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Plasma for Modification of Polymers

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ABSTRACT

The effect of nonpolymer-forming plasma (e.g., plasma of hydrogen, helium, argon, nitrogen) can be viewed as the following two reactions: 1) reaction of active species with polymer, and 2) formation of free radicals in polymer which is mainly due to the UV emitted by the plasma.

The incorporation of nitrogen into the polymer surface by N₂ plasma and the surface oxidation by O₂ plasma are typical examples of the first effect. The latter effect generally leads to incorporation of oxygen in the form of carbonyl and hydroxyl and to some degree of cross-linking depending on the type of substrate; however, the degradation of polymer at the surface manifested by weight loss occurs in nearly all cases when polymers are exposed to plasma for a prolonged period of time.

The effects of polymer-forming plasma is predominated by the deposition of polymer (plasma polymer); however, with some plasma-susceptible polymer substrates the effect of UV emission from polymer-forming plasma cannot be neglected. The mechanism of polymer formation can be explained by the stepwise reaction of active species and/or of an active specie with a molecule, and the chain addition polymerization of some organic compounds (e.g., vinyl monomers) is not the main route of polymer formation.

Plasma polymers contain appreciable amount of trapped free radicals; however, the concentration is highly dependent on the chemical structure of the monomer. In plasma polymerization, 1) triple bond and/or aromatic structure, 2) double bond and/or cyclic structure, and 3) saturated structure are three major functions which determine the rate of polymer formation and the properties of plasma polymers. The changes of some properties of plasma polymers with time are directly related to the concentration of trapped free radicals in plasma polymers. The amount of trapped free radicals in a plasma polymer is also influenced by the conditions of discharge; however, the UV irradiation from the polymer-forming plasma is not the main cause of these free radicals. Excess amount of free radicals are trapped during the process of polymer formation (rather than forming free radicals in the deposited polymer by UV irradiation). The properties of a plasma polymer is generally different from what one might expect from the chemical structure of the monomer, due to the fragmentation of atoms and/or functions during the polymerization process. This is another important factor to be considered for the modification of polymer surfaces by plasma polymerization.

INTRODUCTION

Plasma in the modern definition refers to the more or less ionized gas. Plasma which can be used in the modification of polymer (surface) is often referred to as "low-temperature plasma" which may be characterized by "less ionized" compared to highly ionized "hot plasma." Plasma created by electric glow discharge, for example, may contain a variety of species which are chemically active or energetic enough to cause chemical reactions; e.g., electrons, ions of both charges, excited molecules at various levels of excitation, free radicals, and photons of various energies.

Plasma chemistry of polymers may be categorized into two major types of reactions as 1) surface reaction of polymers and 2) polymerization of monomers by plasma. So far as these two types of reactions are concerned, plasma is very similar to other ionizing radiation, such as γ radiation, x radiation, UV radiation, and high-energy electron beams, which can 1) initiate polymerization of certain monomers, and create free radicals on polymer exposed, which lead to 2) cross-linking of the polymer and/or 3) degradation of the polymer, or can be further utilized as the initiation sites of 4) graft copolymerization.

The characteristic features of plasma are 1) the radiation effect is limited to the surface, and the depth of the layer affected by the plasma is much smaller than that by other more penetrating radiation, and 2) the intensity at the surface is generally stronger than that by the more penetrating radiations. Therefore, plasma treatment provides an ideal means of modifying surface properties of polymers.

GAS PLASMA TREATMENT OF POLYMERS

The major reactions of gas plasma (such as of argon, helium, nitrogen, and oxygen) with organic polymers may be considered as:

1. Direct reaction of activated gases (e.g., surface oxidation by oxygen plasma and nitrogen incorporation by nitrogen plasma).
2. Formation of free radicals and the subsequent reaction of the free radicals (e.g., surface etching, degradation, oxygen incorporation, and graft copolymerization).

Which one of the above reactions that will predominate in the plasma treatment of polymers depends on the combination of 1) type of gas and 2) chemical structure of the polymer.

Typical examples of the first may be seen with polyethylene and polytetrafluoroethylene (Teflon) treated with N_2 and Ar plasma. In Fig. 1 are shown Electron Spectroscopy for Chemical Analysis (ESCA) spectra of polyethylene samples treated with N_2 plasma and Ar plasma, and of the control (untreated sample). Peak heights of these spectra are shown in Table 1. The control shows a symmetrical peak of C 1s at 286.5 eV (peak height, 106,000 counts/scan) and very small peak of O 1s at 534 eV (peak height, 3930 counts/scan). With the Ar-plasma-treated sample, the C 1s peak decreases to 67,000 counts/scan and shows slight widening of the peak toward the high-binding energy side, but no appreciable new shoulder or peak. The O 1s peak increases to 33,100 counts/scan, indicating the obvious incorporation of oxygen at the surface. The appearance of a very small N 1s peak with Ar-plasma-treated sample lacks explanation, but the level of N_2 incorporation is insignificant.

With the N_2 -plasma-treated sample the significant level of nitrogen incorporation is evident. The appearance of a shoulder at 288.5 eV on the C 1s peak may reflect the existence of carbon attached to N. The extent of oxygen incorporation (peak height, 22,500 counts/scan) is significantly lower than that caused by Ar plasma treatment (peak height, 33,100 counts/scan). The similar effects of oxygen incorporation and nitrogen attachment are also observed with Teflon; however, the more dramatic change of C 1s peaks is clearly seen due to the strong chemical shift caused by

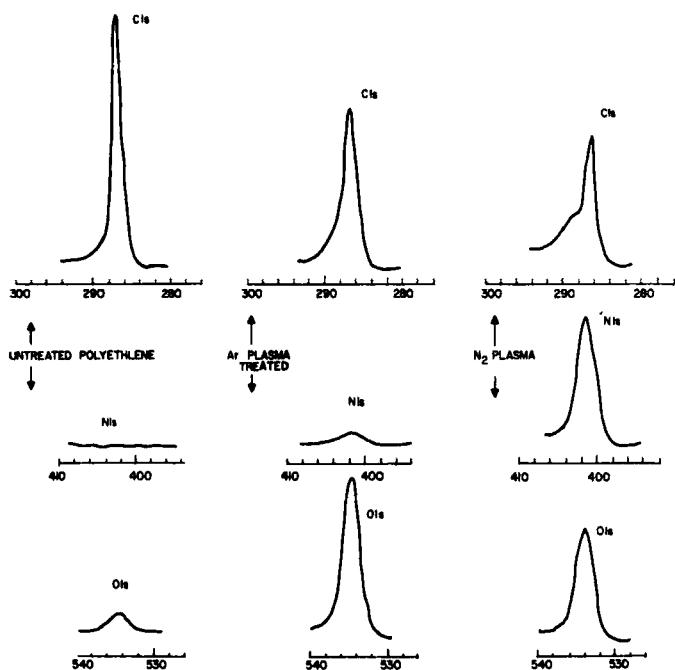


FIG. 1. ESCA spectra (C 1s, N 1s, and O 1s) of polyethylene samples treated with Ar and N₂ plasma.

TABLE 1. Effect of N₂ and Ar Plasma Treatment on ESCA Spectra (given by counts per scan) of Polyethylene

Polymer sample	C 1s		N 1s, 401 eV	O 1s, 534 eV
	288.5 eV shoulder	286.5 eV		
Control	-	106,000	-	3,930
Ar-plasma-treated	-	67,600	2,900	33,100
N ₂ -plasma-treated	(15,700)	52,900	26,300	22,500

the strong binding energy of fluorine. ESCA spectra of C 1s peaks that are observed with Teflon films are shown in Fig. 2, and peak heights are shown in Table 2.

The loss of fluorine atoms from the surface by Ar plasma treatment is evidenced by the decrease of the F 1s peak (peak height decreases from 328,000 counts/scan for the control to 73,700 counts/scan for Ar-plasma-treated sample), and by the change of C 1s peaks. The majority of carbon in Teflon shows a C 1s peak at 295.5 eV. The small peak at binding energy corresponding to ordinary carbons (at 287 eV) might be indicating some degree of oxidation of the surface, since a small peak of O 1s is also found, or the appearance might be due to the artifact due to x radiation damage during the measurement, since spectra

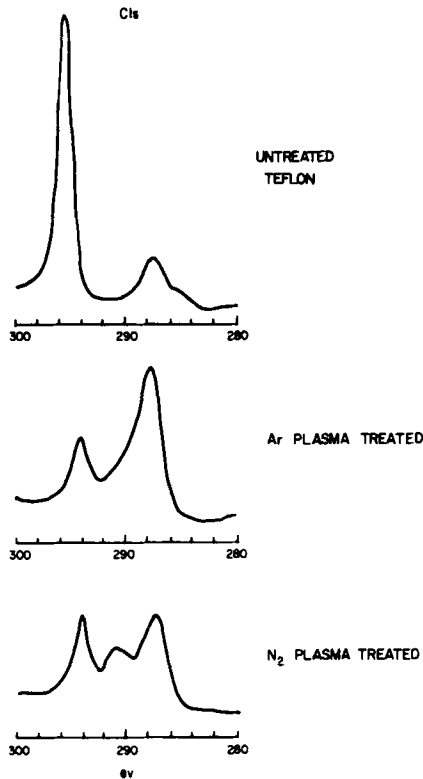


FIG. 2. ESCA C 1s peaks of Teflon samples treated with Ar and N₂ plasma.

