

Polymerization of Organic Compounds in an Electrodeless Glow Discharge. IV. Hydrocarbons in a Closed System

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Synopsis

The polymerization of hydrocarbons was investigated by measuring the hydrogen yield during the glow discharge polymerization in a closed system. It was found that the pressure change in the glow discharge polymerization of hydrocarbons was mainly due to the production of hydrogen and to the loss of vapor phase monomer by polymerization. The opening of triple or double bonds and cyclic structures plays an important role in the polymerization of hydrocarbons; however, these are not exclusive mechanisms. The major polymerization mechanism for saturated normal hydrocarbons seems to be by the formation of free radicals due to hydrogen abstraction and the recombination of these primary radicals. The polymerization due to this mechanism also seems to occur concurrently during the polymerization of hydrocarbons with multiple bond and/or cyclic structures. Aromatic hydrocarbons polymerize with very low hydrogen production, indicating that the utilization of an aromatic double bond is the major mechanism of polymerization.

INTRODUCTION

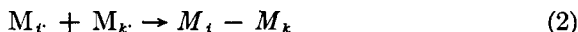
Polymerization of organic compounds in a flow system by an electrodeless glow discharge has been recently reported.^{1,2,3} In these studies, the rates of polymer deposition from various organic vapor plasma in the tail flame (glow region) of an electrodeless discharge by 13.56 MHz rf were studied as a function of flow rate and discharge power. It was generally observed that under the conditions used the rate of polymer deposition is proportional to the monomer feed-in rate. The proportionality constant of polymer deposition based on the mass flow rate, which can be considered as a characteristic polymerization rate of a monomer, is by and large similar regardless of whether an organic compound contains an olefinic double bond.

It was proposed that polymerization of an organic compound in a glow discharge proceeds mainly by coupling of primary radicals (or excited species) generated by ionization of monomer vapor. According to this concept, the polymerization may be represented by the following steps:

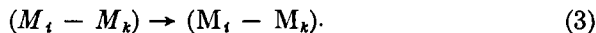
Initiation



Recombination



Reinitiation



where i and k are numbers of repeating unit; i.e., $i = k = 1$ for monomer, $i = k = 2$ for dimer etc. According to this reaction scheme, the glow discharge polymerization corresponds to radiation-induced polymerization at an extremely high dose rate. Westwood et al.⁴ 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 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 reference 3.

It was also found that the fragmentation of some organic compounds occurred in glow discharge and that the extent of fragmentation was related to certain structural features of organic compounds.³

The polymerization of varieties of organic compounds investigated in the previous studies can be explained in a consistent manner by this scheme of polymerization, with the consideration of the fragmentation of organic compounds.

The quantitative investigation of the polymerization mechanism in a flow system is difficult because the observed polymer deposition represents only the polymer formation taking place at the collecting surface whereas any reaction represented by (1), (2), and (3) can occur in the gas phase and at the surface. The observed polymer deposition is not enough to complete the mass balance in a flow system.

Since it is known from the previous studies^{2,3} that the fragmentation of organic compounds manifested by the pressure increase 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.

For this purpose a study of the polymerization of hydrocarbons in a closed system is carried out in this investigation.

PRINCIPLE OF INVESTIGATION AND EXPERIMENTAL

Principle of Approach

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 of 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 vapor phase to solid deposition on the surface.

The word "polymerization" used does not necessarily mean formation of high molecular weight polymer, but merely represents the phenomena of molecules leaving the vapor phase owing to the increase of molecular weight or to the fixation of molecules 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. (This situation is discussed later in more detail.)

3. The cleavage of a C-C bond of a cyclic compound which leads to the formation of a polymer 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., 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 polymer and cannot be considered as a main step of polymerization.

The cleavage of a C-C bond of a noncyclic compound creates complications. However, since it has been confirmed that nearly all hydrocarbons polymerize by nearly similar rates (based on mass flow rate), the opening of a double bond or cyclic structure and hydrogen abstraction seem to be the most probable mechanisms.

