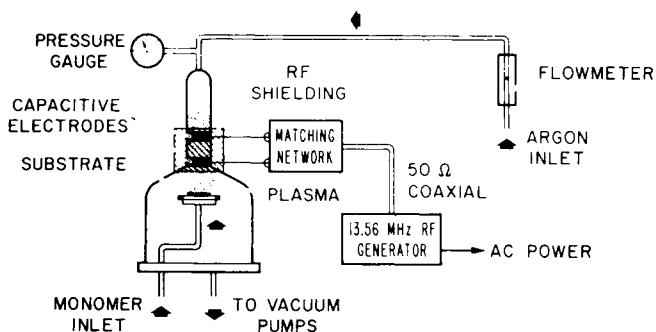


Fig. 5. Schematic representation of a glow discharge reactor with external electrodes. A substrate is placed in the tail-flame portion (not in the portion directly under the external electrodes). [Reproduced from Hollahan and Wydeven (1973).]

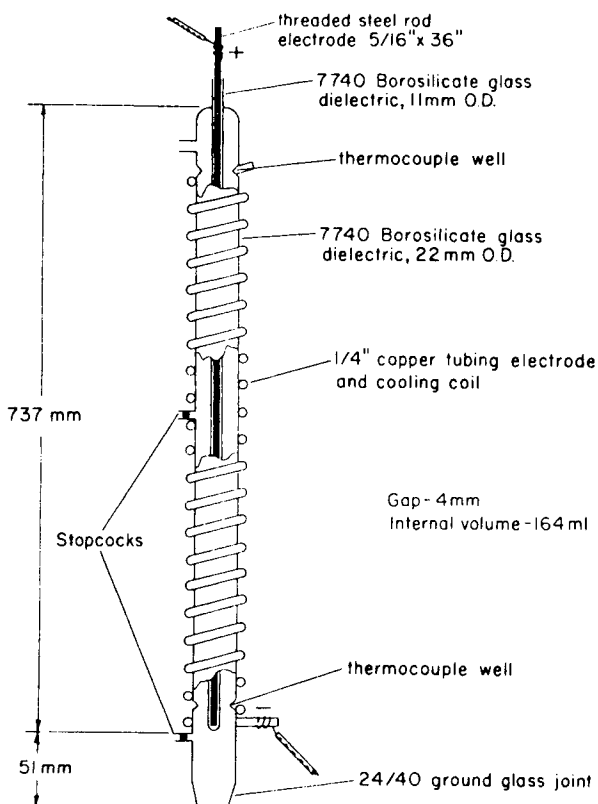


Fig. 6. Schematic representation of a corona reactor. [Reproduced from Ranney and O'Connor (1969).]

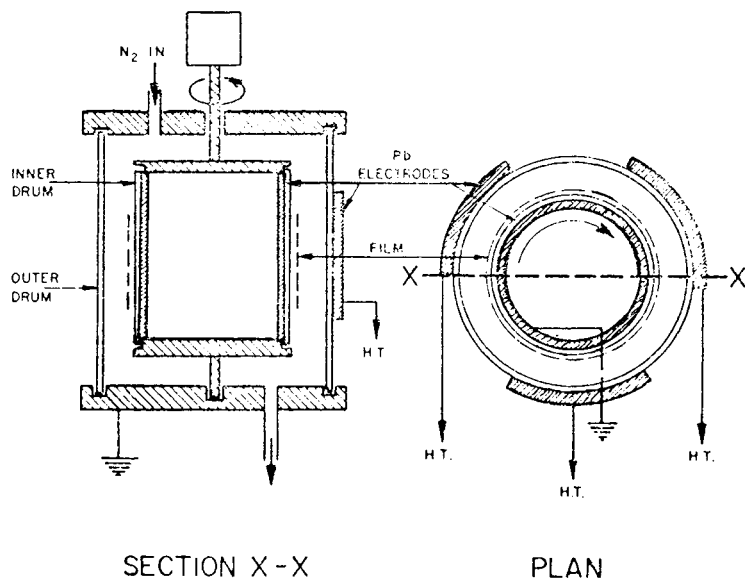


Fig. 7. Schematic representation of a corona reactor with a rotating drum (glass tubing) on which a substrate film is placed. [Reproduced from Blais, Carlsson, and Wiles (1971).]

can be placed either between electrodes or in the tail flame (as shown in Fig. 5).

In Figure 8, an example of an inductively coupled (electrodeless) discharge reactor (No. 10 in Table I) is shown (Yasuda and Lamaze, 1973). A substrate can be placed in the tube directly surrounded by a radio frequency (RF) coil (an entire tube is in the coil). For microwave discharge, the RF coil in Figure 8 is replaced by either a microwave coupling cavity or a slow-wave structure for larger volume plasma (Bosisio, Weissfloch, and Wertheimer, 1972; Bosisio, Wertheimer, and Weissfloch, 1973).

Regardless of the mode of coupling and the type of electrical power source,

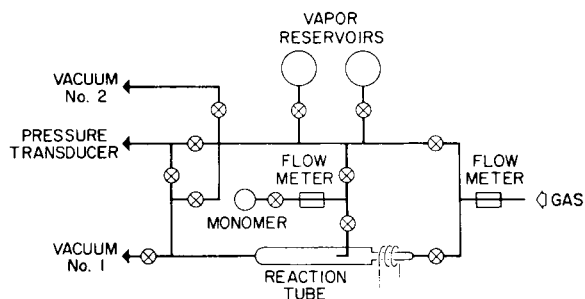


Fig. 8. Schematic representation of an electrodeless glow discharge reactor. [Reproduced from Yasuda and Lamaze (1973a).]

the deposition of polymer seems to occur mainly on the surface that directly contacts the glow (plasma). Some polymer deposition occurs on the surfaces in the nonglow region on the downstream side; however, the deposition is generally much less compared to the deposition that occurs in the glow region.

Electric power sources with a frequency ranging from zero (dc) to gigahertz (microwave) can be used for glow discharge polymerization. The use of a low-frequency electric power source (up to about the audio frequency range) requires internal electrodes. With higher frequency, external electrodes or a coil also can be used.

The use of internal electrodes has the advantage in that any frequency can be used. The glow discharge is more or less restricted to the space between electrodes. The best glow discharge is obtained with internal electrodes at a relatively high pressure (>0.1 Torr). At lower pressure, the glow discharge expands beyond the space between electrodes. At low pressure (<0.02 Torr) the glow occurs mainly in the space outside of the gap between the electrodes, and the system becomes inefficient for glow discharge polymerization. In order to restrict the glow to the space between the electrodes in the low-pressure range, it is necessary to employ magnetic enhancement (Morosoff, Newton, and Yasuda, 1978). Under typical conditions, polymer deposition is mainly onto the electrode surface. With a high-frequency (RF range) power source, the glow tends to stray from the space between the electrodes; however, because of this tendency polymer deposition onto a substrate surface placed in between the electrodes increases (Morosoff, Newton, and Yasuda, 1978).

The systems that employ external electrodes or a coil are suited for large-volume glow discharges. They are particularly suited for the utilization of the tail-flame portion of the glow discharge. The tail flame refers to the glow discharge away from the energy input region (under external electrodes or coil).

Whether a substrate is placed in the energy input region or placed in the tail flame—or in the case of an internal electrodes system, whether a substrate is placed directly onto the electrode surface or placed in between electrodes—it plays an important role in the properties of the polymer formed (O'Kane and Rice, 1976; Yasuda and Hsu, 1978). The relative location of the energy input and the polymer deposition is an important factor to be considered in view of the competitive ablation and polymerization (CAP) scheme of glow discharge polymerization in which the substrate material also plays an important role in glow discharge polymerization. The details of this will be discussed in a later section for mechanisms of polymer formation.

2. *Volume and Intensity of Plasma*

The volume of glow discharge as well as the intensity of glow are highly dependent on the mode of discharge, the discharge power, and the pressure of the system. The volume and the intensity of glow will affect the rate of polymer deposition in different ways, depending on the geometric factors of the reaction vessel. These aspects can be easily visualized by observation of the glow region

in a discharge with parallel electrodes in a bell-jar-type reactor.

The change in volume and intensity of glow as the pressure of the system decreases at a given discharge power is shown in Figures 9–12. Glow discharge is initiated (16 kHz, 100 W) at approximately 0.8 Torr (residual air) using a bell jar with parallel electrodes, and the pressure of the system is reduced, i.e., (a) ca. 0.8 Torr, (b) 0.5 Torr, (c) 0.3 Torr, and (d) <0.1 Torr. With a relatively wide gap (ca. 4.5 cm) between electrodes (see Fig. 9), it is clearly visible that glow is intense in the vicinity of the electrode surfaces and the dark region exists between them at higher pressure (shorter mean free path). As the pressure decreases (mean free path increases), the glow expands more and the dark region becomes smaller. At the same time, the glow reaches the back side of the electrodes. These trends become more clear as the pressure decreases further. At the lowest pressure (largest mean free path), the discharge prefers the longer path and the strongest intensity of the glow shifts to the back side of the electrodes.

With a narrower gap between the electrodes (see Fig. 10), the plasma intensity in the space between the electrodes is much higher at the higher pressures and

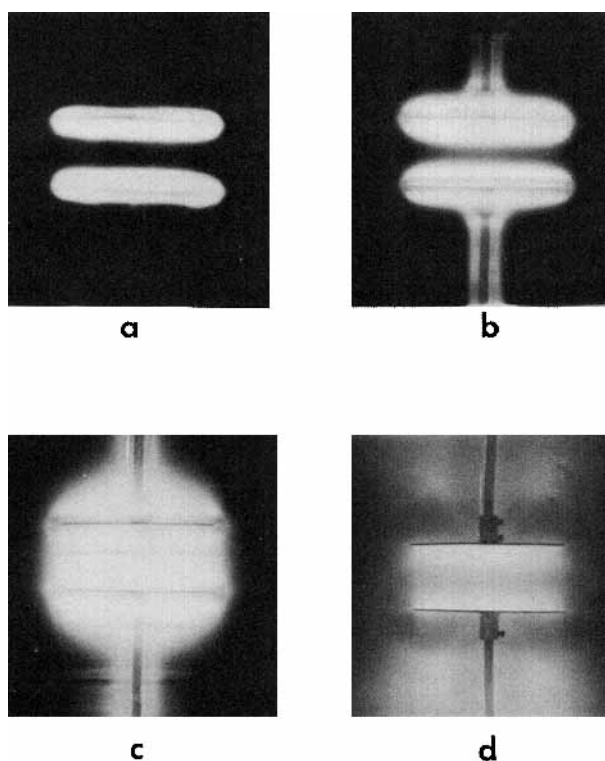


Fig. 9. Dependence of glow discharge on pressure (in mm Hg). Parallel-plate electrodes without insulation, 4.5 cm between plates: (a) 0.8, (b) 0.5, (c) 0.3, (d) <0.1.

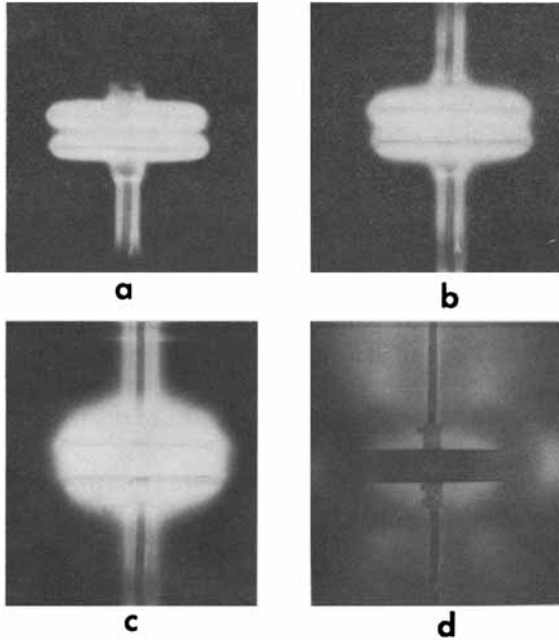


Fig. 10. Dependence of glow discharge on pressure (in mm Hg). Parallel-plate electrodes without insulation, 2.0 cm between plates: (a) 0.8, (b) 0.5, (c) 0.3, (d) <0.1 .

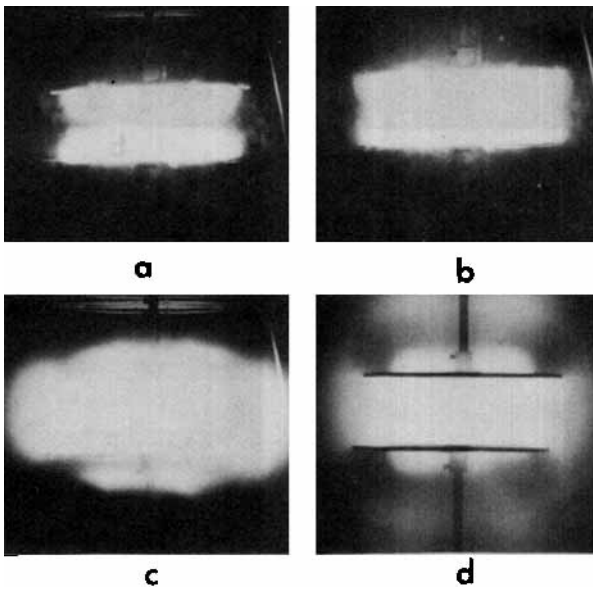


Fig. 11. Dependence of glow discharge on pressure (in mm Hg). Parallel-plate electrodes with insulation, 4.5 cm between electrodes: (a) 0.8, (b) 0.5, (c) 0.3, (d) <0.1 .

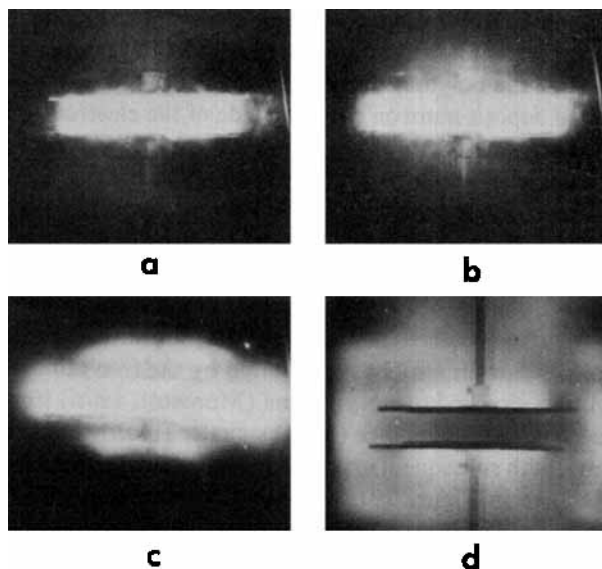


Fig. 12. Dependence of glow discharge on pressure (in mm Hg). Parallel-plate electrodes with insulation, 2.0 cm between electrodes: (a) 0.8, (b) 0.5, (c) 0.3, (d) < 0.1 .

the dark region is much smaller than that found in Figure 9. At the lower pressure, however, the glow shifts nearly exclusively to the outsides of the electrodes and the space between the electrodes appears as a dark region.

By placing insulating material (larger than the electrodes) on the back sides of the electrodes, the glow discharge that occurs in the back sides of electrodes is reduced (see Figs. 11 and 12). However, at low pressure the glow still extends through practically the entire volume of the bell jar. Although the examples shown here represent only limited combinations of factors, it is quite clear that the volume of glow is dependent on the operational factors, which include the area of electrode surface, distance between electrodes, the presence of insulating materials (which prevents longer path discharge in lower pressure), discharge power, and frequency.

Since the majority of polymerization occurs in the plasma (glow region) regardless of whether it occurs in gas phase or at the interface, Figures 11 and 12 clearly point out the heterogeneous aspect of glow discharge polymerization. The following aspects should be taken into consideration when one considers the dependence of polymer deposition on operational factors such as pressure, discharge power, and flow rate.

(a) The total volume and intensity of plasma changes as the operational factors vary. Therefore, the ratio of plasma volume to the total volume of the system also changes.

(b) The surface on which polymer exclusively deposits may change with operational factors. If the polymer deposition rate is measured with a substrate

placed on the inside surface of an electrode, it may lead to a dramatic decrease in the polymer deposition rate at lower pressures. However, it may simply be due to the shift of the polymer deposition surface at lower pressure when the polymer starts to deposit more on the other side of the electrode and also on the wall of the vessel.

(c) The medium in which glow discharge polymerization occurs is not homogeneous. Therefore, the location of the polymer deposition surface and the type of glow to which the surface is exposed are very important factors.

In electrodeless glow discharge, particularly in the tail-flame (after glow) portion not directly under the coil or external electrodes, the plasma seems to be much more homogeneous. The intensity of plasma (in tail flame of electrodeless glow discharge) may be represented by the free radicals formed in a glass (Pyrex) tube exposed to a N_2 plasma (Morosoff, 1976) since glass yields very stable electron spin resonance (ESR) signals. Treatment of the Pyrex tube with N_2 plasma, with subsequent exposure to air, gives rise to a complicated ESR spectrum as shown in Figure 13(a). This may be compared with the "background" from an untreated glass tube, also shown in Figure 13(b). Glass radicals are extremely stable, their population decreasing by only 25% after 6 days in air. Signal intensity is measured from the highest point in the ESR spectrum

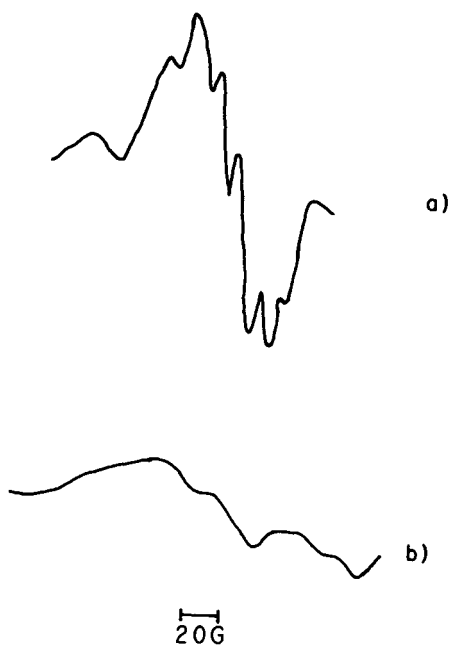


Fig. 13. (a) ESR spectrum of radicals formed by treatment of a glass tube N_2 plasma at an initial pressure of $12 \mu m$ Hg N_2 , 30-W power for 5 min with subsequent exposure of the tube to air. (b) "Background" from untreated glass tube. Relative ordinate scale: 1:1.

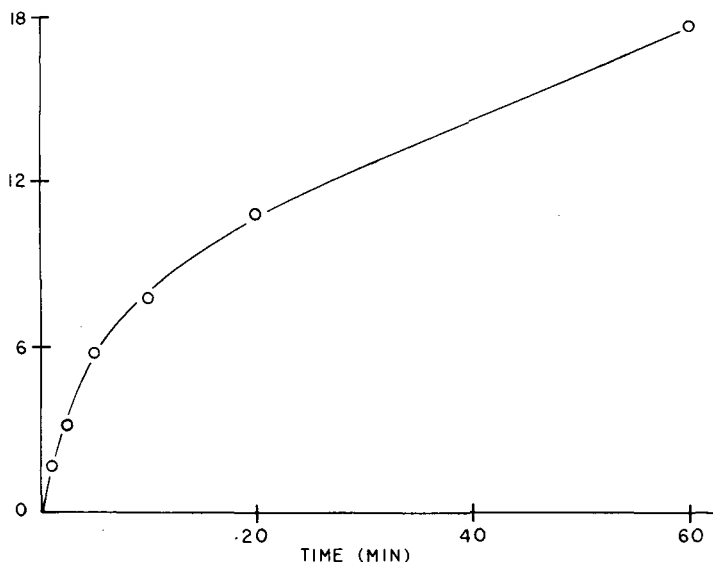


Fig. 14. ESR signal intensity of the glass radical plotted against time of glow discharge treatment. Conditions of treatment are an initial N_2 pressure of $50 \mu\text{m Hg}$ and power of 30 W.

to the neighboring minimum and corrected for the difference in height in the corresponding "background" spectrum.

The trend of signal intensity versus time at constant N_2 pressure and power is shown in Figure 14. The decreasing rate of free radical population growth may indicate either a process of annihilation of glass radicals by radicals in the glow discharge process competing with the formation of glass radicals, or a limited number of sites on the glass surface on which air-stable radicals may be formed.

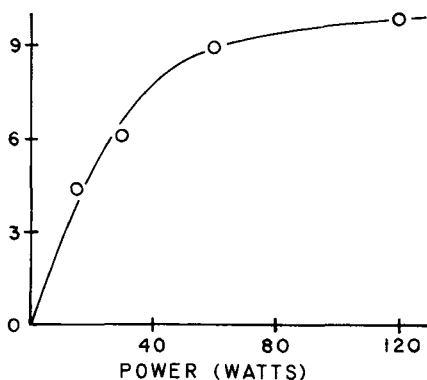


Fig. 15. ESR signal intensity of the glass radical plotted against power used in the glow discharge treatment. The initial pressure of N_2 was kept constant at $50 \mu\text{m Hg}$; the time of treatment was 5 min.

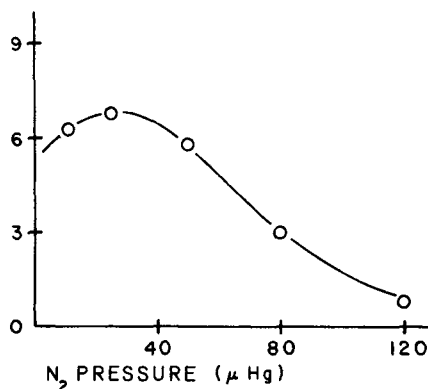


Fig. 16. ESR signal intensity of the glass radical plotted against initial pressure of N_2 used in the glow discharge treatment. The power was kept constant at 30 W.

Of more interest are the effect of power and N_2 pressure on the glass radical population. These are shown in Figures 15 and 16, respectively.

At a given pressure (50 $\mu\text{m Hg}$ of N_2 gas in Fig. 15), increasing power leads to increasing radical concentration up to a plateau region, after which further increments in power have little effect on radical concentration. Increasing pressure, on the other hand, leads to a maximum in the graph of ESR signal intensity versus initial pressure of N_2 . This reflects the fact that the glass tube is in the "afterglow" of the glow discharge rather than in the region encircled by the RF discharge coil, where glow discharge is generated.

At a given power, increasing pressure increases both the number of radicals generated and the possibility of recombination of radicals. The predominance of the latter process at the higher pressure is reflected in the decreasing length of glow as the pressure is increased. The dashed line in Figure 17 is a plot of the power needed to just fill the reaction tube with glow discharge (as ascertained visually) at various preset initial pressures of N_2 . It is seen that the slope (Δ power/ Δ pressure) increases with increasing power.

A similar plot may be obtained from the data in Table II in which the ESR signal height is given for various combinations of power and initial pressure of N_2 . Power levels from 5 to 120 W were sampled; initial pressures range from 10 to 120 $\mu\text{m Hg}$. It can be seen that the character of the plots given in Figures 15 and 16 is quite general. The data in the rows of Table II would fit a Figure 16-type plot; the data in the columns manifests a maximum that is shifted to higher pressures as the power level is increased. Estimates of the pressure corresponding to a maximum ESR signal at a given power were made from the data in Table II, and the results were plotted as a solid line in Figure 17. While the data at the higher power levels appear to lie on a straight line, this line does not pass through the origin, and an increasing (Δ power/ Δ pressure) slope is required for the low-pressure part of the plot.

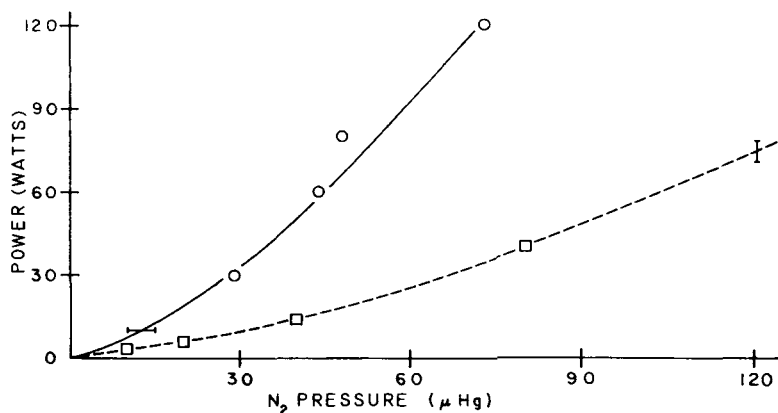


Fig. 17. Plot of the reaction conditions required to fill the reaction chamber (---), as ascertained visually, and (—) to attain the maximum ESR signal intensity in a Fig. 16-type plot as applied to the data in Table II.

The solid line in Figure 17 represents the pressure giving the maximum radical yield (at the position sampled in the reaction chamber) for any given power. For a given pressure, the power should be that which is given by the solid line in Figure 17. Increasing the power above this level will increase radical yield to some extent, but operating at a lower power level tends to favor reaction of excited species (including free radicals, electrons, and excited molecules which cause formation of glass radicals) with surfaces or each other before reaching the sample tube, to the point that radical yield in the tube is reduced.

These results indicate that the "afterglow" region of the plasma appears to consist of a region of fairly even plasma (the body) followed by a "tip" where the intensity gradually drops as a function of distance from the RF coil. As the power is increased at a given pressure, the length of the afterglow is increased, effectively moving the glass tube from the tip to the body of the plasma. After the tube has arrived at the body, further increases in power do not result in any

TABLE II
ESR Signal Intensity (of Pyrex Glass) as a Function of N₂ Pressure and RF Power^a

pressure (μ Hg)	rf Power (watts)					
	5					
10	2.6	3.0	5.1	6.0	6.5	5.7
25	2.0	2.9	5.8	7.4	6.8	8.7
50	0	0.5	5.0	8.0	8.2	9.4
80	-	-	3.0	6.6	6.2	9.8
120	-	-	1.2	5.0	5.5	7.2

^a Data cited from Morosoff et al. (1976).

substantial increase in generated free radicals. The data in Table II are interpreted as demonstrating that at the pressure and power levels sampled the pressure limits the intensity of plasma in the body of the afterglow; the power merely determines how far into the reaction chamber the body of the plasma will extend.

B. Monomer Flow Rate

The flow of a monomer is generally given by the volume of the gas at standard temperature and pressure (STP) per unit time; e.g., $\text{cm}^3(\text{STP})/\text{min}$. In gas phase the pressure and volume decide the number of molecules (or number of moles) of gas in the volume. Consequently, flow rate F_v based on volume at STP is essentially the flow rate based on moles per unit time. Polymer deposition rate, on the other hand, is generally measured by weight of polymer per unit area per unit time; e.g., $\text{g}/\text{cm}^2 \text{ min}$. Therefore, it is quite obvious that the polymer deposition rates of monomers at a given flow rate (F_v) is dependent on the molecular weight of the monomer. The polymer deposition rates of various monomers should be compared on the basis of mass flow rate; otherwise, polymer deposition rates are not directly comparable with polymerization rates. The weight basis flow rate F_w is given by $F_w = F_v M / 2.24 \times 10^4$ where F_v is given by $\text{cm}^3(\text{STP})/\text{unit time}$, F_w is given by grams per unit time, and M is the molecular weight. The dependence of apparent polymer deposition rate based on volume flow rate on the molecular weight of monomers (Yasuda and Lamaze, 1973a) is seen in Figure 18.

The volume of a reactor, V_R , is not always identical to the volume of glow, V_g , where plasma polymerization occurs. For instance, in a bell-jar system, V_g/V_R is most likely less than 0.10, whereas in the electrodeless glow discharge used in a tube-type reactor shown in Figure 8, V_g/V_R is close to unity.

Flow rate of monomer is measured as the flow of monomer fed into V_R . Consequently, the flow rate is a meaningful parameter only for the system which has $V_g/V_R = 1$ or for the system in which V_g/V_R and the flow pattern are well defined.

