

Plasma Polymerization

H. Yasuda

PLASMA POLYMERIZATION

This page intentionally left blank

PLASMA POLYMERIZATION

H. Yasuda

Institute for Thin Film Processing Science
Materials Research Center
University of Missouri–Rolla
Rolla, Missouri

1985



ACADEMIC PRESS, INC.

(Harcourt Brace Jovanovich, Publishers)

Orlando San Diego New York London
Toronto Montreal Sydney Tokyo

COPYRIGHT © 1985, BY ACADEMIC PRESS, INC.
ALL RIGHTS RESERVED.
NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY
INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT
PERMISSION IN WRITING FROM THE PUBLISHER.

ACADEMIC PRESS, INC.
Orlando, Florida 32887

United Kingdom Edition published by
ACADEMIC PRESS INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Yasuda, H.
Plasma polymerization.
Includes index.
1. Polymers and polymerization. 2. Plasma chemistry.
I. Title.
Q0381.8.Y37 1985 547.7 84-24350
ISBN 0-12-768760-2 (alk. paper)

PRINTED IN THE UNITED STATES OF AMERICA

85 86 87 88 9 8 7 6 5 4 3 2 1

Contents

Preface	ix
1 Introduction	
Text	1
References	3
2 Scope of Polymer Formation by Plasma Polymerization	
2.1 Preferred Form of Plasma Polymers	4
2.2 Plasma-State Polymerization versus Plasma-Induced Polymerization	5
2.3 Plasma Polymerization versus Graft Polymerization	7
2.4 Plasma Polymerization versus Radiation Polymerization	9
References	10
3 Fundamental Aspects of Gas-Phase Reactions	
3.1 Gas in a Closed System	11
3.2 Diffusion and Flow of Gas	15
3.3 Flow Rate and System Pressure of Flow	18
References	18
4 Fundamental Aspects of Ionized Gas	
4.1 Plasma for Plasma Polymerization	19
4.2 Macroscopic Treatment of Glow Discharge	20
4.3 Microscopic Treatment of Glow Discharge	23
4.4 Microscopic Treatment of Plasma	35
References	43
5 Fundamental Aspects of Polymerization	
5.1 Classification of Polymerization by Growth Mechanism	44
5.2 Addition Polymerization	49

5.3	Radiation Polymerization	59
5.4	Polymerization in a Vacuum	63
	References	71
6	Kinetic and Mechanistic Aspects of Plasma Polymerization	
6.1	Role of Ionization in Plasma Polymerization	73
6.2	Growth Mechanism of Plasma Polymerization	79
6.3	Reactive Species in Plasma Polymerization	82
6.4	Free Radicals in Plasma Polymers	86
6.5	Incorporation of Nonpolymerizable Gases in Plasma Polymers	115
6.6	Interpretation of Plasma Diagnostic Data	131
6.7	Interpretation of Polymer Properties	143
6.8	Atomic (Nonmolecular) Nature of Plasma Polymerization	166
	References	176
7	Competitive Ablation and Polymer Formation in Plasma	
7.1	Overall Reactions in a Plasma Polymerization System	178
7.2	Classification of Gases for Plasma	183
7.3	Ablation by Plasma	184
7.4	Dependence of Ablation on Operational Parameters	186
7.5	Simultaneous Sputter Coating and Plasma Polymerization	189
	References	195
8	Kinetic and Mechanistic Aspects of Polymer Deposition in Plasma Polymerization	
8.1	Polymerization and Deposition Mechanisms	196
8.2	Mass Balance in a Plasma Polymerization System	201
8.3	Distribution of Polymer Deposition	205
8.4	Dependence of Growth Reactions on Diffusional (Kinetic) Path Length	229
8.5	Polymer Deposition in a Closed System and in a Flow System	253
8.6	Overall Kinetics of Polymer Deposition	260
8.7	Simultaneous Polymerization–Deposition Mechanisms	273
	References	275
9	Operational Parameters of Plasma Polymerization	
9.1	Pressure of a Steady-State Flow System	277
9.2	System Pressure under a Glow Discharge	279
9.3	Factors That Determine Pressure under a Glow Discharge	281
9.4	Monomer Flow Rate	287
9.5	Determination of Flow Rate	288

9.6	Meaning of Flow Rate in a Plasma Polymerization System	290
9.7	Power Input of Plasma Polymerization	292
9.8	Effect of Power on the Volume and Intensity of Plasma	292
9.9	Plasma Energy Density and Input Power	295
9.10	Discharge Power for Polymer-Forming Plasma	298
9.11	Composite Power Parameter for Plasma Polymerization	301
9.12	Domains of Plasma Polymerization	309
9.13	Location of Polymer-Collecting Surface and Frequency of Electric Power Source	313
9.14	Stationary and Moving Substrates	315
9.15	Magnetron Discharge for Plasma Polymerization	319
	References	332
10	General Characteristics of Plasma Polymers	
10.1	Free Radicals in Plasma Polymers	334
10.2	Internal Stress in Plasma Polymers	337
10.3	Solubility and Fusibility of Plasma Polymers	344
10.4	Surface Properties of Plasma Polymers	344
10.5	Permeability Characteristics of Plasma Polymers	355
10.6	Adhesion of Plasma Polymers	359
	References	369
11	Electrical Properties of Plasma-Polymerized Thin Organic Films	
11.1	Historical Background	370
11.2	Dielectric Properties of Plasma-Polymerized Organic Films	372
11.3	Electrical Conduction in Plasma-Polymerized Organic Films	395
11.4	Concluding Remarks	414
	References	416
	Index	419

Introduction

Plasma polymerization refers to the formation of polymeric materials under the influence of plasma (partially ionized gas). Because the most practical means of carrying out plasma polymerization involves the use of an electric glow discharge in a vacuum, the term *glow discharge polymerization* has been used, in every practical sense, synonymously with plasma polymerization, although plasma polymerization can be carried out by means other than glow discharge.