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

Experimental

The apparatus used for this study is identical to the one reported in part II of this series, except that the monomer inlet tube on the reaction tube is replaced by a cold finger. A small U-shaped glass tube with one end closed and with a glass joint on the other end is connected to the monomer inlet in upside-down position so that the closed end of the tube can be used as the cold trap after the glow discharge. The volume of the system including the

pressure gauge is approximately 1000 cm³. The initial pressure p_0 of 150 μm Hg and discharge wattage of 30 W are arbitrarily selected for this study. The monomer vapor is introduced into the closed reaction system which has been degassed to a vacuum of less than 0.2 μm Hg through the vacuum manifold.

After 150 μm of monomer is introduced into the system, the cold finger is surrounded by liquid nitrogen. It is confirmed that the monomer used can be completely trapped by this technique.

Following this preliminary checking and after the pressure of the system returns to the initial pressure p_0 , the glow discharge is initiated and maintained until the pressure recording shows no further change. After the glow discharge is discontinued, the final pressure p_∞ is measured. Then the cold finger is surrounded by liquid nitrogen and the pressure p_{H_2} is measured after confirming that no further pressure change occurs.

The following parameters are calculated from these measurements:

Monomer-type parameter

$$\gamma = \frac{p_\infty}{p_0}$$

Fraction of residual vapor

$$x = \frac{p_\infty - p_{\text{H}_2}}{p_0}$$

Yield of hydrogen

$$y = \frac{p_{\text{H}_2}}{p_0}$$

Yield of polymer

$$z = (1 - x)$$

In order to gain a rough comparison of relative rates of reactions, the half-time of reaction, $t_{1/2}$, is read from the pressure-time recording during the discharge. Many reactions start nearly as the first order in respect to the pressure; however, they generally do not follow the first-order reaction. Nevertheless, the half-time of the reaction provides a means of comparing the rates of reactions for various monomers. Some reactions follow two stages insofar as the pressure change-versus-time relation is concerned. In this case, the half-time of the first step is recorded.

RESULTS AND DISCUSSION

Results expressed in terms of the parameters described above (i.e., γ , x , y , and z) are summarized in Table I. The interpretation of these data is dependent on the meaning of hydrogen yield since the technique employed cannot distinguish H₂ and CH₄ (neither can be trapped by the cold finger at liquid nitrogen temperature). The value observed as hydrogen yield may

include the yield of methane from the monomer. However, it may be a reasonable assumption to consider the gas product that does not condense at the liquid nitrogen temperature to be mostly hydrogen, since methane itself produces hydrogen and forms polymer.⁵

This assumption is further confirmed by the analysis of gas products of glow discharge with propane, cyclopropane, and isobutylene by mass spectroscopy. Because of an extremely high escaping tendency of H₂ gas from the mass spectrometer, an empirical calibration curve of CH₄⁺ peak/H₂⁺ peak versus mole fraction of CH₄ was constructed by using known mixtures of CH₄ and H₂. In these experiments, the time of starting the scanning after the introduction of a sample into the spectrometer was carefully controlled. From the CH₄⁺/H₂⁺ peak ratio, the concentrations of CH₄ in glow discharge products of propane, cyclopropane, and isobutylene are estimated as less than 1%.

It should also be recognized that the rate of reaction roughly expressed by the half-time is not true half-time of the first order reaction due to the following ambiguity and change of condition during the reaction. First, the endpoint is not very clear except with monomers of low γ -value, and the reaction time is dependent on the selection of the end of change in pressure. Secondly, the volume of glow discharge where the reaction occurs is not a constant value during the reaction and also varies from compound to compound depending on the breakdown wattage of the compound and on the change of pressure during the reaction.

Even considering these ambiguities involved in the experiment, the following aspects seem to be clearly evident and are indicative of the mechanism of glow discharge polymerization.












1. The monomer-type parameter γ is nearly identical to the hydrogen yield. In the previous paper,³ it was interpreted that high γ -value is due to the decomposition (or fragmentation) of the monomer molecule. In the case of hydrocarbons, it appears that the increase of pressure is due mainly to the production of hydrogen molecules. All hydrocarbons with unsaturation belong to type A monomer ($\gamma < 1$; i.e., the pressure decreases in glow discharge), and nearly all saturated hydrocarbons (with the exception of cyclopropane) belong to type B monomer ($\gamma > 1$; i.e., the pressure increases in glow discharge).