The flow rate of monomer is often expressed in terms of the volume of gas at the standard state ($p_0 = 1 \text{ atm}$, $T_0 = 273 \text{ K}$); e.g., $\text{cm}^3(\text{STP})/\text{min}$. However, in plasma polymerization which is carried out in a vacuum system, the meaning of flow rate is often misunderstood. First, $\text{cm}^3(\text{STP})$ is not a unit of volume, i.e., $\text{cm}^3(\text{STP}) \neq \text{cm}^3$. The flow rate given in $\text{cm}^3(\text{STP})$ represents the flow in terms of number of moles, but is not directly related to the velocity of a gas flow. In a noncompressive system such as a liquid, the flow rate is directly proportional to the velocity of the flow. Flow rate in the context of flow velocity in a vacuum is given by F/p , where F is the flow rate in $\text{cm}^3(\text{STP})$ and p is the system pressure in atmospheres. Therefore, the same flow rate, e.g., $10 \text{ cm}^3(\text{STP})/\text{min}$, at 0.1 mm Hg has a velocity which is 100 times higher at 10 mm Hg .

Second, the linear velocity of flow is also dependent on the cross-sectional area of the system in which the flow takes place. Therefore, a parameter which de-

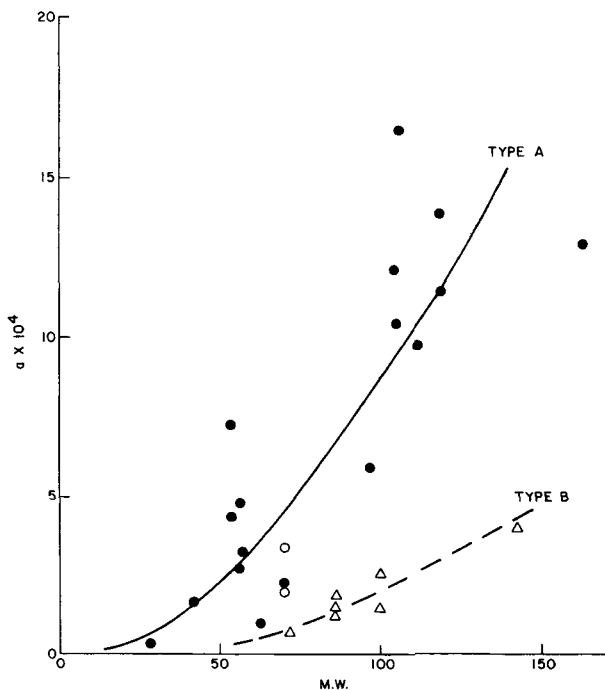


Fig. 18. Dependence of polymer deposition rate constant a on molecular weight (MW) of monomers. The polymer deposition rate R_0 g/cm² min is given by $R_0 = ap_m^2$, where p_m is monomer vapor pressure of a flow system; a in units of g/cm² min (mm Hg)². [Reproduced from Yasuda and Hirotsu (1978a).]

scribes the linear velocity of a flow is given by F/Ap , where A is the cross-sectional area in cm². The value of F/Ap for a flow of 50 cm³(STP)/min introduced into a bell jar of 50-cm diameter at 1 mm Hg is 19.4 cm/min, whereas the value of F/Ap for a flow of 5 cm³(STP)/min maintained in a tube of 5-cm diameter at 0.1 mm Hg is 1936 cm/min. The parameter which is proportional to the resident time should also be calculated based on F/Ap . V/F or lA/F , where V is the volume of a reactor and l is the length of a tube, does not yield a number in units of length. As it is clear for these examples, 50 cm³(STP)/min in the bell-jar system under the given conditions is actually a much slower flow than 5 cm³(STP)/min in the tube system under the given conditions for the latter case, despite the value of F being ten times greater.

The ratio F/V_g is an important factor for describing how fast the monomer is fed into the reaction system, and the value of F/Ap is an important parameter which is related to the resident time of a flow system. By the same token, F alone without detailed description of the system has little value beyond being a controlling parameter of a system. These factors are usually not considered in discussions of plasma polymerization appearing in the literature.

Another important factor to consider in the interpretation of results is whether

the experimental condition is (a) the diffusion-dominating case or (b) the mass-flow-dominating case. Gas molecules have rather high velocity, and in low pressure the diffusion of gas becomes a much faster process than one might expect from the general sense of "diffusion." It was shown by Einstein that one-dimensional displacement \bar{x} executed by a particle during time t in a medium with a diffusion coefficient D is given by $\bar{x}^2 = 2Dt$. The diffusion coefficient in low pressure can be calculated from the diffusion coefficient D_0 at the standard state ($p_0 = 760$ mm Hg and $T_0 = 273$ K) by $D = D_0(T/T_0)^n(p_0/p)$ where n is between 1.75 and 2 (Melville and Gownlock, 1964).

The diffusion coefficient D_0 of most gases is of the order of a few tenths cm^2/sec at STP. The order of magnitude of the diffusive displacement velocity $d\bar{x}/dt$ can be estimated using the value of $D_0(T/T_0)^n = 0.2$ cm^2/sec and can be compared with linear velocity of the center-of-mass movement in a flow system. In a cylindrical tube of i.d. = 40 mm, and a flow rate of 1×10^{-3} $\text{cm}^3(\text{STP})/\text{sec}$ at a pressure of 0.03 mm Hg, the diffusive displacement velocity is about 100 cm/sec , whereas the linear velocity of the mass flow is only 2.02 cm/sec . If the flow rate is increased to 1 $\text{cm}^3(\text{STP})/\text{sec}$ at a pressure of 2 mm Hg in the same tube, the diffusive displacement velocity decreases to 12.3 cm/sec and the linear flow velocity increases to 30 cm/sec . Therefore, it is clearly seen that in the former case (low flow rate and low pressure) the diffusion of gases is more important than the flow, whereas in the latter case (higher flow rate and higher

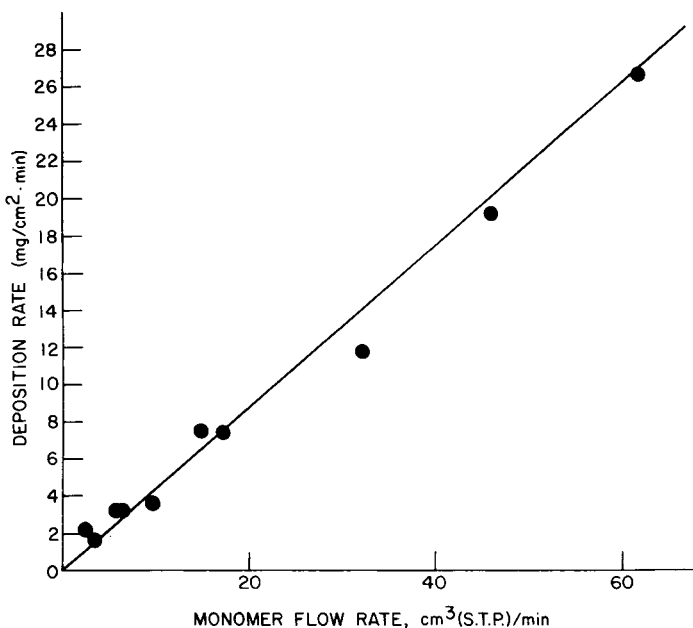


Fig. 19. Dependence of polymer deposition rate on monomer (4-vinylpyridine) flow rate. [Reproduced from Yasuda and Lamaze (1973a).]

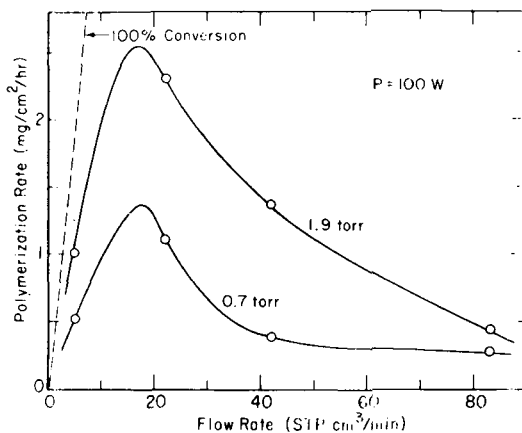


Fig. 20. Effect of monomer flow rate on the rate of polymer deposition. [Reproduced from Kobayashi, Bell, and Shen (1974).]

pressure), the flow plays the more important role. The resident time of monomer molecules in the plasma is dependent on the length of plasma in the direction of displacement (consequently, the volume of plasma) and the mass flow velocity.

In the diffusion-dominant case, nearly all monomer molecules coming into the reaction vessel may polymerize; consequently, the apparent rate of polymer deposition is controlled by the monomer feed-in rate (flow rate), as reported by Yasuda and Lamaze (1973) (see Fig. 19). A similar observation was also made by Kobayashi, Bell, and Shen (1974) in capacitive coupling glow discharge polymerization of ethylene in a bell-jar-type reactor. In such a system, however, the effective flow rate in the plasma volume is not clear. Nevertheless, the deposition rate increases (in the low-flow-rate region) nearly linearly proportionally to the monomer flow rate. As the flow rate increases, the resident time of the monomer in the plasma decreases; consequently, the rate of polymer deposition as well as the yield of polymerization both decrease with increasing flow rate as shown in Figure 20. Similar results are reported by Westwood (1971) for the polymerization of vinyl chloride (see Fig. 21).

It should be noted here that all these observations were made at a fixed discharge wattage. As will be discussed later, none of the parameters such as discharge power, flow rate, and system pressure can be treated as an independent parameter. All factors influence the glow discharge polymerization in an interrelated manner, and such a plot merely represents the slicing of a three-dimensional profile at a fixed plane.

C. System Pressure

The system pressure is perhaps the most misunderstood and ill-treated parameter of glow discharge polymerization. This misunderstanding or mis-

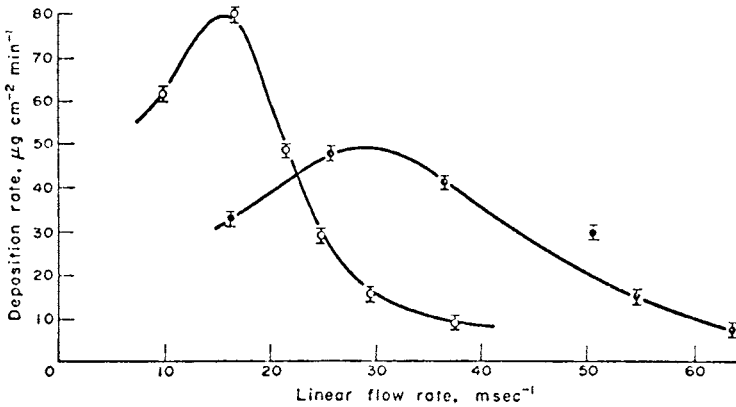


Fig. 21. Deposition rate as function of linear flow rate. Vinyl chloride: 200 V cm^{-1} , 2.29 mA cm^{-2} ; temperature 20°C . [Reproduced from Westwood (1971).]

treatment stems largely from the lack of distinction between nonpolymer-forming and polymer-forming plasmas. As mentioned earlier, efficient glow discharge polymerization is an excellent pump. Consequently, the polymerization itself changes the system pressure. Another factor contributing to the misunderstanding is the failure to recognize the effect of product gas. In many cases, the system pressure observed before glow discharge, p_0 , is cited as though it represents the system pressure during glow discharge polymerization, p_g . Some authors claim that p_g is adjusted to p_0 by controlling the pumping rate. Since p_g is dependent on the production rate of product gas, such an operation is not always possible. Furthermore, in view of the etching effect of the product-gas plasma which is highly dependent on the amount and nature of product gas, such an operation does not seem to have any advantage or significance in controlling the process.

The following points may clarify the meaning of system pressure in glow discharge polymerization:

(1) The system pressure before glow discharge, p_0 , at a given flow rate is entirely dependent on the pumping rate (Yasuda and Hirotsu, 1978). The higher the pumping rate, the lower is the value of p_0 .

(2) The pumping rate of a system is dependent on the nature of the gas and is particularly important when a liquid nitrogen trap or a turbomolecular pump is employed in a vacuum system as shown in Figure 22. These are excellent pumps for most organic vapors (starting material of glow discharge polymerization) and some gases; however, they offer virtually no pumping action for H_2 , which is the main product gas when hydrogen-containing compounds are used as the starting material.

(3) As far as the gas phase is concerned, glow discharge polymerization acts as an additional pump.

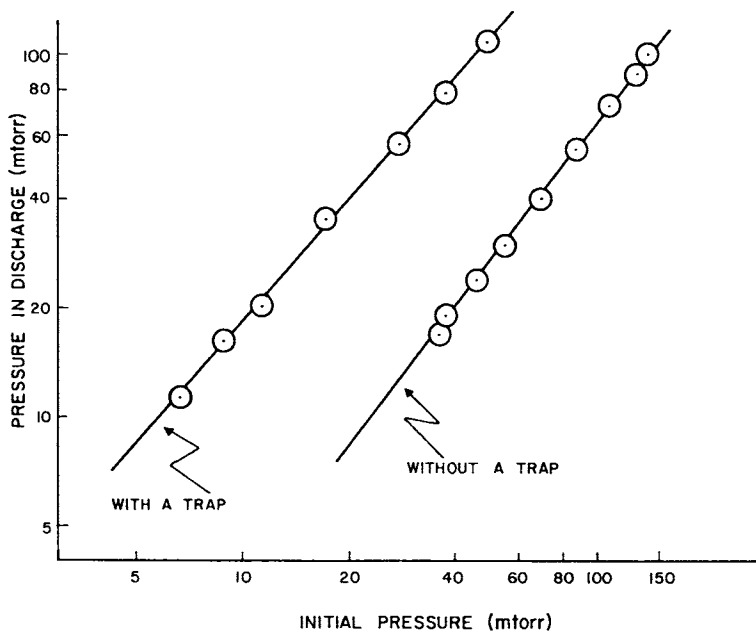


Fig. 22. The dependence of system pressure in the discharge, p_g , on the initial system pressure p_0 for glow discharge polymerization of ethylene. The initial pressure at a given flow rate is dependent on the pumping rate of the system as shown by the two lines representing systems with and without liquid nitrogen traps.

(4) Glow discharge polymerization changes the gas phase from the starting material to the product gas.

(5) Consequently, the system pressure with the glow discharge on, p_g , is largely determined by the pumping efficiency of the product gas, the efficiency of the polymerization, and the production rate of the product gas.

(6) Therefore, there is no unique relationship between p_0 and p_g . In a system where the polymerization yield is maintained at nearly 100%, p_g is determined by the flow rate but not by the value of p_0 , as shown in Figure 23.

Since the velocity and the ionization of gas molecules are dependent on pressure (Bell, 1976) the value of p_g (but not p_0) is important in controlling the distribution of polymer deposition and the properties of polymers formed in glow discharge polymerization; however, p_g cannot be considered as a manipulatable processing factor. The value of p_g can be manipulated to a certain extent, but it is largely determined by the nature of the starting material (i.e., gas production rate).

A change in pressure also changes the volume and intensity of the plasma, which not only changes the relative position of the polymer-collecting surface in the plasma but also the ratio of polymer collected on the surface to the total amount of polymers formed. The discussion of polymer deposition rate is

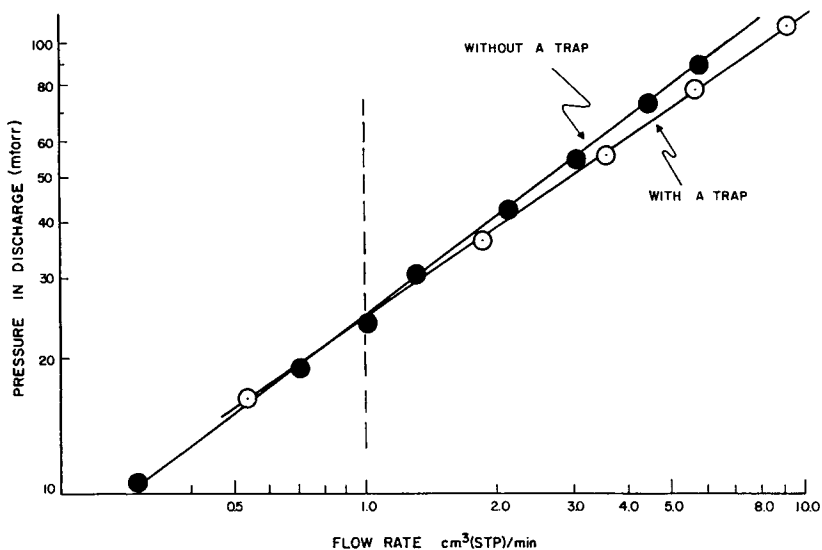


Fig. 23. The dependence of system pressure during the discharge, p_g , on the flow rate of starting material (ethylene). Despite the difference in p_0 's for systems with or without a liquid nitrogen trap, p_g is mainly dependent on the flow rate, indicating that the production rate of the product gas (H_2) and the pumping rate of a system for the product gas determine the value of p_g .

meaningful only when the ratio mentioned above is close to unity or at least does not change significantly within the range of experimental conditions.

Therefore, the dependence of polymer deposition rate on the pressure should be interpreted only in the context that the pressure is an empirical controlling factor of plasma reactor. The apparent dependence of polymer deposition rate on the pressure is shown in Figures 24 and 25.

Figure 24 shows the rate of polymer deposition of vinyl chloride in a flow system as a function of pressure, at a fixed value of flow rate, and of current density (Westwood, 1971). Figure 25 shows the rate of polymer deposition of vinyl chloride in a closed system as a function of pressure at two fixed current densities (Westwood, 1971).

D. Discharge Power

As previously mentioned, the intensity of a nonpolymer-forming plasma is dependent on a combined factor of pressure and discharge power as well as on other factors of the discharge system such as distance between electrodes, surface area of electrodes, and total volume. Therefore, the factors discussed in the sections above (the effect of flow rate and pressure) also apply to the effect of discharge power.

Furthermore, the breakdown energy necessary to initiate the glow discharge of an organic compound is not a constant and is dependent on the nature of each

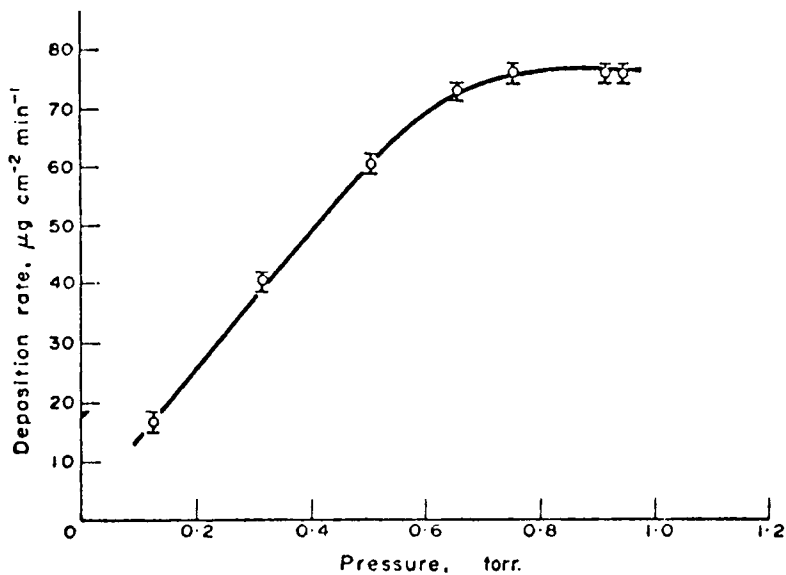


Fig. 24. Flow system. Deposition rate as function of pressure. Vinyl chloride: 200 V cm^{-1} , 2.59 mA cm^{-2} ; linear flow rate: 20 msec^{-1} ; temperature: 20°C . [Reproduced from Westwood (1971).]

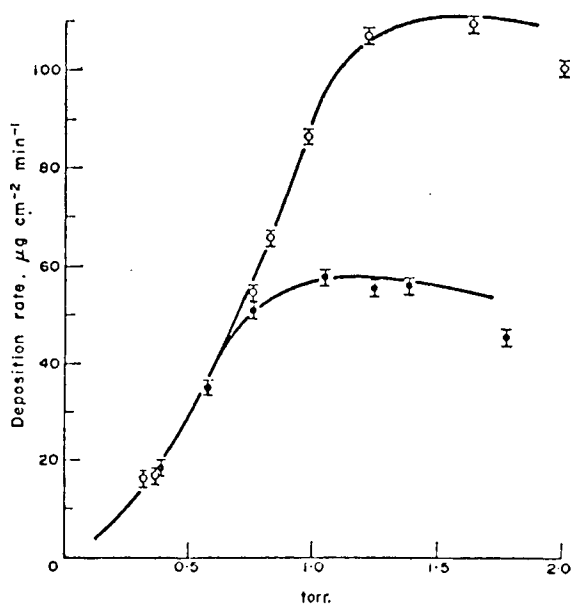


Fig. 25. Deposition of polymer in a glow discharge. Monomer: vinyl chloride; current density: (i) 1.76 mA cm^{-2} , (ii) 1.40 mA cm^{-2} ; temperature: 15°C . [Reproduced from Westwood (1971).]

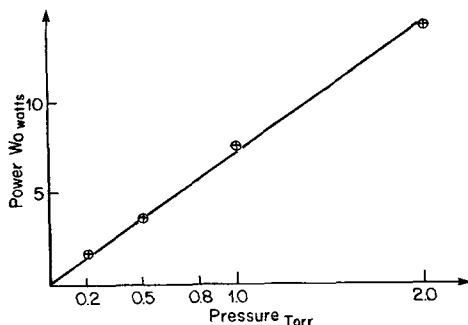


Fig. 26. Minimum power necessary to sustain plasma as function of pressure (benzene). [Reproduced from Duval and Theoret (1973).]

compound. A certain discharge power at a given pressure is not a sufficient parameter to specify plasma, particularly as an operational factor of plasma polymerization. In order to overcome this situation, Duval and Theoret (1973) use a parameter W/W_0 , where W_0 is the minimum power to sustain glow discharge at a given pressure and W is the actual power used in an experiment. The ratio W/W_0 is a parameter for discharge power which is less dependent on the pressure and geometry of the discharge vessel and may be considered a measure of the effective power for glow discharge polymerization.

The minimum discharge power W_0 is dependent on the pressure, as shown in Figure 26 for glow discharge of benzene in a bell-jar-type reactor with parallel electrodes (13.5 MHz). The conversion (g polymer/100 g benzene) is found to be proportional to the product of W/W_0 and the resident time τ , i.e., $(W/W_0)\tau$, as shown in Figure 27.

Williams and Hayes (1966) report that the polymer deposition rate is linearly dependent on the current density in a similar reactor using 10-kHz audio fre-

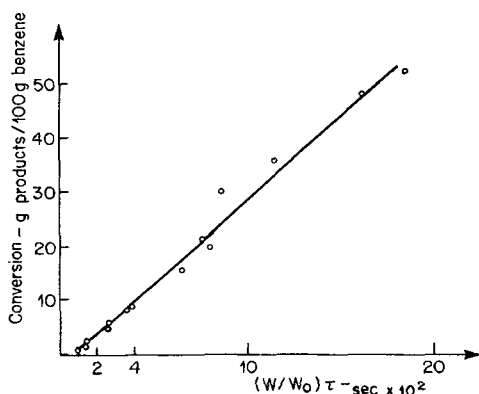


Fig. 27. Conversion of benzene polymerization as a function of $(W/W_0)\tau$, where W/W_0 is the relative wattage and τ is the resident time. [Reproduced from Duval and Theoret (1973).]

quency; i.e., polymer deposition rate = αI , where α is a constant that varies with the degree of adsorption of the monomer onto the electrode surface and I is the current density.

Westwood (1971) uses the current density to describe the energy used in a glow discharge. The dependence of polymer deposition rate on the current density is shown in Figures 28 and 29 for a closed system and a flow system, respectively.

Denaro, Owens, and Crawshaw (1968, 1969, 1970) use the parameter $W \text{ cm}^{-2}$ where W is wattage, to describe the discharge power used in a bell-jar-type reactor with parallel-plate electrodes (2 MHz). The deposition rate generally increases with increasing W , and the deposition rates of vinyl and allyl monomers can be generally expressed by

$$\text{deposition rate} = kW^n \frac{p}{p + 2A}$$

where k and A are parameters related to the kinetics of polymerization [see Denaro, Owens, and Crawshaw (1970) for details of these parameters], and p is the pressure of the monomer. Table III summarizes the values of parameters together with the vapor pressure p_0 of the monomers at 25°C and the maximum experimental pressure used.

In an electrodeless glow discharge, Thompson and Mayhan (1972) report the increase of polymer deposition rate with increasing wattage as shown in Table IV and Figure 30. The dependence of the polymer deposition rate shown can

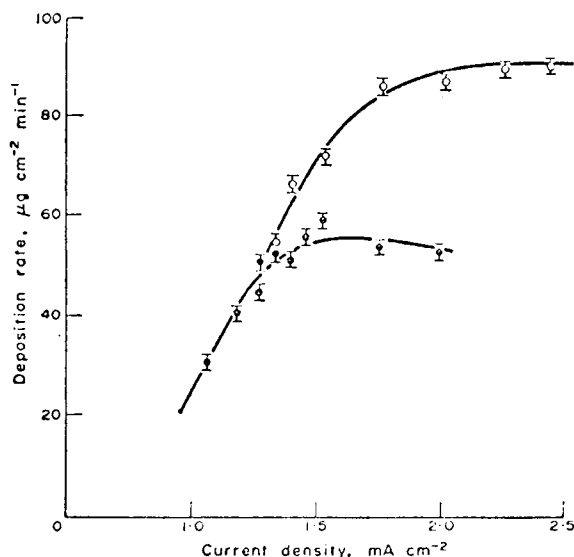


Fig. 28. Deposition of polymer in a glow discharge. Monomer: vinyl chloride; pressure: (i) 0.99 mm Hg, (ii) 0.76 mm Hg; temperature: 15°C. [Reproduced from Westwood (1971).]

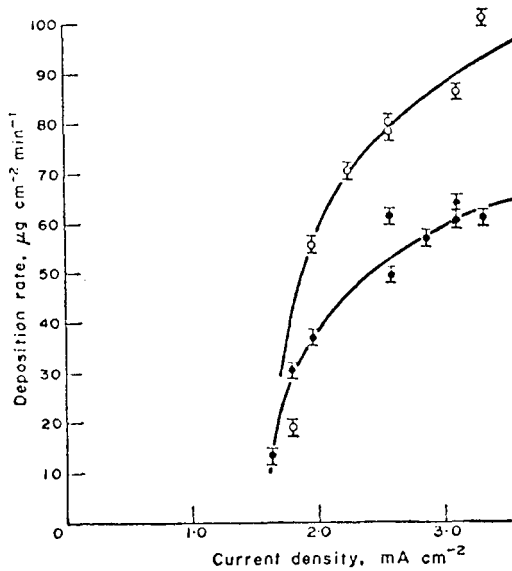


Fig. 29. Flow system. Deposition rate as function of current density. Vinyl chloride: temperature: 20°C, (i) pressure: 1.01 mm Hg, linear flow rate: 14.0 msec⁻¹; (ii) pressure: 0.51 mm Hg, linear flow rate: 27.8 msec⁻¹. [Reproduced from Westwood (1971).]

be expressed by

$$\ln(\text{polymer deposition rate}) = A \exp(-E_a/K'W)$$

where $-E_a$ is the apparent activation energy, W is the power input into the system in watts, and K' is a constant.

The dependence of both polymer deposition rate and conversion percent on the discharge power shown in Table IV and in Figure 30 is in good accordance with the data of ESR signals produced in a glass tube exposed to a glow discharge

TABLE III
Monomer Parameter^a

Monomer	k	n	A	p^0 (torr)	Max. press. (torr)
Styrene	8.5	1.7	0.29	4.2	2.0
α -Methylstyrene	12.3	1.0	0.20	4.2	1.4
ω -Methylstyrene	-	-	0.02	1.0	1.0
Allyl benzene	12.0	1.0	0.55	1.8	1.6
Allyl alcohol	5.8	0.57	1.02	16.2	2.0
Crotyl alcohol	1.4	1.0	0.26	4.5	2.0

^a The values in the table are based on the formula deposition rate = $kW^n[p/(p + 2A)]$. [Reproduced from p. 495 of Denaro, Owens, and Crawshaw (1970), courtesy of Pergamon Press.]

