Polymerization of Organic Compounds in an Electrodeless Glow Discharge. VI. Acetylene with Unusual Comonomers

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Synopsis

Polymerizations of acetylene with nonpolymerizing gases and vapors such as H_2O, N_2, and CO in a plasma generated by inductive coupling of 13.5 MHz radio frequency are investigated. It is found that acetylene copolymerizes with those comonomers and that properties of copolymers are distinctly different from that of plasma polymer of acetylene. The copolymerization with H_2O has a significant effect in reducing the trapped free radicals in the plasma polymer (to a nonexistent level). Infrared and electron spin resonance (ESR) spectroscopies and elemental analysis of polymers are used to investigate the incorporation of H_2O, N_2, and CO into the plasma polymers.

INTRODUCTION

In the previous parts[1,2] of this series of studies, it was found that acetylene and other triple bond-containing compounds polymerize in plasma with an extremely low yield of hydrogen compared to other types of compounds, such as double bond-containing and saturated compounds. This indicates that the opening of triple bond plays the major role in plasma polymerization of these monomers, whereas hydrogen detachment seems to play important roles in plasma polymerization of other types of compounds.

It was also found that N_2 participates in the plasma polymerization of some monomers and that nitrogen atoms are incorporated into plasma polymers.[3] Therefore, it seems to be quite possible that some vapors and gases which do not polymerize independently but form free radicals under the influence of plasma might copolymerize with acetylene and other triple bond-containing compounds.

Since those unusual comonomers have no capability of forming long-chain molecules, the incorporation of some elements may not be termed a kind of copolymerization in the true sense. In plasma polymerization, however, most polymers are formed with short chains, highly branched and crosslinked,[1,2,4] and there may be no distinction between the main chain and branches. Under such a condition, the incorporation of nonpolymerizing gases and vapors into plasma polymer of acetylene might be expressed as copolymerization.

In this study, plasma copolymerization of N_2, H_2O, and CO with acetylene is investigated and some properties of those copolymers are studied.

EXPERIMENTAL

Glow Discharge

Plasma polymerization is carried out by an apparatus which utilizes inductive coupling of 13.5 MHz radio frequency described previously in this series of studies.[5] Acetylene (purified grade from Matheson Gas Product) is used as supplied. The purity of the monomer is regularly checked by the condensibility of the monomer at liquid nitrogen temperature, by recording the pressure change which occurs when a part of the apparatus (cold finger) is surrounded by liquid nitrogen. Since the greatest amount of impurity in a vacuum system is caused by the air leaks, this technique is found to be a very satisfactory means of checking the purity of monomers. All experiments are done with the condensibility higher than 99%. Water vapor is supplied from a flask containing approximately 50 ml distilled water which has been thoroughly degassed prior to the experiment. CO and N_2 are used as supplied (99.99% min.).

Analysis

Pressure Measurement During the Polymerization

The measurement of pressure of the system before and during the plasma polymerization is used to estimate the participation of N_2 and CO in the polymerization.

If nitrogen alone is subjected to plasma, little change is observed between its initial pressure (<150 μm Hg) and its final pressure, that is, the steady-state pressure reached after the plasma is initiated (see Fig. 1). The nitrogen apparently is not broken down, partially or completely, into atomic nitrogen,
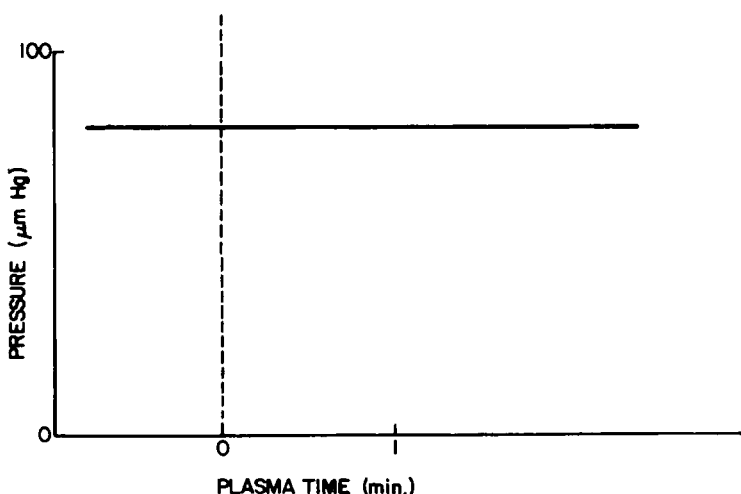

Fig. 1. Schematic representation of pressure change of a flow system of nitrogen when plasma is initiated.
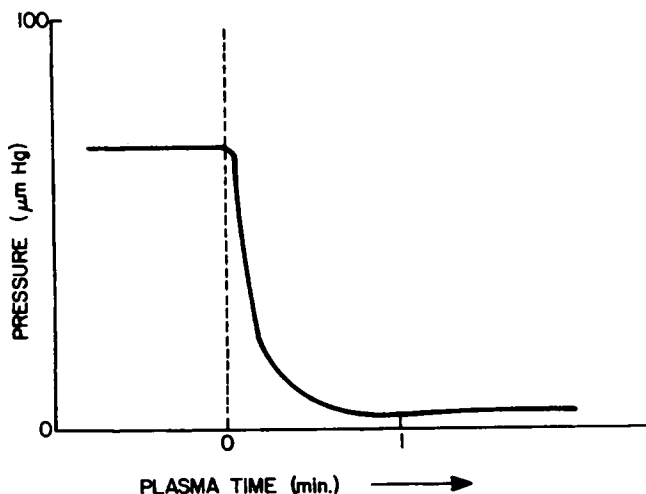
Fig. 2. Schematic representation of pressure change of a flow system of acetylene when plasma is initiated.

since such a reaction should result in a pressure increase, doubling the pressure in the extreme case of complete breakdown.