2. Compounds with olefinic double bond showed relatively high hydrogen yield, indicating that the contribution of polymerization by the opening of double bond is surprisingly small. In the cases of ethylene and propene, the role of hydrogen abstraction is almost equal that of the double bond opening. This does not imply that polymer is formed by hydrogen abstraction without utilizing the double bond, but that the polymerization via hydrogen abstraction is perhaps contributing to the crosslinking of the polymer.

3. The more striking fact is that compounds with triple bond or conjugated double bond, including aromatic and heteroaromatic compounds, polymerize with very small hydrogen yield. This means that the poly-

TABLE I
Hydrocarbon Polymerization Parameters

Compound	Structure	$t_{1/2}$, sec	Monomer type parameter γ	Fraction of residual vapor z	Hydrogen yield y	Polymer yield (1- x)
Methane	CH_4	— ^a	1.22	0.017	1.22	—
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	~3	1.75	0.055	1.70	0.946
<i>n</i> -Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	12	2.62	0.285	2.33	0.715
<i>n</i> -Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	7	2.75	0.133	2.61	0.867
Ethylene	$\text{CH}_2=\text{CH}_2$	0.75	0.647	0.020	0.628	0.980
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	2.25	0.920	0.040	0.880	0.960
<i>trans</i> -2-Butene	$\text{CH}_3\text{CH}=\text{CHCH}_3$	2.75	1.16	0.038	1.12	0.962
Isobutylene	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	3	1.11	0.048	1.07	0.955
1,3-Butadiene	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	3.75	0.471	0.019	0.452	0.981
Allene	$\text{CH}_2=\text{C}=\text{CH}_2$	3	0.135	0.007	0.128	0.994
Acetylene	$\text{CH}\equiv\text{CH}$	1.1	0.103	0.011	0.091	0.989
Methylacetylene	$\text{CH}_3\text{C}\equiv\text{CH}$	2.25	0.179	0.008	0.171	0.992
Dimethylacetylene	$\text{CH}_3\text{C}\equiv\text{CCH}_3$	6	0.326	0.020	0.307	0.980
Ethylacetylene	$\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$	5.5	0.462	0.148	0.447	0.985

Cyclopropane		0.5	0.907	0.033	0.873	0.96
Cyclopentane		2.5	1.41	0.081	1.33	0.92
Cyclohexane		3	1.50	0.043	1.43	0.95
Cycloheptane		3.5	1.69	0.083	1.61	0.91
Cyclohexene		2	0.833	0.033	0.800	0.96
Methylene cyclohexane		—	1.01	0.026	0.979	0.97
Benzene		<2	0.110	0.003	0.107	0.99
Toluene		3	0.174	0.001	0.172	9.90
<i>p</i> -Xylene		4	0.133	0.000	0.133	1.00
Ethylbenzene		6	0.298	0.020	0.278	0.98
Styrene		4	0.105	0.017	0.088	0.98

* Due to small pressure damage, the estimate of endpoint is difficult.

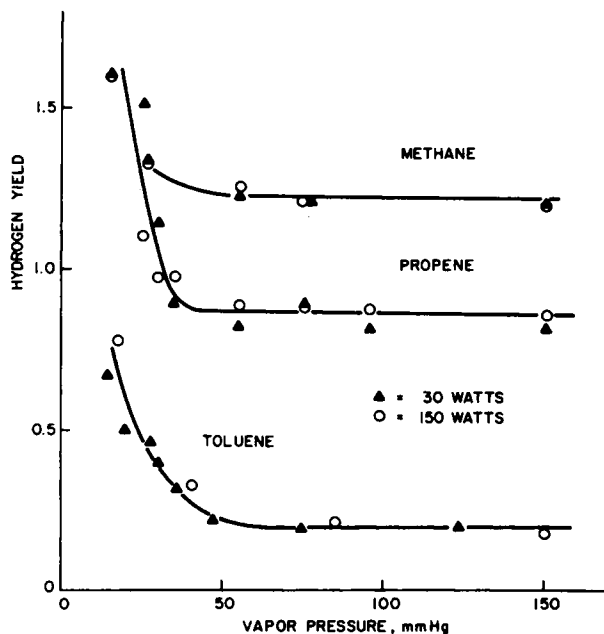


Fig. 1. Dependence of hydrogen yield on vapor pressure for methane, propene, and toluene at discharge power of 30 W and 150 W.

merization of aromatic compounds must proceed by opening of double bonds in the aromatic or heteroaromatic ring.