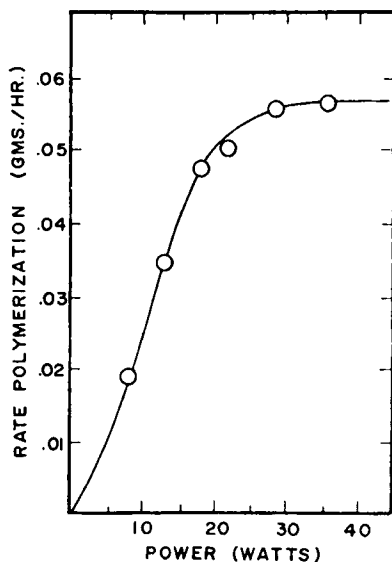


Fig. 30. Rate of polymer formation as a function of power. [Reproduced from Thompson and Mayhan (1972).]

of a similar type (see Fig. 15). However, it also indicates that this dependence may be limited to the relatively low-wattage region in which glow discharge is not fully developed and the conversion is low. As ESR signals indicate, after the glow discharge is fully developed in the entire volume of a reactor, additional wattage does not increase the production of free radicals. Under such conditions the flow rate of monomer becomes the rate-determining step of polymer deposition.

Yasuda and Lamaze (1973, 1971) utilized the fully developed tail-flame (afterglow) portion of an electrodeless glow discharge (13.5 MHz) and found that the polymer deposition rate is independent of wattage (20–150-W region)

TABLE IV
Rate of Polystyrene Formation and Percent Monomer Conversion at Various Power Levels^a

Power (watts)	Deposition rate (g/hr)	Monomer conversion (%)
8	0.019	30–35
13	0.035	60–65
18	0.047	-
22	0.053	80–85
28	0.056	-
36	0.057	100

^a Reproduced from Thompson and Mayhan (1972), p. 2318, courtesy of John Wiley & Sons, Inc.

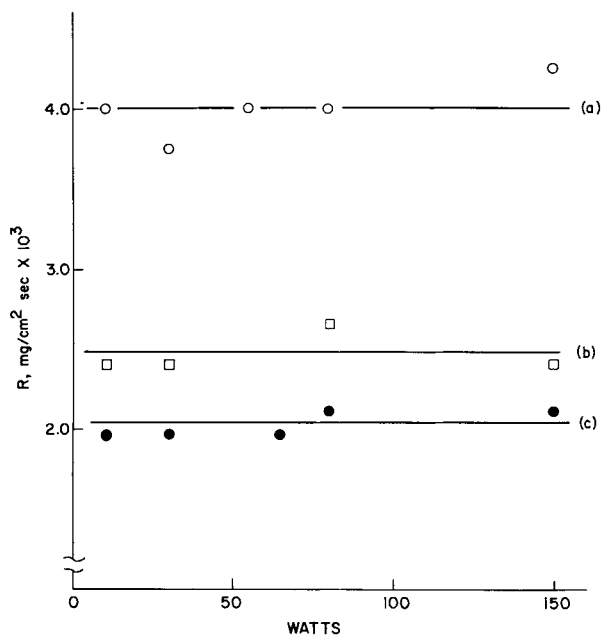


Fig. 31. Dependence of polymer deposition rate on the discharge power (W): (a) 40 μm Hg styrene and 40 μm Hg N_2 ; (b) 20 μm Hg styrene and 40 μm Hg N_2 ; (c) 40 μm Hg styrene. [Reproduced from Yasuda and Lamaze (1971).]

as shown in Figure 31 and is linearly proportional to the flow rate of monomers (see Fig. 19).

The significance of discharge power in glow discharge polymerization is quite different from that for nonpolymer-forming plasmas. In essence (the absolute value of), discharge power itself cannot be considered as an independent variable of the operation, since a certain level of discharge power (e.g., 60 W) in a given set of discharge conditions for one starting material (e.g., ethylene) could not even initiate a glow discharge with another starting material (e.g., *n*-hexane) under otherwise identical conditions. In other words, a relative level of discharge power which varies according to the characteristics of starting materials is needed to describe the discharge power for glow discharge polymerization.

In order to understand the importance of the discharge power parameter for glow discharge polymerization, it is very important to recognize the following characteristics of glow discharge polymerization: (i) the starting material is in the gas phase, but the main product is in the solid phase; (ii) glow discharge polymerization occurs mainly in the glow region of a reactor; and (iii) the glow region of the gas phase is not a simple plasma of the starting material but contains significant amounts of nonpolymer-forming gas product(s). Therefore, in order to describe the discharge power of glow discharge polymerization, it is necessary to express the characteristic power density in the glow volume of a flow system.

Consequently, the discharge power level to describe glow discharge polymerization is a system-dependent parameter, not simply the power input into the system.

For instance, the discharge power necessary for glow discharge polymerization [based on the maximum change which occurs in gas phase (Yasuda and Hirotsu, 1978c)] of various hydrocarbons is shown in Figures 32 and 33 as a function of flow rate of the starting material. As seen in these figures, the discharge power necessary for glow discharge polymerization depends on both the molecular weight and chemical structure of the compounds.

The best first-order approach to dealing with this situation is to use the parameter given by W/FM , where W is the power input, F is the flow rate, and M is the molecular weight of starting material (Yasuda and Hirotsu, 1978c). The parameter W/FM represents the power input per unit mass of the starting material. This parameter does not contain terms which describe the geometric factor of and flow pattern within a reactor, and consequently the absolute value cannot

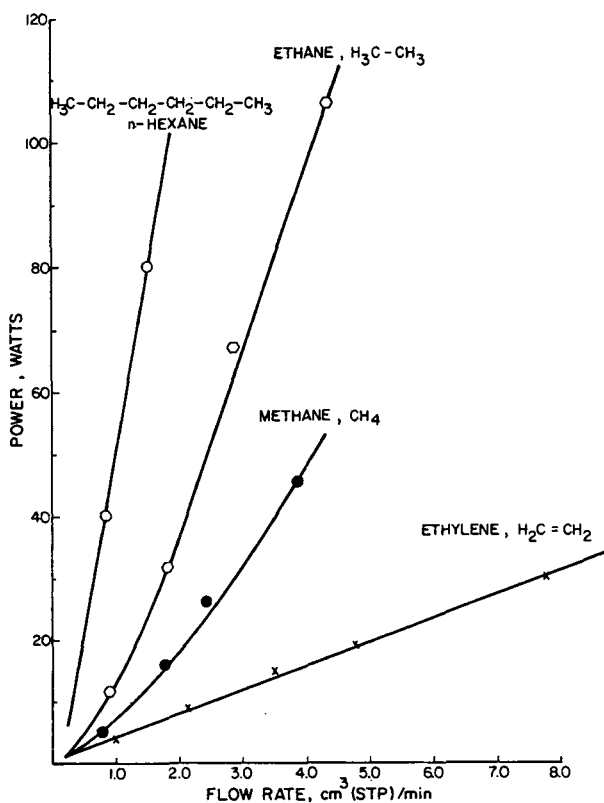


Fig. 32. The dependence of discharge power to obtain a comparable level of glow discharge polymerization on the flow rates of starting materials. The discharge power is greatly dependent on the molecular weights of the starting materials.

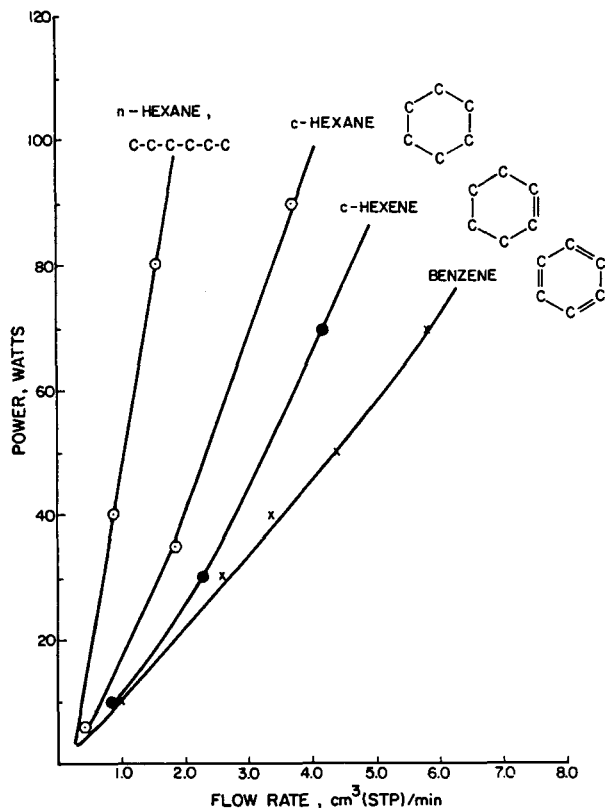


Fig. 33. The dependence of discharge power to obtain a comparable level of glow discharge polymerization on the flow rates of the starting materials for hydrocarbons containing six carbons. The discharge power is also dependent on the structures of starting materials.

be used in general cases. However, it is a useful parameter to describe glow discharge polymerization of different starting materials in a polymerization reactor.

The discharge power which is widespread as shown in Figures 32 and 33 for various compounds becomes roughly comparable when $(W/FM)_c$ is plotted against F , as shown in Figures 34 and 35. $(W/FM)_c$ represents the values of W/FM given by lines shown in Figures 32 and 33. The values $[(W/FM)_c]_{F \rightarrow 0}$ for various hydrocarbons are nearly constant, dependent only on structures of starting materials. It is worth noting here that the slope observed in the plots of $(W/FM)_c$ vs. F is proportional to the hydrogen yield of compounds, as shown in Figure 36.

As mentioned earlier, the effect of W or F cannot be determined independently since glow discharge polymerization is dependent on the combined parameter of W/FM . As long as the W/FM value remains above a critical level $(W/FM)_c$ where energy input is sufficient for polymerization, the major effect of increasing

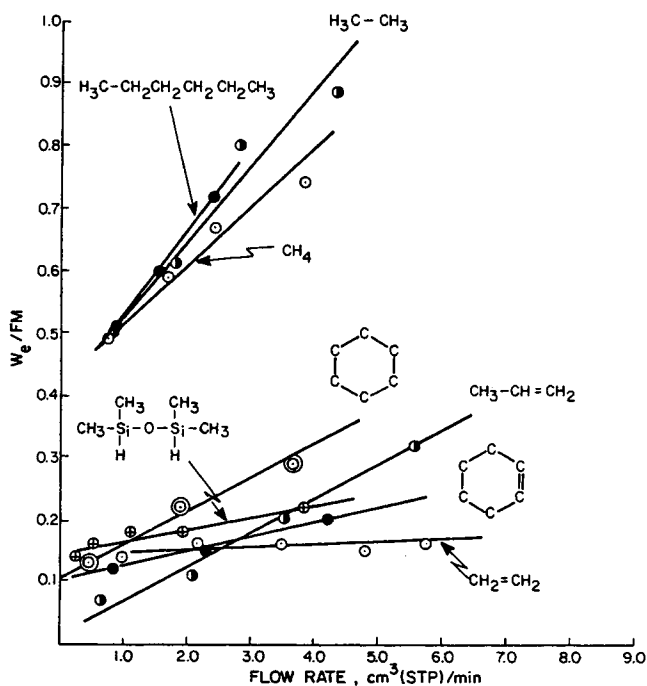


Fig. 34. Plots of $(W/FM)_c$ against the flow rate for various compounds, where W is discharge power for glow discharge polymerization, F is the flow rate, and M is the molecular weight of the starting material, and $(W/FM)_c$ represents the values of W/FM given by lines shown in Figs. 5 and 6.

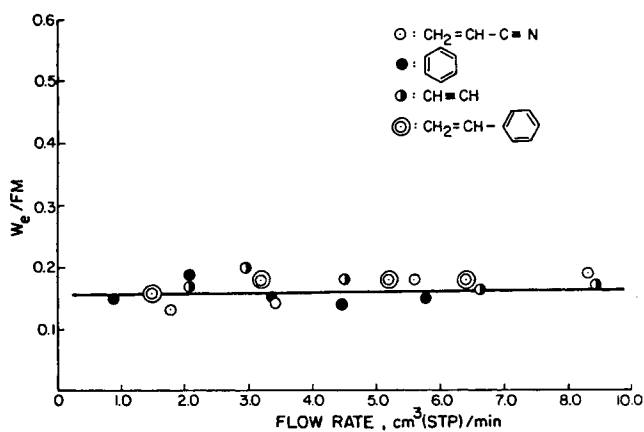


Fig. 35. Plots of $(W/FM)_c$ versus the flow rate of compounds which contain triple bonds and/or aromatic structures. $(W/FM)_c$ is nearly independent of the flow rate for these compounds. (See Fig. 7 caption for definitions.)

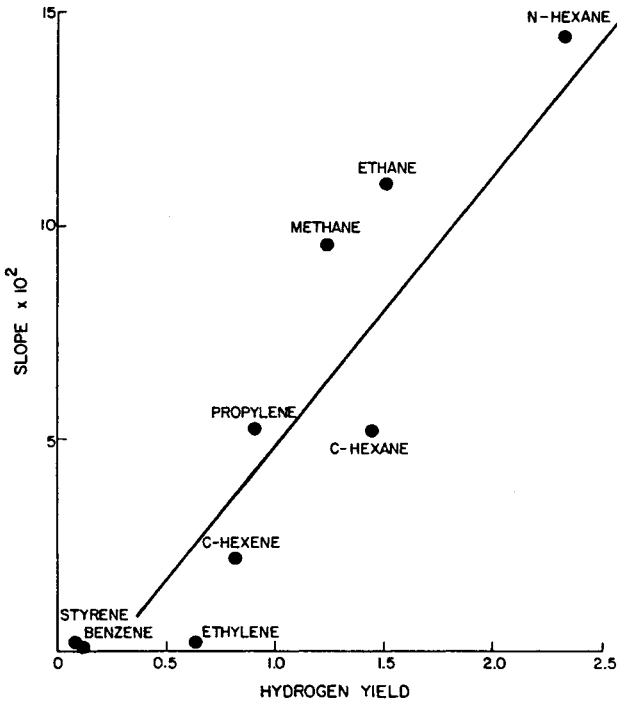


Fig. 36. The dependence of the slopes of $(W/FM)_c$ vs. F plots on the hydrogen yield of compounds. The hydrogen yield is the number of hydrogen molecules evolved when a molecule of starting material is incorporated into the glow discharge polymer.

the flow rate is to increase the feed-in rate, which increases the polymer deposition rate. However, if the W/FM level drops to a certain level as F increases at a constant W , where the discharge power is not sufficient to polymerize all starting materials coming into the reaction system, the polymerization mechanism itself changes. Consequently, the polymer deposition rate decreases despite the fact that more starting materials are supplied to the reaction system. The general situation is shown in the schematic diagrams (Yasuda, 1977) given in Figure 37.

According to the W/FM parameter, the discharge power W must be increased as the flow rate of starting materials increases, and/or as the molecular weight of the starting material increases.

E. Geometrical Factor of Reactor

1. Bypass Ratio of Flow

Not all starting materials fed into a glow discharge polymerization reactor are utilized in the polymer formation. The bypass ratio represents the portion of flow which does not contribute to glow discharge polymerization. Conse-

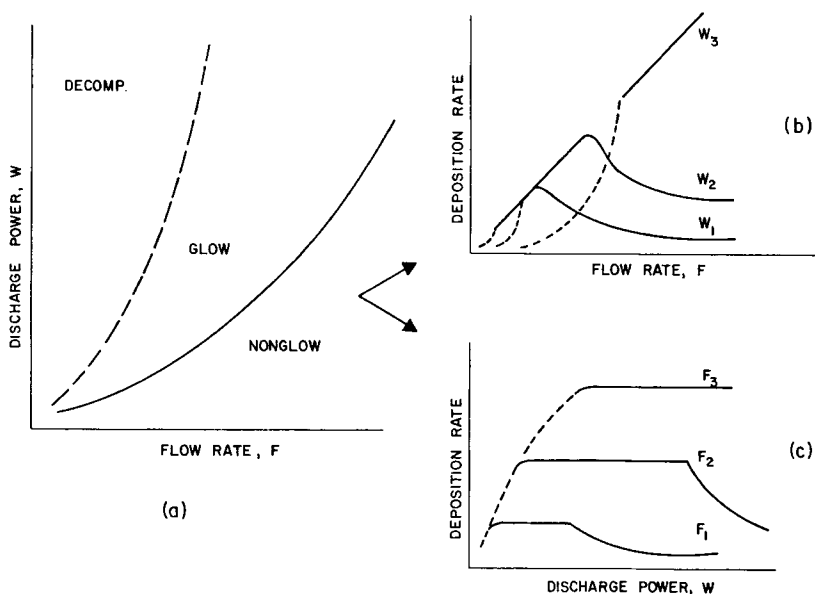


Fig. 37. Schematic representation of the interrelationship of polymer deposition rate with flow rate and discharge power: (a) indicates the power flow domains of decomposition (poor polymer deposition due to predominating ablation process), normal glow where glow discharge polymerization occurs, and nonglow region. (b) and (c) at a fixed level of W or F , change of F or W crosses the domain shown in (a), and consequently the apparent dependence of polymer deposition rate on either F or W is determined by where the change of domain occurs.

quently, the higher the bypass ratio of a reactor, the lower the conversion of the starting material is to the polymer. Clearly, this ratio depends on the ratio of the volume occupied by discharge, V_g , to the total volume of reactor, V_R .

2. Relative Position of Energy Input and Polymer Deposition

In glow discharge polymerization which utilizes internal electrodes, either the substrate is placed directly on an electrode surface or in the space between the electrodes.

With external electrodes or a coil, the location of the substrate can be chosen in a variety of ways. Since the polymer properties and the deposition rate are dependent on the location within a reactor, this is an extremely important factor in practical applications. The relative position is further complicated by the factor described below.

3. Relative Location of the Feed-In of the Starting Material and Flow Pattern

The location where the starting material is introduced is very important for polymer deposition. The importance of flow pattern with respect to the location

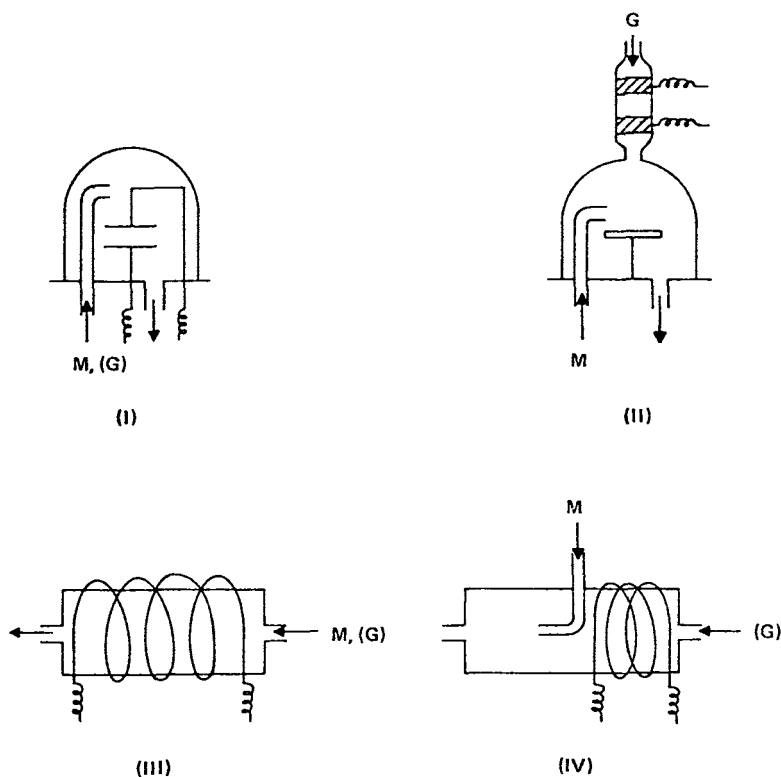


Fig. 38. Schematic representation of some typical arrangements of electric discharge, flow of starting material, M (and carrier gas, G), and the location of polymer deposition.

of energy input and of polymer deposition can be visualized in an example of glow discharge polymerization in a straight-tube reactor with an external coil placed in the middle portion of the tube. In such a system, the volume of glow discharge is generally much larger than the volume of the portion of tube which is directly under the coil. Consequently, polymer deposition occurs even at the upstream side of the coil. The best flow pattern for most practical purposes can be established by avoiding all starting materials passing through the energy-input region, as seen in the examples shown in I, II, and IV of Figure 38. This factor is less obvious in a system with internal electrodes (e.g., in a bell jar).

The importance of these factors (location of the feed-in and flow pattern) will be discussed in more detail in a later section dealing with the distribution of polymer deposition.

F. Nonpolymerizable Gas

Although gases such as helium and argon are commonly used in plasma polymerization, little data dealing with quantitative comparison of the polymer

deposition rates with and without such a gas are available. This is perhaps due to the inherent difficulty associated with the dependence of glow discharge on the pressure and the monomer flow rate. If the flow rate or the partial pressure of a monomer is maintained at a constant value, the glow discharge must be carried out at varying total pressure and flow rate. Conversely, if the total pressure of the system is fixed at a constant value, the monomer flow rate or the partial pressure of monomer must be changed. Therefore, the quantitative effect of gas on the rate of polymer deposition can be examined only under those conditions where the effect of pressure on plasma (nonpolymerizing gas plasma) is relatively small.

Yasuda and Lamaze (1971, 1973) used the tail-flame portion of an electrodeless glow discharge (13.5 MHz) to investigate the effect of a gas on the rate of polymer deposition. In the study, the rate of polymer deposition of pure monomer at a given pressure, R_0 , is measured. Then, a varying amount (pressure) of gas (such as He, N₂, Ar, and H₂) is added to the given pressure of a monomer and the rate of polymer deposition (with a gas), R , is measured. Since the discharge power does not affect the polymer deposition rate in such a system

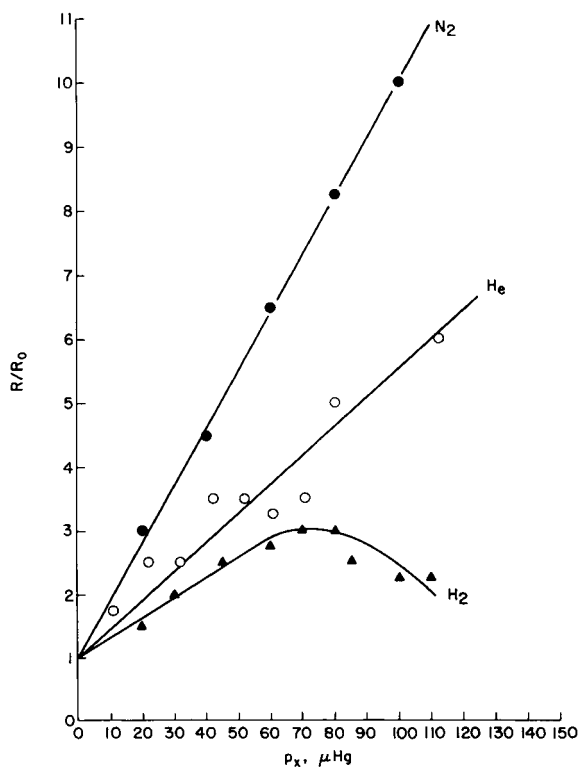


Fig. 39. Dependence of polymer deposition rate on the partial pressure of gas. The relative deposition rate R/R_0 is according to eq. (2). [Reproduced from Yasuda and Lamaze (1971).]

after the discharge power reaches a certain level (see Fig. 31), a discharge power is selected to assure that the glow discharge fills the entire reaction tube at the highest total pressure used in a series of experiments. By this procedure, the effect of the change of total pressure can be minimized, and it is possible to see the effect of gas on the rate of polymer deposition. The ratio R/R_0 is plotted against the partial pressure of a gas. Typical results are shown in Figure 39 where it can be seen that the addition of a gas generally increases the apparent rate of polymer deposition, and the relative rate increase can be given by

$$R/R_0 = 1 + bp_x$$

where b is a constant and p_x is the partial pressure of the gas. Examples of values of b are shown in Table V.

The exceptionally high degree of acceleration with N_2 is partly due to the incorporation of N_2 in the polymer. Hollahan and McKeever (1969) showed that nitrogen was found in the polymer formed in a glow discharge of CO_2 , N_2 , and H_2 , and that its nitrogen content in the polymer is dependent on the flow rate of nitrogen.

Yasuda and Lamaze (1973) report that the pressure of a closed system that contains nitrogen gas and a vinyl monomer (4-vinylpyridine) dropped below the partial pressure of nitrogen, indicating that nitrogen was consumed by plasma polymerization of a vinyl monomer, as shown in Figure 40.

In later studies (Yasuda et al., 1975, 1976) it has been found that many gases and vapors, such as N_2 and H_2O which do not polymerize themselves in plasma, act as comonomers of double-bond- and triple-bond-containing organic compounds in plasma polymerization. This aspect will be discussed in more detail

TABLE V
Constant b for Various Monomers and Gases

Monomer	Gas	Value of $b \times 10^{-1}$ (torr) ⁻¹	Ref.
Styrene	H_2	3.3	(54)
	He	4.5	(54)
	Ar	8.5	(54)
	N_2	9.0	(54)
4-vinylpyridine	N_2	4.5	(40)
α -Methylstyrene	N_2	2.4	(40)
Vinyltoluene	N_2	6.6	(40)
2-vinylpyridine	N_2	5.0	(40)
N-vinyl-2-pyrrolidone	N_2	2.2	(40)
Acrylonitrile	N_2	9.9	(40)
Butadiene	N_2	5.0	(40)
Allylamine	N_2	5.9	(40)
Vinyl chloride	N_2	1.4	(40)

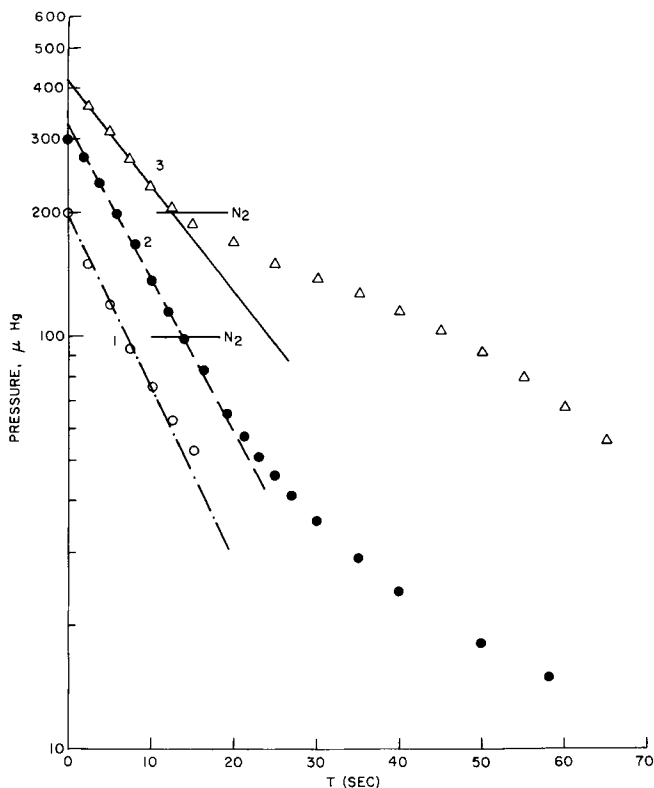


Fig. 40. Pressure change of a closed system, which contains (1) 200 μm Hg styrene, (2) 200 μm Hg styrene and 100 μm Hg N_2 , and (3) 200 μm Hg styrene and 200 μm Hg N_2 with time of glow discharge at 60 W. [Reproduced from Yasuda and Lamaze (1973a).]

in the following section where the properties of plasma polymers are discussed.