It was known for many years that some organic compounds form solid deposits in plasma generated by some kind of electrical discharge (1–9). In most cases, however, the deposits were recognized as by-products of phenomena associated with electric discharge; consequently, little attention was paid either to the properties of these materials (undesirable by-products) or to the process as a means of forming useful materials.

At these early stages of discovery, the concept of polymers was not well developed, and obviously these processes had never been considered to be polymerization, that is, plasma polymerization or glow discharge polymerization. Only since the 1960s has the formation of materials in plasma been recognized as a means of synthesizing polymers, and the process, when used to make a special coating on metals, has been referred to as plasma polymerization or glow discharge polymerization (10–14).

Following the advancement of polymer science, the formation of organic solids or films in plasma has attracted considerable attention, and the process has been generally recognized as plasma polymerization or glow discharge polymerization. The American Chemical Society has held symposiums (1970, 1974, 1978, and 1982) on this subject.

In these developments (i.e., up to the 1970s), however, the concept of plasma polymerization has been based on the application of the concept of polymerization and/or of polymers developed in preceding decades to the formation of organic material under plasma conditions. In other words, the process has attracted the attention of scientists and engineers as an exotic method of polymerization. Although a great number of research studies have

been published and numerous potential applications and the uniqueness of the polymer formation process have been demonstrated, the subject has not drawn much academic interest as a new subject area of polymer science. This is due largely to the fact that the very unique and advantageous feature (in certain applications) of forming insoluble, infusible polymers has hampered the basic study of the process at the molecular level.

In more recent years, however, the question of whether the concepts of polymers and of polymerization can be applied to plasma-formed materials and to plasma polymerization, respectively, has been reexamined (15). The well-recognized concept of polymerization today is based on the molecular processes by which the size of molecules increases. The arrangement of the atoms that constitute the molecules of a monomer is accomplished during the organic synthesis of the monomer. During the polymerization of a monomer, rearrangement of atoms within the molecule seldom occurs.

In contrast to such molecular processes, polymer formation in plasma has been recognized as an atomic (nonmolecular) process (15). If one adopted such an atomic process to form materials in which the reaction of new covalent bonds between atoms played a predominant role, one could find numerous new processes and resulting materials that would play vitally important roles in modern technologies. The processes recognized as chemical vapor deposition, plasma chemical vapor deposition, ion-assisted vapor deposition, and sputter coating of polymers all fall into this category.

Plasma polymerization was dealt with in the 1960s and 1970s as a method of polymerization. Although some important differences in polymer formation mechanisms and the properties of resultant polymers were recognized, the underlying concept was an extension of the concepts of polymerization and polymers developed with conventional polymers. Consequently, the underlying concept was represented, for example, by the preparation of a thin layer of polystyrene by the plasma polymerization of styrene or the preparation of a thin layer of polytetrafluoroethylene by the plasma polymerization of tetrafluoroethylene. In other words, plasma polymerization was conceived as a new and exotic method of polymerization.

Plasma polymerization today is gaining recognition as an important process for the formation of entirely new kinds of materials. The materials obtained by plasma polymerization are significantly different from conventional polymers and are also different from most inorganic materials. Thus, plasma polymers lie somewhere between organic polymers and inorganic materials. Plasma polymerization should be considered a method of forming such new types of materials rather than a method of preparing conventional polymers. Consequently, the term *plasma polymerization* should not be limited to the formation of organic materials but should cover a wider area that includes metallic or inorganic elements, although the major portion of studies

covered in this volume involve the formation of polymeric materials from organic compounds.

To take full advantage of the new kinds of materials recognized as plasma polymers and of the process by which they are made, it is important to recognize that we are not dealing with conventional polymers and polymerization in the strict sense, although these terms are used. Therefore, considerable effort is spent comparing plasma polymerization with conventional polymerization.

References

1. P. DeWilde, *Ber. Dtsch. Chem. Ges.* **7**, 4658 (1874).
2. A. Thenard, *C. R. Hebd. Seances Acad. Sci.* **78**, 219 (1874).
3. C. S. Schoepfle and L. H. Connell, *Ind. Eng. Chem.* **21**, 529 (1929).
4. J. B. Austin and I. A. Black, *J. Am. Chem. Soc.* **52**, 4552 (1930).
5. E. G. Linden and A. P. Davis, *J. Phys. Chem.* **35**, 3649 (1931).
6. W. B. Harkins and J. M. Jackson, *J. Chem. Phys.* **1**, 37 (1933).
7. H. Koenig and G. Helwig, *Z. Phys.* **129**, 491 (1951).
8. K. Otazai, S. Kume, S. Nagai, T. Yamamoto, and S. Fukushima, *Bull. Chem. Soc. Jpn.* **27**, 476 (1954).
9. P. B. Weisz, *J. Phys. Chem.* **59**, 464 (1955).
10. J. Goodman, *J. Polym. Sci.* **44**, 551 (1960).
11. G. J. Arguette, U.S. Patent 3,061,458 (1962).
12. J. H. Coleman, U.S. Patent 3,068,510 (1962).
13. M. Stuart, *Nature (London)* **199**, 59 (1963).
14. A. Bradley and J. P. Hammes, *J. Electrochem. Soc.* **110**, 15 (1963).
15. H. Yasuda, *Contemp. Top. Polym. Sci.* **3**, 103 (1979).