4. The hydrogen yield of cyclic compounds is smaller than the corresponding normal hydrocarbon. This means that the opening of the cyclic structure is contributing to the polymerization.

Another important observation is that the yield of polymer is surprisingly high even with type B monomers ($\gamma > 1$). This is consistent with the fact that high values of γ for hydrocarbons are mostly due to the high hydrogen yield.

Data presented in Table I were taken at fixed pressure (150 $\mu\text{m Hg}$) and fixed wattage. The effects of discharge power and monomer pressure were examined with methane, propane, and toluene, and results are shown in Figure 1. In all cases, the hydrogen yield is nearly independent of discharge wattage and monomer pressure in the range above 40 $\mu\text{m Hg}$. This is consistent with the observations obtained in a flow system that the polymer deposition rate is not dependent on the discharge power. No change in hydrogen yield due to higher wattage means that the polymerization mechanism is not changed by higher discharge power. Consequently, in a flow system where monomer feed-in rate is the controlling factor, no change of polymer deposition rate is expected. The sharp increase of hydrogen yield may be an indication of higher degree of crosslinking of glow discharge polymer formed in low pressure.

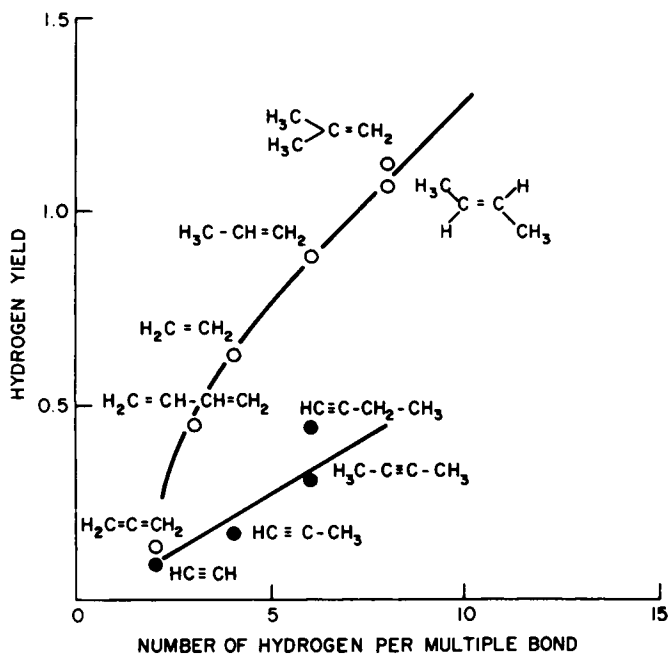


Fig. 2. Dependence of hydrogen yield on the number of hydrogen per multiple bond.

The hydrogen yield provides the most interesting information from this simple experiment; therefore, it may be worth examining the meaning of the values obtainable by possible reactions. Let us consider the simple case of $\gamma = y$, i.e., no production of condensible organic vapor, for polymerization of methane. In this process of polymerization, each step of forming a C-C bond produces one hydrogen molecule. If a kinetic chain length of n produced a molecular weight high enough to leave the gas phase (criterion of polymer in this study), the corresponding value of hydrogen yield is

$$(n - 1)/n = 1 - \frac{1}{n}.$$

This means that if polymerization proceeds by consecutive steps of recombination of radicals formed by hydrogen abstraction, the theoretical maximum value of hydrogen yield is unity.

The addition onto already formed polymer does not change this situation. Therefore, in order to have hydrogen yield higher than unity, hydrogen must be abstracted from the polymer either by (1) introduction of double bond or (2) crosslinking of two polymers already formed.

The introduction of one crosslink or unsaturation to a polymer of kinetic chain length n yields