It should be also noted here that a part of the increase in polymer deposition rate due to the addition of gas is due to a change of the distribution pattern of polymer deposition as will be discussed in the following section.

G. Distribution of Polymer Deposition

The distribution of polymer deposition is directly related to the uniformity of the thin film formed by glow discharge polymerization. Distribution of polymer deposition is dependent on (1) the geometrical arrangement of the inlet of starting material, the outlet of the system, and the region of energy input; (2) the operating pressure of the discharge (not the initial pressure); and (3) the reactivity of a starting material to form polymers. The effects of these factors on the distribution of polymer deposition may be visualized from the data shown

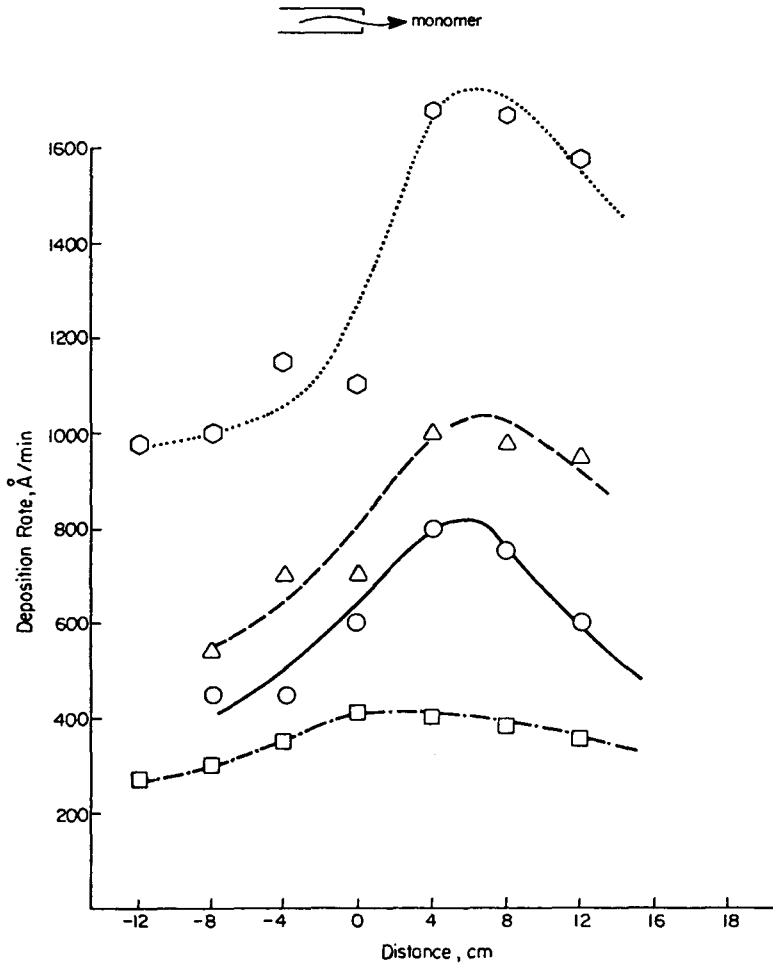


Fig. 41. Distribution of polymer deposition in glow discharge polymerization of acetylene at various flow rates. F denotes flow rate in $\text{cm}^2(\text{STP})/\text{min}$, and p_g denotes the system pressure in the glow discharge given in $\mu\text{m Hg}$. The distance is taken from the point of the starting material inlet in the direction of flow. See Yasuda and Hirotsu (1978a) for details of the reactor.

in Figures 41–46 obtained from an RF (inductively coupled) discharge (Yasuda and Hirotsu, 1978a, 1978b, 1978d). The general trends are as follows.

(1) The lower the discharge pressure, the wider (more uniform) is the distribution of polymer deposition. The lower the pressure, the larger is the mean free path of gas molecules, and the diffusional displacement becomes more efficient. Therefore, the polymer formation is not localized at either the region of excitation or the site of introduction of the starting material.

(2) The higher the reactivity of the starting material (to form polymer), the

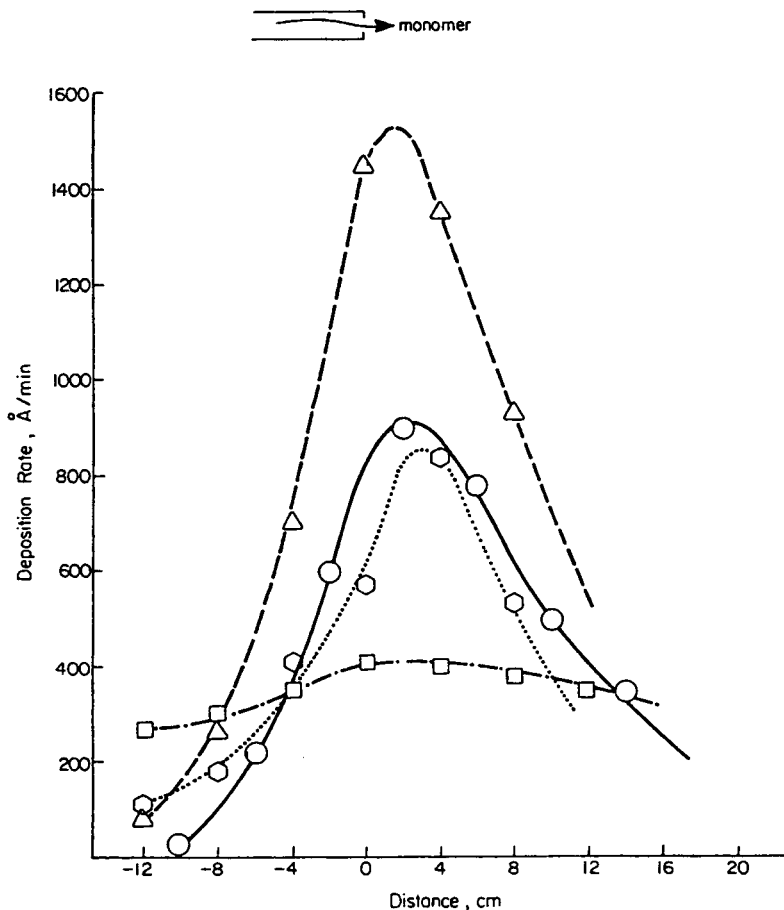


Fig. 42. Distribution of polymer deposition in glow discharge polymerization of acetylene with the addition of a carrier gas. H_2/Ac , Ar/Ac , and N_2/Ac denote the mole ratios of carrier gas to acetylene. The flow rate of acetylene is maintained constant in all cases. Other notation and units are the same as those in Fig. 41.

narrower is the distribution curve of polymer deposition, which has the maximum in the vicinity of the starting material inlet.

(3) With starting materials that have low reactivity to form polymer, the maximum peak is shifted toward the downstream side of the inlet. Consequently, the minimum (rather than the maximum) in the distribution curve is often observed at the vicinity of the inlet.

(4) Addition of nonpolymer-forming gas (e.g., Ar) tends to narrow the distribution curve, and polymers tend to deposit in the vicinity of the monomer inlet.

The distribution of polymer deposition onto the surface of internal electrodes

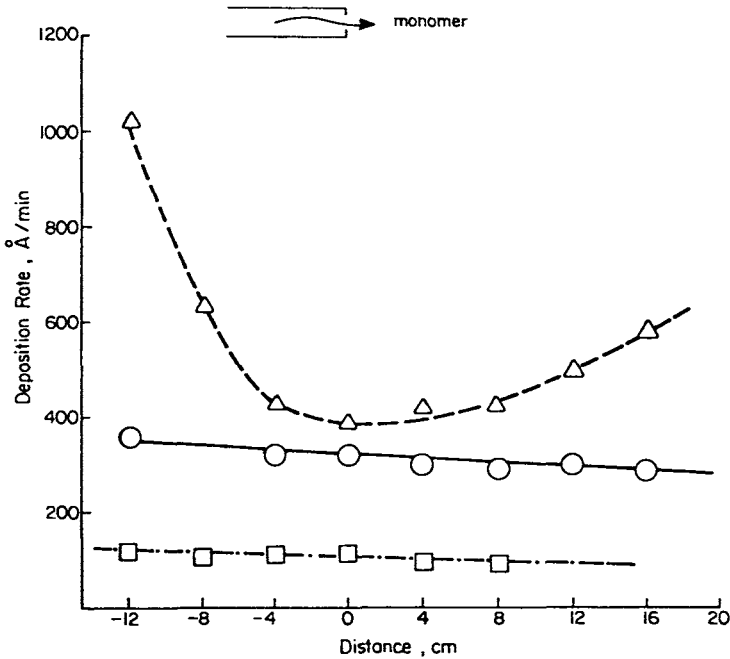


Fig. 43. Distribution of polymer deposition in the glow discharge polymerization of ethylene. All notation and units are the same as those in Fig. 41. Ethylene is a less reactive material than acetylene, as far as glow discharge polymerization is concerned. The increase of flow rate yields a maximum of deposition in the downstream side of the inlet, consequently the apparent minimum is observed near the inlet.

is generally very smooth, unless the starting material inlet is placed too close to the electrodes or too small an electrode gap (in relation to the mean free path of gases) is used. The effect of inlet-outlet locations in a bell-jar-type reactor is shown in Figure 47 (Kobayashi, Bell, and Shen, 1976).

Regardless of the mode of electric discharge or type of reactor, the region where glow discharge polymerization occurs is located in the direct or tortuous pathway of the starting material from the inlet to the outlet. On this pathway, starting material is consumed to form a polymer, and simultaneously the gas phase changes from the starting material to the gas product as polymerization proceeds. Therefore, an uneven distribution always exists if the polymer is collected on a stationary substrate surface. A moving substrate will average out this inherent uneven distribution of polymer deposition and provides a practical means of yielding a uniform coating (Morosoff, Newton, and Yasuda, 1978).

The distribution of polymer deposition should be taken into consideration when the polymer formation is monitored at a fixed location. The shift of the distribution curve due to changes in operational factors could be misinterpreted as a change in the polymer deposition rate itself.

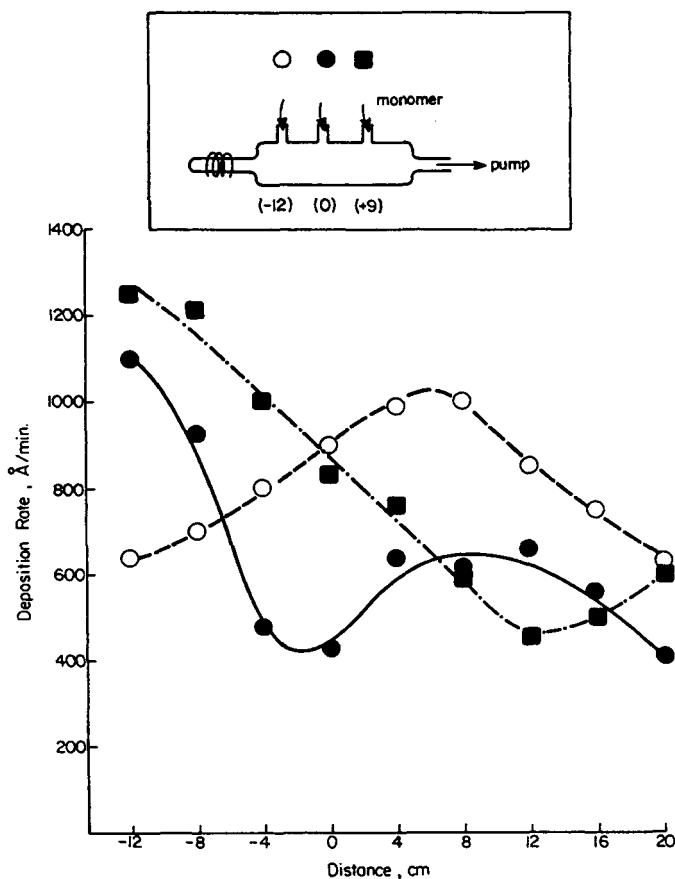


Fig. 44. The effect of location of the starting material (ethylene) inlet on the distribution of polymer deposition. The location of the inlet is shown in the insert. The flow rate of ethylene is maintained constant [$F = 9.8 \text{ cm}^3(\text{STP})/\text{min}$] in all cases.

H. Properties of Polymers

Since glow discharge polymerization is system dependent, the properties of polymers formed by glow discharge polymerization are also dependent on the conditions of the process. The properties of polymers are dependent not only on the kind of reactor used but also on the location within a reactor where polymer deposition occurs.

The diagrams in Figure 48 (Kobayashi, Shen, and Bell, 1974) show what kinds of polymer are formed from a given starting material, depending on the apparent operational factors described. Because the strict meaning of parameters, such as flow rate, pressure, etc., depends on the geometrical factors of a reactor and the type of starting material, generalization of trends should not be made from

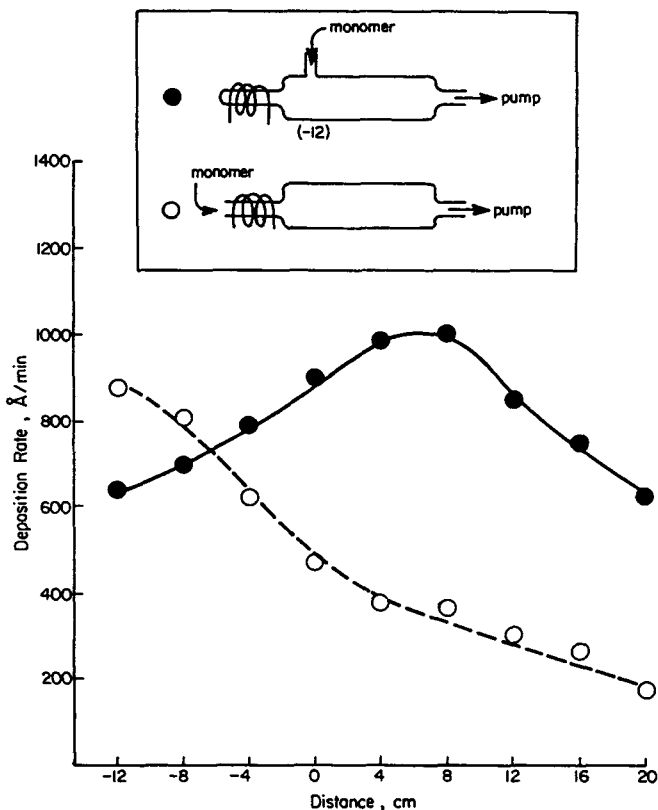


Fig. 45. The effect of flow passing through the RF coil (energy input region) on the distribution of polymer deposition in glow discharge polymerization of ethylene. $F = 9.8 \text{ cm}^3(\text{STP})/\text{min}$ for both cases.

such a diagram. However, it clearly shows the important fact that the properties of polymers formed by glow discharge polymerization are entirely dependent on how the polymerization is carried out.

Analysis of polymers collected in different sections of a system, and of polymers formed by different electric discharges, also shows considerable differences in their properties (Duval and Theoret, 1973, 1975).

A study of the properties of polymers formed from tetrafluoroethylene by glow discharge polymerization investigated by electron spectroscopy for chemical analysis (ESCA) (Yasuda and Morosoff, 1979) provides further evidence of the importance of processing factors. Tetrafluoroethylene is an ideal starting material to illustrate the CAP scheme of glow discharge polymerization. Therefore, some results are shown in Figures 49–51.

The ESCA C_{1s} spectrum of conventionally prepared polytetrafluoroethylene shows a single intense peak at 292 eV corresponding to the $-\text{CF}_2-$ carbon

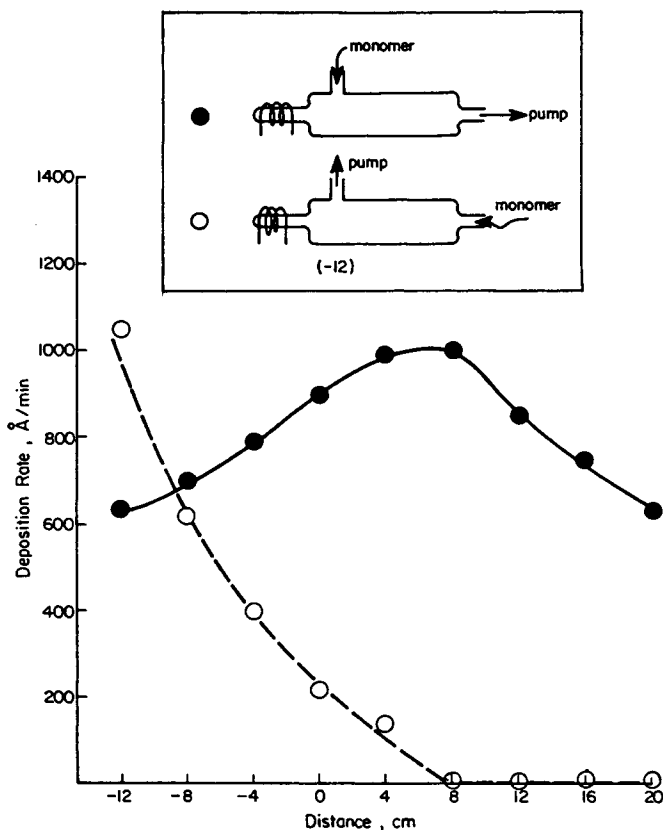


Fig. 46. The effect of direction of flow in relation to the RF coil (energy input region) on the distribution of polymer deposition in glow discharge polymerization of ethylene. All other conditions are maintained constant for both cases.

bond. The peaks at binding energy levels of less than 291 eV represent the presence of crosslinks ($>CF-$, $>CF<$) and carbons bonded to other substituents, including nitrogen- and oxygen-containing groups.

Characteristic shapes of the C_{1s} peaks shown in Figure 49 indicate that polymers that are formed at locations in the upstream and downstream sides of the RF coil are quite different when a relatively low discharge power is used. The polymer formed in the upstream side contains considerable amounts of CF_3 and CF besides the expected CF_2 . This is undoubtedly due to the elemental or atomic nature of glow discharge polymerization rather than conventional molecular polymerization.

The polymer formed in the downstream side of the RF coil at this low discharge power contains much less F (i.e., much smaller peaks for higher binding energy) and the peak at 284.6 eV becomes the major peak. This is a dramatic display of the effect of the energy input zone (i.e., tube directly under RF coil)

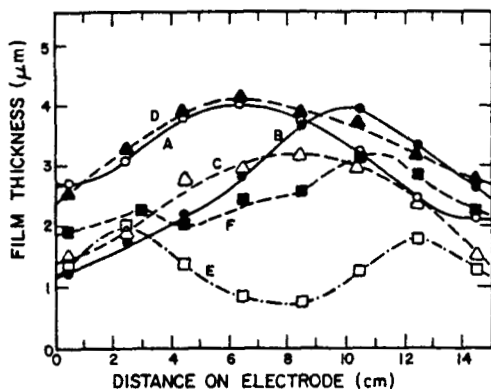
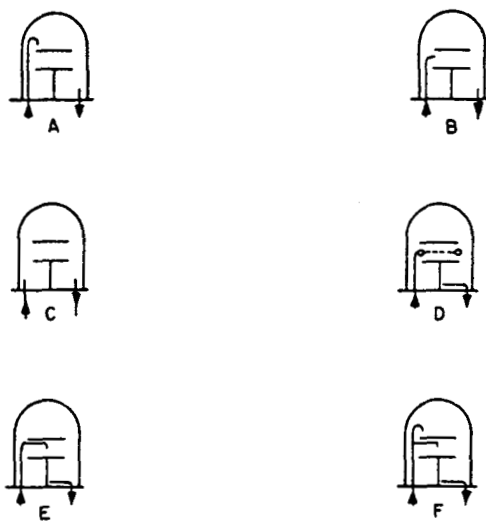


Fig. 47. Effect of relative location of starting material inlet, outlet, and electrodes on the distribution of polymer deposition onto electrode surfaces. See Kobayashi, Bell, and Shen (1976) for details of conditions. $p = 2$ Torr, $P = 100$ W, $F = 80$ cm³/min.

on the properties of glow discharge polymers. As the discharge power is increased, this severe effect of the energy input zone expands eventually to the entire length of the tube, and at a high discharge power the polymer formed in the upstream side of the RF coil becomes similar to the polymer formed in the downstream side, as seen in Figure 50.

When a system in which the flow does not pass through the energy input zone

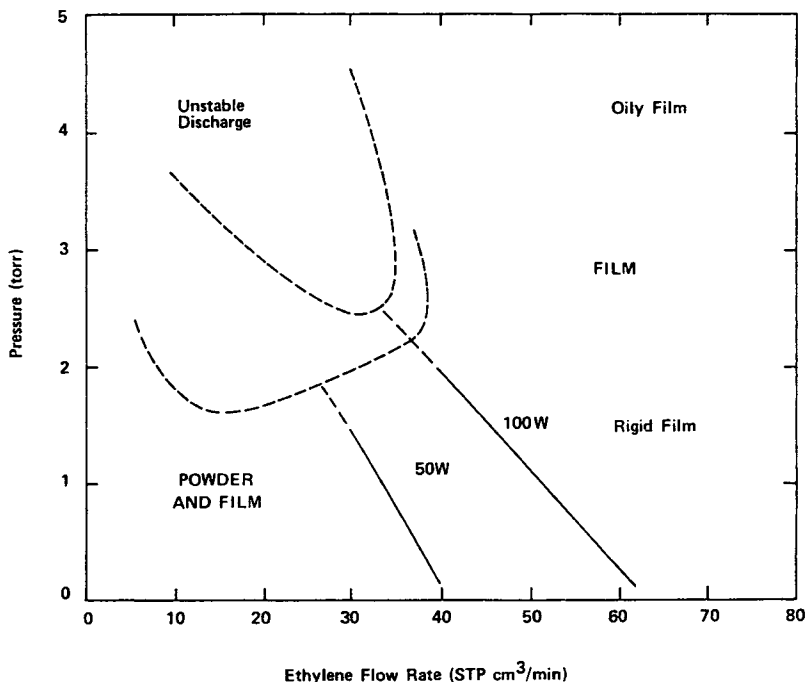


Fig. 48. An example of the dependence of the type of polymer formed on the apparent operational factors of power, pressure, and flow rate.

and glow discharge polymerization is carried out in the tail-flame portion of the glow discharge, the polymer formed at the downstream end of a reactor is not necessarily the same as that formed in the downstream end of a straight tube. Results given in Figure 51 show that the polymer formed in the nonglow region, although it is located at the downstream end of a reactor, is nearly identical to the conventional polytetrafluoroethylene. This means that polymers formed under such conditions are formed mainly by *plasma-induced polymerization*.

As mentioned earlier, tetrafluoroethylene is a special starting material which reflects the effects of operational factors in a very sensitive manner. Therefore, some effects (e.g., the increase of ablation by the increase of discharge power and by the location within a reactor) might be much smaller with other starting materials. However, the important aspects of (i) atomic rather than conventional molecular polymerization and (ii) system-dependent polymerization would undoubtedly be applicable to many other starting materials. These effects should be taken into consideration in designing the reactor, during processing, and in interpretation of results.

Many investigators recognized that coherent and uniform films are obtained when polymers are formed slowly. The number of particles observed on the

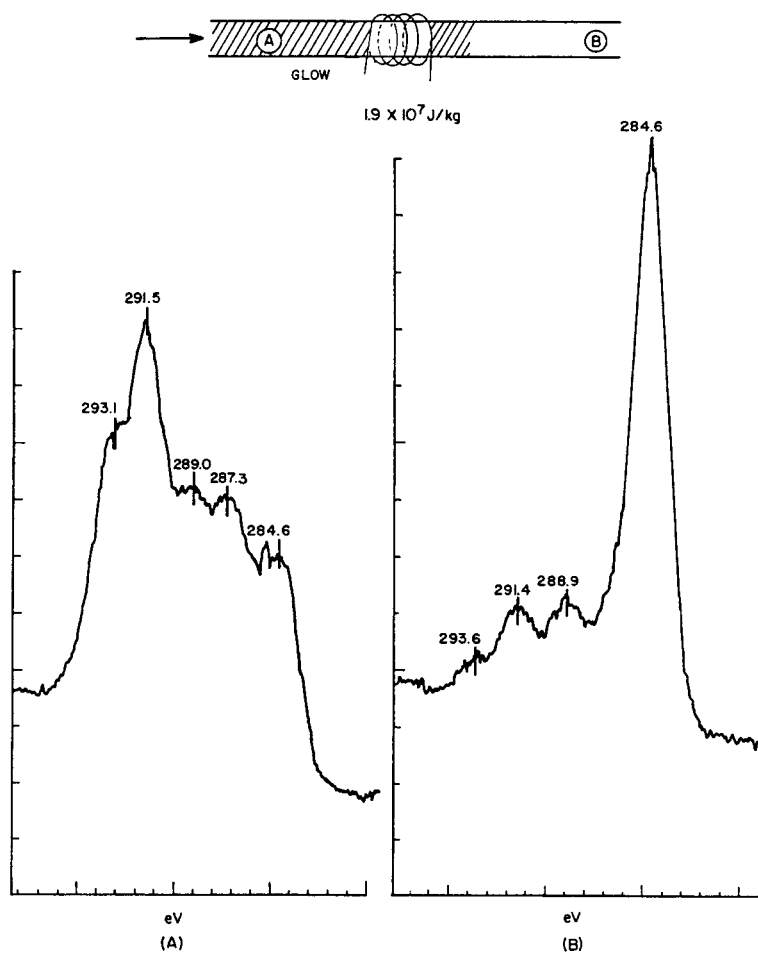


Fig. 49. Dependence of the ESCA C_{1s} peaks of glow discharge polymers of tetrafluoroethylene on discharge conditions and the location of polymer deposition. Polymer deposit occurred at two locations (A) before the RF coil, and (B) after RF coil. Discharge power level is $1.9 \times 10^7 \text{ J/kg}$.

surface of polymer deposition in a film form also decreases as the rate of polymer deposition decreases (Tien, Smolinsky, and Martin, 1972) as shown in Figure 52.

Formation of polymer powders or particles either embedded in a film deposition or dusting on the surface has been reported by many investigators (Thompson and Smolinsky, 1972; Liepins and Sakaoku, 1972; Kobayashi, Bell, and Shen, 1973; Niimomi et al., 1973; Havens et al., 1978; Havens, Mayhan, and James, 1978). X-ray scattering (small angle) data of polymer deposition which is absent of visible microspheres indicated the presence of two distinguishable phases.

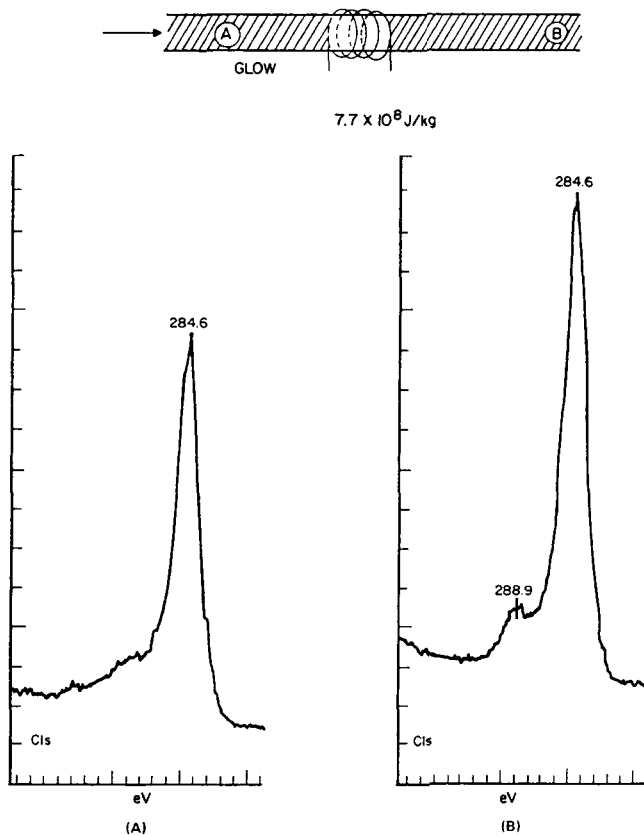


Fig. 50. ESCA C_{1s} peaks of glow discharge polymers of tetrafluoroethylene in the same reactor shown in Fig. 22, but at the higher discharge power level of $7.7 \times 10^8 \text{ J/kg}$.