A pressure drop which would be indicative of polymerization into multi-molecular nitrogen chains was not observed. Such chains would, of course, be highly unstable and are certainly not expected. The absence of a pressure drop also indicates that nitrogen is not reacting with the wall of the reactor.

If acetylene alone is subjected to plasma, however, a marked decrease in pressure results. The pressure falls from an arbitrary initial value (<150 μm Hg) to a small residual pressure (4–6 μm Hg). Such a drop represents fairly complete polymerization (see Fig. 2), since this level of residual pressure is expected from the hydrogen yield of acetylene polymerization in plasma.[1]
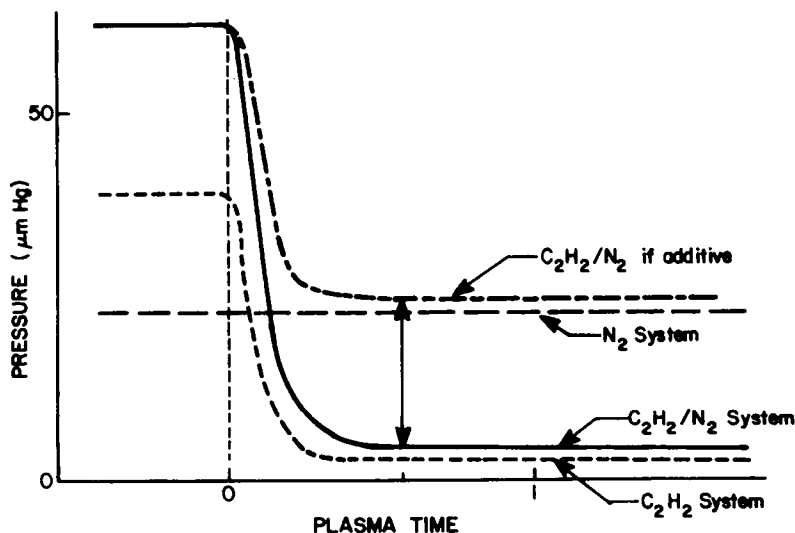

Fig. 3. Schematic representation of pressure change of a system which contains acetylene and nitrogen when plasma is initiated.

The interesting case occurs when the two gases are combined. It is found that the pressure changes are not additive, based on N_2 being considered a nonreactive gas; that is, in an acetylene–nitrogen system, the observed drop is in excess of that expected from acetylene alone (see Fig. 3). This fact directly implies an incorporation of nitrogen into the polymer.

Assuming that acetylene reacts completely irrespective of the presence of nitrogen, the relative amount of acetylene and nitrogen in the polymer can be calculated as follows:

$$(\Delta p - \Delta p_{\text{acetylene}})/p_{\text{acetylene}} = (N_2/C_2H_2)_{\text{polymer}}$$

where Δp is the observed pressure drop. A similar method and calculation is applied to the evaluation of CO incorporation into the polymer.

Elemental Analysis and IR Spectroscopy

Polymer samples are deposited on glass slides placed in the reaction tube and are scraped from the glass plate with a razor blade. Samples are sent for microanalysis by Galbraith Laboratory, Inc., Knoxville, Tenn.

IR spectra are taken by depositing the polymer on the surface of a NaCl crystal. This is often performed simultaneously with the preparation of samples for elemental analysis.

Electron Spin Resonance (ESR) Spectroscopy

A 4-mm glass tube (approximately 10 cm long) is placed on the monomer inlet using a glass joint into which the glass tube fits snugly. The monomer is fed into the reaction tube through this glass tube, and the polymer deposition per unit area is measured by either weighing the tube or by placing a small cover glass below the glass tube for weight increase determination.

The ESR signal is measured by placing the tube into the cavity approximately 5 min after the coated glass tube is taken out from the plasma reactor and exposed to air.

RESULTS AND DISCUSSION

The amount of N_2 incorporated in the polymer formed from acetylene–N_2 mixture in plasma is shown in Figure 4 as a plot of $(N_2/C_2H_2)_{\text{polymer}}$ versus $(N_2/C_2H_2)_{\text{gas}}$, which is given by $p_{N_2}/p_{C_2H_2}$. The partial pressure of acetylene is maintained at 20 μm Hg, and discharge power is kept at 30 watts.

At the low ratio of N_2/C_2H_2, nearly all N_2 is incorporated into polymer, and the curve reaches a maximum around $(N_2/C_2H_2)_{\text{gas}} = 2$. At this point, the amount of nitrogen in polymer is slightly less (1.75) than in the gas phase (2.0).