TABLE 2. Effect of N₂ and Ar Plasma Treatment on ESCA Spectra (given by peak heights in counts per scan) of Polytetrafluoroethylene

Polymer sample	C 1s				F 1s, 693 eV	N 1s, 403 eV	O 1s, 535.5 eV
	295.5 eV	294 eV	290.5 eV	287 eV			
Control	41,000	-	-	6,830	328,000	-	2,990
Ar-plasma-treated	-	10,240	-	21,500	75,100	1,880	17,600
N ₂ -plasma-treated	-	11,900	7,850	14,000	73,700	12,800	13,300

were taken by two scans. A more careful examination of the latter effect is in progress, and the results will be presented elsewhere.

The plasma treatments cause not only the decrease of the C 1s peak at higher binding energy, but they also cause the shift of the peak from 295.5 to 294 eV, which might indicate a decrease of the number of fluorine attached to a carbon. Here again, the oxygen incorporation is higher with Ar-plasma-treated sample than with N₂-plasma-treated sample, and the nitrogen attachment to the surface is clear in both the appearance of the N 1s peak and of a new peak of C 1s spectra.

The nitrogen attachment may represent the direct reaction of activated gases, and the oxygen incorporation by Ar plasma may represent the formation of free radicals and the subsequent reaction of the free radicals. The latter effect, particularly the formation of free radicals, can be more directly investigated by Electron Spin Resonance (ESR) spectroscopy, and some of the results obtained by ESR studies seem to cast more insight into the mechanism of free-radical formation by plasma treatment.

In order to investigate the possible mechanism of free-radical formation, a series of experiments to elucidate the location of free radicals were carried out recently [1, 2], and their results may be briefly summarized as follows.

ESR signals are examined with glass rods coated with polymer which are exposed to N₂ plasma, and the signals in the polymer layer and in the glass are distinguished by subtracting the ESR signal due to the spins in the polymer by wiping off the polymer coating. The results of the experiments carried out with polyethylene-coated tubes are shown in Table 3. The situation involved in the experiment is schematically represented in Fig. 3. The thickness of polyethylene coating is of the order of 3 to 10 μm, and the glass rod does not directly contact the N₂ plasma. If the plasma treatment as manifested by the formation of free radicals is limited to the interface of plasma and polymer, all free radicals should be concentrated at the surface of the polyethylene coating.

The results indicate that 1) not many free radicals are formed in the polyethylene layer, and 2) free radicals are formed in the glass which did not contact the plasma. The small amount of free radical in the polyethylene layer may in part be due to the quick reaction of free radicals after the sample is exposed to air for ESR measurement; however, the fact that strong signals come from free radicals in the glass strongly indicates that free radicals are formed by some energetic species which have some penetrating capability. Therefore, electrons (low energy), ions, and excited gas molecules do not seem to be responsible for the formation of the majority of free radicals by plasma. This effect is not limited to the N₂ plasma, for similar results are obtained with hydrogen plasma.

TABLE 3. ESR Signals Observed with Polyethylene-Coated Glass Tubes Exposed to N₂ Glow Discharge (120 μmHg)

PE coating mass (mg)	PE coating thickness (μm)	Plasma gas	Plasma power (W)	Time of exposure to plasma (hr)	Time of subsequent exposure to air (hr)	EPR signal intensity (a.u.) ^a
4.6	2.6	N ₂	75	1	0.25	5.2
					20	4.9
					20	4.1
Wipe off polyethylene coating						
6.2	3.5	N ₂	75	1	0.17	2.2
Wipe off polyethylene coating						
12	6.8	N ₂	75	0.17	0.17	0
17.3	9.3	N ₂	75	1	0.33	1.9
14.4	7.8	N ₂	75	1	0.17	1.4
15.2	8.2	H ₂	100	0.33	0.25	1.5
No PE		H ₂	100	0.33	0.17	32

^a Arbitrary unit.

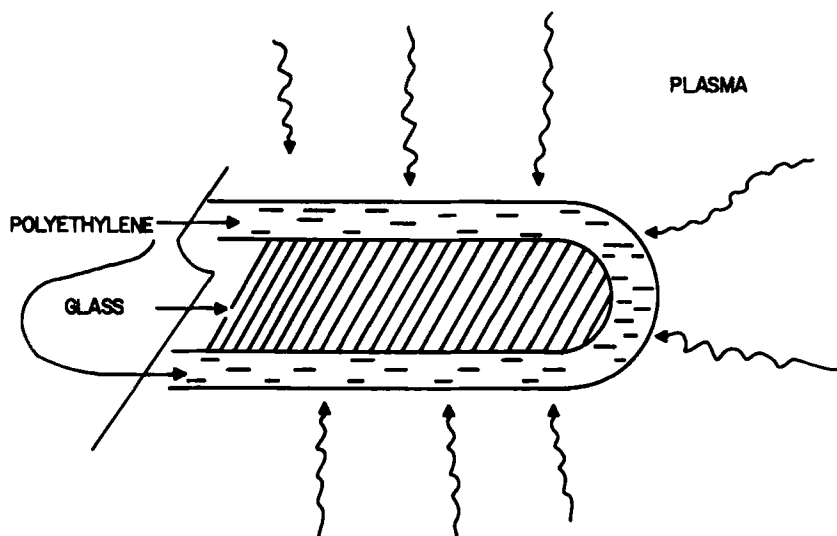


FIG. 3. Schematic representation of ESR probe used for the investigation of the location of free radicals formed by plasma.

The above observations strongly suggest that UV emission from plasma (glow discharge) may be the primary cause of the free radical formation by plasma. This scheme of free-radical formation is supported by the experiments in which a glass rod is encased inside a sealed tube. The situation involved in this experiment is schematically shown in Fig. 4. The glass rod (ESR probe) is enclosed in a quartz or glass envelope with a nitrogen, oxygen, or vacuum environment inside the envelope. The entire sealed tube is placed in a plasma reactor (in vacuum) and is exposed to N_2 plasma. Results of these experiments are shown in Table 4.

Substances that do not absorb UV radiation of wavelengths greater than 1650 \AA (i.e., quartz, vacuum, and nitrogen) result in a substantial spin concentration in the glass rod, whereas the presence of glass or oxygen between the plasma and the glass rod leads to a substantial reduction (oxygen) or complete absence (glass) of free radicals in the glass rod. By these demonstrations it seems clear that free radicals which can be detected by ESR spectroscopy are caused mainly by UV irradiation in glow discharge, and that their population is not limited to the surface.

The free radicals formed on the polymer surface by the exposure to gas plasma can be utilized to initiate graft copolymerization. The mechanism of graft copolymerization is similar to radiation-induced

TABLE 4. ESR Signals Observed with a Glass Rod Placed Inside a Sealed Tube and Subjected to N₂ Plasma (80 μmHg, 120 W)^a

Material of tube	Gas inside	Pressure of gas	Time of plasma treatment (hr)	Signal intensity (a. u.) ^b
Quartz	Vacuum	5×10^{-6} μmHg	3	4.4
Glass	Vacuum	10^{-6} μmHg	3	0
Quartz	Air	1 atm	3	1.0
Glass	Air	1 atm	3	0
Quartz	N ₂	664 μmHg	3	5.2
Quartz	O ₂	678 μmHg	3	1.3
Control, bare glass tube exposed directly to plasma			1	8.7

^aGlow discharge does not contact the glass rod.

^bArbitrary unit.

graft copolymerization; however, the plasma-initiated graft copolymerization yields surface grafting in a more strict sense compared to those obtained by more penetrating radiations.

The interaction of plasma with a polymer surface may be represented by the schematic diagram of reactions shown in Fig. 5. The practical use of plasma in the modification of polymer surfaces (such as cleaning of the surface, cross-linking, increasing bonding strength, and increasing wettability of the surface) depends on the combination of the chemical structure of polymer and the type of gas used; however, the overall effects may be explained by the two major reactions described above.

Nearly all polymers lose weight when they are exposed to plasma, and the rate of weight loss is proportional to the time of exposure and is somewhat dependent on the type of gas used. The weight loss is strongly dependent on the discharge wattage, probably because the UV emission of plasma is highly dependent on the discharge wattage [3]. The weight loss rate of some polymers is shown in Table 5.

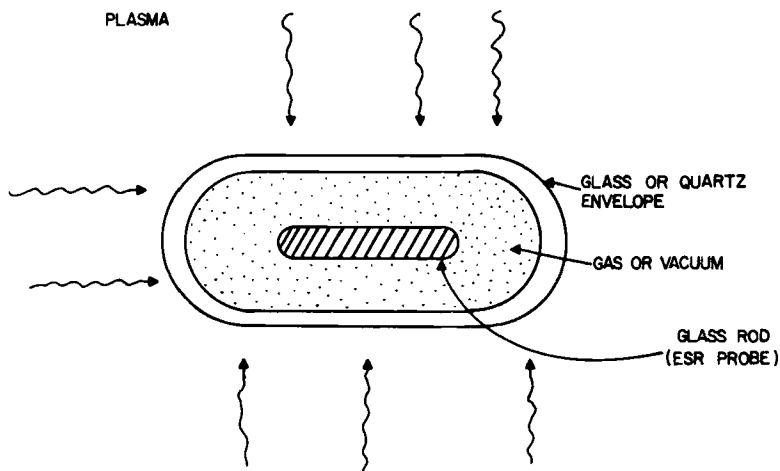


FIG. 4. Schematic representation of ESR probe (glass rod) used for the investigation of effect of UV on the formation of free radicals.