Fundamental Aspects of Ionized Gas

4.1 Plasma for Plasma Polymerization

The term *plasma* describes the state of ionized gas (e.g., glow discharge) (*I*). An ionized gas consists mainly 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 greater than 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, although its density is much lower.

The classical definition of plasma limits the term 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 of plasma is less restrictive; the term simply denotes 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*. Plasma in this sense may be *cold*. Plasma created by an electric glow discharge is often called *low-temperature* plasma to distinguish it from *hot* plasma.

In the laboratory, plasma is generated by combustion, flames, electric discharge, controlled nuclear reactions, shocks, and other means. Because 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 of maintaining the plasma state continuously for a relatively long period of time, the most obvious and most common method is the use of an electric discharge. For this reason, most experimental work, particularly in the study of polymerization, is carried out using some kind of electric discharge.

There are many types of electric discharges, all characterized by the presence of free electrons and/or an electric field. Among the many types of electric discharge, glow discharge is by far the most frequently used in plasma polymerization. Consequently, the term *glow discharge polymerization* can be used nearly synonymously with *plasma polymerization*, although the latter covers polymerization obtained by a variety of technical processes.

4.2 Macroscopic Treatment of Glow Discharge

In its simplest form, a glow discharge can be established by passing a dc electric current through a gas under low pressure between two electrodes. Electric multiplication is due to an increase in the energy of the primary electrons as they move through the applied electric field until they gain sufficient energy to ionize the gas molecules, which collide with electrons. When a glow discharge is established, the space between the electrodes becomes visible by a characteristic glow. The actual distribution of light in the glow discharge is significant and is dependent on the voltage–current characteristics of the discharge. The general shape of the current–voltage characteristics of gaseous discharges for pressure in the range 0.1–10 torr is shown in Fig. 4.1, which delineates the conditions under which various discharges are stable. (*I*).

Glow discharge is characterized by the appearance of several luminous zones and by a constant potential difference between the electrodes independent of current. The relative size of these zones varies with pressure and the distance between the electrodes. A typical distribution is shown in Fig. 4.2a; the distribution of potential among different zones is shown in Fig. 4.2b.

As the pressure decreases, the negative glow and the Faraday dark space expand at the expense of the positive glow, which may disappear altogether. If the distance between the electrodes decreases, the positive glow diminishes while the size of the other zones remains intact. This indicates that the positive glow is not an essential feature of the discharge, as are the zones in the neighborhood of the cathode (*I*).

Apart from the cathode region, the resultant space charge is practically zero over the whole length of the tube, and the gas in the tube is in the form of a plasma. An important factor is that the density of the plasma in the negative glow is 10–100 times greater than that of the positive column (*I*).

The electric field is much higher in the cathode region. Right at the cathode, most of the current is carried by ions flowing to the cathode; in the rest of the discharge, including the negative glow and the Faraday dark space, nearly all of the current is carried by electrons. The Faraday dark space is dark because there is little or no accelerating electric field in this region.

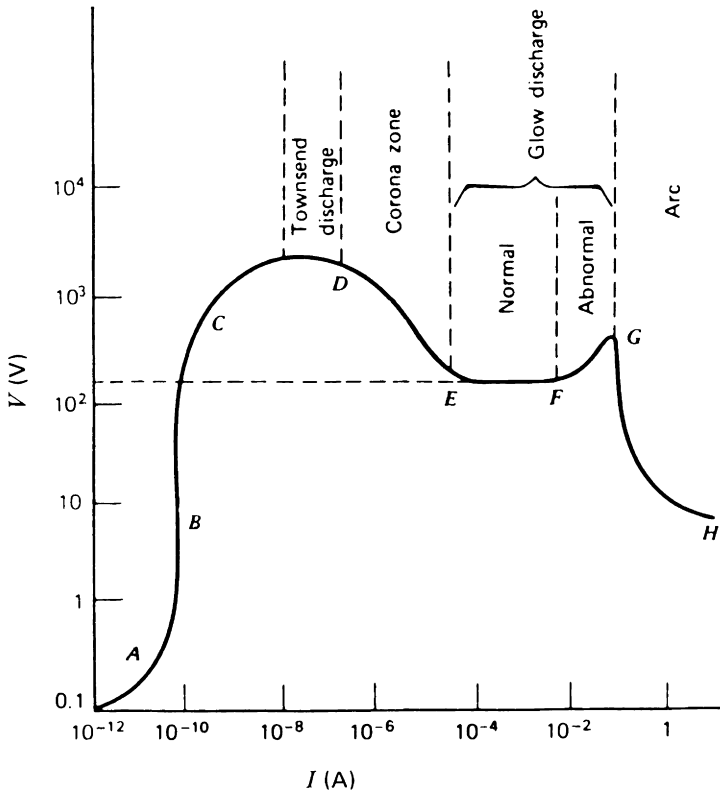


Fig. 4.1 Voltage-current characteristics of a dc discharge. From Shakin (*I*, Fig. 10). Copyright 1971 John Wiley & Sons, Inc.