The presence of an apparent maximum may be due to the effect of the increasing total pressure at a given discharge wattage, since the partial pressure of acetylene is kept at a constant and the ratio of N_2/C_2H_2 is varied. In order to see the effect of total pressure, similar experiments are carried out at different partial pressures of acetylene, and the results are shown in Figure 5. The maximum of the curves shift with the partial pressure of acetylene; i.e.,
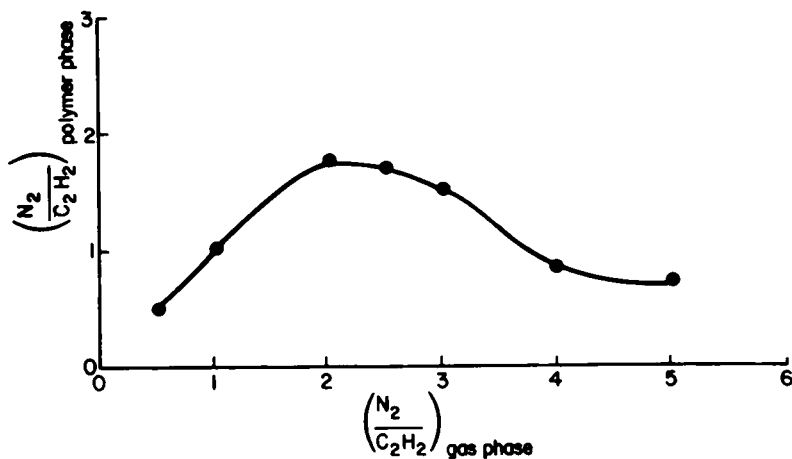
Fig. 4. Amount of nitrogen incorporated into the plasma polymer of acetylene and nitrogen as a function of the ratio of N_2/acetylene in the gas phase.

at 10 μm Hg partial pressure, $(N_2/C_2H_2)_{polymer} = 2.7$ at $(N_2/C_2H_2)_{gas} = 3$; but at 40 μm Hg, $(N_2/C_2H_2)_{polymer} = 1.4$ at $(N_2/C_2H_2)_{gas} = 1.7$. For a given ratio of $(N_2/C_2H_2)_{gas}$, more nitrogen can be incorporated into the polymer at lower total pressure, except at lower $(N_2/C_2H_2)_{gas}$ ratio where 100% of the gas phase nitrogen seems to be incorporated into the polymer.

When the pressure of gas is increased at a constant discharge power, the volume of plasma tends to decrease,[6] and it may affect the deposition of polymer. In order to see the effect of discharge power, a similar experiment (partial pressure of acetylene at 20 μm Hg) is carried out at higher wattage, at 80 watts, and the results are shown in Figure 6. Results indicate that the ob-
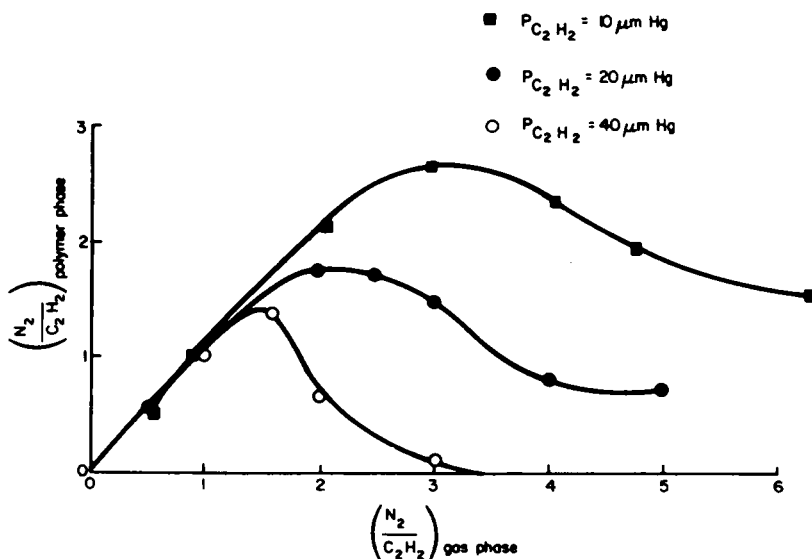