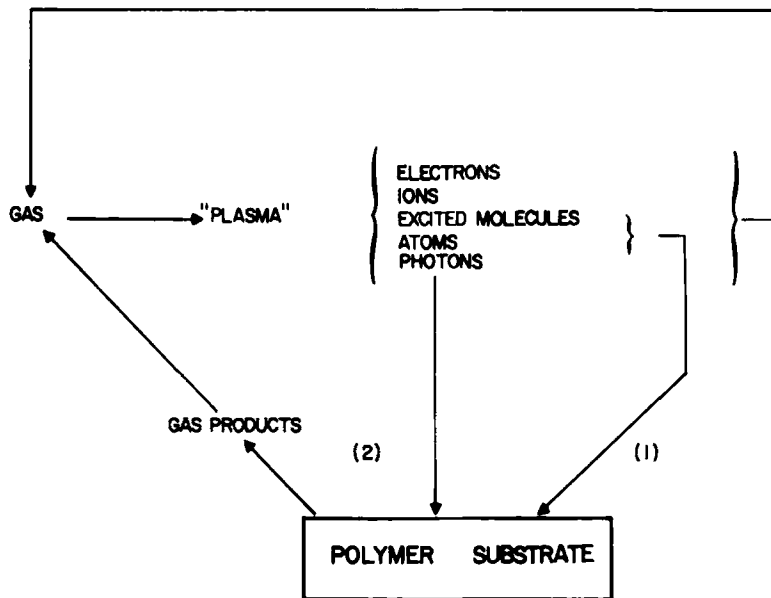


FIG. 5. Schematic representation of the interaction of plasma with a polymer surface.

TABLE 5. Plasma Susceptibility of Polymers Measured by the Rate of Weight Loss in Helium Plasma

Polymer	Weight loss rate ^a (mg cm ⁻² min ⁻¹ × 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

^aHe plasma (100 μmHg) at 30 W.

The change of morphology of the surface by exposure to plasma is more complicated since the localized melting and recrystallization of polymer might occur as superimposed on the surface reactions and the degradation of the polymer. The change of morphology of the surface is highly dependent on 1) type of gas, 2) discharge wattage, and 3) treatment time. Some results showing the change of morphology of the surface are shown in Fig. 6 for (a) untreated polypropylene, (b) polypropylene treated with N₂ plasma (150 μmHg) at 100 W for 60 min, and (c) polypropylene treated with He plasma (150 μmHg) at 100 W for 30 min. It was generally observed that He plasma treatment causes more drastic changes in the morphology of polymer surfaces. In shorter treatments by plasma, the changes in morphology of the surfaces are much smaller and, in many cases, at the negligible level.

PLASMA POLYMERIZATION

When an organic vapor such as of argon or helium is introduced into plasma, or plasma of the organic vapor is created (without

addition of plasma gas), polymerization of the vapor occurs and the polymer deposits. If the polymer deposition is allowed to occur onto an appropriate polymer substrate, the method provides a means of surface coating or surface grafting since such a polymer deposition can be formed as highly cross-linked and strongly bonded to the substrate polymer.

The polymerization of an organic monomer in plasma is quite different from the conventional polymerization of the monomer. Furthermore, polymerization in plasma is dependent on the conditions of plasma, e.g., types of electric discharge and geometrical factors of the reaction vessel. Consequently, the mechanism of polymerization by which an organic vapor polymerizes under the influence of plasma is quite complex and cannot be specifically described for the general case. However, the following aspects seem to apply to nearly all cases, though their relative importance varies depending on conditions.

1. The monomer may undergo considerable decomposition or fragmentation of chemical functions under plasma conditions. For instance, when acrylic acid is polymerized by plasma, the polymer shows a great deficiency of carboxylic acid groups and is rather hydrophobic, indicating fragmentation of carboxylic acid groups during the polymerization.
2. Polymerization proceeds by a unique mechanism under plasma (plasma polymerization).
3. Polymerization of certain monomers (e.g., vinyl monomers) could proceed by the conventional addition polymerization mechanism initiated by active species of plasma (plasma-induced polymerization).

Plasma-induced polymerization can proceed after the plasma is extinguished as long as the monomer is available to the reactive sites (e.g., free radicals) already formed, whereas plasma polymerization proceeds only under plasma conditions. The extent of plasma polymerization and that of plasma-induced polymerization can be visualized by a comparison of the deposition rates of vinyl compounds and their corresponding saturated compounds. Some examples are shown in Table 6.

The deposition rates cited in Table 6 may need further comment. In most work appeared in literature, the deposition rate is given by g polymer/cm²min or g polymer/cm²min at a given flow rate (based on volume of gas); however, the deposition rate given in such a unit does not represent the characteristic polymer formation rate of a specific monomer since the amount of monomer molecules involved in gas phase is not specified. The deposition rate given in such a unit is useful in obtaining a certain thickness of deposition and can be used to compare the polymer deposition rates of various compounds

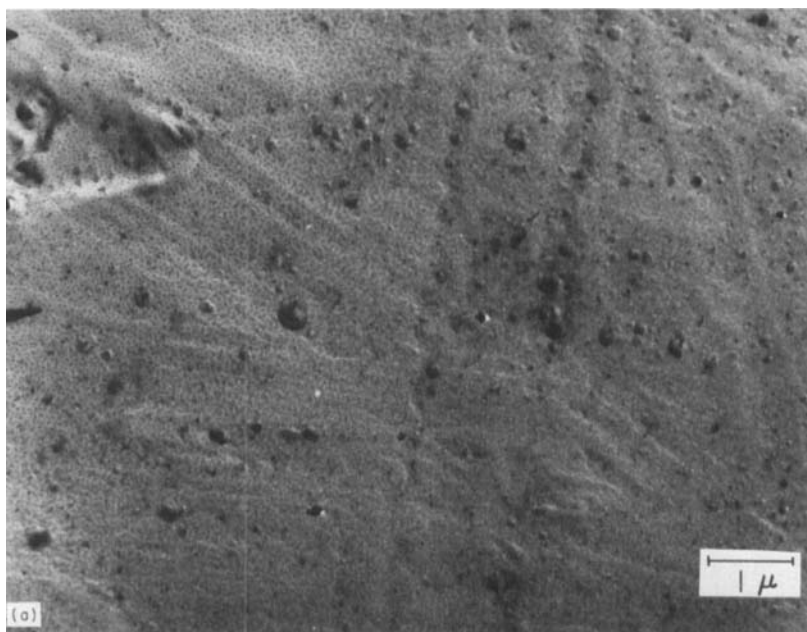


FIG. 6a. Electron microscope picture (transmission) of the surface of untreated polypropylene sample.

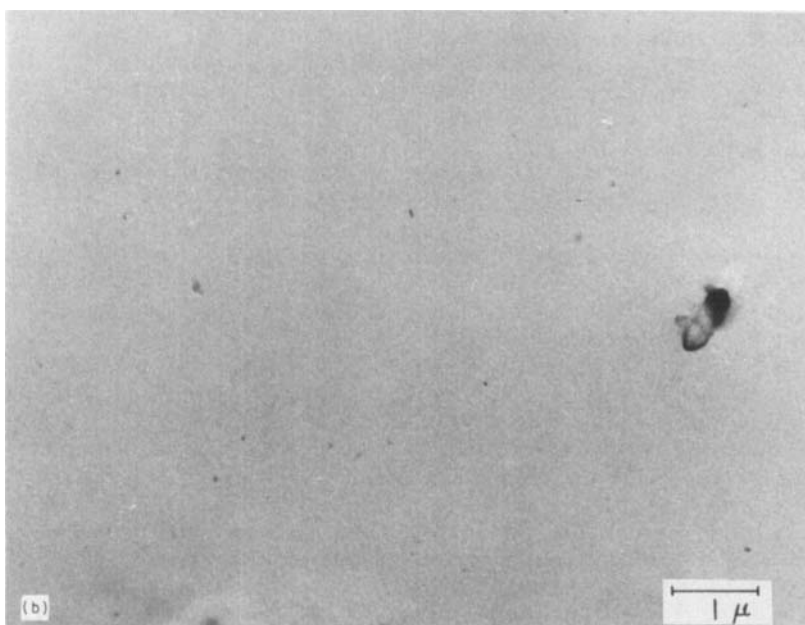


FIG. 6b. Electron microscope picture (transmission) of the surface of polypropylene sample treated with N_2 plasma (100 W, 60 min).

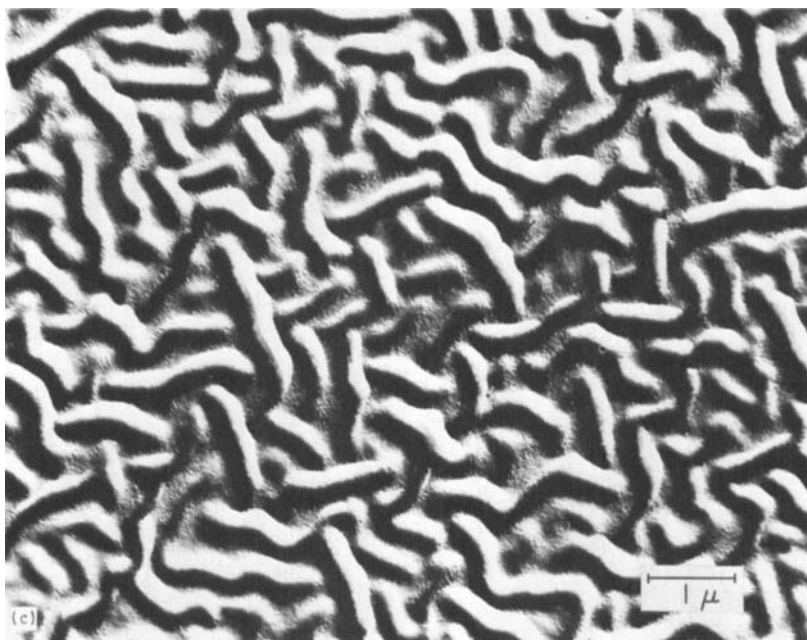


FIG. 6c. Electron microscope picture (transmission) of the surface of polypropylene sample treated with He plasma (100 W, 30 min).

within the same conditions using the same apparatus. The gas flow rate is usually given by the volume, and the volume of gas (STP) represents the number of molecules. On the other hand, the deposition rate is measured by the weight of polymer but not the number of molecules. Therefore, a little more specific deposition rate can be given by the deposition rate based on the weight-basis flow rate. This ideal situation applies only to some systems where the total volume of plasma and the surfaces on which the polymer deposits are well defined [6].