Since the dependence of polymer deposition rate on operational factors such as flow rate, pressure, and discharge wattage is different depending on the type of reactor, the properties of polymers depend differently on those factors. For instance, the slower deposition rate is obtained with a high flow rate of monomer by the bell-jar-type reactor used by Kobayashi, Shen, and Bell (1974), but the slower deposition is attained by the lower flow rate in the tail-flame reactor used by Yasuda and Lamaze (1973). Nevertheless, it is a general observation that highly coherent films are formed under conditions that deposit polymer slowly.

A recent work by Sharma, Millich, and Hellmuth (1978) indicated that adhesion of the glow discharge polymer—propylene—to a glass substrate was excellent when polymer was deposited at a slow deposition rate at a high flow rate (after passing the maximum in the deposition rate–flow rate dependence such as the ones shown in Figs. 20 and 21); whereas polymer obtained at lower

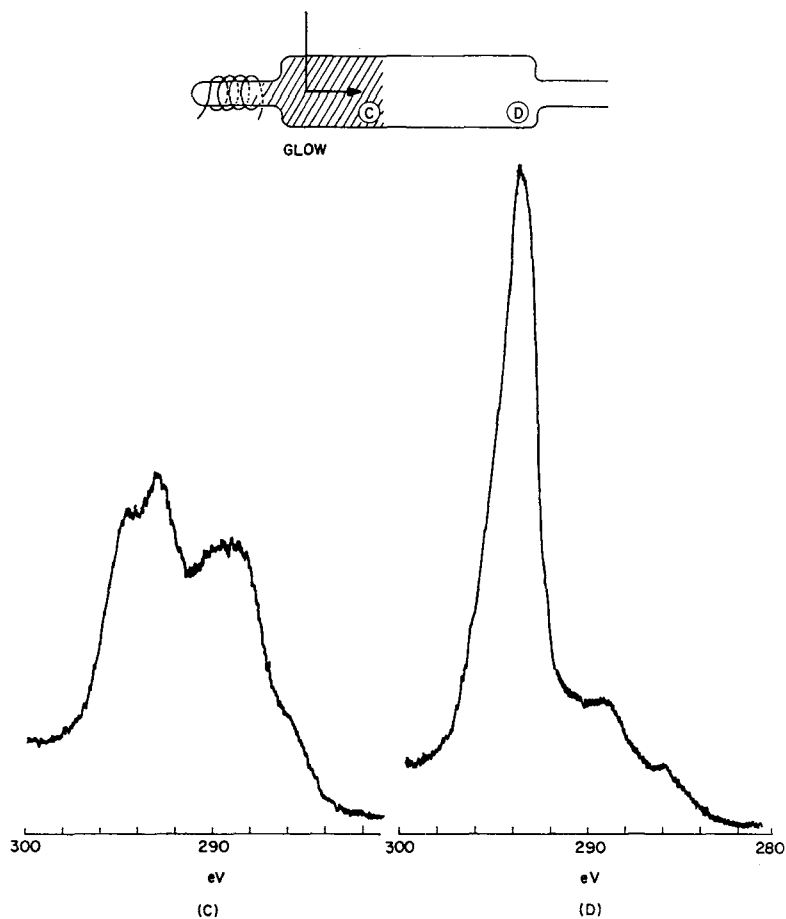


Fig. 51. ESCA C_{1s} peaks of glow discharge polymers of tetrafluoroethylene prepared in a reactor shown in the insert: (C) at the end of the glow region and (D) at the end of the tube in the nonglow region.

flow rate, which is on the other side of the maximum, has poor adhesion.

Duval and Theoret (1973) investigated the molecular weight distribution of soluble compounds formed in a glow discharge of benzene (13.5 MHz) collected from the electrodes' surface, the wall of the reactor (bell jar), and the cold trap placed between the reactor and vacuum pump. Their molecular weight distribution, as obtained by gel permeation chromatography (GPC), is given in Figures 53–55. When pressure is reduced (lower rate of polymer deposition) polymers with higher molecular weights are formed. The overall film (mechanical) strength decreases with increasing pressure, discharge power, and film thickness.

Perhaps the most distinct differences between plasma polymers and con-

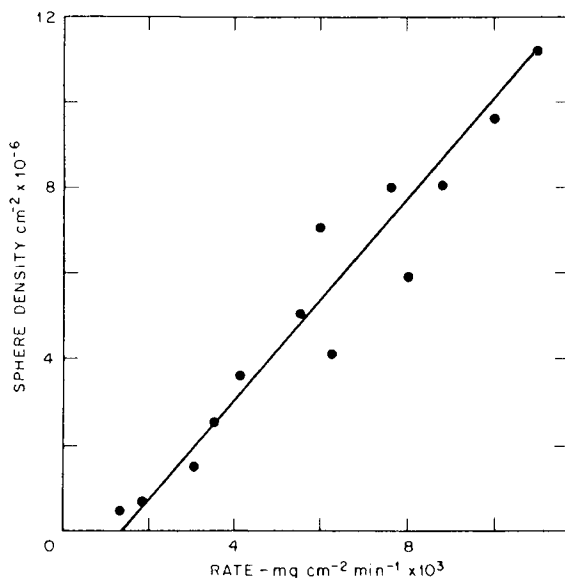


Fig. 52. Sphere density as a function of growth rate of TMS film. [Reproduced from Thompson and Smolinsky (1972).]

ventional polymers are (a) the H/C ratio of plasma polymers is smaller than the value expected from the monomer, and (b) oxygen is found in nearly all cases in plasma polymers. The low H/C ratio is undoubtedly caused by the polymerization mechanism in which the formation of active species such as free radicals by hydrogen elimination plays an important role. The incorporation of oxygen is most likely due to the postpolymerization reaction of trapped free radicals in the plasma polymers with atmospheric oxygen and possibly water vapor.

Elemental analyses of glow discharge polymers obtained by electrode glow discharge (3.14 MHz) of vinyl chloride, vinyl fluoride, and vinylidene fluoride at various conditions are shown in Tables VI and VII. Using these data, Westwood (1971) notes that polymers formed under different sets of experimental conditions from the same monomer are seen to differ in chemical composition, particularly as regards oxygen content; however, apart from the oxygen data, the variations are relatively small and polymers from a particular monomer have a more or less distinctive infrared spectrum.

Tien, Smolinsky, and Martin (1972) report that the oxygen content of glow discharge polymers can be controlled by the treatment of plasma polymers. The oxygen content of glow discharge polymer from vinyl trimethylsilane increases when the film is heat-treated in an oxygen atmosphere. Exposure of films first to nitric oxide and then to air reduces the oxygen content to about 2% compared to 10–15% for films exposed to air directly.

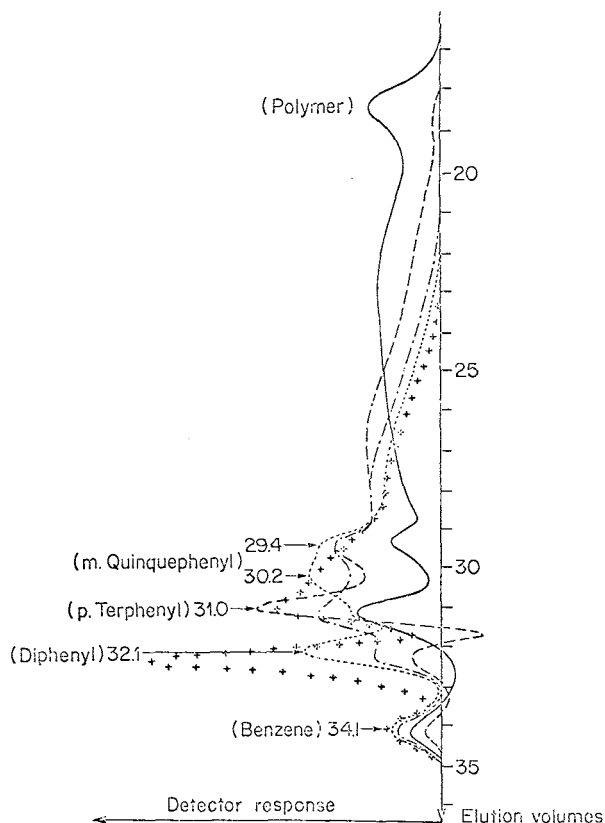


Fig. 53. GPC spectra of soluble compounds deposited on reactor walls at constant power ($W/W_0 = 1.5$) as function of pressure (in mm Hg): (—) 0.2, (---) 0.5, (-·-) 0.3, (···) 1.0, (+) 2.0. [Reproduced from Duval and Theoret (1973).]

TABLE VI
Chemical Analysis of Glow Discharge Polymers^a

Polymer	Discharge conditions	Empirical formula
PVC	116 V/cm, 1.75 mA/cm ² , 0.76 torr	C ₂ H _{2.06} Cl _{0.51} O _{0.40}
PVC (vinyl chloride/argon)	240 V/cm, 2.95 mA/cm ² , 1.14 torr	C ₂ H _{1.97} Cl _{0.57} O _{0.28}
PVF	148 V/cm, 2.25 mA/cm ² , 1.52 torr	C ₂ H _{2.32} F _{0.31} O _{0.16}
PVF	113 V/cm, 1.95 mA/cm ² , 0.57 torr	C ₂ H _{2.25} F _{0.24} O _{0.37}
PVDF	100 V/cm, 1.72 mA/cm ² , 0.88 torr	C ₂ H _{1.45} F _{0.95} O _{0.15}
PVDF (powder form)	100 V/cm, 1.72 mA/cm ² , 0.88 torr	C ₂ H _{1.46} F _{0.98} O _{0.16}
PVDF	109 V/cm, 1.85 mA/cm ² , 0.95 torr	C ₂ H _{1.69} F _{0.99} O _{0.07}

^a Reproduced from Westwood (1971), p. 378, courtesy of Pergamon Press.

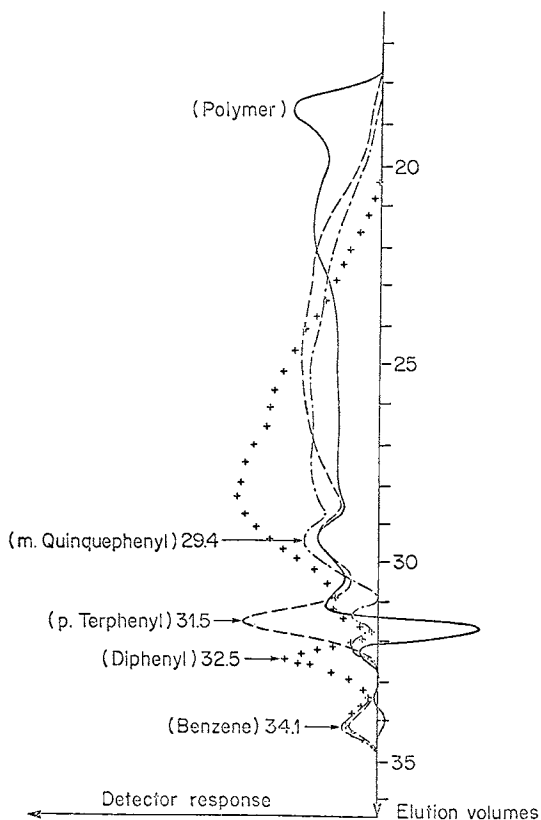


Fig. 54. GPC spectra of soluble compounds deposited on electrodes at constant power ($W/W_0 = 1.5$) as function of pressure (in mm Hg): (—) 0.2, (---) 0.5, (-·-·-) 0.3, (+) 2.0. [Reproduced from Duval and Theoret (1973).]

TABLE VII
Variation of Chemical Analysis with Temperature^a

Polymer	Discharge conditions	Temp. (°)	Empirical formula
PVC	2.50 mA/cm ² , 1.10 torr	-10	C ₂ H _{2.14} Cl _{1.68} O _{0.24}
	2.50 mA/cm ² , 1.10 torr	20	C ₂ H _{1.97} Cl _{1.56} O _{0.27}
	2.50 mA/cm ² , 1.10 torr	40	C ₂ H _{1.85} Cl _{1.57} O _{0.33}
PVF	2.05 mA/cm ² , 1.12 torr	-10	C ₂ H _{2.63} F _{0.23} O _{0.45}
	2.05 mA/cm ² , 1.12 torr	20	C ₂ H _{2.14} F _{0.29} O _{0.32}
	2.05 mA/cm ² , 1.12 torr	40	C ₂ H _{2.09} F _{0.28} O _{0.28}

^a Reproduced from Westwood (1971), p. 378, courtesy of Pergamon Press.

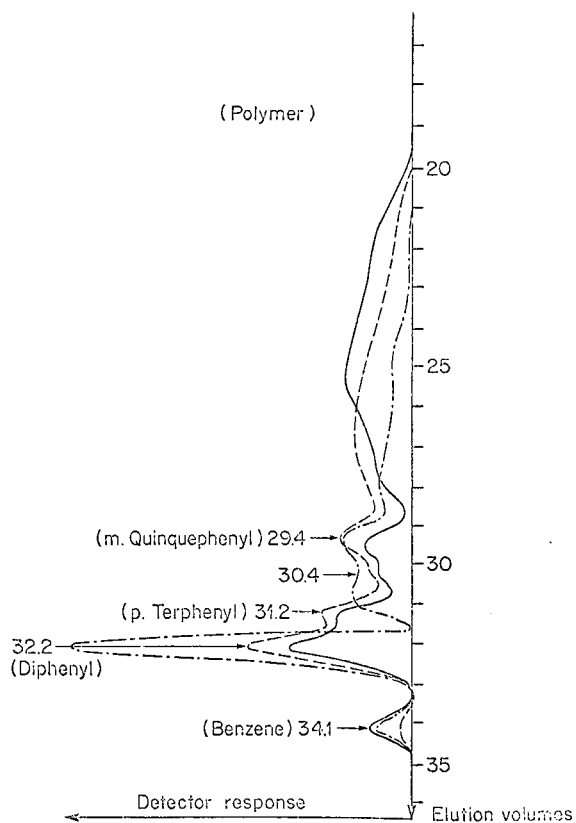


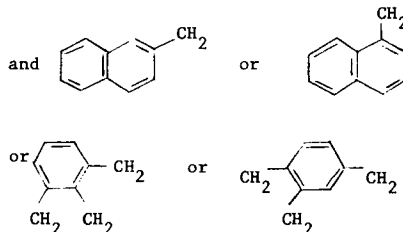
Fig. 55. GPC spectra of soluble compounds in traps at constant power ($W/W_0 = 1.5$) as function of pressure (in mm Hg): (—) 0.2, (---) 0.5, (- - -) 0.8. [Reproduced from Duval and Theoret (1973).]

The increase of oxygen content reflects the infrared spectra of glow discharge polymers. On allowing the polymer film to be exposed to air, the growth of a broad carbonyl band in the $1700\text{--}1720\text{-cm}^{-1}$ region was observed by many investigators with a variety of plasma polymers.

Jesch, Bloor, and Kronick (1966) studied IR spectra of glow discharge polymers formed from pentane, ethylene, butadiene, benzene, styrene, and naphthalene and summarized the structures of plasma polymers as shown in Table VIII. Whether the monomer is aromatic, olefinic conjugated, unconjugated, or fully saturated, the glow discharge polymer is highly branched and crosslinked and contains identifiable unsaturation in the form of both olefinic bonds and free valences. While aromaticity is not produced in the reaction, it is (partially) preserved in the products formed from aromatic compounds. For instance, *n*-pentane, ethylene, and butadiene yield similar polymers, with some small but reproducible variation due to the monomer structure. Benzene, styrene,

TABLE VIII
Structures in Glow Discharge Polymers from Hydrocarbons^a

Starting vapor	Functional groups in polymers
Pentane	Branches at each pentane molecule, methyl chain ends, ($-\text{CH}=\text{CH}-$)
Ethylene	($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), methyl chain ends, ($-\text{CH}=\text{CH}-$), crosslinks at saturated carbons
Butadiene	($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), ($-\text{CH}=\text{CH}-$), methyl chain ends, and crosslinks at saturated and unsaturated carbons
Benzene	($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), ($-\text{CH}=\text{CH}-$), ($-\text{C}=\text{C}-$) or ($-\text{C}\equiv\text{C}-$), methyl chain ends, and phenyl side-groups
Styrene	Same as benzene, (C_6H_5) $-\text{CH}_2-$
Naphthalene	($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), ($-\text{CH}=\text{CH}-$), ($-\text{C}=\text{C}-$) or ($-\text{C}\equiv\text{C}-$), methyl chain ends,



^a Reproduced from Jesch, Bloor, and Kronick (1966), p. 1496, courtesy of John Wiley and Sons, Inc.

and naphthalene produce polymers containing the features of the nonaromatic condensates, plus acetylene groups and the aromatic function of each starting material. This summary seems to cover all trends observed with various glow discharge polymers formed under a variety of glow discharge conditions by many investigators.

Chemical structure of a plasma polymer seems to be affected by the position of polymer deposition. Yasuda, Baumgarner, and Morosoff (1974) investigated elemental analysis of glow discharge polymer from hexamethyldisiloxane collected in different parts of an electrodeless glow discharge (13.5 MHz); i.e., (i) inside the RF coil, (ii) between the RF coil and the monomer inlet, and (iii) in the tail-flame portion usually used for polymer collection. The relative positions in a glow discharge reaction tube are shown in Figure 56. Results of elemental analysis are shown in Table IX. It is important to note that the surface at location 1 is also the energy input surface whereas the surface at locations 2 and 3 are decoupled from the energy-feeding process. In this respect, the electrode surface is similar to the surface in location 1, although the aspect of energy input may be much stronger at the electrode surface. It seems quite clear from these results that the tail-flame portion is quite different from the portion that is directly under

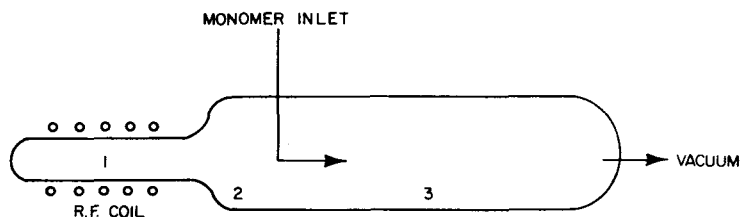


Fig. 56. Schematic representation of relative positions in a glow discharge reaction tube used to collect polymer samples for elementary analysis.

the RF coil insofar as the glow discharge polymerization is concerned. It also suggests that some of the distinct differences found in the results obtained by different reactors, particularly electrode discharge versus electrodeless discharge, may be due to the condition of whether or not the polymer-collecting surface is also the energy input surface.

1. Polymers from Mixed Monomers

(a) *Mixture of organic compounds*: As expected from the reaction mechanism which will be discussed later, glow discharge polymerization has the unique characteristic of being able to copolymerize nearly all monomers, since the reactivity of monomers is by and large the same. Consequently, the properties of polymers formed from a mixture of two monomers are nearly proportional to the composition of the two components in the monomer mixture. Refractive indices (Tien, Smolinsky, and Martin, 1972) of glow discharge polymers formed from mixtures of hexamethyldisiloxane and vinyl trimethylsilane are shown in Figure 57.

(b) *Mixture of an organic compound and nonpolymerizing vapor*: The properties of glow discharge polymers of certain types of organic compounds can be modified to a great extent by the incorporation of nonpolymerizing gases

TABLE IX
Elemental Analysis of Glow Discharge Polymers of Hexamethyldisiloxane (40 μ m Hg, 30 W)^a

Location of polymer deposition	Percent				Ratio and Color			
	C	H	Si	O	C	H	Si	O
1. Inside Coil	47.0	5.1	29.8	18.1	1	1.30	0.27	0.29
							brown	
2. Between coil and monomer inlet	31.3	6.3	40.6	21.8	1	2.42	0.55	0.52
							yellow	
3. Normal place for substrate	30.0	7.5	40.2	22.2	1	2.99	0.57	0.56
							white	

^a Data cited from Yasuda, Lamaze, and Sakaoku (1973).

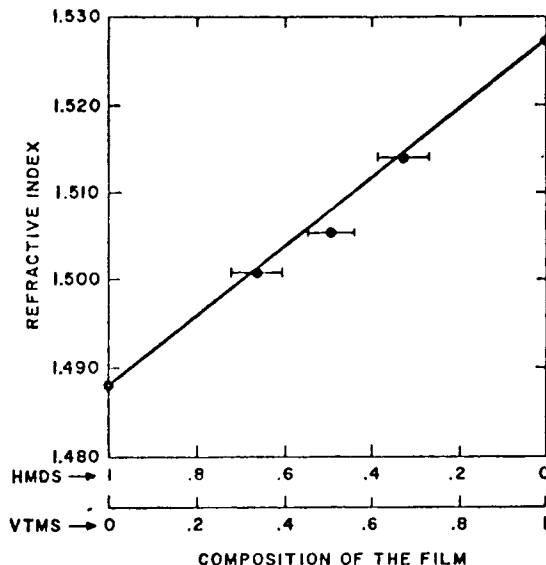


Fig. 57. Refractive indices of the films prepared by mixing VTMS and HMDS monomers before deposition. [Reproduced from Tien, Smolinsky, and Martin (1972).]

and vapors as comonomers. Although results obtained are limited to a small number of examples, it seems that organic compounds containing double or triple bond(s) can easily incorporate gases and vapors that have a radical-forming capability.

Some examples are shown in Table X and Figure 58. As evident in these re-

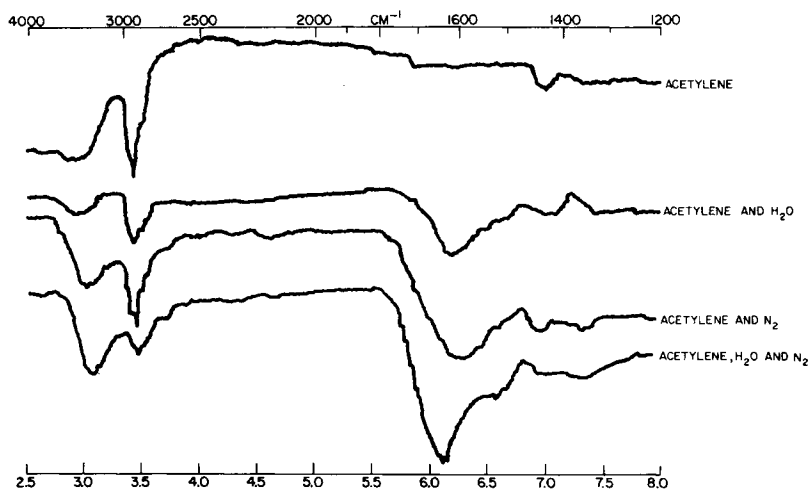


Fig. 58. Infrared spectra of the acetylene series (see Table X for conditions).

TABLE X
Elemental Analysis of Glow Discharge Polymers of Acetylene Monomer Series^{a,b}

Monomer	Percent				Ratio and color				
	C	H	N	O	C : H : N : O				
Acetylene (40–50 $\mu\text{m Hg}$)	79.5	5.4	–	15.1	1	0.81	–	0.14	dark brown
Acetylene/ N_2 (50 $\mu\text{m Hg}$) (33 $\mu\text{m Hg}$)	64.0	5.8	16.7	13.5	1	1.08	0.23	0.16	dark brown
Acetylene H_2O (40 $\mu\text{m Hg}$) (20 $\mu\text{m Hg}$)	66.5	7.6	–	25.9	1	1.37	–	0.29	off white
Acetylene/ $\text{N}_2/\text{H}_2\text{O}$ (30 $\mu\text{m Hg}$) (20 $\mu\text{m Hg}$) (15 $\mu\text{m Hg}$)	53.2	6.5	15.7	24.6	1	1.45	0.25	0.35	brown

^a Data cited from Yasuda, Lamaze, and Sakaoku (1973).

^b All polymerizations at 30 W.

sults, nitrogen and water vapor (perhaps a source of oxygen and OH) participate in the polymerization of acetylene. Infrared (IR) spectra of plasma polymers obtained from ethylene oxide with and without nitrogen are distinctly different as shown in Figure 59.

2. Substrate and Reactor Materials

Since the most important form of glow discharge polymers is a thin coating, the effects of substrate on the polymer deposition rate and on the properties of polymers are important in the practical applications of glow discharge polymers.

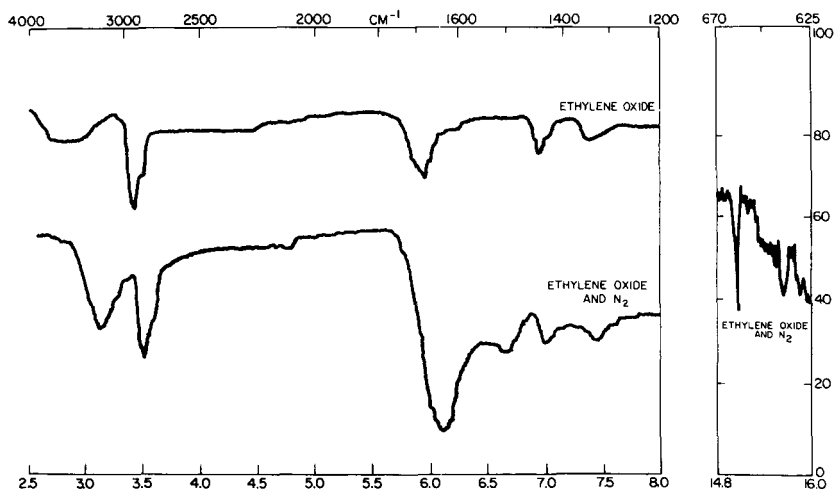


Fig. 59. Infrared spectra of the ethylene oxide series. Ethylene oxide: 40 $\mu\text{m Hg}$, 30 W, total of 5.5 hr. Ethylene oxide/ N_2 : 40/40 $\mu\text{m Hg}$, 30 W, total of 6.7 hr.

TABLE XI
Hexamethyldisiloxane (HMDS) and Vinyl Trimethylsilane (VTMS) Films Deposited on Different Surfaces^a

Surface	(Number of spheres/cm ²) × 10 ⁻⁴			
	HMDS/Ar	HMDS/He	HMDS/H ₂	VTMS/Ar
Aluminum	7.6	4.0	8.0	6.0
Copper	1.0	0.1	2.0	2.0
Gold	0.5	0.2	0.1	1.0
Nichrome	0.08	0	0.8	0
Silicone	0	0	0	0
Silicon Dioxide	0	0	0	0
β-Tantalum	0.2	0.1	0.2	-
Titanium	0.3	0.1	0.2	-
Tungsten	0	0	0.01	0

^a Reproduced from Thompson and Smolinsky (1972), p. 1181, courtesy of John Wiley and Sons, Inc. VTMS films prepared at 0.1 mm Hg argon at 150 W; HMDS films prepared at 0.05 mm Hg HMDS and 0.15 mm Hg inert gas at 100 W. Films were deposited simultaneously on each surface in the same run for each set of conditions.

Thompson and Smolinsky (1972) report that the number of small particles in the plasma polymer films deposited on metal surfaces are affected by the substrate materials, although the rate of film growth is unaffected. These workers consider that the particles probably result from vapor phase polymerization of monomer and that their concentration is a function of the substrate surface and the rate of film growth. The surface effect on the population density of particles is shown in Table XI.

When an organic polymer is used as the substrate in the plasma polymerization, the plasma susceptibility of the polymer is an important factor that affects both the rate of polymer deposition and the surface properties of the coating. When polymer films are exposed to a glow discharge (of nonpolymerizing gas such as He and Ar), most polymers lose weight during prolonged treatment.

The weight loss is generally linearly proportional to the exposure time. Therefore, the rate of weight loss under a given condition can be used to express the plasma susceptibility of a polymer. In Table XII the plasma susceptibility of various polymers (Yasuda, Lamaze, and Sakaoku, 1973) is shown by the values of weight loss rate observed in the tail-flame region of inductively coupled glow discharge (13.5 MHz).