Fig. 5. Amount of nitrogen incorporated into the plasma polymer of acetylene and nitrogen as a function of the ratios of N_2/acetylene in the gas phase at different partial pressures of acetylene.
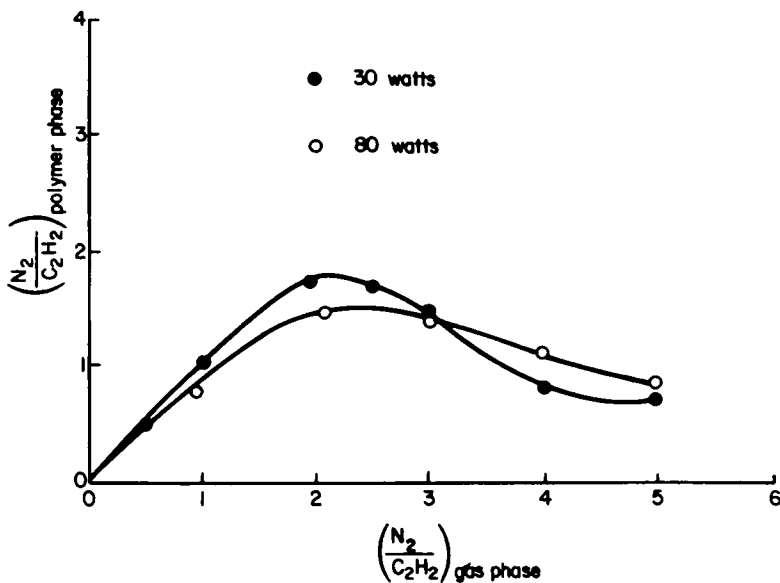
Fig. 6. Comparison of nitrogen incorporation into plasma polymer of acetylene and nitrogen at different discharge wattages.

served maximum is not due to the decrease of plasma volume at increased pressure but to the characteristic reaction mechanism.

At lower ratio of $(N_2/C_2H_2)_{gas}$, the chance of nitrogen–nitrogen collisions is minimized. The polymer-forming reactions (e.g., acetylene–nitrogen and acetylene–acetylene) predominate, and available nitrogen may be captured by the forming polymer. At higher $(N_2/C_2H_2)_{gas}$ ratios, excessive nitrogen is available and the effects of total system pressure become important. In a flow system, pressure not only changes the frequency of collisions but also changes the resident time of reactant molecules (in the system used for this study). Lower pressure results in longer resident time, thus significantly increasing the chances for productive molecular collisions. Such increased resident time effects seem to overcome the effects resulting from any decrease in the frequency of collisions at lower pressure. This does not seem unreasonable considering the fact that plasma is maintained by the continuous feed-in of the excitation energy.

Similar results are obtained with an acetylene–CO system, and the results are shown in Figure 7. The incorporation of CO by acetylene is very much similar to that of N_2.

The incorporation of nitrogen in the polymer is evident in the results of elemental analysis shown in Table I. All samples are dried overnight at 40–50°C under vacuum before the analysis. The content of oxygen is calculated from data for the elemental analysis of C/H and N.

It may be worth noting that the addition of N_2 seems to reduce the hydrogen detachment during polymerization. The empirical formula for plasma polymer of acetylene/N_2 may be given as $C_2H_2N_{0.5}O_{0.3}$. The increase in H/C ratio with addition of water is direct evidence of the incorporation of water (probably as OH) into the plasma polymer of acetylene/N_2/H_2O, which can be given as $C_2H_{2.9}N_{0.5}O_{0.7}$.

TABLE I
Elemental Analysis of Glow Discharge Polymers of Acetylene with H_2O, N_2, and CO

Monomer	C, %	H, %	N, %	O, %	Empirical formula	Color
Acetylene (50 μm Hg)	79.5	5.4	—	15.1	$C_2H_{1.6}O_{0.3}$	dark brown
Acetylene/N_2 (50 μm Hg)/(33 μm Hg)	64.0	5.8	16.7	13.5	$C_2H_2N_{0.5}O_{0.3}$	dark brown
Acetylene/H_2O (40 μm Hg)/(20 μm Hg)	66.5	7.6	—	25.9	$C_2H_{2.7}O_{0.4}$	off white
Acetylene/N_2/H_2O (30 μm Hg)/(20 μm Hg)/ (15 μm Hg)	53.2	6.5	15.7	24.6	$C_2H_{2.9}N_{0.5}O_{0.7}$	brown
Acetylene/CO (30 μm Hg)/(20 μm Hg)	82.6	6.9	—	10.5	$C_2H_{1.8}O_{0.2}$	dark brown
Acetylene/CO/H_2O (30 μm Hg)/(20 μm Hg)/ (15 μm Hg)	72.0	8.4	—	19.6	$C_2H_{2.8}O_{0.4}$	light brown

All plasma polymers in this study have oxygen incorporated in the polymer, as generally found in various plasma polymers by many investigators. Results of elemental analysis are based on direct analysis of C/H and N and not direct analysis of O. However, the presence of O in the polymer is evident in the electron spectroscopy for chemical analysis (ESCA) spectra. The details of study with ESCA will be presented elsewhere.

Part of the oxygen in most plasma polymers, and all of oxygen in plasma polymer of acetylene alone, is the consequence of the postplasma reaction of trapped free radicals (in the polymer) with atmospheric oxygen and possibly
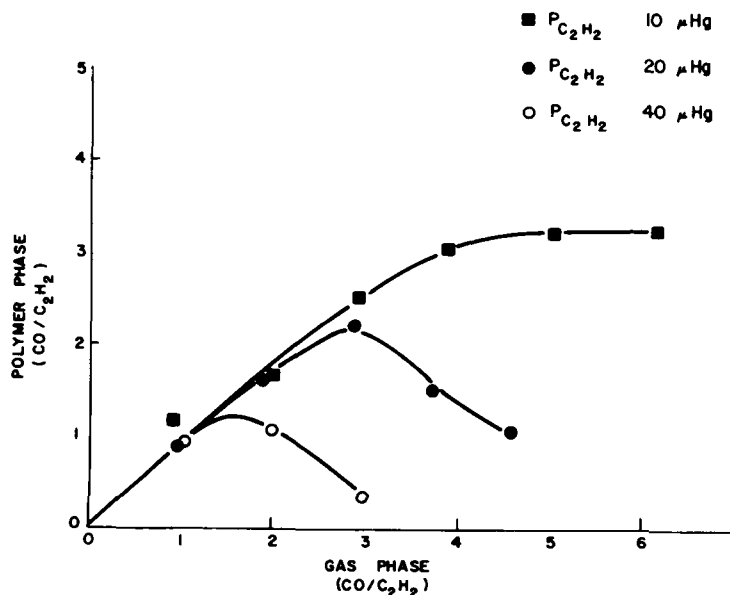