The values of deposition rates for various monomers expressed by the unit based on the volume flow rate are spread over a wider range than those based on weight-basis flow rate as shown in Table 5, since the monomers of higher molecular weight contribute more when they deposit as repeating units of the polymers.

The polymerization of vinyl monomers may be simultaneous polymerization by plasma polymerization and plasma-induced vinyl polymerization. It should also be noted that saturated compounds are not monomers by conventional polymerization mechanisms.

TABLE 6. Comparison of Polymer Deposition Rates^a for Vinyl and Saturated Vinyl Compounds

Compound	Vinyl monomer		Saturated vinyl monomer	
	Compound	$k \times 10^4$ (cm^{-2})	Compound	$k \times 10^4$ (cm^{-2})
4-Vinylpyridine		7.59	4-Ethylpyridine	4.72
α -Methylstyrene		5.33	Cumene	4.05
Styrene		5.65	Ethylbenzene	4.52
N-Vinylpyrrolidone		7.75	N-Ethylpyrrolidone	3.76
Acrylonitrile		5.71	Propionitrile	4.49
Vinylidene chloride		5.47	1,1'-Dichloroethane	2.98
Allylamine		2.86	n-Butylamine	2.52
Methyl acrylate		0.99	Methyl propionate	0.57

^a Polymer deposition rate R in $\text{g}/\text{cm}^2 \cdot \text{min}$ is given by $R = kF_w$; F_w is the weight basis flow rate (g/min) [4, 5].

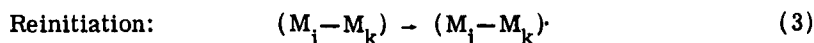
Nevertheless, the polymer deposition rates of these two groups of monomers are by and large the same, indicating that plasma polymerization rather than plasma-induced polymerization is responsible for a major portion of polymer formation.

This implies that any reaction scheme of addition, irrespective of the reactive intermediate—such as (shown by free radical as the reactive intermediate specie) $R \cdot + M \rightarrow RM \cdot$ for the formation of polymer—does not play a major role in plasma polymerization.

The detailed mechanism of plasma polymerization is not well understood. However, it seems to be quite reasonable to rule out, as the major polymerization routes, the polymerization mechanisms that include plasma-induced polymerization in which the growth of molecular weight is solely dependent on the addition of reactive intermediate species (such as free radicals, cations, and anions) onto the monomer molecules. The question of what kinds of reactive species (i.e., ions or free radicals) are involved in plasma polymerization is not the main issue at this point. Due to the complexity of glow discharge conditions, and also due to the variety of reactive species involved in the actual process of polymer formation under plasma conditions, many species can possibly contribute to the polymerization. In view of the utilization of glow-discharge polymerization for the modification of polymer surfaces, knowledge both of the chemical structure of organic compounds which can be easily polymerized by glow discharge and of the properties of the polymer formed (in relation to the chemical structure of the monomer) are vitally important regardless of the polymerization mechanism.

In order to emphasize the characteristic difference of plasma polymerization from plasma-induced polymerization, the following polymerization mechanisms are presented by using the free radicals as the reactive species; however, the free radicals shown in certain reactions may be replaced by any other reactive species or molecules as long as the rapid propagation by chain reactions is ruled out.

Polymerization of organic compounds in a glow system by an electrodeless glow discharge has been recently reported [4, 5]. In these studies the rates of polymer deposition from various organic vapor plasmas in the tail flame (glow region) of an electrodeless discharge by 13.56 MHz rf were studied as a function of flow rate and discharge power. It was generally observed under the conditions used that the rate of polymer deposition is proportional to the monomer feed-in rate. It was proposed that polymerization of an organic compound in a glow discharge proceeds mainly by the coupling of primary radicals (or excited species) generated by the ionization of monomer vapor. According to this concept, the polymerization may be represented by the following steps:



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

According to this reaction scheme, the glow-discharge polymerization corresponds to radiation-induced polymerization at an extremely high dose rate. Westwood et al. [7] have estimated that the dose rate in glow discharge is 10^6 times higher than the ordinary dose rate used in γ -ray irradiation. At an extremely high dose rate of irradiation, the concentration of primary radicals increases and, consequently, in a flow system the concentration of (unexcited) monomer decreases. Therefore, the recombination of primary radicals is favored over the propagation of a radical via addition onto vinyl or olefinic double bonds. Consequently, vinyl compounds and saturated vinyl compounds polymerize by nearly the same rate (in order of magnitude) as shown in Table 6.

It was also found that fragmentation of some organic compounds occurred in glow discharge and that the extent of fragmentation was related to certain structural features of organic compounds [4, 5]. Since the fragmentation of organic compounds shown by the pressure increases in a glow discharge is not directly correlated to the lower rate of polymer deposition, it is extremely interesting to investigate the cause of the pressure increase of certain organic compounds in glow discharge.

Studies of the polymerization of hydrocarbon [8] and some nitrogen-containing compounds [9] in a closed system have been recently carried out in order to obtain information about glow-discharge polymerization which might relate to the properties of the polymers. The details of experimental procedures and results will be seen in the references, and only a brief digest is presented here.

If the polymerization of hydrocarbon in a glow discharge can be represented by Reactions (1), (2), and (3), the analysis of the gas phase would provide important information concerning the type of radicals that are formed and participate in polymerization. Free radicals can be formed from a hydrocarbon molecule (which

contains only carbon and hydrogen) by three possible steps: (a) opening a double or triple bond, (b) hydrogen abstraction, and (c) cleavage of a C—C bond.

The contribution of these three possible steps can be conveniently investigated by measuring the change of pressure of a closed system, since the pressure of a fixed volume represents the number of gas molecules in the system. In such a closed system the decrease of pressure is caused only by polymerization, which transforms organic molecules in the vapor phase to solid deposition on the surface.

The types of radical formation can be related to the pressure change of a closed system in the following cases:

1. If polymerization proceeds via recombination of radicals formed by the opening of a double bond (or a triple bond), the polymerization would lead to the decrease of pressure and no hydrogen production, since the opening of a double bond per se does not change the total number of molecules.
2. If radicals are formed by only hydrogen abstraction, the total pressure of the system will remain constant, since the production of hydrogen gas molecules compensates for the loss of an organic molecule due to the polymerization.
3. The cleavage of a C—C bond of a cyclic compound will be similar to the opening of a double bond so far as the pressure change of the system and the production of hydrogen molecules are concerned; i.e., a decrease in pressure and no hydrogen production.
4. The cleavage of a C—C bond in a noncyclic molecule will not contribute to the formation of a polymer and cannot be considered as a main step of polymerization.

The investigation of the pressure change of a closed system and the estimation of hydrogen production, therefore, would provide further information pertaining to the mechanism of polymerization.

As it turned out, nitrogen in most nitrogen-containing organic compounds is retained in the glow-discharge polymers although the original chemical bond may not be retained. Consequently, the situations discussed above for hydrocarbons also apply to amines and nitriles. Glow-discharge polymerization of hydrocarbons, amines, and nitriles can be characterized by the numbers of hydrogen liberated by the polymer formation; this is expressed by "hydrogen yield" (numbers of hydrogen gas liberated from a molecule of monomer during the process of glow-discharge polymerization). In conventional addition polymerization of vinyl compounds, no hydrogen is liberated in the polymer formation (i.e., hydrogen yield = 0).

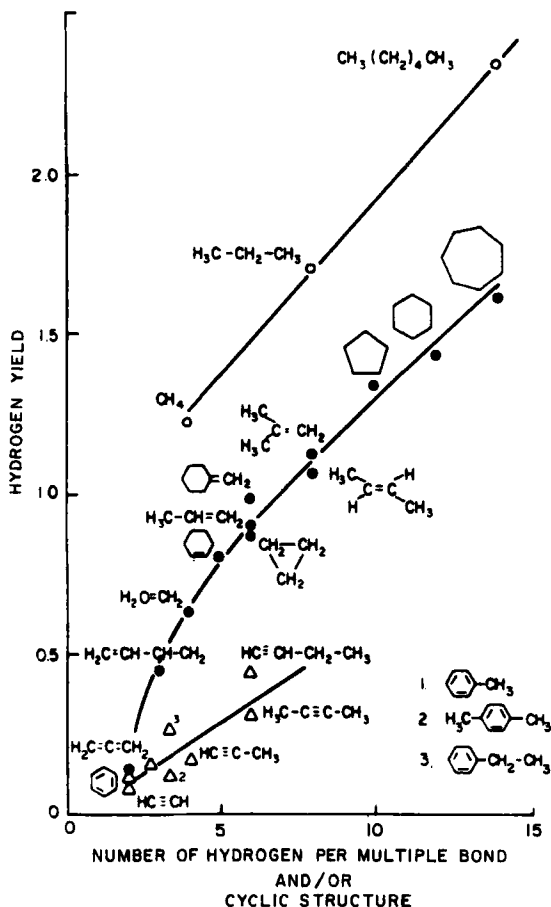


FIG. 7. Hydrogen yield observed with the plasma polymerization of organic compounds.