The polymer-forming plasma has a much less damaging effect on the substrate than gas (nonpolymerizing) plasma. This is partly due to the shielding effect of polymer formed on the surface and also to the fact that polymer-forming plasmas consume energy and transmit much less energy to the surface. This aspect will be discussed in more detail in the section on mechanisms of polymer formation.

TABLE XII
Plasma Susceptibility of Polymers Measured by the Rate of Weight Loss in Helium Plasma^a

Polymer	Weight loss rate, ^b
	(mg cm ⁻² min ⁻¹) x 10 ³
Poly(oxymethylene)	17.0
Poly(acrylic acid)	16.2
Poly(methacrylic acid)	15.4
Poly(vinylpyrrolidone)	11.9
Poly(vinyl alcohol)	9.4
Poly(ethylene terephthalate)	1.7
Polyethylene	1.2
Nylon 6	1.1
Polypropylene	0.8

^a Reproduced from Yasuda, Lamaze, and Sakaoku (1973), p. 148, courtesy of John Wiley & Sons, Inc.

^b He plasma (100 μm Hg) at 30 W.

By utilizing the difference in dependence of polymer deposition and degradation of a substrate polymer on the operational factors (particularly discharge power), the effect of the substrate polymer can be minimized. In Table XIII, the deposition rates of styrene are compared using (a) glass plate and (b) polyoxymethylene which has very high plasma susceptibility (Yasuda, Lamaze, and Sakaoku, 1973).

TABLE XIII
Effect of Plasma Gas on Degradation of Polyoxymethylene and Polymerization of Styrene onto the Substrate^a

Plasma	Substrate	Rate of weight change, (g cm ⁻² min ⁻¹) x 10 ⁶	
		30 W	100 W
Vacuum (0.2 μm Hg)	POM	-3.50	-15.8
100 μm Hg He	POM	-3.13	-14.6
100 μm Hg N ₂	POM	-2.00	-11.0
40 μm Hg ST	glass slide	+1.88	+ 1.88
40 μm Hg ST	POM	+1.25	0.0
80 μm Hg N ₂ + 20 μm Hg ST	glass slide	+4.40	+ 4.40
80 μm Hg N ₂ + 20 μm Hg ST	POM	+1.50	+ 1.63
80 μm Hg He + 20 μm Hg ST	glass slide	+2.50	+ 2.50
80 μm Hg He + 20 μm Hg ST	POM	-0.25	- 0.83

^a Reproduced from Yasuda, Lamaze, and Sakaoku (1973), p. 144, courtesy of John Wiley & Sons, Inc.

At low wattage, the rate of polymer deposition from pure monomer onto polyoxymethylene is close to that onto glass surface, indicating that at low wattage the deposited polymer partly shields the plasma-susceptible substrate. However, at high wattage, a weight loss rather than weight gain is observed despite the visible presence of polymer coating, indicating that a considerable amount of substrate polymer is lost during glow discharge polymerization.

Analogous to the polymer substrate, the spattering tendency of metals is an important factor, depending on the conditions of the glow discharge polymerization. In any case, knowledge of the characteristic properties of substrate materials under plasma conditions is essential for the successful use of glow discharge polymerization.

The dependence of overall weight change observed with styrene polymerization onto polyoxymethylene is due to the difference between the wattage dependence of polymerization and that of the degradation of polyoxymethylene, the rate of which is highly dependent on the wattage, whereas the polymer deposition rate is independent of wattage in the system used. The dependence on the discharge wattage of degradation of polyoxymethylene and of polymerization of styrene observed in the same system is shown in Figures 31 and 60, respectively.

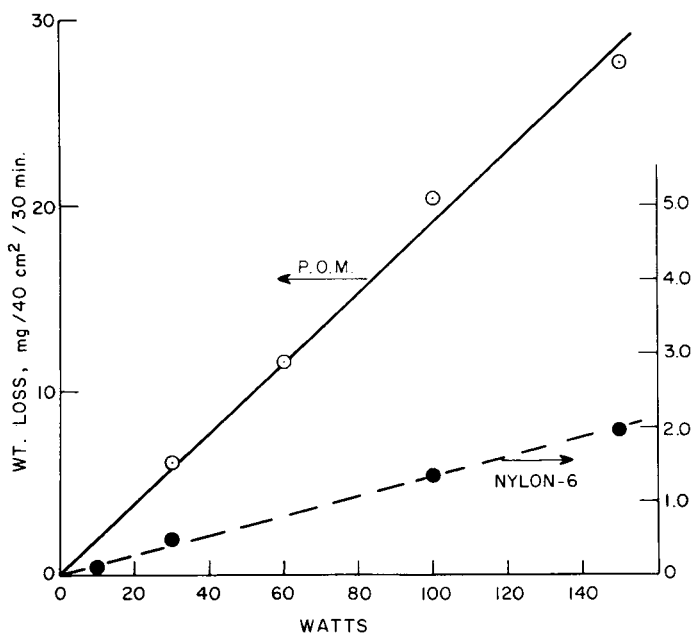


Fig. 60. Effect of discharge wattage on the rate of weight loss for polyoxymethylene and nylon 6. He plasma, 150 μ m Hg. [Reproduced from Yasuda, Lamaze, and Sakaoku (1973).]

IV. MECHANISMS OF POLYMER FORMATION

The reaction mechanisms by which polymerization proceeds under plasma conditions are not well understood. Some of the difficulty of studying the polymerization mechanism stems from the complexity of reactions that can occur in plasma and their dependence on the experimental conditions. A reasonable reaction mechanism for glow discharge polymerization must reasonably explain all of the following general aspects of plasma polymerization:

- (1) Nearly all organic compounds can be polymerized by plasma.
- (2) Conventional monomers such as vinyl monomers and their corresponding saturated compounds (e.g., styrene versus ethyl benzene, and ethylene versus ethane) polymerize with rates that are by and large similar.
- (3) Within a homolog series, polymer deposition rate increases with increasing molecular weight.

Consequently, any reaction mechanism that is specific to a specific monomer structure is very unlikely to be the major route of glow discharge polymerization. For instance, many of the reaction mechanisms appearing in the literature for glow discharge polymerization of vinyl monomers involve addition polymerization via vinyl double bonds by either free radicals or ions; however, such a mechanism cannot be applied to the propagation step of nonvinyl monomers and therefore cannot be considered as the predominant mechanism of glow discharge polymerization.

There is no doubt that ions are involved in some stage of plasma polymerization since the plasma requires a certain degree of ionization. The rate of polymer deposition is greatly influenced by electric potential of the polymer-collecting surface. In dc discharge, polymer deposition takes place almost exclusively on the cathode (Westwood, 1971). In ac discharge, polymer deposits on both electrodes since polarity of the electrodes is alternating. However, when a 60-Hz glow discharge is biased by a dc potential, polymer deposits more heavily on the electrode surface that has a negative potential (Coleman, 1973). A similar phenomenon is observed with deposition on a grid surface that is biased either positively or negatively with respect to the electrodes used in a 3.14-MHz glow discharge (Westwood, 1971); i.e., the negative potential increases and the positive potential decreases the polymer deposition as shown in Figure 61.

These observations indicate that positively charged organic ions are involved in the process of glow discharge polymerization. How these positive ions are involved in glow discharge polymerization is not clear; however, it may be similar to the fundamental ion-molecule interaction that occur in the formation of free radicals by ionizing radiation such as x-ray and electron beams. So far as the polymerization mechanism is concerned, it seems more likely that the ions themselves are not involved in the polymer formation reactions, but rather exist in the intermediate stage of forming excited molecules that subsequently form free radicals.

Ions of similar charge repel each other and a propagation reaction based on an ionic mechanism is possible only with double-bond-containing monomers.

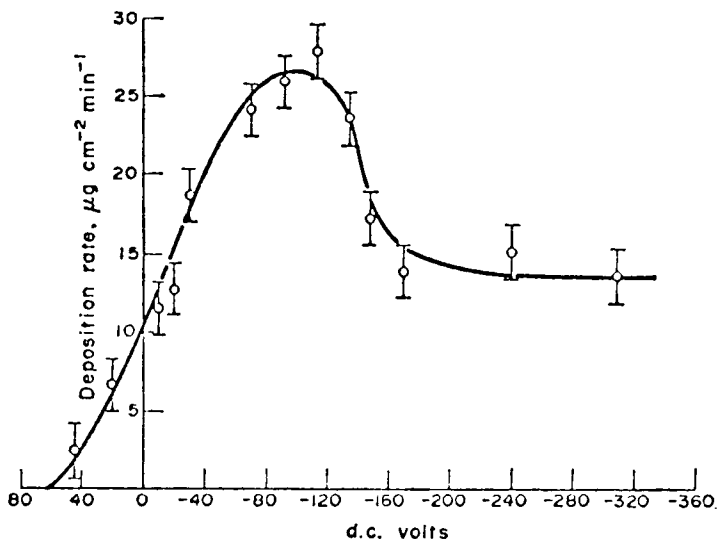


Fig. 61. Deposition rate against dc voltage (comb experiment). Vinyl chloride: pressure, 1 mm Hg; constant RF power on comb. 212 V, 19 mA, 3.14 MHz. Distance between comb and collector plate, 0.46 cm. [Reproduced from Yasuda et al. (1975).]

Therefore, the higher deposition of polymer on a surface of negative potential may be more reasonably explained by an increase of available monomer ions in the vicinity of the negatively charged electrode surface due to the electric attraction of positively charged ions.

Thompson and Mayhan (1972) have suggested an anionic polymerization mechanism for the glow discharge polymerization of styrene. Their main reason for considering anionic mechanism is that radical scavengers (such as NO_2) do not affect the glow discharge polymerization of styrene. This reasoning may require careful reexamination. Radical scavengers in conventional liquid phase or gas phase reactions are not necessarily, and are very unlikely to be, radical scavengers in plasma (which consists of ions and excited molecules). This situation is analogous to the roles of helium in conventional gas reaction and in plasma. Helium does not react in gas phase molecular reactions; it acts as a diluent or a quenching agent. In plasma, however, helium (which consists of helium ions and excited helium atoms) initiates the polymerization of monomers.

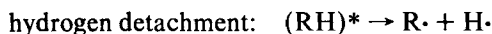
Besides the fact that polymer deposition occurs on the surface having negative potential (which suggests the existence of monomer cations), there seems to be no direct evidence to support a polymerization mechanism in which ions are involved. On the other hand, there is ample evidence to support polymerization mechanisms based on free radicals as mentioned before.

Strong evidence to support radical polymerization was recently presented by Brown and Bell (1973). They found that the concentration of free radicals in

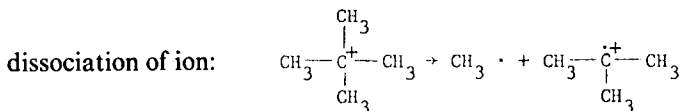
a plasma is usually 5 to 6 orders of magnitude higher than that of ions. It therefore seems reasonable to employ a free radical mechanism in discussing glow discharge polymerization.

Although the initial step of creating plasma from vapor of an organic compound is ionization, the polymer-forming plasma generally consists of ions and excited and unexpected molecules. It therefore seems appropriate to consider here some of the mechanisms or primary processes that have been suggested to explain radical formation in the radiolysis of hydrocarbons. These processes include (i) dissociation of excited molecules, (ii) dissociation of ions, (iii) neutralization of ions, and, (iv) ion-molecule reactions (Gaumann and Haigne, 1968).

The dissociation of excited molecules can be represented by the following two types:

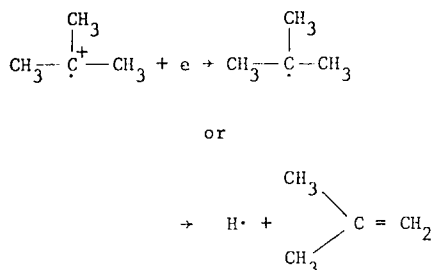


The formation of radicals from ions may be illustrated by the following examples. In the radiolysis of neopentane, where the yield of methyl radical was far greater than that of pentyl radical, the elimination of a methyl group from the molecular ion leaving a *t*-pentyl carbonium ion has been suggested.

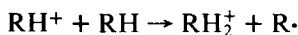


Subsequent neutralization of the ion formed may lead to *t*-butyl radicals or a hydrogen atom and isobutene.

neutralization of ion (radical):



Ion-molecule reactions can be represented by



These processes indicate that the variety of possible reactions involved in ionization of molecules (generation of plasma) could lead to the production of free radicals.

Primary processes shown above merely indicate the possibility of forming free radicals from ionized vapors (plasma); however, the processes *per se* are essentially cracking or degradation of the starting organic compound (monomer) and do not lead to polymers.

For polymerization of conventional monomers (which contain olefinic double bond), the polymerization can be easily explained once the source of free radicals is evident. However, it must be remembered that organic compounds that do not have an olefinic double bond also polymerize in plasma and that their characteristic rates of polymerization are by and large similar to those of conventional monomers. Therefore, it is obvious that addition polymerization of olefinic double bond based on a radical mechanism is not the predominant process of glow discharge polymerization, although such addition polymerization undoubtedly would occur whenever such monomers are subjected to free radicals.

A question that then arises is the possibility of forming structures that can undergo addition polymerization from a monomer by the influence of plasma as an intermediate species or precursor. There is ample evidence that such precursor structures as ethylene and acetylene can be formed in glow discharge of alkanes so that possibility of this kind of polymerization mechanism cannot be categorically eliminated. However, one must also consider the fact that in experimental conditions in which such precursor (e.g., acetylene) is formed with a good yield, the yield of polymer formation is small. On the other hand, under certain conditions acetylene polymerizes very quickly in plasma with very high yield of polymer. Consequently, the fact that such a precursor structure can be formed in plasma does not necessarily support the polymerization mechanism in which such precursors are first formed and subsequently polymerized by free radicals formed by plasma.

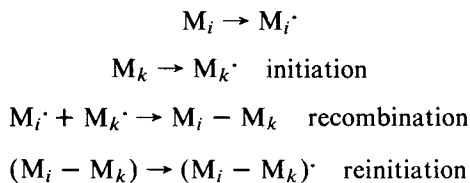
One must also consider the fact that the increase of free radical concentration inevitably increases the recombination of free radicals and also decreases the concentration of nonradical species. Under such conditions, the propagation by addition of free radicals onto an olefinic double bond becomes unfavorable. This situation seems to be the same one we are facing in glow discharge polymerization. Westwood (1971) noted that the rate of energy input in a glow discharge polymerization is 10^6 times greater than that used in radiation-induced polymerization reactions and that chain termination rather than propagation will be favored by these very high energy input rates.

Analogous to radiation-induced polymerization, glow discharge polymerization can be considered a case in which an extremely high dose rate is used. Under such a high-dose-rate experiment, one must not overlook the fact that the recombination of two free radicals does not terminate the entire reaction, since the molecules formed by recombination of two free radicals are not immune to the continuous energy input that occurs at a very high input rate and causes the formation of free radicals.

If the primary radicals are formed from excited molecules by a molecular detachment mechanism, the entire reaction is a vicious cycle of polymerization

and degradation, and it seems very unlikely that such reactions constitute a major mechanism of polymerization. However, if the primary radicals are formed by hydrogen abstraction (by plasma) from excited molecules, the consecutive steps of radical formation, recombination of radicals, and reexcitation of the recombination product to form radicals that are larger in molecular weight than the starting compound will quickly lead to formation of polymers.

This scheme of radical polymerization can be represented schematically by



where i and k are number of repeating units, i.e., $i = k = 1$ for the monomer.

This scheme of polymerization is not restricted to a mode of radical formation. Consequently, any radical formation mechanism that does not accompany fragmentation of molecules by the breaking of a C—C bond can contribute to the polymerization. A study by Yasuda, Bumgarner, and Hillman (1975) has shown that opening of multiple bond(s), opening of cyclic structure, and hydrogen abstraction all contribute to the glow discharge polymerization of organic compounds, depending on the statistical weight of these mechanisms attributable to the structure of a monomer.

Yasuda and Lamaze (1973) have observed that the pressure of a flow system changes as a glow discharge is initiated and that its change (positive or negative in respect to the pressure of the flow system before a glow discharge is initiated) is related to the structure of organic compounds (Yasuda and Lamaze, 1973). The investigation of gas phase components in glow discharge polymerization was extended in a study (Yasuda, Bumgarner, and Hillman, 1975) to a closed system in which analysis of gas phase after the polymerization was carried out. According to the results, nearly all hydrocarbons are converted to polymer with yield varying from 85% to over 99% in a relatively short time under the conditions used, and the gas phase after the reaction (excluding condensible organic vapor which is 0–15% of monomer depending on the polymer yield) consists mainly of hydrogen. Less than approximately 1% of the gas phase consists of methane, indicating that methane formation by fragmentation does not occur.

The hydrogen yield accompanied by glow discharge polymerization of hydrocarbons increases with an increasing number of hydrogen atoms in a molecule as shown in Figure 62. Strikingly regular dependence of hydrogen yield on the number of hydrogen atoms in a molecule indicates that every C—H bond has an equal probability of creating a free radical and participating in the polymerization.

In plasma, therefore, an organic compound with an olefinic double bond such

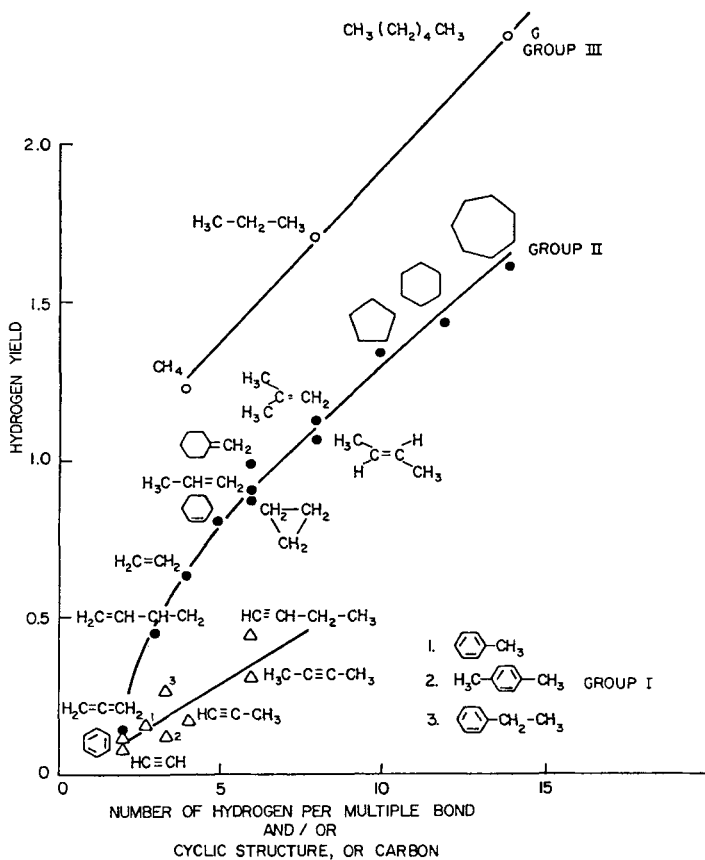


Fig. 62. Number of hydrogen molecules evolved per molecule of starting material when hydrocarbons polymerize (hydrogen yield) as a function of chemical structure.

as ethylene and propylene does not polymerize exclusively via the double bond, and the contribution of the double bond becomes smaller as the molecular weight of the monomer increases.

The contributions of double bonds and cyclic structures to the overall polymerization are quite similar as can be seen in Figure 62; however, the exact role of these bonds and structure is not quite clear, i.e., whether these structures act as the source of the primary radicals by the opening of multiple bonds or cyclic structure, or simply lengthen the kinetic chain length by addition of an already formed free radical.

In the case of glow discharge polymerization of vinyl-type monomers, the latter mechanism can be easily accepted. However, in the cases of cyclic and aromatic compounds, the latter mechanism does not seem to be highly probable, since aromatic and cyclic structures generally remain intact in many free radical reactions including irradiation by x-ray and electron beam. In other words, a free

radical does not break cyclic and aromatic structures. Therefore, it seems more reasonable to consider that the opening of a multiple bond or a cyclic structure is caused by initial stages of ionization, excitation, and formation of radicals. This consideration is supported by the glow discharge polymerization of hexafluorobenzene which polymerizes at a rate similar to that of benzene without forming any gas (Yasuda, Bumgarner, and Hillman, 1975). No production of gas indicates that hexafluorobenzene polymerizes without fragmentation (including fluorine abstraction). This is possible only by the opening of double bonds or the opening of the aromatic structure as the primary reaction under plasma condition.

So far as overall polymerization is concerned, however, the mechanism of propagation or steps by which the molecular weight increases is more important, and it can be dealt with without complete elucidation of the primary steps.

The relatively high concentration of residual (trapped) free radicals in glow discharge polymers can be easily explained by the above-mentioned mechanism. As the molecular weight of an organic compound increases, the probability of recombination of free radicals decreases due to (a), the increase of possible sites to form a free radical within a molecule, (b) the decrease in mobility of a molecule, and (c) the increasing steric hindrance.

It is also expected from the mechanism that polymers formed by glow discharge polymerization have a very short kinetic chain length with a high degree of branching and crosslinking. Many investigators have found that plasma polymers are generally characterized by these factors.

A. Gas Phase Reaction Versus Surface Reaction

The question of whether polymerization takes place in (gas phase) plasma or at the surface of the wall has been a point of debate in an attempt to elucidate the mechanism of glow discharge polymerization. However, it must be noted that this is not an essential question of the polymerization mechanism unless completely different and exclusive mechanisms can be assigned to reactions in plasma and at the surface.

Because it is the nature of plasma to follow the law of fluid mechanics, the vapor phase reaction and wall reaction cannot be clearly separated. The emphasis on one over the other depends on the many factors of empirical nature. At least the following factors should be taken into consideration for a proper understanding of the results and also for the design of a plasma reactor.

1. *Energy Input Surface and Reaction Media*

As mentioned earlier, in order to achieve continuous glow discharge: it is necessary to feed in energy as fast as plasma loses its energy. In the case of electric discharge: the energy is generally fed into the gas phase through a surface, e.g., an electrode surface in electrode discharge and a glass wall in inductive electrodeless discharge. However, the surface on which polymer deposition oc-

curs is not necessarily and not always the same surface of the energy input. In case of capacitive discharge and the electrode surface as the substrate, the energy input surface and the deposition surface are identical. In the case of a substrate surface being placed between two electrodes, and also in the case of tail-flame portion of electrodeless inductive discharge: the substrate surface is not the surface through which energy to sustain plasma is supplied. In the former case, obviously, the role of the surface reactions is greater than in the latter case. This factor of substrate surface versus energy input surface is dependent on the design of the reaction system as well as the type of discharge used in the reactor.

2. Fluid Mechanic Factors of Plasma

Whether plasma phase reaction or wall surface reaction plays the predominant role in polymer deposition can be judged by the fluid mechanics aspect of plasma. The approximate ratio of gas phase reaction/wall surface reaction can be estimated from the number of collisions between molecules and the number of collisions with a surface. For simplicity of discussion, let us consider a simple monomer system and treat the monomer as an ideal gas. From the kinetic theory of gases, the number of collisions between like molecules per unit volume and per unit time, $Z(AA)$, is given by

$$Z(AA) = (4\pi RT/M_A)^{1/2} \sigma_{AA}^2 N_A^2$$

where M_A is the mass of molecule A , N_A is the number of molecules per cm^3 , and σ_{AA} is the collision diameter, which equals the molecular diameter for collisions between like molecules. Substituting the known numerical values, one obtains

$$Z(AA) = 3.23 \times 10^4 (T/M_A)^{1/2} \sigma_{AA}^2 N_A^2$$

when M_A is the molecular weight of gas A .

Since the number of molecules per cm^3 at a pressure of p mm Hg and temperature T (K) is given by

$$N_A = 9.652 \times 10^{18} p/T$$

$Z(AA)$ can be written as a function of p and T as

$$Z(AA) = 3.01 \times 10^{42} p^2 T^{-3/2} M^{-1/2} \sigma_{AA}^2$$

The number \dot{n} molecules striking a unit area per second is given by the kinetic theory of gases as

$$\dot{n} = N_A (RT/2\pi M)^{1/2}$$

and therefore,

$$\dot{n} = 3.51 \times 10^{22} p M^{-1/2} T^{-1/2}$$

The ratio of $Z(AA)/\dot{n}$ is given by

$$Z(AA)/\dot{n} = 8.58 \times 10^{19} p \sigma_{AA}^2 / T$$

The ratio ϕ of gas-wall collision/gas-gas collision in the total system is given by

$$\phi = \frac{S\bar{n}}{VZ(AA)} = \frac{S}{V} 1.17 \times 10^{-20} \frac{T}{p\sigma_{AA}^2}$$

This equation indicates that the ratio ϕ is dependent on the surface-volume ratio (S/V), temperature, pressure, and the size of the gas molecule. For a given monomer at fixed pressure and temperature, the ratio ϕ is directly proportional to the surface-volume ratio (S/V) of the system.

Yasuda and Hsu (1976) have examined the dependence of polymer deposition rate on the size of reaction tube by creating a constriction in a glass tube reactor. For a cylindrical tube, S/V is given by $2/r$, where r is the radius of a tube. Under such a condition: the dependence of polymer deposition rate on the ratio ϕ can be examined by the plot of polymer deposition rate versus $1/d$, where d is the inner diameter of the constriction. The results are shown in Figure 63, which clearly indicate that the polymer-forming plasma can be dealt with as a uniform

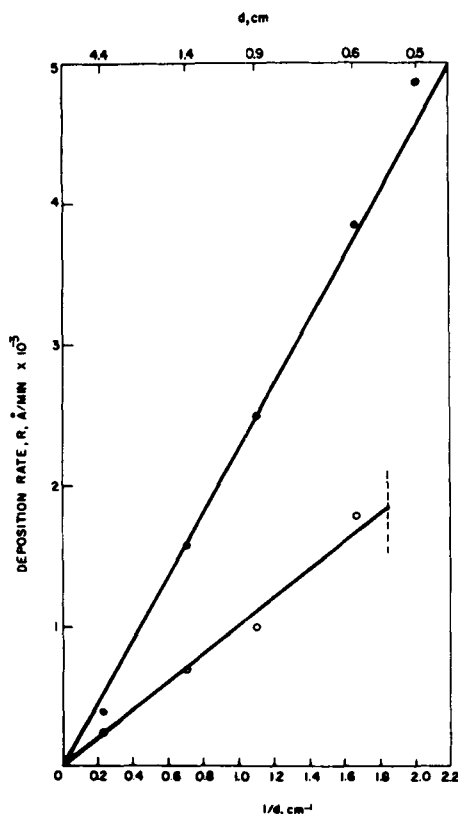


Fig. 63. Dependence of polymer deposition rate on the diameter d of the constriction.

plasma phase and the polymer deposition rate is influenced by the surface-volume ratio of the reactor in a predicted manner.

The formation of polymer powder has been observed by many investigators as mentioned earlier. It has also been confirmed (Kobayashi, Bell, and Shen, 1973) that chemical properties of powder (formed in gas phase) and of polymer film deposition are essentially identical, indicating that the polymers are formed in gas phase and at the surface by the same mechanism. Therefore, debate of gas phase polymerization versus surface polymerization is not an essential problem pertinent to the polymerization mechanisms; however, information concerning the kind of operational conditions wherein noncoherent powder is formed rather than coherent film and vice versa would undoubtedly be very useful in controlling the process and the properties of plasma polymers.

Therefore, some aspects pertinent to the importance of vapor phase reaction are presented here. In view of the fact that plasma is sustained by gas phase collision of electrons and molecules, there is no doubt that the polymerization in gas phase is an essential reaction. If the polymerization did not occur in gas phase, the glow discharge polymerization would have no distinction from radiation-induced polymerization, i.e., polymerization of adsorbed monomer molecules (at the surface) by the bombardment of electrons, ions, and excited molecules. In the latter mechanism, the propagation mechanism is by the addition chain reaction of free radicals, ion radicals, and ions (cations and anions). Therefore, the monomers that can be polymerized by this mechanism must possess double or triple bonds which undergo the chain addition reaction. The fact that many organic compounds that do not contain multiple bonds polymerize in plasma just as easily as those that contain multiple bonds is sufficient to disprove the reaction mechanism based on the surface reaction (polymerization of adsorbed monomer at the surface). The polymerization of adsorbed monomer would undoubtedly occur in the actual polymerization of certain monomers (e.g., olefinic monomers) in plasma, particularly under certain conditions in which condensation or adsorption of monomer is favored. Such a reaction should be considered as plasma-induced (conventional) addition polymerization, and should be distinguished from the more unique plasma state polymerization.