Of the three main parts of the glow discharge, the cathode fall region is probably the least understood from a theoretical viewpoint. Although some theoretical treatments exist, Ingold considers the cathode fall, negative glow, and Faraday dark space together by assuming that they form a diode (2). This is because these regions are related to cathode properties, whereas the positive column is independent of the cathode.

It is important to note that the operation of the glow discharge depends critically on the role of the cathode dark space. In order to have a steady state, each electron emitted by the cathode must produce sufficient ionization and excitation to effect the release of a sufficient number of secondary electrons from the cathode upon impact of the ions.

In the positive column, the axial component of the electric field is constant, and hence all of the measurable quantities—particle densities, current densities, and particle temperature—vary with radial position only. The low

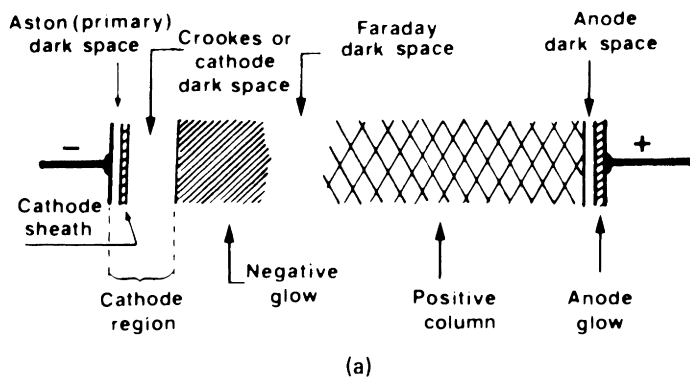
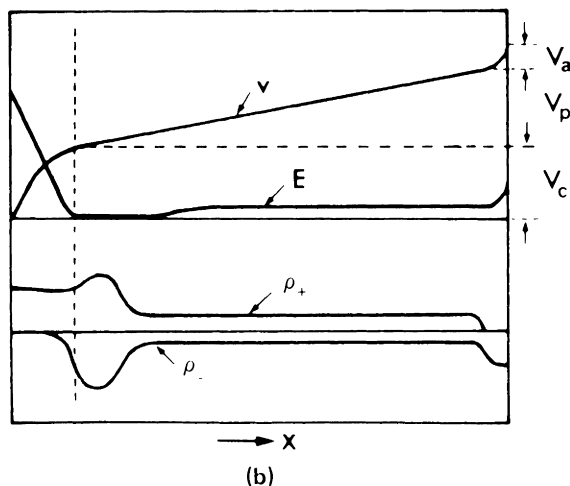


Fig. 4.2 (a) Normal glow discharge; the shaded areas are luminous. (b) Distribution of potential among luminous zones (4). From Shakin (*I*, p. 299, Fig. 11). Copyright 1971 John Wiley & Sons, Inc.

field as well as the uniform appearance of the positive column indicates that ionization is not obtained from the drift velocity of electrons in the field direction, but rather from their large random velocity acquired by numerous elastic collisions in the electric field (*I*).

The role of the anode is to transform current from the glow discharge to the external circuit. When there is no positive column, the anode is usually in the Faraday dark space. In this case, the anode fall of potential can be very small, or even negative, because ions and electrons diffuse together to the anode from

the negative glow in such a way that charge neutrality is maintained (2). In the presence of a positive column, however, a negative space charge is generally present in the neighborhood of the anode. The anode fall potential is of the order of the ionization potential of the gas, because it is in this region of the discharge that most of the ions that traverse the position column are generated (1, 2).

In the region of normal glow discharge (E–F, Fig. 4.1) the effect of a rise in current is to increase the diameter of the discharge so that the current density will remain constant. For an abnormal glow discharge (F–G, Fig. 4.1) the current density rises with an increase in total current, causing both the cathode and the gas to become more heated.

4.3 Microscopic Treatment of Glow Discharge

4.3.1 IONIZATION OF MOLECULES BY AN ELECTRON BEAM

If a free electron is somehow produced in a gas and a dc electric field is imposed, the electron will respond according to Newton's law,

$$a = \frac{q}{m_e} E, \quad (4-1)$$

where a is the acceleration of the electron, q its electric charge, m_e its mass, and E an electric field, and will begin to accelerate in free fall. Three types of collisions can occur between the electron and a gas molecule. At low energies, elastic collisions will take place. At high energies, a large amount of energy can be lost by the electron in exciting the molecules to a higher energy level. At still higher energy levels, ionization of the molecule can occur. The last process is essential for maintaining an electric discharge.

Although we do not intend to review the fundamentals of ionization or electric discharge in this book, some important aspects that are relevant to plasma polymerization are presented in a simplified way in this chapter. A more detailed treatment of ionization and discharge can be found elsewhere (3–5). In the following sections, the excellent illustrations of Hatta (6) are adapted to explain the basic concept.

4.3.2 CROSS SECTION OF ELECTRON–ATOM COLLISIONS

To express the frequency of collision, the term *cross section of collision* or simply *cross section* is generally used. The collisions of electrons with gas atoms can be determined by the experiment described in Fig. 4.3, where K is a

Kinetic and Mechanistic Aspects of Plasma Polymerization

As pointed out in Chapter 5, the level of vacuum generally used in plasma polymerization (10^{-3} – 10^1 torr) is too low to form polymers in a practical manner by ordinary polymerization such as the addition polymerization of olefinic monomers. At this point, the most important thing to recognize is that plasma polymerization is an entirely different type or category of polymerization than the polymerizations discussed in Section 5.2. In this chapter, the kinetic and mechanistic aspects of plasma polymerization are discussed as an extension of the comparisons presented in Section 5.4.