Fig. 7. Amount of CO incorporated into plasma polymer of acetylene and CO as a function of the ratios CO/acetylene in gas phase at different partial pressure of acetylene.
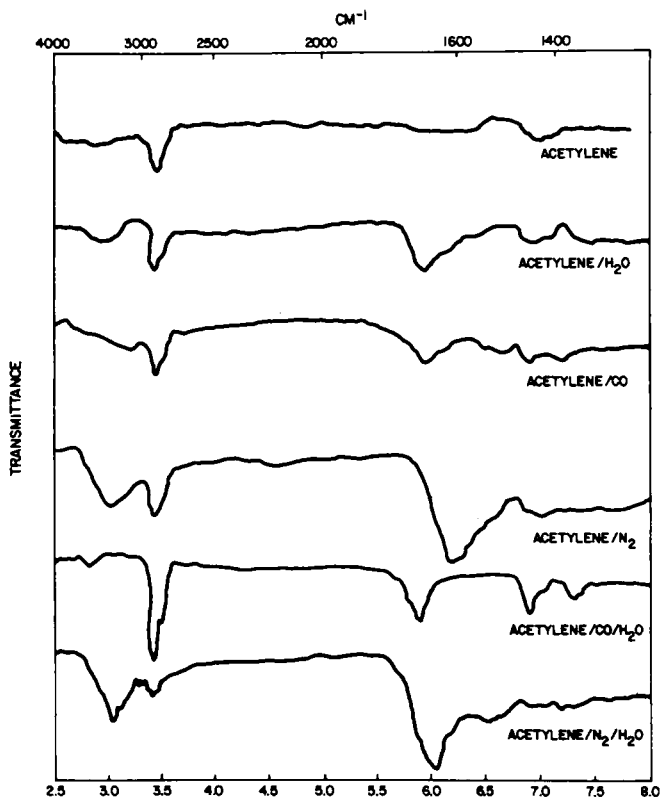
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Fig. 8. Infrared spectra (4000 cm^{-1}–1250 cm^{-1}) of plasma copolymers of acetylene.

with water vapor. However, a major portion of oxygen in copolymers with H_2O, and H_2O, and nitrogen results from the copolymerization of water. The following results of ESR and IR spectra seem to support this interpretation.

The complex nature of glow discharge polymer makes precise interpretation of infrared spectra difficult. However, much useful information concerning the general nature of the polymer can be obtained, especially in light of other data such as free-radical concentration and elemental analysis. The infrared spectra of the six glow discharge polymers considered in this study are shown in Figures 8 and 9, and a summary is presented in Table II.

Discharge polymers of acetylene and the unusual comonomers are thought to be random and highly branched hydrocarbon chains with varying hydroxyl, carbonyl, and nitrogen-containing functions. The highly branched nature is made evident by the lack of strong absorption in the 720–770 cm^{-1} region characteristic of straight chains of four or more methylene groups. The hydrocarbon nature of these chains produces the C—H stretching bands near 2900 cm^{-1} observed in each polymer. Except for the acetylene/N_2/H_2O system, the polymers also produce the C—H bending modes around 1400 cm^{-1}.

Regardless of the mechanism, the polymerization of acetylene should result in some form of hydrocarbon. Electron spectroscopy for chemical analysis (ESCA), however, reveals the presence of oxygen in the discharge polymer. In fact, ESCA and elemental analysis have indicated the presence of oxygen in all discharge polymers investigated. It is most reasonable to attribute the

TABLE II

Infrared Absorption Characteristics of Electrodeless Glow Discharge Polymers[a]