In an electrodeless glow discharge, particularly in the tail-flame portion of a discharge, the energy necessary to sustain plasma is transmitted through the vapor phase. In other words, the gas phase collision is the main route of transmitting energy of plasma. Therefore, the analysis of the amount of energy consumed in the polymer-forming plasma versus the amount of energy transmitted to the wall surface by the polymer-forming plasma provides further insight into the importance of vapor phase reaction and of surface reaction.

As described earlier, the ESR signal of glass tube exposed to plasma can be utilized as a dosimetry of the (radiation) free radical yield of plasma. When a polymer is deposited on the surface of a glass tube, the ESR signal of the tube consists of the combined signals of the free radicals of the glass and of the free radicals trapped in the polymer deposition. The shapes of the glass signal and the polymer signal are different, and in many cases the polymer deposition can

TABLE XIV
Sealing Thickness and the Film Growth Rates of Some Glow Discharge Systems^a

Monomer system	Sealing thickness (Å)	Polymer deposition rate (Å/min)
Picoline (30 μm Hg) + N ₂ (30 μm Hg)	400	142
Acetylene (30 μm Hg) + H ₂ O (10 μm Hg) + N ₂ (20 μm Hg)	1,200	67
Acetylene (60 μm Hg)	70	33
Hexamethyldisiloxane (30 μm Hg) + N ₂ (30 μm Hg)	200	192
Ethylene oxide	400	33

^a Data cited from Yasuda, Bumgarner, and Morosoff (1974).

be removed by a combination of swelling in a solvent and mechanical wiping off. Accordingly, the amount of glass signal and polymer signal can be quantitatively investigated. The size of polymer signal increases linearly with polymerization time (the polymer signal is proportional to the amount of polymer deposition); however, the size of glass signal reaches the plateau value in relatively short polymerization time, and further polymerization does not increase the glass signal. This observation indicates that the polymer deposition shields the substrate (glass) from the plasma.

The hypothetical "sealing thickness" of a glow discharge polymer can be calculated from the time the glass signal reaches the plateau value together with the rate of polymer deposition. The higher the value of sealing thickness, the stronger the energy transmitted to the wall surface (glass surface) by the polymer forming plasma.

The values of sealing thickness calculated for various monomer systems are shown in Table XIV. No correlation between the glass signal (sealing thickness) and the rate of polymer deposition seems to exist.

If the polymerization occurs in the adsorbed monomer layer at the surface, the concentration of free radicals in the plasma polymer is expected to be higher with a polymer that has a higher rate of polymer deposition since the residual free radicals are only a portion of free radicals created at the surface. In Table XV, spin concentrations observed by ESR spectroscopy of plasma polymers are compared with the rate of polymer deposition (film growth rate).

No correlation between the film growth rate and the free radical concentration in the plasma polymer seems to exist. These data can be interpreted to support either hypothesis (i.e., vapor phase reaction and surface reaction) together with other factors such as adsorption rates and the propagation rates of various monomers. However, the fact that the polymer-forming plasma (of organic compounds) has much less radiation effect on the wall surface seems to indicate that the polymerization starts in the vapor phase, and the vapor phase reaction

TABLE XV
Spin Concentrations and Film Growth Rates of Some Plasma Polymers^a

Monomer system	Spin concentration (spins/cm ³)	Film growth rate (Å/min)
Picoline (30 μm Hg) + N ₂ (30 μm Hg)	2×10^{18}	142
Hexamethyldisiloxane (30 μm Hg) + N ₂ (30 μm Hg)	4×10^{17}	192
Acetylene (60 μm Hg)	4×10^{20}	33

^a Data cited from Yasuda, Bumgarner, and Morosoff (1974).

is an essential part of unique plasma polymerization (distinguished from conventional plasma-induced polymerization).

Further evidence that some gases, such as nitrogen, which is not adsorbed on the surface at ordinary temperature of experiments, participate in the propagation of the polymer is strongly against the mechanism based on surface reaction.

B. Polymerization Rates and Monomer Structure

As mentioned earlier, the polymer deposition rates observed in a glow discharge system constitute an empirical parameter to express the rate by which the polymer deposition occurs under a certain condition and cannot be used to compare the reactivities of organic compounds as monomers in plasma polymerization.

In a series of experiments carried out by Yasuda and Lamaze (1971, 1973a, 1973b), and Yasuda, Lamaze, and Sakaoku (1973), conditions are selected so that (i) polymerization occurs in the diffusion dominating condition; (ii) consequently, the rate of polymer deposition is linearly proportional to the monomer feed-in rate; and (iii) the rate of polymer formation is independent of the discharge power.

Under such conditions (obtained by utilizing a tail-frame portion of an inductively coupled electrodeless glow discharge), the reactivities of organic compounds as monomers for plasma polymerization can be compared.

The rate of polymer deposition, R (g/cm² min), is related to the weight-based monomer flow rate F_w (g/min) by

$$R = kF_w$$

where k is a rate constant (cm⁻²).

Thus defined, the rate constant k may be used as the characteristic overall polymerization rate constant to compare the reactivities of organic compounds. It should be noted that k is not a rate constant of the chemical reaction in a strict sense. The values of k obtained by a system cannot be directly compared with values obtained by other systems.

In order to obtain the k value for an organic compound, a series of experiments are carried out at various flow rates (three to five different rates). The discharge power is selected from the necessary wattage to maintain a glow discharge in the entire reaction tube at the highest flow rate (highest pressure) used in a series. From the slope of a plot of polymer deposition rate versus flow rate, the value of k for the monomer is calculated.

The flow rate as well as the pressure of the monomer is determined before glow discharge is initiated. The pressure of the flow system changes to a new steady-state flow pressure during the plasma polymerization. The change of pressure is noted as a parameter δ which is given by $\delta = p_g/p_m$, where p_g is the pressure of the system during the polymerization and p_m is the pressure of monomer flow prior to the initiation of plasma.

With polymers that polymerize without evolving gas, the value of δ is smaller than unity. The value of δ is greater than unity for monomers that polymerize with evolution of gas(es). The parameter δ is used as a monomer-type parameter to distinguish the behavior of organic compounds in plasma. The monomers that have $\delta < 1$ are called type A monomers and those that have $\delta > 1$ are called type B monomers.

The values of k and δ for various organic compounds are shown in Tables XVI–XIX. The comparison of k and δ values for vinyl compounds and the

TABLE XVI
Polymerization of Olefinic Monomers—Type A^a

Monomer	Molecular weight	$k \times 10^4$, cm ⁻²	Wattage	$p_g/p_m = \delta$
4-Vinylpyridine	105	7.59	30	3/30 = 0.10
α -Methylstyrene	118	5.33	30	8/30 = 0.26
1-Phenylbutene-2	162	6.56	60	8/50 = 0.16
Styrene	104	5.65	30	5/50 = 0.10
Vinyltoluene	118	6.16	30	3/38 = 0.08
2-Vinylpyridine	105	4.81	30	3/40 = 0.08
N-vinyl-2-pyrrolidionone	111	7.76	60	22/36 = 0.61
Acrylonitrile	53	5.71	30	5/30 = 0.16
Vinylidene chloride	97	5.47	60	33/47 = 0.70
Butene-1	56	4.94	60	10/30 = 0.33
Butadiene	54	4.44	60	12/40 = 0.30
Allylamine	57	2.86	30	30/45 = 0.66
<i>trans</i> -Butene-2	56	2.11	60	30/40 = 0.75
Isobutylene	56	2.62	60	42/60 = 0.70
3-Methylbutene-1	70	1.47	60	18/37 = 0.49
Propylene	42	2.24	60	26/40 = 0.65
Vinyl chloride	63	1.02	100	28/40 = 0.70
Ethylene	28	0.36	100	75/90 = 0.83

^a Data cited from Yasuda and Lamaze (1973a).

TABLE XVII
 Polymerization of Olefinic Monomers—Type B^a

Monomer	Molecular weight	$k \times 10^4$, cm^{-2}	Wattage	$p_g/p_m = \delta$
Glycidyl methacrylate	142	1.91	30	45/22 = 2.05
2-Methylbutene-2	70	2.22	60	43/41 = 1.05
Methyl methacrylate	100	1.41	150	105/40 = 2.62
2-Methylbutene-1	70	1.20	100	62/60 = 1.03
Methacrylic acid	86	1.54	100	100/45 = 2.22
Methyl acrylate	86	0.99	150	150/50 = 3.00
Butyl vinyl ether	100	0.79	150	160/60 = 2.67
Vinyl acetate	86	0.79	100	61/50 = 1.22
Vinylene carbonate	86	0.80	150	80/40 = 2.00
Acrylic acid	72	0.76	150	140/50 = 2.80

^a Data cited from Yasuda and Lamaze (1973a).

 TABLE XVIII
 Polymerization of Unconventional Monomers—Type A^a

Monomer	Molecular weight	$k \times 10^4$, cm^{-2}	Wattage	$p_g/p_m = \delta$
4-Methylbenzylamine	121.2	10.99	60	10/33 = 0.30
5-Ethyl-2-methylpyridine	121.2	7.38	30	10/43 = 0.23
Benzylamine	107.2	7.94	30	6/35 = 0.17
<i>tert</i> -Butylbenzene	134.2	4.41	30	14/40 = 0.35
2-Phenylpropane	120.2	4.05	60	8/50 = 0.16
4-Ethylpyridine	107.2	4.72	30	6/40 = 0.15
Ethylbenzene	106.2	4.52	60	7/52 = 0.13
4-Picoline	93.1	5.83	60	4/50 = 0.08
3,5-Lutidine	107.2	5.82	30	7/56 = 0.13
1-Methyl-2-pyrrolidone	99.1	5.24	30	48/48 = 1.00
Toluene	92.1	5.03	60	4/50 = 0.08
<i>tert</i> -Butylpyridine	135.2	3.81	30	9/40 = 0.23
2-Methylfuran	82.1	4.96	30	8/35 = 0.23
Pyridine	79.1	5.81	30	3/30 = 0.10
2,5-Lutidine	107.2	4.28	30	7/40 = 0.18
Furan	68.1	5.59	30	7/42 = 0.17
Pyrrole	67.1	5.03	30	6/55 = 0.11
Benzene	78.1	4.35	30	3/55 = 0.05
Propionitrile	55.1	4.49	30	23/65 = 0.35
N-Methylpyrrole	85.1	4.01	30	7/50 = 0.14

^a Data cited from Yasuda and Lamaze (1973a).

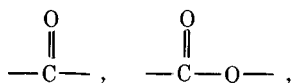
TABLE XIX
Polymerization of Unconventional Monomers—Type B^a

Monomer	Molecular weight	$k \times 10^4$, cm^{-2}	Wattage	$p_g/p_m = \delta$
Triethylsilane	116.2	6.33	100	98/50 = 1.96
N-Methylpyrrolidine	85.2	4.01	60	78/60 = 1.30
Pyrrolidine	71.1	4.18	60	84/60 = 1.40
1-Ethyl-2-pyrrolidone	113.2	3.76	60	75/47 = 1.60
1,1-Dichloroethane	99.0	2.98	60	64/55 = 1.16
sec-Butylamine	73.1	2.68	60	95/60 = 1.58
n-Butylamine	73.1	2.52	60	126/65 = 1.94
1,3-Diaminopropane	74.1	2.80	60	134/65 = 2.06
Morpholine	87.1	2.50	100	160/65 = 2.46
tert-Butylamine	73.1	2.14	60	88/53 = 1.66
n-Hexane	86.2	1.74	60	128/60 = 2.10
Cyclohexane	84.1	1.71	30	95/60 = 1.58
Cyclopentanone	84.1	1.44	60	89/48 = 1.85
γ -Butyrolactone	86.1	1.24	60	101/38 = 2.66
Dimethylformamide	73.1	1.15	100	220/80 = 2.75
Cyclohexanol	100.2	0.81	60	117/50 = 2.34
1-Hexanol	102.2	0.79	60	110/40 = 2.75
Methyl propionate	88.1	0.57	100	178/50 = 3.56
Ethylene oxide	44.1	0.86	60	85/38 = 2.23
Dimethyl sulfoxide	78.1	0.40	100	130/56 = 2.32
Tetrahydrofuran	72.1	0.32	100	138/70 = 1.97

^a Data cited from Yasuda and Lamaze (1973b).

corresponding saturated vinyl compounds are presented in Table XX. From these results the following trends are evident:

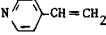
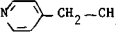
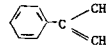
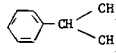
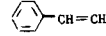
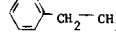
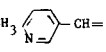
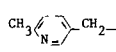
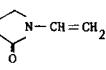
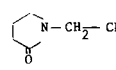
- Within a homologous series, k is higher with higher molecular weight materials.
- The value of k increases with the number of multiple bonds in a molecule, counting aromatic double bonds and triple bonds such as $-\text{C}\equiv\text{N}$.
- A cyclic structure increases the value of k .
- Oxygen-containing groups (e.g.,



$-\text{O}-$, and $-\text{OH}$) decrease k unless those groups are situated in between. $\text{C}=\text{C}$ double bonds or attached to a cyclic or an aromatic structure.

- No direct correlation between k and δ exists, although some organic

TABLE XX
Polymerization Parameters: Vinyl Versus Saturated Vinyl Compounds^a

	Vinyl monomer ^b			Saturated vinyl monomer	
	k	δ		k	δ
	7.59	0.10		4.72	0.10
	5.33	0.26		4.05	0.16
	5.65	0.10		4.52	0.14
	7.65	0.16		7.38	0.24
	7.75	0.61		3.76	1.60
$\text{CH}_2=\text{CH}-\text{CN}$	5.71	0.16	$\text{CH}_3-\text{CH}_2-\text{CN}$	4.49	0.35
$\text{CH}_2=\text{C} \begin{matrix} \text{Cl} \\ \text{Cl} \end{matrix}$	5.47	0.70	$\text{CH}_3-\text{CH} \begin{matrix} \text{Cl} \\ \text{Cl} \end{matrix}$	2.98	1.16
$\text{CH}_2-\text{CH}(\text{CH}_2-\text{NH}_2)$	2.86	0.66	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	2.52	1.94

^a Data cited from Yasuda and Lamaze (1973b).

^b k in units of $\text{cm}^{-2} \times 10^4$; $\delta = p_g/p_m$, where p_g is pressure in glow discharge and p_m is pressure of monomer (before glow discharge).

compounds that do not polymerize easily in plasma have relatively high values of δ .

Together with data of hydrogen yield accompanied by the polymerization of hydrocarbons (see Fig. 62), it seems most probable that the plasma polymerization is initiated by free radical formation by hydrogen elimination, opening of cyclic structure, and opening of multiple bonds. Therefore, the total numbers of (a) hydrogen, (b) double bond, (c) triple bond, (d) cyclic or aromatic structure, and (e) element heavier than carbon such as silicone, which attaches directly to carbon and is not labile to plasma, in a molecule would decide the overall polymerization rates of organic compounds. The high values of δ can be attributed to two major causes, i.e., high hydrogen yield and evolution of gases that do not participate in the polymerization. The former leads to higher k values and the latter yields lower k values. Therefore, the classification of organic compounds by type A and type B monomers is based on the empirical behavior in plasma and is not on the mechanism of the plasma polymerization. The quantitative analysis of values of δ is seen in Yasuda and Hirotsu (1978).

The study of glow discharge polymerization is greatly hampered by the fact that those polymers having advantageous characteristics for potential application are highly crosslinked and branched and are thereby insoluble and infusible. In other words, the very features that make them usable actually hamper their characterization and hinder the study of their polymerizing mechanisms.

Consequently, most studies concerning them are based on a preconceived concept that their formation is a kind of polymerization. This situation is somewhat analogous to the basic concept of “radiation polymerization” or “radiation-induced polymerization,” in which the initial step is the direct consequence of the radiation process, but these polymer-forming processes are essentially identical to those initiated by conventional means.

The formation of a polymer in glow discharge is not only a complex phenomenon, but interpretation of the formation mechanism is further complicated by use of the misleading term “polymerization.” It may, therefore, be worth examining the widely accepted definition of this term. Conventionally, polymerization means that the molecular units (monomers) are linked together by the “polymerizing” process. Specifically, rearrangement of the atoms or elements that constitute the molecules of a monomer seldom occurs during the polymerizing process. For instance, the polymerization of styrene by conventional means is accomplished by the opening of a double bond without losing or rearranging the atoms. Thus, the resulting polymer’s name is formed by using the term “poly” + the name of the monomer. In the case of styrene, the polymer formed by the polymerization of *styrene* is named *polystyrene*. In other words, polymerization in the accepted sense refers to *molecular* polymerization, i.e., the chemical structure of a polymer is denoted by the chemical structure of the monomer.

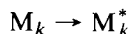
Strictly speaking, the usual process of polymerization is not the same as the process that occurs in glow discharge. In this context, polymer formation in a plasma state takes place via a “nonpolymerizing” process. Thus, polymer formation of this type may be characterized as *elemental* or *atomic* polymerization in contrast to *molecular* polymerization, which describes the conventional process. The following discussion may illustrate the *atomic* nature of polymer formation in a plasma state.

C. Plasma-Induced and Plasma-State Polymerizations

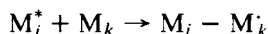
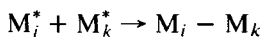
With regard to the preconceived concept of conventional (molecular) polymerization, the majority of monomers that have been studied are conventional types, such as styrene, ethylene, and vinyl chloride. Because the ionization of gas or vapor involves many highly energetic species, which can trigger the polymerization of such monomers, and as long as these monomers are used in plasma polymerization, it will continue to be difficult to distinguish clearly between *atomic* and *molecular* polymerization. For the sake of discussion, the conventional (molecular) type of polymerization is triggered by a reaction such as plasma-induced polymerization. The atomic process, which occurs in a plasma state, can then be identified as “plasma-state polymerization.”

Plasma-state polymerization can be represented by the following mechanisms:

Initiation or reinitiation:



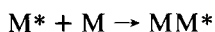
Propagation and termination:



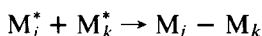
In these formulas, i and k are the numbers of repeating units, i.e., $i = k = 1$ for the starting material, and M^* represents reactive species, which can be an ion of either charge, an excited molecule, or a free radical produced from M but not necessarily retaining the molecular structure of the starting material; i.e., M can be a fragment or even an atom detached from the original starting material. In this type of polymerization, the polymer is formed by the repeated stepwise reaction described above.

Plasma-induced polymerization may be schematically represented by a chain propagation mechanism as follows:

Propagation:



Termination:



It should be noted that plasma-induced polymerization does not produce a gas phase byproduct, because the process proceeds via utilization of a polymerizable structure. Overall, polymerization in a glow discharge consists of both plasma-induced polymerization and plasma-state polymerization. Which of these two mechanisms plays the predominant role in the polymer formation in a glow discharge depends not only on the chemical structure of the starting materials but on the conditions of the discharge.

One of the most significant differences between plasma-induced polymerization and plasma-state polymerization is the fact that plasma-state polymerization produces gas phase byproducts, which are not incorporated into the polymer. This means that the components of the plasma phase change as soon as plasma-state polymerization occurs. Consequently, the influence of the product gas plasma on the entire system is an important factor.

D. Effect of Product Gas Plasma

In an efficient glow discharge polymerization system, a monomer tends to polymerize in the vicinity of the monomer inlet, and the range in which polymer deposition is observed is much narrower than the range in which glow discharge

is observed. This situation is a reflection of the fact that the plasma phase consists mainly of a product gas (e.g., H₂) and contains only a small amount of the monomer or growing species. Because of this situation, gas phase analyses have failed to detect substantial amounts of oligomers.

Because the gas phase changes from a monomer to product gases as soon as glow discharge polymerization occurs, what the product gas plasma does to the system (which consists of the monomer, the intermediate species, a polymer, substrate material, and the wall of the reaction vessel) becomes an important factor. This factor depends on what kind and how much of the product gas (or gases) evolves during the process.

The major effects of the product gas plasma may be seen by examining the processes of (i) emission of photons and (ii) etching by chemical reaction. As far as the material balance in the system is concerned, these two processes can be represented by ablation. Consequently, the entire glow discharge polymer-

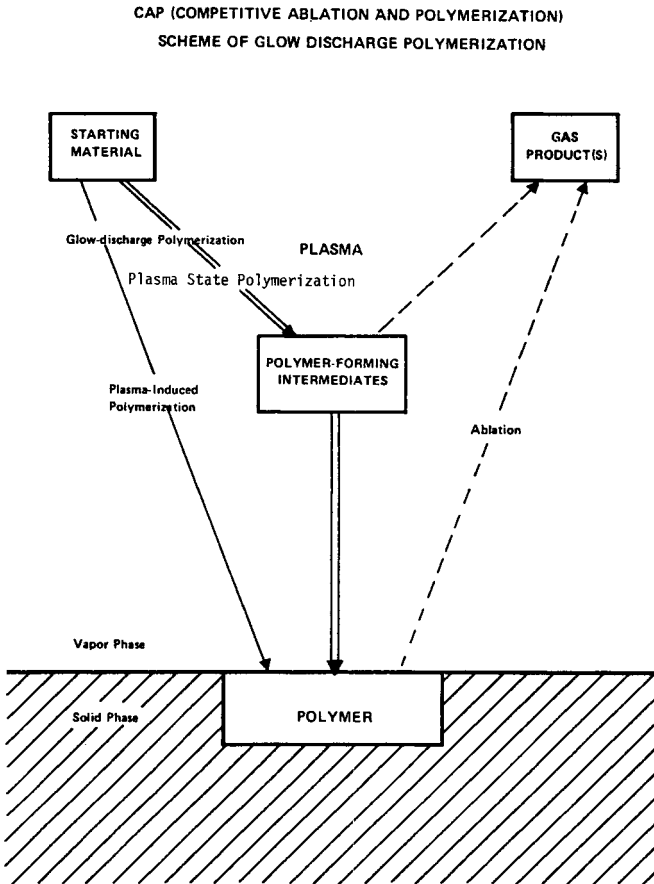


Fig. 64. Overall mechanism of glow discharge polymerization.

ization can be represented schematically by the competitive ablation and polymer formation (CAP) mechanism (Yasuda and Hsu, 1978) shown in Figure 64.

Because most of the literature on glow discharge polymerization deals with hydrocarbons, which produce hydrogen as the product gas, the effect of ablation does not appear to be too great. Consequently, the complete neglect of ablation does not make a significant difference in the overall picture of glow discharge polymerization; however, when a fluorine- or oxygen-containing compound is used as the starting material, the extent of ablation becomes predominant, and the amount of polymer formation depends entirely on the quantity of gas produced.

Perhaps the most dramatic demonstration of the effect of ablation was given by Kay (1977) in the glow discharge polymerization of CF_4 . It had been thought that CF_4 was one of the very few organic compounds that does not polymerize in a glow discharge. On the other hand, CF_4 has been used as one of the most effective gases in plasma etching. Kay observed that no polymer deposition occurs under normal conditions in spite of the fact that the C—F bonds are broken in the glow discharge, a fact which is confirmed by mass spectroscopic analysis of the gas phase. However, when a small amount of hydrogen is introduced into the discharge, the polymer is deposited. When the hydrogen flow is stopped, the polymer deposit ablates.

The situation observed in the above example may be visualized by comparing the bond energies. It should be noted that the energy level involved in a glow discharge is high enough to break any bond (Clark and Dilks, 1977; Wehner and Anderson, 1970). That is, C—F is broken, although its bond is stronger than C—H and C—C. The important factor is the stability of the product gas. The bond energy for F—F is only 37 kcal/mole, whereas H—F is 135 kcal/mole; which is higher than the 102 kcal/mole for a C—F bond. The introduction of hydrogen into the monomer flow evidently produces HF and removes F from the discharge system, thus reducing the etching effect of the product gas (F_2) plasma and shifting the balance between polymerization and ablation in favor of polymerization. Although the term F_2 plasma is used to describe the effect of the detached F in the plasma, F_2 is not detected in the plasma state, perhaps because of its extremely high reactivity (Smolinsky, 1977).

It is interesting to note that F and O are two elements that reduce the rate of polymer formation from compounds that contain one of them. They are the two most electronegative elements. Of course, the bond energy itself is not a measure of the etching effect of the plasma. For instance, the N—N bond is only 32 kcal/mole. However, N_2 plasma does not etch polymer surfaces; instead, the incorporation of N into the surface predominates (Yasuda et al., 1977). Nevertheless, the importance of the ablation process shown in Figure 64 seems to be well demonstrated by the deficient polymer formation in the glow discharge polymerization of CF_4 , C_2F_6 , and oxygen-containing compounds (Yasuda, 1977).

The polymer formation and properties of polymers formed by glow discharge polymerization are controlled by the balance among plasma-induced polymer-

ization, plasma-state polymerization, and ablation; i.e., polymer formation is a part of the CAP scheme shown in Figure 64. Because of this type of glow discharge polymerization, the gas evolved from the substrate also plays an important role, particularly at the early stage of coating.

E. Molecular Polymerization Versus Atomic Polymerization

Atomic polymerization is the principal element of the CAP mechanism, but a similar result may be expected if one conceives of a polymerizable precursor. The formation of polymers from organic compounds, which do not polymerize under normal conditions, may be postulated by assuming that polymerizable precursors are formed in the plasma state and form polymers by conventional polymerization mechanisms. For instance, the slower polymer deposition from ethylene compared to that from acetylene has been attributed to the slower process of forming acetylene, which is assumed to be the precursor of glow discharge polymerization (Kobayashi, Shen, and Bell, 1974). According to this concept, saturated hydrocarbons, such as methane and ethane, will polymerize via plasma synthesis of acetylene and subsequent (molecular) polymerization. The frequently disputed subject of vapor phase polymerization versus surface polymerization is discussed in the context of precursor concept (although it is usually not mentioned explicitly), because one cannot explain the polymerization of a saturated hydrocarbon, such as CH_4 , without assuming such a precursor.

There is no clear-cut answer as to whether atomic polymerization theory or precursor theory explains the actual process of polymer formation in glow discharge. All experimental data in glow discharge polymerization can be interpreted only as circumstantial evidence so far as the mechanism of polymer formation is concerned. Therefore, the following discussion presented is not intended to disprove any other concept but is intended to present a new way of recognizing glow discharge polymerization. The most important point is that any theory must cover all possible cases and must satisfactorily explain not only one aspect of glow discharge polymerization, e.g., polymer deposition rate, but all other aspects, e.g., distribution of polymer deposition and change of polymer properties associated with the distribution, in a consistent manner.

1. Correlation between Polymer Deposition Rate and Chemical Structure of Monomer

When polymer deposition rates are compared for various pairs of monomers, which have similar chemical structures with and without vinyl double bonds, the difference between those with olefinic vinyl double bonds and those without is very small (Yasuda, 1976) as shown in Table XX. Furthermore, the differences among various kinds of monomers are surprisingly small. In other words, nearly all hydrocarbon monomers polymerize at rates that vary only within an order of magnitude. These two aspects indicate that no specific structure (necessary

for the precursor theory) is needed for the glow discharge polymerization of organic compounds.

The dependence of polymer deposition rates on the molecular weight of monomers is another important aspect. For instance, if one takes a homologous series of saturated hydrocarbons, the probability of their forming precursor structures, e.g., acetylene, decreases rapidly as the number of carbons increases, whereas the number of hydrogen molecules evolved during glow discharge polymerization increases monotonously with the number of carbons as shown in Figure 62. This indicates that every hydrogen atom has an equal probability for hydrogen abstraction. Therefore, if a precursor is formed first, the polymer deposition rate should decrease with an increase in the number of carbons in a hydrocarbon molecule. Contrary to this expectation, the polymer deposition rate increases with the molecular weight of the monomer as shown in Figure 65. These correlations are in accordance with the atomic mechanism.