$$y = \frac{n - 1}{n} + 1 = 2 - \frac{1}{n}.$$

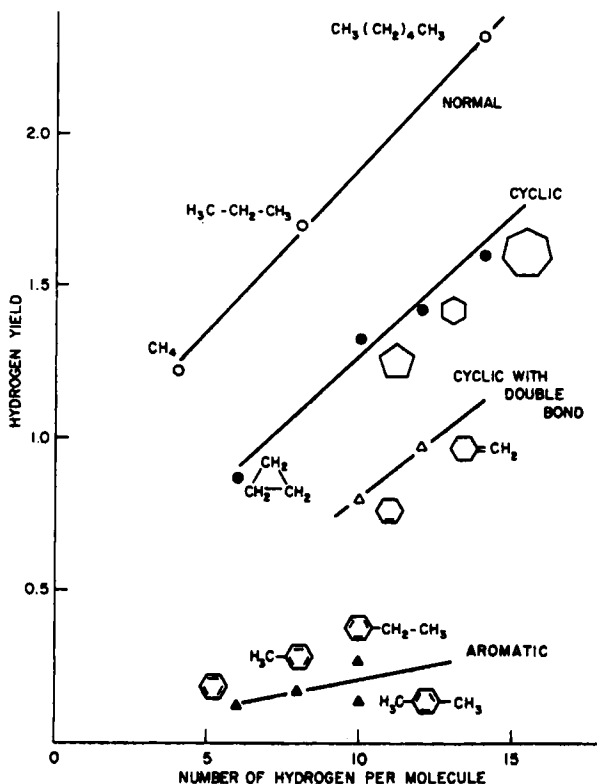


Fig. 3. Dependence of hydrogen yield on the number of hydrogen per molecule for normal, cyclic, and aromatic hydrocarbons.

Two crosslinks or unsaturation per polymer yields

$$y = \frac{n-1}{n} + 2 = 3 - \frac{1}{n}$$

It has been recognized that glow discharge polymers generally contain both crosslinks and unsaturation. The relatively high values of hydrogen yield obtained by normal hydrocarbons and olefins are consistent with those observations.

Other possible routes of polymerization of methane are (1) via formation of ethylene and (2) via formation of acetylene. In the first case, the expected maximum hydrogen yield is unity, in the second case, 1.5.

The observed hydrogen yield of 1.2 can be interpreted as a case of stepwise addition polymerization with crosslinking or as a case of acetylene formation, or by the combination of these two mechanisms. With higher alkanes, however, it seems rather unlikely that polymerization through formation of acetylene is the major route since the process involves two hydrogen abstraction from the same C-C bond without affecting the rest of the hydrogens.

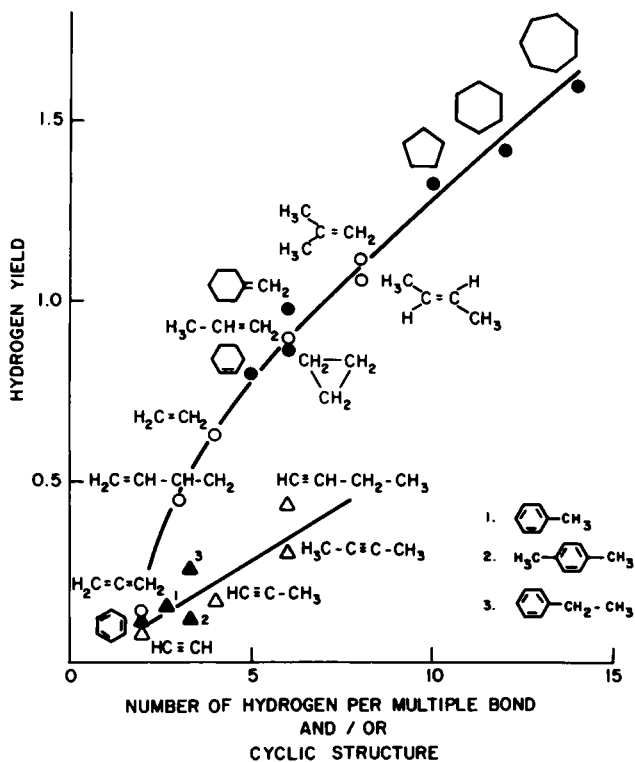


Fig. 4. Dependence of hydrogen yield on the number of hydrogen per multiple bond and/or cyclic structure for aromatic, cyclic, and multiple bond(s) containing hydrocarbons.

Polymerization by the (saturated) ring opening mechanism is quite evident if we compare the hydrogen yields as a function of numbers of hydrogen in a monomer molecule. In Figures 2 and 3, hydrogen yields were plotted against numbers of hydrogen in the monomer or numbers of hydrogen per multiple bond. As seen in Figure 2, the hydrogen yield is linearly proportional to the numbers of hydrogen per multiple bond, and all double bond-containing monomers and triple bond-containing monomers belong to respective lines. As seen in Figure 3, the hydrogen yield of cyclic compounds is much smaller than for normal compounds, and its dependence on the numbers of hydrogen is nearly the same as that of double bond-containing monomers (see Fig. 4).