In Fig. 7, hydrogen yield as a function of the numbers of hydrogen in the monomer molecules per multiple bond and/or cyclic structure are shown for hydrocarbons. These results indicate the following important features of glow-discharge polymerization:

1. Compounds with olefinic double bonds show a relatively high hydrogen yield, indicating that the contribution of polymerization by the opening of double bonds is surprisingly small. In the cases of ethylene and propylene, the role of hydrogen abstraction is almost equal that of the double-bond opening.

2. The more striking fact is that compounds with triple bonds or conjugated double bonds polymerize with a very small hydrogen yield. This means that the polymerization of aromatic compounds must proceed by the opening of double bonds in the benzene ring.
3. The hydrogen yield of cyclic compounds is smaller than that of corresponding normal compounds. The contribution of the opening of a cyclic structure to polymerization is similar to that of an olefinic double bond, as seen in Fig. 7.

It seems to be extremely important to reckon that the hydrocarbons can be grouped into three characteristic groups as shown in Fig. 7. The very smooth increase of hydrogen yield (within a group) as a function of the number of hydrogen atoms in the monomer suggests that the following three major routes of polymerization occur simultaneously in plasma polymerization; i.e., free radical formation by 1) hydrogen detachment, 2) opening double-bond and cyclic structure, and 3) opening triple-bond (including $C\equiv N$) and aromatic and heteroaromatic structures. With these initiation mechanisms the overall mechanisms of polymer formation by glow discharge seem to be well represented by the scheme shown by Reactions (1), (2), and (3).

This scheme of plasma polymerization via stepwise recombination of free radicals also suggests that many small molecules which are not considered as "monomer" in general polymerization can be copolymerized or incorporated into the plasma polymers. It is indeed found that unusual comonomers such as N_2 , CO, and H_2O can be used in copolymerization with organic compounds. Such a copolymerization is particularly efficient with monomers containing triple-bond, double-bond, or aromatic structures. Some of the results pertaining to this effect are shown in Table 7 and Figs. 8 and 9. The details of the copolymerization or the incorporation of these gases and vapor can be seen in Refs. 10 and 11.

The plasma-polymerization mechanism with stepwise recombination of free radicals and reexcitation of the recombination products shown above also explains the existence of free radicals in the plasma polymers. Free radicals in the plasma polymer could be introduced by UV irradiation of the polymer-forming plasma since this seems to be the main cause of free-radical formation in polymers exposed to plasma. However, this mechanism does not seem to play a major role as can be seen by the set of experiments described below.

It is found that the ESR signals of glass tubes on which plasma polymers are deposited consist of signals of plasma polymer and also of the glass signal [1]. There is a clear correlation that the higher the ESR signal of polymer, the lower is the ESR signal of glass and vice versa. For instance, when plasma polymer of

TABLE 7. Results of Elemental Analysis of Some Plasma Polymers

Plasma polymer of	% Elements found				Empirical formula of repeating unit	
	C	H	N	O		
Acrylonitrile	59.16	5.61	24.68	10.55	-	$C_3H_3N_1O_{0.4}$
Propionitrile	55.19	7.3	18.56	18.95	-	$C_3H_{4.7}N_1O_{0.8}$
Propylamine	63.23	8.89	18.02	9.86	-	$C_3H_5N_1O_{0.4}$
Allylamine	60.48	7.86	18.43	13.23	-	$C_3H_{4.7}N_1O_{0.4}$
Ethylene	74.13	8.11	-	17.77	-	$C_2H_{2.6}O_{0.4}$
Ethylene/N ₂	49.38	6.26	18.51	25.85	-	$C_2H_3N_{0.6}O_{0.8}$
Allene	78.26	8.13	-	13.61	-	$C_3H_{3.7}O_{0.4}$
Allene/H ₂ O	73.15	8.63	-	18.22	-	$C_3H_{4.2}O_{0.6}$
Allene/N ₂	62.68	6.71	17.73	12.88	-	$C_3H_{3.8}N_{0.7}O_{0.5}$
Allene/N ₂ /H ₂ O	63.77	7.86	10.79	17.58	-	$C_3H_{4.4}N_{0.45}O_{0.5}$
Acetylene	79.5	5.4	-	15.1	-	$C_2H_{1.6}O_{0.3}$
Acetylene/N ₂	64.0	5.8	16.7	13.5	-	$C_2H_{2.2}N_{0.5}O_{0.3}$
Acetylene/H ₂ O	66.5	7.6	-	25.9	-	$C_2H_{2.7}O_{0.6}$
Acetylene/N ₂ /H ₂ O	53.2	6.5	15.7	24.6	-	$C_2H_{2.9}N_{0.5}O_{0.7}$
Ethylene oxide	72.6	9.0	-	18.4	-	$C_2H_{2.9}O_{0.4}$
Hexamethyldisiloxane	30.0	7.5	-	22.2	40.2 (Si)	$C_{3.5}H_{10.5}Si_2O_2$
Tetrafluoroethylene	27.8	-	-	5.28	66.92 (F)	$C_2F_3O_{0.3}$

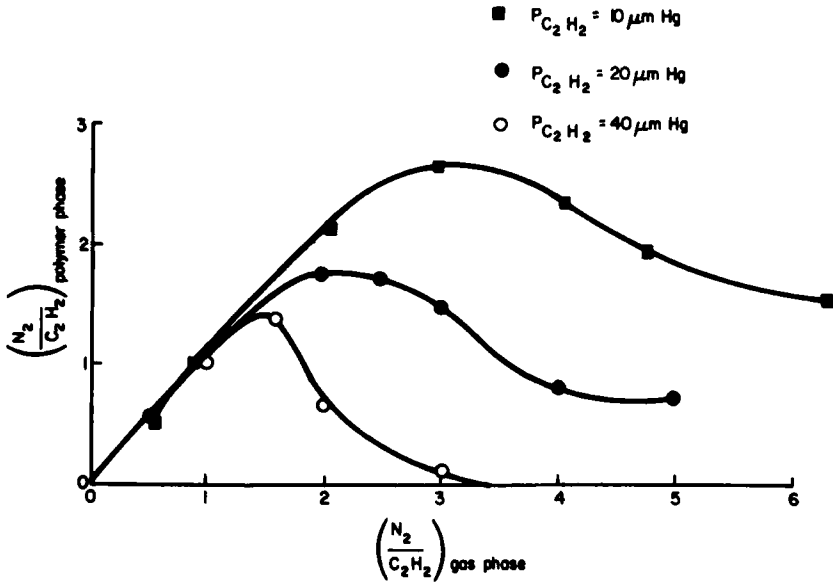


FIG. 8. The amount of N_2 incorporated into the plasma polymers of acetylene and nitrogen as functions of the ratio of N_2/C_2H_2 in the gas phase.

acetylene is deposited onto a glass tube, the entire signal observable by ESR is the polymer signal, and no glass signal can be detected. With plasma polymer of acetylene/ H_2O , on the other hand, the entire ESR signal is glass signal, and no polymer signal can be detected. Should UV irradiation play the major role, there must be a great difference in the UV absorption characteristics of these polymers; i.e., the plasma polymer of acetylene should have a high absorption of UV, and the plasma polymer of acetylene/ H_2O should be transparent to UV. However, the UV absorption characteristics (to wavelength of 1600 Å) of these two polymers are nearly identical.

The absence of any significant difference between the UV spectra of these polymers, which cover a wide variation in the ability to induce free radicals in the substrate, suggests that the cause of free radicals formed in the substrate exposed to the polymer-forming plasma is to be found in the emission characteristics (especially UV emission) of the (polymer-forming) plasma rather than in the UV absorption (protective) characteristics of the polymer deposits. By the same token, the variation in the concentration of free radicals in plasma polymer is to be found in the plasma-polymerization

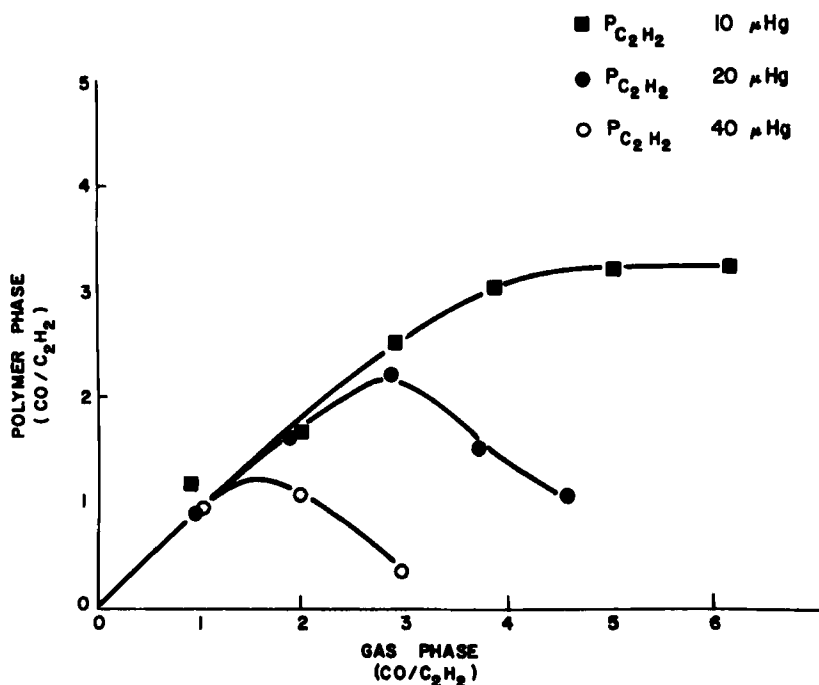


FIG. 9. The amount of CO incorporated into the plasma polymers of acetylene and CO as functions of the ratio of CO/C₂H₂ in the gas phase.

mechanism of these polymers. Here again, the plasma-polymerization scheme presented earlier seems to be useful in postulating the concentration of free radicals in the plasma polymers.