Characteristics of atomic polymerization are directly seen in the incorporation of gases or vapors, such as N_2 , CO , and H_2O , by polymers formed in glow discharge, when these gases or vapors are mixed with the vapor of an organic compound.

If the basic step of forming a polymer is molecular polymerization of the precursor species created in a plasma, the incorporation of such gases or vapors cannot be explained. This gas incorporation in glow discharge polymerization is also an indication of the atomic nature of the polymer formation process, i.e., gases and vapors provide atoms but are not incorporated as molecules.

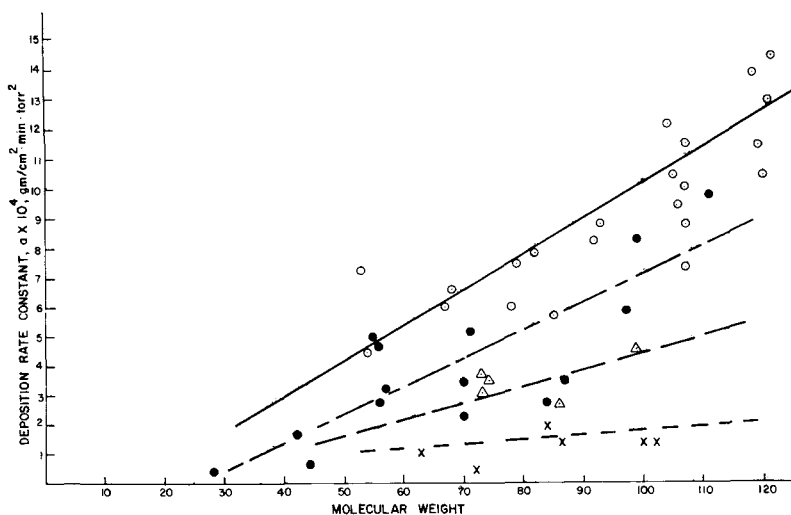


Fig. 65. Dependence of polymer deposition rate on molecular weight of monomer. Group I: triple-bond-containing, aromatic, and heteroaromatic compounds; group II: double-bond-containing and cyclic compounds; group III: compounds without above-mentioned structures; group IV: oxygen-containing compounds. (○) Group I, (●) group II, (△) group III, (×) group IV.

2. Trapped Free Radicals in Polymers

One of the most significant features of glow discharge polymerization is that large amounts of free radicals are trapped in the polymer. Although the amounts of trapped free radicals vary with the types of monomers and conditions of glow discharge polymerization, it is safe to consider that glow discharge polymers contain trapped free radicals. An explanation of how these free radicals are formed could provide important information for how polymeric materials are formed in the glow discharge of organic compounds.

Obviously, molecular polymerization, e.g., free radical polymerization of vinyl monomers, does not yield polymers with trapped free radicals. Therefore, if one considers molecular polymerization of precursors as the main polymer-forming mechanism, it is necessary to take into account separate mechanisms for creating free radicals in polymers. An easily conceived mechanism is free radical formation by radiation, because glow discharge can be considered as a kind of radiation process. There are many energetic species, such as electrons, ions, excited molecules, free radicals, and photons, in glow discharge; consequently, such a hypothesis is not at all unreasonable. Therefore, the trapping of free radicals in a glow discharge polymer as a function of the chemical structure of monomers should be examined.

First, there is a definite correlation between the spin concentration measured by ESR and the chemical structure of monomers. Glow discharge polymers of monomers that contain triple bond, aromatic, and heteroaromatic rings and $\text{—C}\equiv\text{N}$ produce the highest level of free spins. Hydrocarbons can be grouped into three major types based on their behavior in glow discharge polymerization. These can be tentatively referred to as group I, group II, and group III monomers as used in Figures 62 and 65. Group I monomers are those mentioned above. They polymerize with evolution of the least amount of hydrogen and contain the highest level of free spins among polymers. Group II monomers are compounds containing an olefinic double bond and/or a cyclic structure. Group III monomers are saturated compounds, which do not contain the structures mentioned in groups I and II. Group III monomers polymerize with evolution of the highest level of hydrogen and contain the least amount of free spins. Group II monomers lie in between these two extremes, i.e., they evolve a moderate amount of hydrogen and exhibit an intermediate level of free spin concentration.

The free spin concentration in glass can be attributed to ultraviolet irradiation in the glow discharge polymerization system. If trapped free radicals are formed by the irradiation of the formed polymer by molecular polymerization of the plasma-synthesized precursor and, consequently, impart no free radicals in the polymer, the level of ultraviolet irradiation manifested by the free spin concentration in glass should be proportional to the free spin concentration in glow discharge polymer. In other words, the highest free spins in glass should be obtained by the glow discharge polymerization of group I monomers. Contrary to this expectation, the highest level of ultraviolet emission is associated with

TABLE XXI
ESR Spin Concentration in Plasma Polymers and Glass Substrates

Monomer	$C_g^* \times 10^{-19}$, spins/cm ³		$C_g \times 10^{-15}$, spins/cm ² *	
	Continuous	Pulsed	Continuous	Pulsed
C ₂ H ₂	8.6	15.6	0	0
C ₆ H ₆	3.2	1.6	0	0
C ₆ F ₆	7.4	5.4	0	0
Styrene	3.8	0.54	0	0
C ₂ H ₄	1.36	14.5	4.0	0.85
C ₂ F ₄	13.0	8.4	11.2	1.8
Cyclohexane	0.84	0	1.1	0
Ethylene oxide	0.75	0.5	6.6	1.6
Acrylic acid	0.76	1.85	4.4	0
Propionic acid	1.0	1.0	6.3	1.6
Vinyl acetate	0.42	0.33	6.1	1.8
Methyl acrylate	0.31	0.15	6.4	1.5
Hexamethyldisilane	0.5	0.24	0	0
Tetramethyldisiloxane	0.49	0.05	0	0
Hexamethyldisiloxane	0.21	0	0	0
Divinyltetramethyldisiloxane	0.15	0.05	0	0

* Total spins divided by surface area of glass.

group III monomers, which yield the least amount of free spins in the polymer as shown in Table XXI. This trend is in accord with the intensity of the glow observed in the glow discharge polymerization of monomers. Specifically, the glow observed for group I is very weak, whereas the one observed for group III is the most intense. In other words, the level of ultraviolet emission is proportional to the evolution of hydrogen in the glow discharge polymerization system. Consequently, the hypothesis that trapped free radicals are formed by irradiating polymers does not explain the forming of trapped free radicals in glow discharge polymers. That means that a radically new approach is needed to explain the formation of polymers in glow discharge.

F. Internal Stress in Glow Discharge Polymerization

One of the unique characteristics of polymers formed by glow discharge polymerization is their strong tendency to exhibit internal (expansive) stress in the polymer layer during the process of deposition. When a thin layer of glow discharge polymer is deposited on a thin polymer film, the coated film tends to curl as a result of the internal stress in the coating. By knowing the thicknesses of both layers and Young's modulus of the substrate film, the curling force and the internal stress can be calculated from the radius of the curled sample (Yasuda, Hirotsu, and Olf, 1977). Typical cases are shown in Figure 66.

This high level of internal stress sometimes causes self-destruction of the coating when too thick a layer is deposited. An important aspect is that the buildup of internal stress, manifested by the curling of the coated substrate, occurs during the process of polymer deposition. This aspect, therefore, should

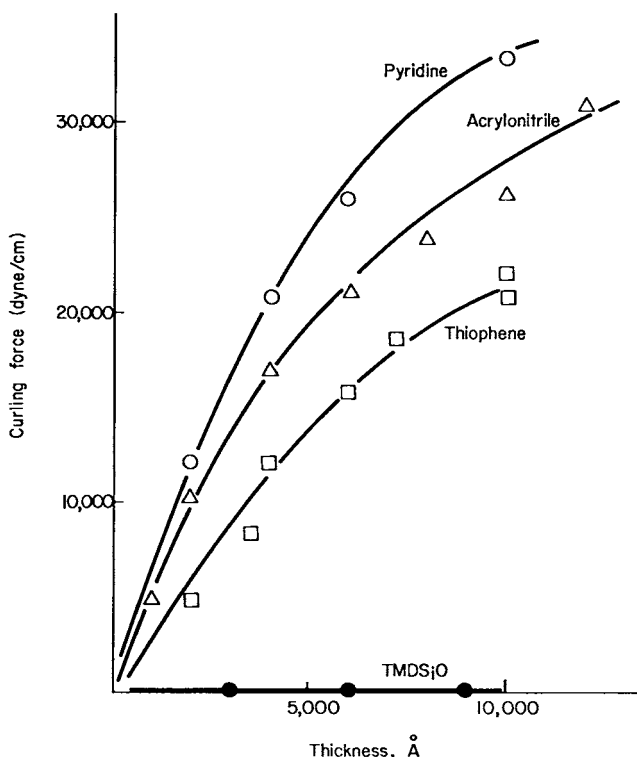


Fig. 66. The curling force, which is the product ($\sigma_s d$) of the internal stress (σ_s) and the thickness (d) of the plasma-deposited layer, is plotted versus d . The three curves correspond to layers obtained by plasma polymerization of the indicated monomers.

be directly related to the mechanism of polymer formation. Another possible cause of the internal stress is the absorption of oxygen by trapped free radicals and subsequent absorption of water vapor by the oxygen-containing functions. These two phenomena, which occur in general cases, will cause expansion or swelling of the polymer deposit. However, it has been found that there is no direct correlation between the free spin concentration observed by ESR and the reported internal stress (Yasuda and Hirotsu, 1977). This indicates that the major portion of the buildup of internal stress occurs during the process of polymer deposition.

Polymers formed by glow discharge polymerization have much greater densities than corresponding conventional polymers (Knidemeyer, Peace, and Mayhan, 1974). For instance, the density of the glow discharge polymer of ethylene was found to be as high as 1.3, but the polymer has no crystallinity. The presence of high density and high expansive internal stress in the absence of crystallinity can be explained by the continuous impinging process in atomic polymerization.

G. Structural Difference of Monomer and Polymer

The aspect of atomic polymerization can be seen clearly in the molecular structural difference of monomers and polymers, but with the glow discharge polymers of hydrocarbons, without appropriate analytical tools, it is difficult to demonstrate the difference in a (semi)quantitative manner, although such tests as elemental and IR spectra analyses generally show that glow discharge polymers are quite different from corresponding conventional polymers. Specific analysis is hampered by the characteristic insolubility of most glow discharge polymers. However, the use of electron spectroscopy for chemical analysis (ESCA) to study the glow discharge polymers of perfluorocarbons provides a unique opportunity to overcome these difficulties. The results of ESCA studies of glow discharge polymers of tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$, are reviewed below in view of atomic polymerization.

Because of the strong electron negativity of fluorine atoms, the binding energy of the core-level electron of carbon is shifted enough so that the amount of shift can be measured by the ESCA C_{1s} spectrum. Consequently, ESCA can distinguish carbons that have one, two, or three fluorine atoms attached. Conventional polytetrafluoroethylene (Teflon) shows a singlet C_{1s} peak, which corresponds to $-\text{CF}_2-$ at 291.5 eV. This peak is shifted from the C_{1s} peak of normal carbons (bound to H or C) at 284.5 eV.

If a polymer is formed by plasma-induced polymerization in a glow discharge, the C_{1s} peak should be a singlet at 291.5 eV as it is in the case of polytetrafluoroethylene. If a polymer is formed via a triple bond containing a precursor, as it is proposed for the glow discharge polymerization of hydrocarbons, the C_{1s} peak should be at a lower binding energy level (289 eV) than that for $-\text{CF}_2-$, because the formation of such a structure requires the abstraction of two fluorine atoms from two adjacent carbons to yield polymers with less fluorines. In the most typical cases, however, the C_{1s} peak of the glow discharge polymer of tetrafluoroethylene contains a considerable amount of $-\text{CF}_3$, $-\text{CF}_2-$, and intermediate peaks in between $-\text{CF}_2-$ and C as shown in Figure 49. This strongly indicates that polymers are formed by neither molecular polymerization of the monomer nor (molecular) polymerization of the plasma-synthesized precursor. This situation is exactly what is to be expected of the atomic polymerization mechanism described earlier for plasma state polymerization. (Namely M^* can be a fragment of a molecule including a single atom.)

Other evidence, which supports the concept of atomic polymerization, may be seen under certain conditions in the codeposition of aluminum (used as a substrate) in the glow discharge polymer of tetrafluoroethylene. When an excessive discharge power is used for the glow discharge polymerization of tetrafluoroethylene, the fluorine detachment and the consequent ablation prevail in the polymer formation (Yasuda and Hsu, 1978). Under such conditions, the ESCA C_{1s} peak indicates very little $-\text{CF}_3$, $-\text{CF}_2-$, and the major peak becomes a broadened peak around 285.5 eV. When this happens, the polymer deposition rate decreases drastically, and the ESCA spectrum shows the presence

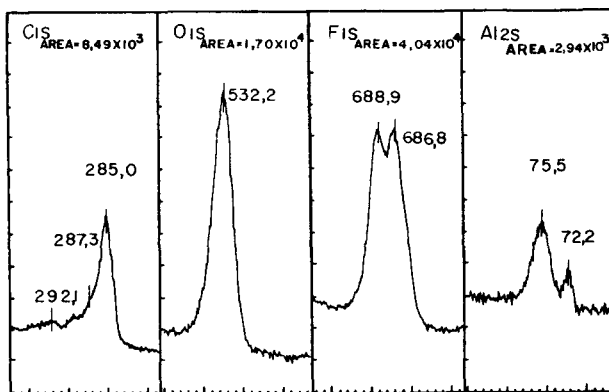


Fig. 67. ESCA spectrum of glow discharge polymer of tetrafluoroethylene polymerized at high energy input (*W/FM*).

of Al as shown in Figure 67. The ESCA Al_{2s} peak observed in this case is not identical to that of the Al foil used as the substrate, and the F_{1s} peak also shows a conspicuous doublet, indicating that AlF is formed and codeposited in the glow discharge polymer.

Atomic polymerization is not polymerization in the conventional sense, because the molecular structure of the monomers is not retained in the polymer. For instance, the glow discharge polymers of acetylene and benzene are very much alike. Their copolymerization characteristics are nearly identical. When N_2 and H_2O are added to benzene or acetylene, considering that one molecule of benzene is equivalent to three molecules of acetylene in glow discharge polymerization, nearly identical polymers are formed (Yasuda, Marsh, and Tsai, 1975). However, the glow discharge polymer of acetylene or benzene is not quite the same as the glow discharge polymer of either methane or ethane. Therefore, the chemical structures of the monomers do play an important role in glow discharge polymerization, although the original structures or their derivatives may not be retained in the polymer structures. In this sense, absolute atomic polymerization can be seen in carbon films deposited from hydrocarbons when subjected to glow discharge. As shown in Figure 64, the overall glow discharge polymerization generally occurs by simultaneous atomic and molecular polymerizations.

V. CONCLUDING REMARKS

Glow discharge polymerization can be visualized as a process consisting of three discharge processes. These are (1) controlled discharge of monomer, (2) electric discharge (glow discharge), and (3) glow discharge polymerization of the monomer.

Before the electric discharge is initiated, a steady-state flow of the monomer

is generally established. During this controlled discharge of the monomer (without electric discharge), adsorption of the monomer onto the solid surfaces in a reactor and degassing of a substrate, etc., take place.

When glow discharge is initiated, it is generally assumed, intuitively, that glow discharge polymerization occurs; however, it is important to recognize that (i) glow discharge does not necessarily mean glow discharge polymerization and (ii) glow discharge polymerization does not necessarily replace the controlled discharge of the monomer. In many cases, the above-mentioned three processes continue to occur simultaneously under the conditions of glow discharge. For instance, under a typical condition of glow discharge polymerization in a bell-jar reactor with capacitive discharge at relatively high pressure and high flow rate, the conversion rate of a monomer to polymer is often less than few percent, which means that the majority of monomer is merely dumped through the system. In a strict sense, the major process under such a condition is the controlled discharge of the monomer.

Another example is seen in glow discharge polymerization of ethylene oxide in an inductively coupled tube reactor with a sufficient discharge power. In this case, nearly 100% of the monomer is subjected to glow discharge and the simple controlled discharge of the monomer no longer takes place; however, very little polymer deposition occurs indicating that glow discharge of a monomer does not necessarily mean glow discharge polymerization.

True understanding of glow discharge polymerization cannot be obtained without recognizing the overall process. There is no reaction which can be described by glow discharge or plasma polymerization of a monomer (e.g., ethylene). There is no material that can be specified by glow discharge or plasma polymer of ethylene. Although it is generally recognized that glow discharge polymerization is system dependent, one tends to reach a conclusion by generalizing the observation beyond the boundary of experimental conditions. Many apparently contradictory findings can be attributed to vastly different conditions employed. This critical review was written with the aim of finding the boundary of glow discharge polymerization.

Although it was not included in this review, much research has been done in application of glow discharge polymerization, and its potential appears to be great. It is anticipated that many unique applications will be accomplished through better understanding of factors such as discussed in this article.

REFERENCES

- Argnette, G. J. (1962), U.S. Pat. 3,061,458.
Austin, J. B., and Black, I. A. (1930), *J. Am. Chem. Soc.* **52**, 4552.
Baddour, R. F., and Timmins, R. S., Eds. (1967), *The Application of Plasmas to Chemical Processing*, MIT Press, Cambridge, MA.
Bamford, C. H., and Ward, J. C. (1961), *Polymer* **2**, 277.
Bamford, C. H., Jenkins, A. D., and Ward, J. C. (1960), *Nature* **186**, 712.
Bell, A. T. (1976), *J. Macromol. Sci. Chem.* **10**(3), 309.
Blais, P., Carlsson, D. J., and Wiles, D. M. (1971), *J. Appl. Polym. Sci.* **15**, 129.

- Bosisio, R. G., Weissfloch, C. F., and Wertheimer, M. R. (1972), *J. Microwave Power* **7**(4), 325.
- Bosisio, R. G., Wertheimer, M. R., and Weissfloch, C. F. (1973), *J. Phys. E* **6**, 628.
- Bradley, A., and Hammes, J. P. (1963), *J. Electrochem. Soc.* **110**, 15.
- Brown, L. C., and Bell, A. T. (1973), private communication.
- Clark, D. T., and Dilks, A. (1977), "Characterization of Metal on Polymer Surface," in *Polymer Surfaces*, Academic, New York, Vol. 2.
- Coleman, J. H. (1973), private communication.
- Coleman, J. H. (1962), U.S. Pat. 3,068,510.
- Denaro, A. T., Owens, P. A., and Crawshaw, A. (1968), *Eur. Polym. J.* **4**, 93.
- Denaro, A. R., Owens, P. A., and Crawshaw, A. (1969), *Eur. Polym. J.* **5**, 471.
- Denaro, A. R., Owens, P. A., and Crawshaw, A. (1970), *Eur. Polym. J.* **6**, 487.
- DeWilde, P. (1874), *Ber.* **7**, 4658.
- Duval, M., and Theoret, A. (1973), *J. Appl. Polym. Sci.* **17**, 527.
- Duval, M., and Theoret, A. (1975), *J. Electrochem. Soc.* **122**, 581.
- Duval, M., and Theoret, A., private communication.
- Gaumann, T., and Haigne, J., Eds. (1968), *Aspects of Hydrocarbon Radiolysis*, Academic, New York.
- Goodman, J. (1960), *J. Polym. Sci.* **44**, 551.
- Gould, R. F., Ed. (1969), *Advances in Chemistry Series No. 80*, Am. Chem. Soc., Washington, DC.
- Harkins, W. D., and Jackson, J. M. (1933), *J. Chem. Phys.* **1**, 37.
- Havens, M. R., Mayhan, K. G., and James, W. J. (1978), *J. Appl. Polym. Sci.* **22**, 2799.
- Havens, M. R., Mayhan, K. G., James, W. J., and Schmidt, P. (1978), *J. Appl. Polym. Sci.* **22**, 2793.
- Hollahan, J. R., and McKeever, R. P. (1969), "Chemical Reactions in Electrical Discharge," *Advances in Chemistry Series No. 80*, Am. Chem. Soc., Washington, DC.
- Hollahan, J. R., and Wydeven, T. (1973), *Science* **179**, 500.
- Jesch, K., Bloor, J. E., and Kronick, P. L. (1966), *J. Polym. Sci. A-1* **4**, 1487.
- Kay, E. (1977), paper presented at Int. Round Table on Plasma Polymerization and Treatment, *IUPAC Symp. Plasma Chem.*
- Kikuchi, Y., and Tsuda, S. (1961), *Denki Kagaku* **29**, 389.
- Knidemeyer, W. W., Peace, B. W., and Mayhan, K. G. (1974), *J. Appl. Polym. Sci.* **18**, 301.
- Kobayashi, H., Bell, A. T., and Shen, M. (1973), *J. Appl. Polym. Sci.* **17**, 885.
- Kobayashi, H., Bell, A. T., and Shen, M. (1974), *Macromolecules* **7**, 277.
- Kobayashi, H., Bell, A. T., and Shen, M. (1976), *J. Macromol. Sci. Chem.* **10**, 491.
- Kobayashi, H., Shen, M., and Bell, A. T. (1974), *J. Macromol. Sci. Chem.* **8**, 373.
- Koenig, H., and Helwig, G. (1951), *Z. Phys.* **129**, 491.
- Liepins, R., and Sakaoku, K. (1972), *J. Appl. Polym. Sci.* **16**, 2633.
- Linder, E. G., and Davis, A. P. (1931), *J. Phys. Chem.* **35**, 3649.
- McTaggart, F. K. (1967), *Plasma Chemistry in Electrical Discharges*, Elsevier, New York.
- Melville, H., and Gowenlock, B. G. (1964), *Experimental Methods in Gas Reaction*, MacMillan, London.
- Millard, M. M., Windle, J. J., and Pavlath, A. E. (1973), *J. Appl. Polym. Sci.* **17**, 2501.
- Morita, S. (1976), *J. Macromol. Sci. Chem.* **10**(3), 501.
- Morosoff, N., Newton, W., and Yasuda, H. (1978), *J. Vac. Sci. Technol.* **15**(6), 1815.
- Morosoff, N., Crist, B., Bumgarner, M., Hsu, T., and Yasuda, H. (1976), *J. Macromol. Sci. Chem.* **10**(3), 451.
- Niinomi, M., Kobayashi, H., Bell, A. T., and Shen, M. (1973), *J. Appl. Phys.* **44**, 4317.
- O'Kane, D. F., and Rice, D. W. (1976), *J. Macromol. Sci. Chem.* **10**, 567.
- Osada, Y., Bell, A. T., and Shen, H. (1978), *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **19**(2), 482.
- Osada, Y., Shen, M., and Bell, A. T. (1978), *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **19**(2), 477.

- Otazai, K., Kume, S., Nagai, S., Yamamoto, T., and Fukushima, S. (1954), *Bull. Chem. Soc. Jpn.* **27**, 476.
- Raney, M. W., and O'Connor, W. P. (1969), "Chemical Reactions in Electrical Discharge," in *Advances in Chemistry Series No. 80*. Am. Chem. Soc., Washington, DC.
- Schoepfle, C. S., and Connell, L. H. (1929), *Ind. Eng. Chem.* **21**, 529.
- Sharma, A., Millich, F., and Hellmuth, E. W. (1978), *J. Appl. Phys.* **49**, 5055.
- Smolinsky, G. (1977), private communication.
- Stancell, A. F., and Spencer, A. T. (1972), *J. Appl. Polym. Sci.* **16**, 1505.
- Stuart, M. (1963), *Nature* **199**, 59.
- Thenard, A. (1874), *C. R.* **78**, 219.
- Thompson, L. F., and Mayhan, K. G. (1972), *J. Appl. Polym. Sci.* **16**, 2317.
- Thompson, L. F., and Smolinsky, G. (1972), *J. Appl. Polym. Sci.* **16**, 1179.
- Tien, P. K., Smolinsky, G., and Martin, R. J. (1972), *Appl. Opt.* **11**, 637.
- Venugaopalan, M., Ed. (1971), *Reactions Under Plasma Conditions*, Wiley, New York.
- Wehner, C. K., and Anderson, G. S. (1970), in *Handbook of Thin Film Technology*, L. I. Maissel and R. Glang, Eds., McGraw-Hill, New York.
- Weisz, P. B. (1955), *J. Phys. Chem.* **59**, 464.
- Westwood, A. R. (1971), *Eur. Polym. J.* **7**, 363.
- Westwood, A. R. (1971), *Eur. Polym. J.* **7**, 377.
- Williams, T., and Hayes, M. W. (1966), *Nature* **209**, 769.
- Yasuda, H. (1976), *J. Macromol. Sci. Chem.* **10**, 383.
- Yasuda, H. (1977), *Proc. IUPAC 3rd Int. Symp. Plasma Chem.*
- Yasuda, H., and Hirotsu, T. (1977), *J. Polym. Sci. Polym. Chem. Ed.* **15**, 2749.
- Yasuda, H., and Hirotsu, T. (1978a), *J. Polym. Sci. Polym. Chem. Ed.* **16**, 229.
- Yasuda, H., and Hirotsu, T. (1978b), *J. Polym. Sci. Polym. Chem. Ed.* **16**, 313.
- Yasuda, H., and Hirotsu, T. (1978c), *J. Polym. Sci. Polym. Chem. Ed.* **16**, 743.
- Yasuda, H., and Hirotsu, T. (1978d), *J. Polym. Sci. Polym. Chem. Ed.* **16**, 2587.
- Yasuda, H., and Hirotsu, T. (1978e), *J. Appl. Polym. Sci.* **22**, 1195.
- Yasuda, H., and Hsu, T. (1976), *J. Appl. Polym. Sci.* **20**, 1769.
- Yasuda, H., and Hsu, T. (1977a), *J. Polym. Sci. Polym. Chem. Ed.* **15**, 81.
- Yasuda, H., and Hsu, T. (1977b), *J. Polym. Sci. Polym. Chem. Ed.* **15**, 2411.
- Yasuda, H., and Hsu, T. (1978), *Surf. Sci.* **76**, 232.
- Yasuda, H., and Lamaze, C. E. (1971), *J. Appl. Polym. Sci.* **15**, 2277.
- Yasuda, H., and Lamaze, C. E. (1973a), *J. Appl. Polym. Sci.* **17**, 1519.
- Yasuda, H., and Lamaze, C. E. (1973b), *J. Appl. Polym. Sci.* **17**, 1533.
- Yasuda, H., and Morosoff, N. (1979), *J. Appl. Polym. Sci.*, in press.
- Yasuda, H., Bumgarner, M. O., and Hillman, J. J. (1975), *J. Appl. Polym. Sci.* **19**, 531.
- Yasuda, H., Bumgarner, M. O., and Morosoff, N. C. (1974), Ann. Rep. to Natl. Heart and Lung Inst., NIH, Rep. No. NIH-NHLI-73-2913-1. Available from National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22151.
- Yasuda, H., Hirotsu, T., and Olf, H. G. (1977), *J. Appl. Polym. Sci.* **21**, 3179.
- Yasuda, H., Lamaze, C. E., and Sakaoku, K. (1973), *J. Appl. Polym. Sci.* **17**, 137.
- Yasuda, H., Marsh, H. C., and Tsai, J. (1975), *J. Appl. Polym. Sci.* **19**, 2157.
- Yasuda, H., Bumgarner, M. O., Marsh, H. C., and Morosoff, N. (1976), *J. Polym. Sci. Polym. Chem. Ed.* **14**, 195.
- Yasuda, H., Marsh, H. C., Brandt, E. S., and Reilley, C. N. (1977), *J. Polym. Sci. Polym. Chem. Ed.* **15**, 991.
- Yasuda, H., Marsh, H. C., Bumgarner, M. O., and Morosoff, N. (1975), *J. Appl. Polym. Sci.* **19**, 2845.