Absorption region, cm^{-1}	Source	Acetylene	Acetylene/ H$_2$O	Acetylene/ CO	Acetylene/ N$_2$	Acetylene/ CO/H$_2$O	Acetylene/ N$_2$/H$_2$O
1370–1380	C—H sym. bend, methyl			W		M	
1325–1440	C—C aldehyde			W		M	
1430–1470	C—H asym. bend, methyl	W	M	W	W	M	
1445–1485	C—H asym. bend, methylene	W	W	W	W	M	
1490–1580	N—H bend, secondary amine				W		W
1515–1570	N—H bend, secondary amide				S		
1560–1640	N—H bend, primary amine						
1630–1680	C=O stretch, secondary amide						S
1630–1670	C=O stretch, tertiary amide						S
1665–1685	C=O stretch, α,β-unsat. ketone		S	M			S
1680–1705	C=O stretch, α,β-unsat. aldehyde		S	M		S	S
1705–1725	C=O stretch, sat. ketone		M	W		S	
1710–1740	C=O stretch, sat. aldehyde					M	
2843–2863	C—H sym. stretch, methylene	M	S	S	S	S	M
2916–2936	C—H asym. stretch, methylene	S	S	S	S	S	M
2862–2882	C—H sym. stretch, methyl	S	S	S	S	S	M
2952–2972	C—H asym. stretch, methyl	S	M	S	S	S	M
3070–3100	N—H stretch, secondary amide bonded NH, cis or trans						W
3140–3180	N—H stretch, secondary amide bonded NH, cis						M
3270–3370	N—H stretch, secondary amide bonded NH trans			W			S
3310–3350	N—H stretch, dialkyl amine				S		
3400–3500	N—H stretch, primary amine				M		
3200–3600	O—H stretch, bonded hydroxyl	S	M[b]	W	M	W[b]	M

[a] Given as peaks—strong (S), medium (M), and weak (W).
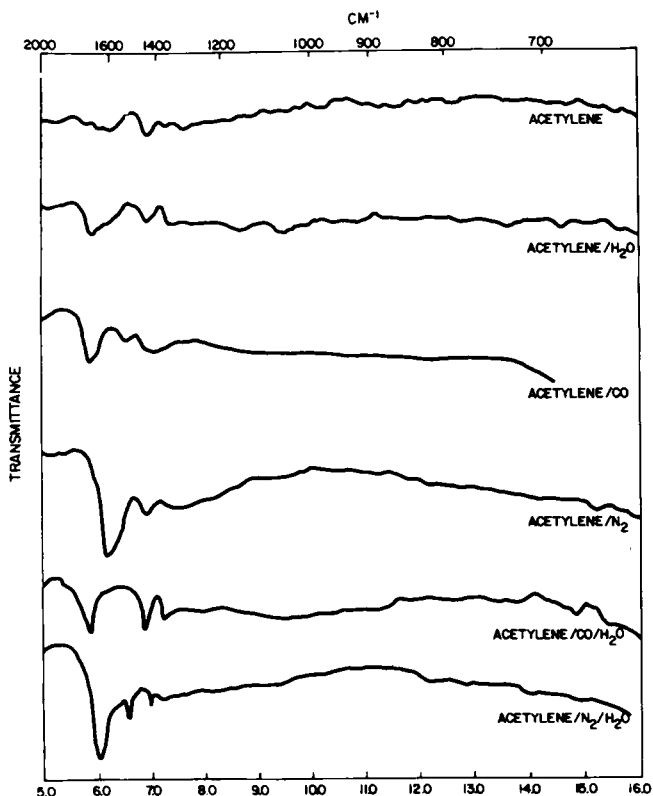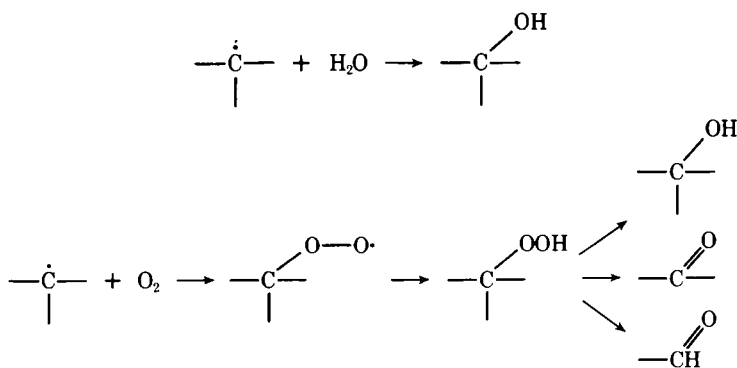[b] Possibly carbonyl overtone.

Fig. 9. Infrared spectra (2000 cm^{-1}–625 cm^{-1}) of plasma copolymers of acetylene.

oxygen to postplasma reaction with the atmosphere. Such an explanation is especially appealing because of the high concentrations of free radicals found in most discharge polymers. There also seems to be correlation between

free-radical concentration and the subsequent increase of carbonyl and possibly hydroxyl groups as a function of time. Free radicals in the discharge polymer may capture molecular oxygen or water producing hydroxyls and carbonyls:
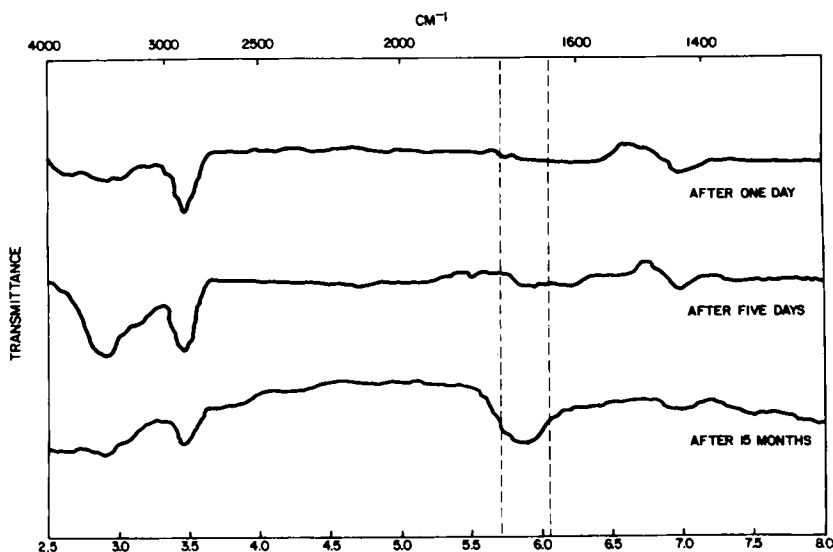
Fig. 10. Infrared spectra of plasma polymer of acetylene taken at various times after the polymerization.