Most studies dealing with the kinetic and mechanistic aspects of plasma polymerization have been based on an *a priori* concept of polymerization, such as (addition type) chain-growth polymerization, which is, according to the considerations discussed in Section 5.4, very unlikely to play a significant role in plasma polymerization or any polymerization that occurs in a vacuum.

Another prevailing trend in studies of the kinetics or mechanisms of plasma polymerization has been the direct application of theories of, or data on, the ionization of gases (the majority of data having been obtained with nonreactive gases such as monoatomic inert gases and relatively simple diatomic gases including N_2 , O_2 , etc.) to polymerizable monomers such as vinyl monomers. In this sense, perhaps too much emphasis has been placed on the ionization aspects of plasma, and too little attention has been paid to the elementary steps of polymer formation (the growth mechanism of polymerization).

Among the polymerizations described in Chapter 5, the closest to plasma polymerization are radiation polymerization and Parylene polymerization. The former involves the ionization of monomers as the primary step of the

initiation of polymerization, and the latter involves the polymerization mechanism by which polymer depositions in a vacuum occur. Radiation polymerization does not yield polymers in a vacuum, and Parylene polymerization does not involve the ionization process. Therefore, neither is a true model of plasma polymerization; however, plasma polymerization can be visualized as a hybrid of these two polymerization mechanisms. In this sense, it is worth examining how plasma polymerization differs from radiation and Parylene polymerizations to gain insight into the mechanisms of plasma polymerization.

6.1 Role of Ionization in Plasma Polymerization

The ionization of a molecule by collision with an accelerated electron is an essential process for creating plasma of a monomer (with or without carrier gas). It is premature to assume, however, that the ionization of molecules is the first elementary step of plasma polymerization. Here, we must recognize the difference between the ionization of atoms and that of molecules, particularly relatively complex organic molecules. With atoms, the ionization can occur only by the elimination of an electron from an electron orbital, and the process requires a relatively high energy (e.g., 13–25 eV for inert gas atoms). Therefore, in the ionization of inert gases, electrons having energies lower than the ionization potential or off-centered collisions that do not result in the transfer of the entire energy of an electron to an atom do not contribute to the ionization.

In the ionization of molecules, particularly organic molecules, this is not a complete picture of the ionization step in plasma. First of all, the ionization energy of greater than 10 eV is far above the bond energies of primary bonds involved in organic compounds. Typical bond energies are given in Table 6.1. In Table 6.2, the dissociation energy, metastable energy, and ionization energy for noble gases and diatomic gases are compared. The low-energy electrons and/or off-centered collisions that cannot ionize molecules can break bonds in organic molecules or create excited species, which can trigger chemical reactions. These side reactions associated with ionization are absent in the ionization of atoms.

Thus, the ionization of an organic molecule is far more complex than the ionization of an atom, and one can easily estimate the extent of the side reactions associated with the ionization by comparing the energies necessary for the side reactions and the ionization energy of a molecule. The following examples provide some indication of the energies involved in the side reactions that occur in the glow discharge of organic molecules [the

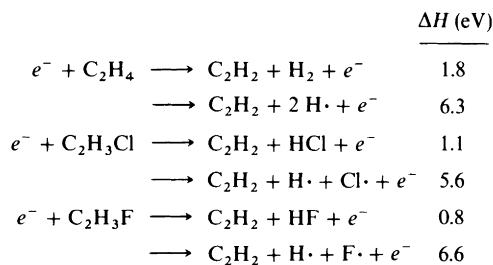
Table 6.1
TYPICAL BOND ENERGIES

Bond	Dissociation energy (eV)
C—C	3.61
C=C	6.35 (2.74 for π bond)
C—H	4.30
C—N	3.17
C=N	9.26
C—O	3.74
C=O	7.78
C—F	5.35
C—Cl	3.52
N—H	4.04
O—H	4.83
O—O	1.52

Table 6.2
DISSOCIATION ENERGY, METASTABLE ENERGY,
AND IONIZATION ENERGY FOR NOBLE AND
DIATOMIC GASES

Gas	Dissociation energy (eV)	Metastable energy (eV)	Ionization energy (eV)
H	—	19.8	24.6
Ne	—	16.6	21.6
A	—	11.5	15.8
Kr	—	9.9	14.0
Xe	—	8.32	12.1
H ₂	4.5	—	15.6
N ₂	9.8	—	15.5
O ₂	5.1	—	12.5

enthalpies of reaction (I) are given in units of electron volts]:



Whereas most ionizations require energy greater than 10 eV, the dissociation of a molecule requires much less energy. It seems noteworthy that the dehydrogenation, dehydrochlorination, dehydrofluorination, and so on, of an organic molecule require very little energy in comparison with the ionization energy.

The relative ease with which such dissociation reactions occur should depend on the activation energy associated with each reaction. However, a rough estimate by the magnitude of the heats of reaction seems to provide reasonably accurate comparisons between the dissociation and ionization of a molecule (*I*).

Ionization is the essential step in creating and sustaining plasma but is not necessarily the primary step in initiating plasma polymerization. The scission of bonds occurs with a far greater frequency than the formation of ions. Bell estimated that the concentration of free radicals in plasma is usually five to six orders of magnitude higher than that of ions (*I*). In other words, the scission of bonds does not occur as the consequence of the ionization of molecules but rather occurs simultaneously with ionization.