The presence of free radicals in the plasma polymers can be explained by the balance between the production of free radicals and the consumption of free radicals by the recombination mechanism. It should be reckoned that the rate of free-radical production and the rate of the consumption of free radicals formed are dependent on different factors, and the balance of these two processes is not necessarily required in the polymerization mechanism.

The chemical structure of the monomers as classified in the three major groups shown in Fig. 7—i.e., 1) aromatic, hetero-aromatic, and triple bond containing compounds; 2) compounds with cyclic structure and/or double bond; and 3) saturated compounds—seems to have a definite correlation to the free radicals in the plasma polymers formed from these compounds. In Table 8

TABLE 8. ESR Signals Observed with Glass Tubes Coated with Plasma Polymers

Components of monomer gas mixture	Spin concentration in polymers (spins/cm ³) × 10 ⁻¹⁹	Glass radical spin concentration (spins/cm ²) × 10 ⁻¹⁵
Acetylene	28	-
Acetylene/N ₂	18	0.3
Acetylene/N ₂ /H ₂ O	0.9	3.3
Acetylene/H ₂ O	-	3.8
Allene	10	1.1
Allene + N ₂	1.0	0.8
Allene + N ₂ + H ₂ O	5.3	2.0
Allene + H ₂ O	-	3.6
Ethylene	0.7	3.7
Tetramethyldisiloxane	0.07	-
Tetrafluoroethylene	-	10.2
Benzene	2.2	0.6
Propionic acid	-	7.0

the ESR spin concentration (spins/cm³) in the plasma polymer and the ESR spins found in the glass substrate (given by spins/cm² because of the uncertainty of the depth in which free radicals exist) are shown for various plasma polymers. It is interesting to note that a high concentration of free radicals is found in polymers from compounds of group 1, fewer free radicals with compounds of group 2, and very small amounts of free radicals are found in plasma polymers of compounds of group 3.

The trends found with these results seem to suggest that triple bonds and double bonds are easily opened under plasma condition, yielding diradicals. It seems to be rather unlikely that both radicals (in a diradical) react simultaneously with other free radicals to

form a product. If one radical of a diradical react with another radical, the probability of the left-over radical reacting with another radical would become smaller due to the steric hindrance. This postulation seems to be supported by the dramatic changes in free radicals found in plasma polymers of acetylene copolymers as shown in Table 8. The addition of water into the plasma system reduces the free radicals in the plasma copolymers of acetylene to the nonexistent level. Water seems to act as the radical scavenger and increases the consumption rate of free radicals formed.

It is important to note that the addition of water increases the deposition rate (based on the same flow rate of acetylene) of the plasma polymer above that of acetylene alone, which seems to imply that the increase of dissipation rate of free radicals rather than the decrease of production rate of free radicals by the addition of water occurs.

The balance in rates of production and dissipation (by coupling) of free radicals can also be visualized by the use of pulsed rf plasma. Results obtained by pulsed rf plasma in which 13.5 MHz rf is pulsed so that rf is on for 100 μ sec and off for 900 μ sec. Under these conditions the production of free radicals (based on the duration of plasma) decreases to 1/10 of normal (unpulsed) plasma and allows free radicals more time to complete coupling. As can be seen in Table 9, the pulsed rf significantly reduces the concentration of free radicals in the plasma polymers in most but not all cases. It is rather surprising that radicals in plasma polymers of ethylene and acetylene increase nearly by an order of magnitude by pulsing rf. These phenomena presently lack a satisfactory explanation; however, they may be due to the increased breakdown steps in pulsed rf plasma, whereas in the continuous

TABLE 9. ESR Signals Observed with Plasma Polymers Formed by the Continuous and the Pulsed rf Plasma

Monomer	Spin concentration (spins/cm ³ × 10 ⁻¹⁹)	
	Continuous plasma	Pulsed plasma
Tetramethyldisiloxane	0.07	0.007
Benzene	2.2	0.6
Ethylene	0.7	14.0
Acetylene	7.6	13.8

plasma the initial breakdown step occurs only once when plasma is initiated. It is known that much higher wattage is generally required to initiate plasma than to maintain plasma. The high induced voltage at the breakdown step might cause production of more free radicals from these compounds than the production of free radicals under the steady-state condition.

Some aspects of polymer-forming plasma as a means for the surface modification of polymers are schematically shown in Fig. 10. An overall view of the formation of free radicals in the polymer substrate and also in the plasma polymers may be presented as follows.

The numbers of spins in the substrate polymer can be correlated to the deposition rate of polymer using assumptions that:

1. The intensity of UV after passing through a polymer film of thickness ℓ can be given by

$$I = I_0 A e^{-a\ell}$$

where I_0 is the intensity of incident light, and A and a are proportionality constants.

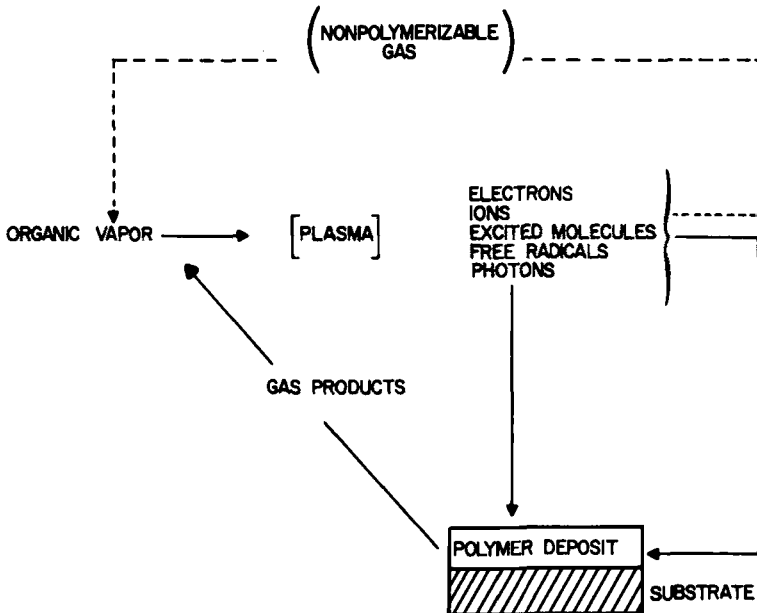


FIG. 10. Schematic representation of the interaction of polymer-forming plasma with a polymer surface.

2. The numbers of spin S is proportional to exposure time, i.e., $dS = kI dt$.
3. The thickness of polymer deposition is proportional to the deposition time, i.e., $l = rt$, where r is the polymer deposition rate constant. Then, the total numbers of spins S can be given by

$$S = \frac{kI_0A}{ar} (1 - e^{-art})$$

This relationship indicates 1) that S is proportional to the intensity of UV emission I_0 , 2) that S is inversely proportional to the rate of polymer deposition r , and 3) that S approaches a constant value as the deposition time increases, which is indeed found in experiments with glass rods as the substrate.

In actual systems the reduction of S with larger r is more pronounced because the UV emission from the polymer-forming plasma with a high rate of polymer deposition is small. This relationship can be visualized by a schematic representation shown in Fig. 11. In Fig. 11 an excited state of a molecule is shown by M^* which could be an ion, a free radical, or an excited molecule. If the monomer does not polymerize, the major portion of the energy may be lost by emission of light $(h\nu)_4$. If the monomer polymerizes, the portion of molecules which contribute the emission of light will be decreased. This situation may be represented by the average energy contributing

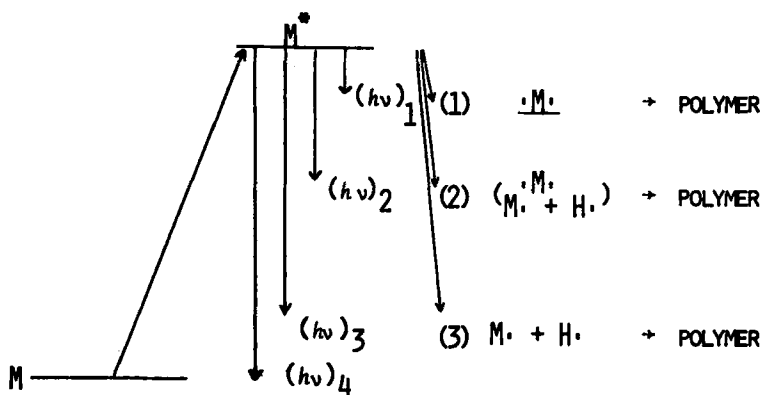


FIG. 11. Schematic representation of correlation between UV emission and plasma polymerization of three major groups of organic compounds.

to the UV emission as shown in Fig. 11 for three groups of compounds $(h\nu)_1$, $(h\nu)_2$, and $(h\nu)_3$.

Therefore, the small numbers of spins in the substrate exposed to polymer-forming plasma can be explained in terms of larger r and smaller I_0 in the above equation. The numbers of spins in the plasma polymer may be best explained by the mechanism of polymerization as described before, since high spin concentrations are found with systems which emit lower levels of UV.