Aromatic compounds have smaller hydrogen yields than those of triple bond-containing monomers. However, it is interesting to note that if the number of hydrogens per double bond is taken, the plot coincides with the line for triple bond-containing monomers. This aspect, together with the fact that polymers are formed with very small hydrogen yield, may suggest that aromatic compounds polymerize through formation of acetylene derivatives. This possibility is further explored with benzene as a model monomer of aromatic compounds. Possible intermediates which can lead to the polymerization of benzene⁶ are represented in Figure 5.

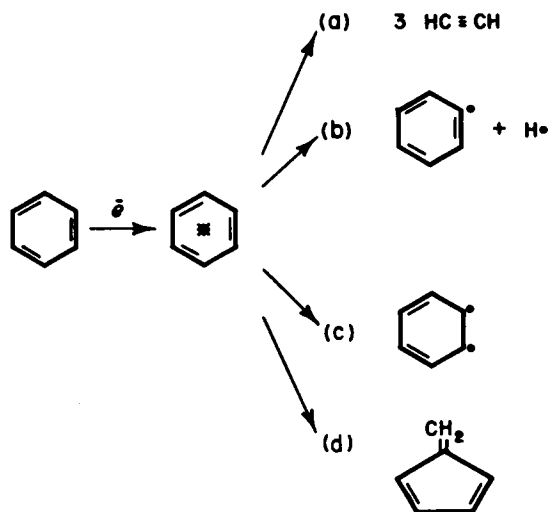


Fig. 5. Possible intermediate species which could lead to the polymerization of benzene in plasma

The reactions (a), (c), and (d) with consecutive utilization of remaining double bonds are the only possible mechanisms of forming polymer without producing hydrogen molecules. Therefore, the fact that the hydrogen yield per hydrogens in a monomer coincides with that of triple bond-containing monomers may be a strong indication that mechanism (a) is at least an important if not the exclusive mechanism. It is significant to note that a strong peak of $\cdot\text{C}\equiv\text{C}\cdot$ is observed in the emission spectra of benzene glow discharge.⁷ The small hydrogen yield may result from production of $\cdot\text{C}\equiv\text{C}\cdot$ from $\text{HC}\equiv\text{CH}$. The majority of acetylene might polymerize by opening of a triple bond followed by either addition or recombination of radicals, since acetylene polymerizes rapidly with small hydrogen yield in plasma.

It is interesting to note that hexafluorobenzene polymerizes without yielding any gas. Namely, $\gamma = p_{\infty}/p_0$ for hexafluorobenzene is zero, indicating that no C-F bond is broken in the polymerization of hexafluorobenzene. This observation also implies that either opening of the aromatic structure (including formation of acetylene derivatives) or opening of the double bond occurs as the primary process of the free-radical formation since the rates of polymerization manifested by the half-time for benzene and for hexafluorobenzene are essentially identical.

It may be concluded that (1) the polymerization mechanism of glow discharge polymerization under conditions used in this study seems to be well represented by the scheme shown by reactions (1), (2), and (3) mentioned earlier; (2) saturated hydrocarbons mainly polymerize by radicals formed by hydrogen abstraction; (3) hydrocarbons with olefinic double bond and cyclic structure polymerize via radicals formed by opening of the double bond or cyclic structure and also by hydrogen abstraction; and

(4) hydrocarbons with triple bond and aromatic structure polymerize predominantly by the opening of multiple bonds, with hydrogen abstraction playing a small role.

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References

1. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **15**, 2277 (1971).
2. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 1519 (1973).
3. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 1533 (1973).
4. A. W. Westwood, *Eur. Polym. J.*, **7**, 363 (1971).
5. J. P. Wightman and N. J. Johnston, *Advan. Chem. Ser.*, No. **80**, 322 (1969).
6. M. W. Ranney and W. F. O'Connor, *Advan. Chem. Ser.*, No. **80**, 297 (1969).
7. A. Théorêt, Institute de recherche de l'Hydro-Québec, Varennes, Québec, Canada, private communication.

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