In this respect, there is a significant difference between radiation polymerization and plasma polymerization. Namely, in radiation polymerization (Section 5.3) the formation of the chain-carrying species such as the cation, anion, or free radical is a consecutive process to the ionization of a monomer, whereas in plasma polymerization, the reactive species are not necessarily formed as the consequence of the ionization. Thus, ironically, ions play a much less important role in plasma polymerization than in radiation polymerization. Nevertheless, the role of ions in plasma polymerization should be examined.

In comparing the effects of ions in plasma polymerization with their effects in radiation polymerization, one must focus attention on the following factors.

6.1.1 REACTIVITY OF CARBOCATIONS

Carbocations are generally very unstable, and it was only after procedures for the rigorous drying of monomers had been applied that the role of cationic polymerization in radiation polymerization became evident. Under ordinary conditions of plasma polymerization, the quantity of impurities is far greater than that in the superdried monomer used in radiation polymerization.

The ordinary plasma reactor contains a large quantity of impurities with respect to the polymerization. At the level of 10^{-3} torr or higher without addition of a monomer, an ample amount of water vapor exists in the system, particularly in relation to the amount of monomer to be introduced. Furthermore, as soon as plasma is initiated, a large amount of by-product gases is formed, and there are many species that can react with cations,

including the free electrons in plasma. Therefore, it is very unlikely that the cations produced in the first step of ionization would play any significant role in plasma polymerization.

6.1.2 CHEMICAL NATURE OF MONOMERS

Although cations are formed by the ionization of a monomer, cationic polymerization can occur only with a limited group of monomers in which the substituent groups to the olefinic double bond are nucleophilic and, consequently, the electron density at the double bond is high. Olefinic monomers with electrophilic substituents cannot polymerize by cationic polymerization (see Table 5.4).

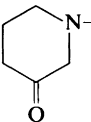
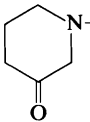
Conventional polymerizations are therefore highly dependent on the structure of the monomer, and a particular monomer can be polymerized only by limited polymerization mechanisms dictated by the monomer structure. This implies that, without considering the monomer structure, one cannot automatically assume that the cations formed by the ionization are the chain-carrying species.

In plasma polymerization, in contrast to this restriction, not only monomers that can be polymerized by addition polymerization, but also any organic compound without a polymerizable structure such as a double bond, polymerize. Furthermore, the rates at which monomers polymerize are by and large similar regardless of the structures of the monomers (e.g., styrene versus ethylbenzene, ethylene versus ethane, etc.).

It should be emphasized that the chemical reactions involved in conventional polymerizations are very specific to the chemical structure and mechanisms. As shown in Fig. 5.4, the rate constant of propagation k_p for styrene varies by seven orders of magnitude, depending on the mechanisms of the polymerization. In other words, when we refer to fast polymerization or slow polymerization, the difference corresponds to several orders of magnitude in the rate constants. It should also be emphasized that such a large difference in the polymerization rates of a monomer (e.g., styrene) is caused by the difference in the polymerization mechanisms.

The study of polymerization kinetics is commonly employed to elucidate polymerization mechanisms. With this background, a comparison of the polymer formation rates of various monomers by plasma polymerization would provide an overview of the kind of reaction mechanism responsible for the plasma polymerization. The variation in the plasma polymer deposition rates for vinyl monomers versus saturated vinyl monomers is only within an order of magnitude (2) (Table 6.3).

Table 6.3**POLYMERIZATION PARAMETER: VINYL VERSUS SATURATED VINYL COMPOUNDS**

Vinyl compounds	k^a	Saturated vinyl compounds	k^a
	7.59		4.72
	5.33		4.05
	5.65		4.52
	7.65		7.38
	7.55		3.76
$\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$	5.71	$\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{N}$	4.49
	5.47		2.98
$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{NH}_2$	2.86	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	2.52

^a Parameter k is expressed in units of $\text{cm}^{-2} \times 10^4$; $r = kF_w$, where r is the rate of polymer deposition ($\text{g}/\text{cm}^2 \cdot \text{min}$) and F_w the weight-based monomer flow rate (g/min).

It should be reiterated that the polymerization rates of vinyl and saturated vinyl monomers polymerized by the conventional process are different in orders of magnitude (i.e., polymerization and no polymerization). These data indicate that (1) plasma polymerization is nonspecific, and (2) not all the polymerization mechanisms discussed in Chapter 5 seem to apply to plasma polymerization. Thus, the direct initiation of polymerization by a cation formed by the ionization of an organic molecule is very unlikely, and cationic (chain-growth) polymerization can be ruled out as a possible plasma polymerization mechanism.

6.1.3 DOSE-RATE (INITIATION-RATE) DEPENDENCE

As another important comparison to radiation polymerization, the dose-rate dependence of polymerization should be considered for plasma polymerization. As mentioned in Section 5.3, in radiation polymerization by the free radical mechanism (in the presence of impurities), the rate of polymerization is proportional to the square root of the dose rate, and the degree of polymerization is inversely proportional to the square root of the dose rate.

In plasma polymerization, the empirical deposition rate of polymer is dependent on energy input (e.g., discharge wattage); however, there are two distinctly different cases insofar as the dependence of polymer deposition rate on the discharge power is concerned, and the dependence in both cases differs significantly from that in radiation polymerization.