Data on free-radical concentrations from ESR measurements can be found in Table III.

Consider first the change in the infrared spectra with time of the acetylene-only discharge polymer. Figure 10 clearly indicates an increasing signal in the carbonyl region (ketones and aldehydes absorb generally 1665–1740 cm^{-1}). There is also an apparent increase in the bonded hydroxyl O—H stretch band (3200–3600 cm^{-1}) relative to the C—H stretching signal (ca. 2900 cm^{-1}).

Concurrent to carbonyl formation observed in the infrared is a decrease in free-radical concentration. Over a 15-month period, the free-radical concentration as measured by ESR drops by 87%. The loss of free radicals is a very slow process as is the oxidation of the polymer film. This indicates stability of the radicals and impenetrability of the film to oxygen. Resonance stabili-

TABLE III
Free Radicals in Plasma Polymers of Acetylene with H_2O, N_2, and CO

Monomer and pressure, μm Hg	Spin concentration, (spins/cm^3) $\times$ 10^{-18}
Acetylene	280
Acetylene/N_2 (30)/(30)	180
Acetylene/N_2/H_2O (30)/(10)/(20)	9
(30)/(20)/(10)	9
Acetylene/H_2O (30)/(20)	0
Acetylene/CO (30)/(20)	217
Acetylene/CO/H_2O (30)/(20)/(15)	1.5

zation of the radicals and impenetrability would be expected of a very highly branched and crosslinked polymer.

Besides the absence of methylene chain signals, the infrared spectra give other indications of a branched polymer. The strong broad O—H stretch absorption shifted down from the high to mid and lower 3000's cm^{-1} results from intramolecular hydrogen bonding fully expected in a branched hydrocarbon polymer.

The glow discharge polymer of acetylene can now be described as highly branched and crosslinked hydrocarbon with a fairly large free-radical concentration. Subsequent exposure to the atmosphere results in the incorporation of carbonyl and hydroxyl groups through reaction with the free radicals.

A plasma of acetylene and nitrogen produces a polymer which shows "amine-like" characteristics with N—H stretching and bending of a both primary and dialkyl amines. Since hydroxyl and carbonyl stretches are found in the same general region as the N—H stretch and N—H bend respectively, and since both regions produce broad and fairly strong signals, the nature of the oxygen incorporated cannot be directly inferred. The amount of oxygen in the polymer as determined by elemental analysis is the same as in the acetylene-only polymer and is similarly best explained by atmospheric oxidation.

Increased exposure to the atmosphere unquestionably intensifies absorption in the carbonyl (1665–1740 cm^{-1}) (see Fig. 11). Again, the effects on the hydroxyl absorption are less clear. This is due primarily to the coincidence of the N—H and O—H stretch regions of absorption, a problem which is complicated, as before, by the effects of hydrogen bonding.

In the acetylene/N_2/H_2O case, the C—H stretching modes are attenuated, and the bending modes undetected. The polymer displays more polyamide than hydrocarbon character (see Figs. 8, 9, and 12). The N—H stretch at 3300 cm^{-1}, the C=O stretch at 1650 cm^{-1}, and the N—H deformation 1515–1570 cm^{-1} provide strong indications of a secondary amide. Further-
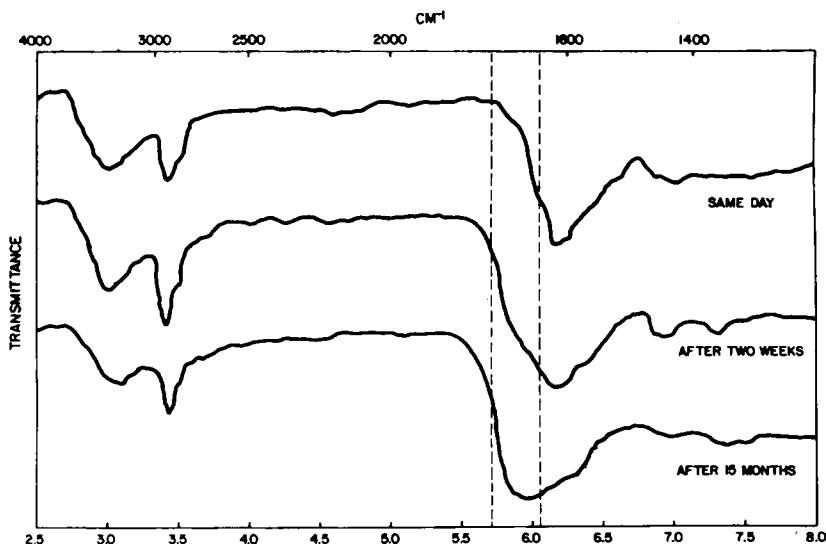