The effect of gas products that are evolved from the substrate polymer may influence, depending on the plasma susceptibility of the substrate, the plasma polymerization of monomers to a significant level. The deposition rates observed with highly plasma-susceptible substrate (polyoxymethylene) are shown in Table 10. If the deposition rate from a polymer-forming plasma is low, the substrate is exposed for a prolonged time to obtain a sufficient polymer deposition and subsequently subjected to UV irradiation for longer periods of time. Furthermore, as shown in the ESR study, the polymer-forming plasma of low polymer deposition

TABLE 10. Effect of Plasma Gas on Degradation of Poly-(oxymethylene) and Polymerization of Styrene onto the Substrate

Plasma ^a	Substrate	Rate of weight change [(g cm ⁻² min ⁻¹) × 10 ⁶]	
		30 W	100 W
Vacuum (0.2 μ)	POM	-3.50	-15.8
100 μ He	POM	-3.13	-14.6
100 μ N ₂	POM	-2.00	-11.0
40 μ ST	Slide	+1.88	+1.88
40 μ ST	POM	+1.25	0.0
80 μ N ₂ + 20 μ ST	Slide	+4.40	+4.40
80 μ N ₂ + 20 μ ST	POM	+1.50	+1.63
80 μ He + 20 μ ST	Slide	+2.50	+2.50
80 μ He + 20 μ ST	POM	-0.25	-0.83

^a μ = μmHg.

rates are generally more stronger UV emission sources. Therefore, the modification of surfaces by plasma polymerization should be carried out with careful consideration of all these characteristics of both plasma and the substrate polymers.

CHARACTERISTIC PROPERTIES OF PLASMA POLYMERS

The properties of polymers formed by plasma polymerization are often very much different from those of the corresponding

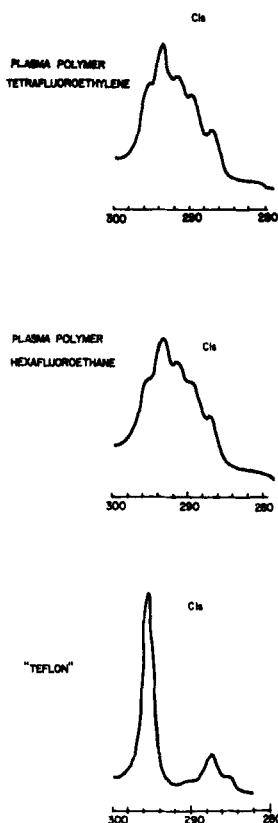


FIG. 12. Comparison of ESCA C 1s spectra for plasma polymer of tetrafluoroethylene, plasma polymer of hexafluoroethane, and Teflon (polytetrafluoroethylene).

conventional polymers. It generally is safe to consider that plasma polymer from a monomer is entirely different from the conventional polymer made from the same monomer. Typical examples may be seen in the following discussion.

In Fig. 12 are shown ESCA spectra of C 1s for plasma polymer of tetrafluoroethylene, plasma polymer of hexafluoroethane, and conventional polytetrafluoroethylene (Teflon). It is clearly evident that plasma polymer of tetrafluoroethylene is very much different from polytetrafluoroethylene. Furthermore, plasma polymer of tetrafluoroethylene is virtually identical to that of hexafluoroethane. These spectra seem to indicate that the detachment of fluorine (similar to hydrogen detachment in hydrocarbon) plays the major role in the polymerization of these fluorocarbons. If tetrafluoroethylene polymerized mainly by the double bond, C 1s peaks of the polymer should be closer to those of polytetrafluoroethylene and should also be different from those for the plasma polymer of hexafluoroethane. Thus the difference of the properties of plasma polymers from those of the corresponding conventional polymer is mainly due to the different mechanism by which polymers are formed under the plasma condition.

The difference in properties of plasma polymers from the conventional polymers is also evident in IR spectra, contact angle, or wettability of the surface. In Fig. 13, IR spectra (by multiple internal reflectance using germanium plates) of plasma polymers of acrylic acid are shown. When acrylic acid is polymerized by the continuous rf (inductive) glow discharge, the polymer surface is rather hydrophobic; i.e., the contact angle of water is 67° ($\cos \theta = 0.39$) and the IR spectrum shows the presence of a little carbonyl group. However, as the same monomer is polymerized by the pulsed rf discharge, the surface becomes more hydrophilic; i.e., the contact angle of water is 11° ($\cos \theta = 0.98$) and the presence of more carbonyl groups is evident in the IR spectrum. In this particular case the fragmentation of monomer molecules occurs more severely in the continuous rf discharge and the use of a pulsed rf discharge decreases the fragmentation of the monomer. The reduced fragmentation is reflected not only in the properties of plasma polymer but also in the increase of polymer deposition rate in spite of the fact that the total duration of plasma is reduced to one-tenth of the continuous rf discharge. The similar trends are also seen with plasma polymers of methylacrylate, whose IR spectra are shown in Fig. 14, although no increase in deposition rate is obtained by the pulsed rf discharge in this case.

The use of pulsed rf discharge provides more insight into the balance of free-radical formation and its dissipation by coupling, and into the extent of the fragmentation, but the overall effects

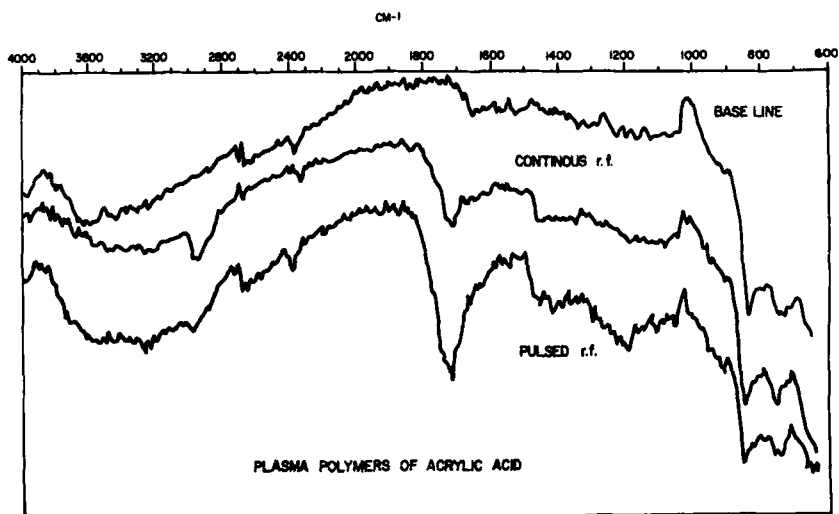


FIG. 13. Infrared (multiple internal reflectance) spectra of plasma polymers of acrylic acid polymerized by a continuous and a pulsed rf discharge.

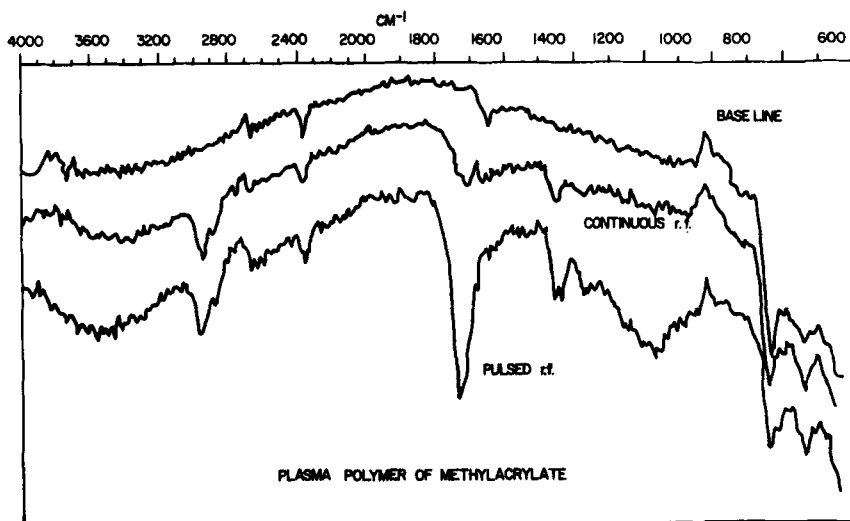


FIG. 14. Infrared (multiple internal reflectance) spectra of plasma polymers of methylacrylate polymerized by a continuous and a pulsed rf discharge.

produced by the pulsing are not always in the same direction. In Fig. 15 the IR spectra of plasma polymers of ethylene oxide are shown.

Ethylene oxide yields more typical "carbonyl-containing" plasma polymers, as polymerized by pulsed rf, which are very much alike regardless of the starting compounds. For instance, the IR spectrum of plasma polymer of acrylic acid by continuous rf discharge (in Fig. 13), that of methylacrylate by the continuous rf discharge (in Fig. 14), and that of ethylene oxide by pulsed rf discharge are nearly identical. Thus, in the case of ethylene oxide, the loss of characteristic features of the monomer is more severe with the pulsed rf discharge than with the continuous discharge.