Plasma polymerization can be generally divided into two cases according to the rate-determining process dictated by the experimental conditions. These are (1) the flow-rate-controlled case and (2) the discharge-power-controlled case. In the former case, ample electric power is provided, and the rate-determining factor of the process is the monomer feed-in rate, and in the latter case, ample monomer is available but the power input rate is the rate-determining factor. In the former case, the polymer deposition rate is independent of the discharge power, that is,

$$\text{Polymer deposition rate} \propto (\text{initiation rate})^0,$$

and in the latter case, the polymer deposition rate is proportional to the discharge power, that is,

$$\text{Polymer deposition rate} \propto (\text{initiation rate})^1.$$

These dose-rate dependencies indicate again that the basic mechanisms of polymer formation are completely different from those applicable to radiation polymerization.

Another important implication of the dose-rate dependence of polymerization can be pointed out. What kind of polymer could be formed by plasma polymerization if one intuitively assumed that the same principle that is applicable to radiation polymerization applied to plasma polymerization? Westwood pointed out, on the basis of the radiation yield (G value) of polymerization, that the dose rate employed in typical plasma polymerization is 10^6 times greater than the typical dose rate used in radiation polymerization (3).

If one applies this figure to the dose-rate dependence of the degree of polymerization [i.e., $(\text{dose rate})^{-1/2}$ dependence], the degree of polymerization is found to be of the order of one one-thousandth that obtained by radiation polymerization in nearly all practical cases. This turns out to be less than 1,

because the degree of polymerization obtainable by radiation polymerization is usually smaller than 1000. Thus, even if chain-growth radiation polymerization were possible, the polymer could not be formed at such a high dose rate, the recombination of primary free radicals would predominate.

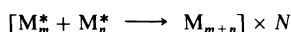
In reality, at such a high dose rate, polymer would be formed by different mechanisms, as evidenced by plasma polymerization. In this sense, the study of plasma polymerization would lead to a prediction of what one could expect if the dose rate in radiation polymerization were increased by a few orders of magnitude. Namely, in such a case, the square root dependence on the dose rate would not be obeyed, and polymers would be formed by the rapid step-growth mechanism.

6.2 Growth Mechanism of Plasma Polymerization

The discussions presented so far suggest that chain-growth polymerization, represented by

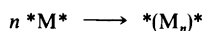


where M^* is the reactive chain-carrying species and M the monomer molecule, would not play a significant role in plasma polymerization and also that the growth mechanism of plasma polymerization would very likely be the rapid step-growth reaction,

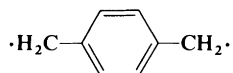


where N represents the number of repetitions of similar reactions. This reaction mechanism differs from conventional step-growth polymerization, in which the reaction occurs between molecules.

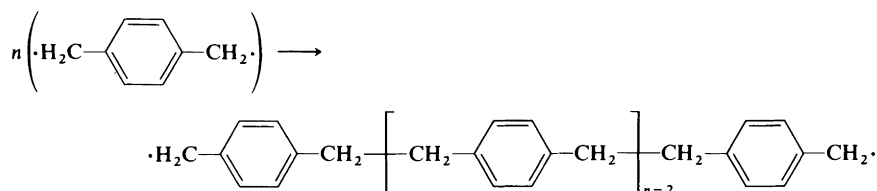
In case of Parylene polymerization, $*M^*$ is a difunctional reactive species and the overall polymerization can be represented by



that is, if we take the diradical form of *p*-xylylene,



the reaction can be written as



(The exact mechanism of the propagation of *p*-xylylene is not well elucidated, and this mechanism is a model representing the rapid step-growth mechanism based on the difunctional reactive species.) Thus, the polymer formed should contain a considerable quantity of unreacted free radicals. It was found that *as*-polymerized polymers of Parylene indeed contain a measurable quantity of free radicals.

If the reactive species represented by M^* is monofunctional, such as a free radical $R^\bullet$, the reaction given by $M_m^\bullet + M_n^\bullet \rightarrow M_{m+n}$ is essentially a termination process that occurs in free radical polymerization and does not contribute to growth without additional elementary steps.

In the case of monofunctional reactive species, a single elementary step is indeed a termination process; in plasma polymerization, however, the product of the reaction is not immune to the activation process that produced the active species considered in the reaction. In other words, the reactivation of the product of an elementary reaction is bound to occur in plasma, as pointed out by Yasuda and Lamaze in 1973 (2).

The overall polymerization mechanism based on the rapid step-growth principle is shown in Fig. 6.1. There M_x refers to a neutral species that can be the original monomer molecule or any of the dissociation products including some atoms such as hydrogen, chlorine, fluorine, and others. The activated species that are capable of participating in the chemical reaction to create a covalent bond are given by $M^\bullet$. Difunctional activated species are shown by $\bullet M^\bullet$. The subscripts *i*, *j*, and *k* merely indicate the difference in the size of

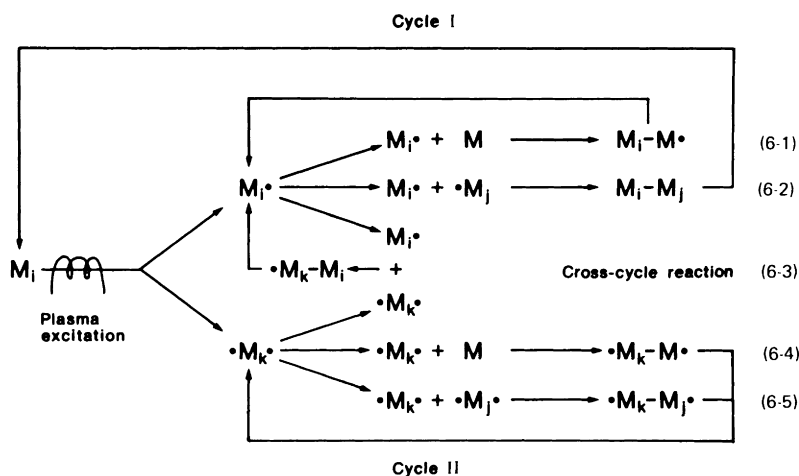
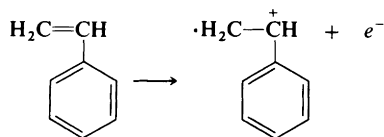