Fig. 11. Infrared spectra of plasma polymer of acetylene and N_2 taken at various times after the polymerization.
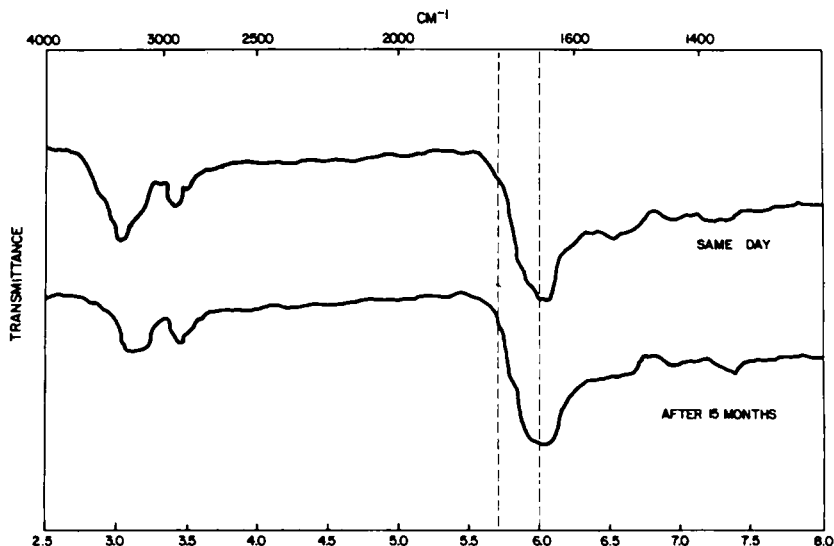
Fig. 12. Infrared spectra of plasma polymer of acetylene, N_2, and water taken at various times after the polymerization.

more, the N—H stretch at 3300 cm^{-1} rather than 3400 cm^{-1} implies intramolecular hydrogen bonding as might be expected in a highly branched polymer. One cannot, however, rule out the possibility of hydroxyl or carbonyl groups coexisting with the amides. Indeed, the absorption bands are quite broad and ill defined, and the superimposing of peaks to some extent seems quite likely. Remembering the fairly equal incorporation of nitrogen and oxygen from elemental analysis, it seems best to term this discharge polymer as "amide-like."

Duration of contact with the atmosphere seems to have little effect on the acetylene/N_2/H_2O polymer (see Fig. 12). This is consistent with a free-radical concentration in the newly produced polymer several orders of magnitude lower than in the acetylene or acetylene/N_2 polymers. Quick conclusions, however, should be avoided since the newly formed polymer produces fairly broad and strong hydroxyl and carbonyl signals, making increases difficult to detect. It is not unreasonable, however, to suggest that the glow discharge polymer of acetylene/N_2/H_2O is less susceptible to atmospheric oxidation due to a lower initial free-radical concentration.

The presence of water in the acetylene plasma seems to have two major effects on the resultant polymer: (1) a marked decrease in the number of free radicals in the polymer, and (2) the incorporation of carbonyl groups.

Whether the inclusion of water in the plasma contributes to oxygen incorporation in hydroxyl form can not be determined, since hydroxyl absorption is generally characteristic of discharge polymers. Thus, the glow discharge polymer of acetylene/water seems to be a highly branched hydrocarbon with hydroxyl and carbonyl groups, and which exhibits a fair degree of stability against oxidative reaction with the atmosphere.

The addition of carbon monoxide to the acetylene plasma apparently results in carbonyls in the polymer, but no appreciable decrease in the free-radical concentration (see Figs. 8 and 9). The primary difference, then, between

TABLE IV
General Character of Discharge Polymers from Infrared Data

Monomer system	Functional character of polymer
Acetylene	hydroxyl
Acetylene/H_2O	hydroxyl-carbonyl
Acetylene/CO	carbonyl
Acetylene/N_2	amine
Acetylene/CO/H_2O	carbonyl
Acetylene/N_2/H_2O	amide

the acetylene/H_2O and the acetylene/CO polymer should be found in terms of stability. Conclusive evidence of this, however, has yet to be obtained.

The acetylene/CO/H_2O seems a likely enough hybrid of the preceding two (see Figs. 8 and 9). The hydrocarbon C—H stretching and bending signals are quite strong. The hydroxyl signal is very weak.

It can be concluded that the addition of water, nitrogen, carbon monoxide, or various combinations of these comonomers to a glow discharge polymerization of acetylene produces chemically distinct polymers. The characteristic nature of these polymers may be summarized as given in Table IV. The polymers are in general highly branched and contain some form of oxygen subsequent to exposure to the atmosphere. The copolymerization of H_2O reduces the trapped free radicals in the plasma polymers in a remarkable manner and enhances the stability of the polymers.

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