One of the most important features of plasma-treated surface and plasma (polymerized) polymers is that the surface has a rather high concentration of oxygen. The oxygen at the surface is most likely due to the postreaction of trapped, free radicals with atmospheric oxygen and water vapor. It is generally found that plasma polymers from monomers which do not have oxygen contain 10 to 20% oxygen by elemental analysis (see Table 7). Although the exact chemical forms in which oxygen is incorporated are not

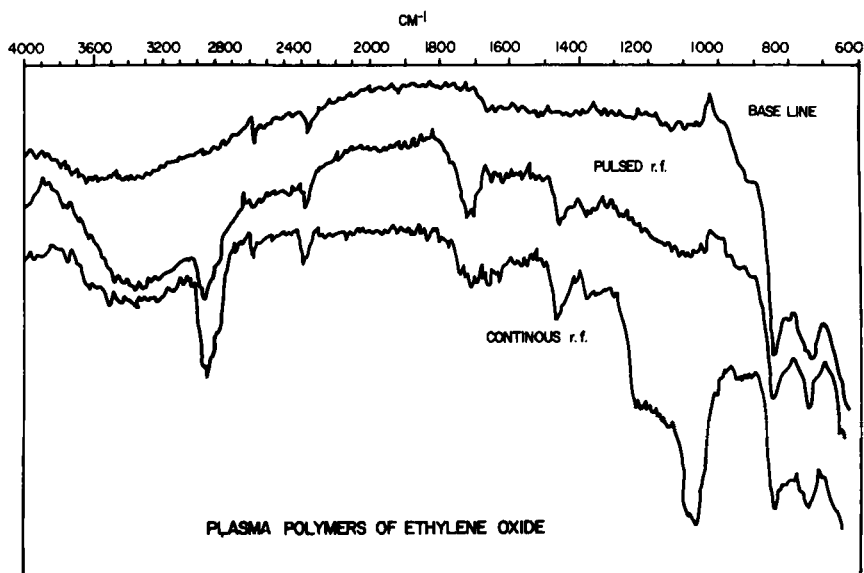


FIG. 15. Infrared (multiple internal reflectance) spectra of plasma polymers of ethylene oxide polymerized by a continuous and a pulsed rf discharge.

known, this high concentration of oxygen seems to play vital roles in the practical use of plasma treatment or plasma polymerization. Whether this aspect is advantageous or disadvantageous is dependent on the types of applications. For instance, the high values of $\tan \delta$ and the change of capacity of films with time (aging of films), which may be attributed to the oxygen incorporation, are troublesome problems when using plasma polymers in electrical applications [12]. The high concentration of trapped, free radicals and/or the high oxygen content in plasma polymers may hamper the use of plasma polymers for protective coating against water vapor and aqueous systems. The same aspect, on the other hand, seems to play an important and favorable role in the use of plasma polymers as semipermeable membranes in which high water throughput is required [13].

The aging effect or the change of properties with time of plasma polymers is closely related to the concentration of trapped, free radicals. In Figs. 16 through 19 the aging effect of polymers are examined by the change of IR spectra with time after the polymerization. The freshly prepared plasma polymer of acetylene contains a high free-radical concentration (2.8×10^{20} spins/cm²) and the IR spectrum shows no carbonyl stretching. With time, a carbonyl signal develops along with a simultaneous drop in the

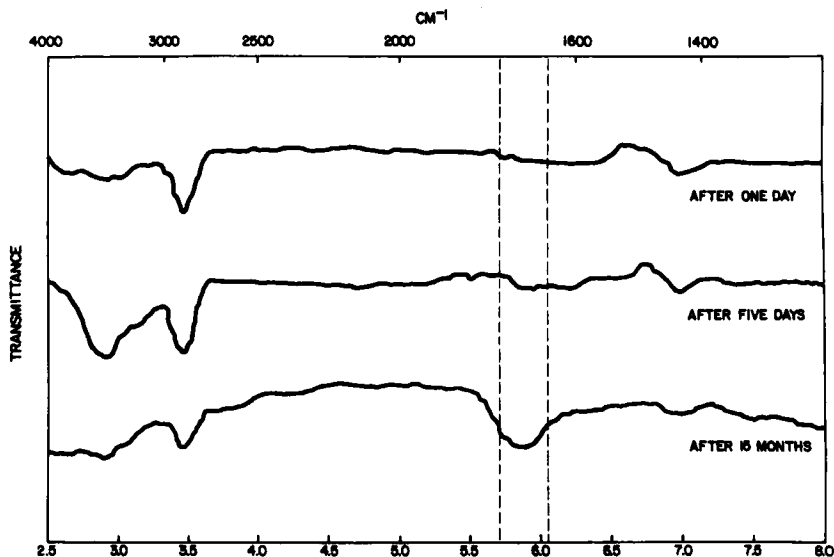


FIG. 16. Infrared spectra of plasma polymer of acetylene taken at various times after the preparation.

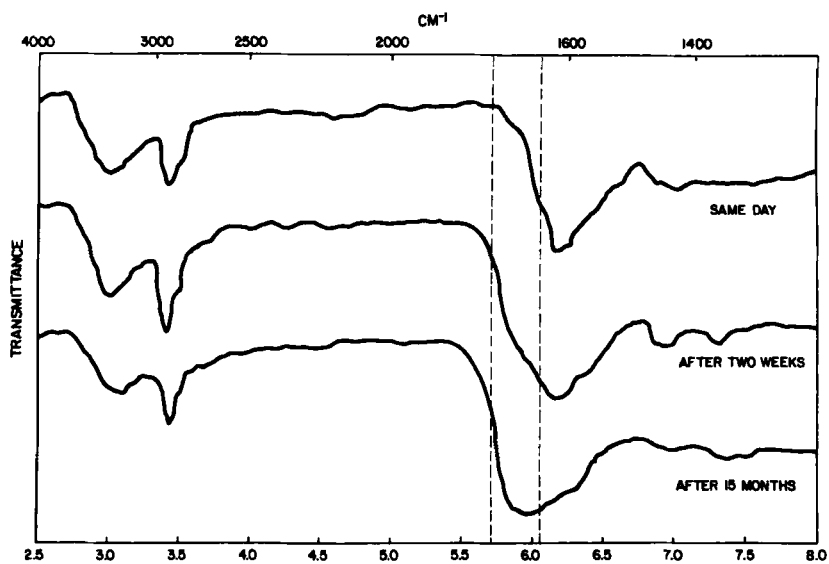


FIG. 17. Infrared spectra of plasma polymer of acetylene/nitrogen taken at various times after the preparation.

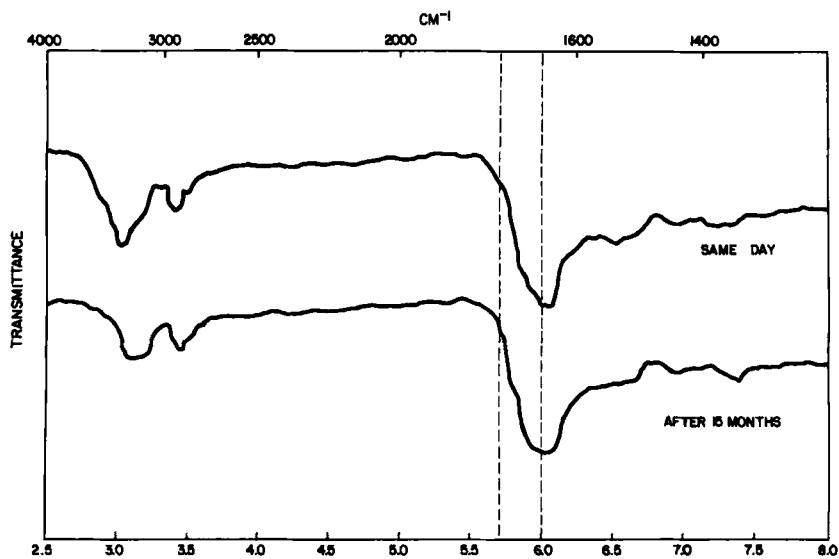


FIG. 18. Infrared spectra of plasma polymer of acetylene/nitrogen/water taken on the same day as the preparation and after 15 months.

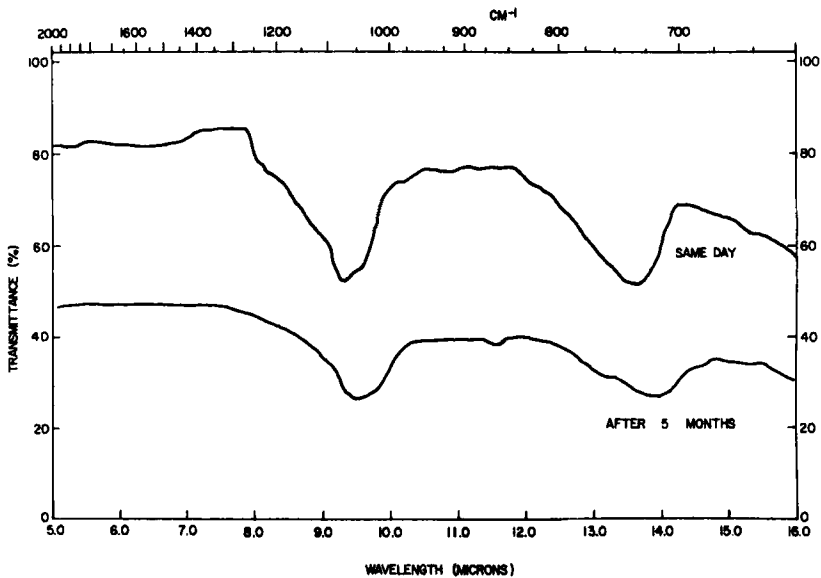


FIG. 19. Infrared spectra ($4000\text{--}1250\text{ cm}^{-1}$) of plasma polymer of tetrafluoroethylene taken on the same day as the preparation and after 5 months.

free radical concentration (see Fig. 16). Over a 15-month period, the free radical concentrations as measured by ESR dropped by 87%.

With polymers which show an IR absorption peak in the range close to that for carbonyl, the aging effect is seen by the shift of peak as seen in Fig. 16 for plasma polymer of acetylene/nitrogen. The freshly prepared plasma polymer of acetylene/nitrogen/water shows no detectable free radicals by ESR, and its IR spectrum shows no appreciable change after a 15-month period (see Fig. 18).

The freshly prepared plasma polymer of tetrafluoroethylene revealed a very low concentration of free radicals in the polymer, and its IR spectrum lacks a carbonyl stretch ($1700\text{--}1650\text{ cm}^{-1}$), both in the freshly prepared sample and in the sample run 5 months later (see Fig. 19).

These examples indicate that the problem of aging can be solved by selecting the monomer and the polymerization conditions. One advantageous feature of plasma polymers is the high degree of cross-linking; however, the process of introducing cross-links tends to leave excess free radicals in the polymer and to cause

troublesome problems in the practical uses. The development of methods to obtain a good balance between these two counteracting effects is important for the proper application of plasma.

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