Fig. 6.1 Schematic representation of bicyclic step-growth mechanism of plasma polymerization.

species involved ($i = j$ is possible); thus, $i = j = 1$ corresponds to the original monomer.

Although the activated species are represented by the symbol for a free radical, for simplicity and reasons to be explained later, any activated species can be considered in the reactions shown in Fig. 6.1. For instance, the opening of a double bond by ionization produces an ion-radical, as shown in Sec-



tion 5.3. The ionization of styrene yields a cation-radical, represented by the symbol $\cdot\text{M}^+$, indicating that the species has two reactive sites. Thus, the opening of a double bond and of a cyclic structure in plasma (not by the addition of a reactive species) produces the difunctional reactive intermediate $\cdot\text{M}^+$.

As shown in Fig. 6.1, the overall reaction contains two major routes of rapid step growth. Cycle I is via the repeated activation of the reaction products from monofunctional activated species, and cycle II is via difunctional or multifunctional activated species similar to what is found in Parylene polymerization. As shown in later sections, plasma diagnostic analysis indicates that ample difunctional species such as $\cdot\text{CH}_2\cdot$ and $\cdot\text{CF}_2\cdot$ are found in plasmas of organic compounds. Therefore, it seems likely that cycle I and cycle II may play equally significant roles. In both cases, however, the growth mechanism of polymerization is rapid step-growth polymerization (RSGP).

Chain-growth polymerization carried by the activated species, particularly free radicals, of certain monomers is possible under certain conditions. For instance, if the plasma polymerization of a vinyl monomer such as styrene were carried out at high vapor pressure and low substrate temperature (low enough to condense the liquid monomer), addition polymerization by the activated species created in plasma would occur. The infrared (IR) spectrum of the plasma polymer of styrene carried out under such conditions indicates that the polymer is almost identical to conventional polystyrene.

Reactions (6-1) and (6-4) in Fig. 6.1 are essentially the same as the first step of propagation by the addition mechanism. Therefore, those reactions require a chemical structure that allows for the addition of M^+ . For the reasons mentioned in Chapter 5, consecutive addition to a sizable kinetic chain length does not occur in a vacuum. Reaction (6-2) is essentially a termination by the recombination mechanism. Reaction (6-3) is similar to reaction (6-2), but one reactant is bifunctional. The loss of a reactive site due to disproportionation in free radical polymerization can be included in reactions (6-2) and (6-3). Reaction (6-4) is the same as reaction (6-1), except that a reactant is

bifunctional. Reaction (6-5) is a combination of bifunctional intermediates, which may play a major role in certain monomers under certain conditions. This reaction represents the principal growth mechanism in the Parylene polymerization discussed in Section 5.4.2. Some of the reactions involved may be identical to those in free radical addition polymerization; a major distinction, however, is the absence of the chain-growth mechanism.

If we examine these mechanisms further, the types of activated species, $M\cdot$, that can contribute to this kind of RSGP become clear. Namely, ionic species can contribute in this scheme via the reaction between a cation and an anion, that is, $M_i^+ + M_k^- \rightarrow M_{i+k}$, because M^+ cannot react with M^+ , and M^- cannot react with M^- , due to the similar charge they carry.

As discussed in Chapter 4, in most plasma, the number of positive ions, n_+ , is equal to the number of electrons, n_e . Therefore, such a contribution of ionic species would be possible only in plasma that contained a considerable quantity of negative ions (i.e., plasma containing negative ions of halogens and/or oxygen). Thus, it seems quite probable that plasma polymerization proceeds mainly via reactions of neutral species (4), although ions do indeed exist in plasma.

6.3 Reactive Species in Plasma Polymerization

Although plasma cannot be created without ionizing monomer molecules used for plasma polymerization, it is more appropriate to consider plasma polymerization as a side reaction of the ionization process. Without recognition of this situation, some plasma diagnostic data cannot be appropriately interpreted. Namely, one falls into the situation in which everything found in a plasma must be correlated with the plasma polymerization. It may be, however, that many species in the plasma do not contribute to the plasma polymerization but rather contribute to the ablation. Therefore, it is important to recognize the regime of the plasma polymerization within the overall plasma that exists in the reactor.

Among the possible neutral activated species that can participate in the RSGP mechanism given by Fig. 6.1, the free radical is the most probable and important species. Direct support for this assumption is the fact that most polymers formed in plasma contain a high concentration of free radicals (i.e., 10^{17} – 10^{20} spins per cubic centimeter). Although a number of possible alternative mechanisms can be written for the presence of free radicals in plasma polymers, the most probable one is based on this polymer formation mechanism.

Direct proof that the residual free radicals involved in the RSGP mechanism remain in the polymer as trapped free radicals can be seen in Parylene polymerization, in which an alternative mechanism such as the