

## Polymerization of Benzene in a Capacitively Coupled RF Plasma

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### Synopsis

The influence of various parameters on the polymerization reaction of benzene in a capacitively coupled rf plasma has been investigated, with particular emphasis on coatings structure and quality. Molecular weight distribution studies by gel permeation chromatography indicate that the degree of polymerization is mainly influenced by pressure and power. A two-stage mechanism of polymer formation is proposed on the basis of experimental data: oligomers or polymers are first formed in the gas phase and then diffuse to the electrodes and reactor walls, where they may undergo an emulsion-type polymerization. Sputtering and pyrolysis effects are suggested to explain the additional observations on the lowest- and highest-pressure films.

### INTRODUCTION

In the past decade, there has been much interest in the deposition of polymers in thin layer from organic vapors subjected to a glow discharge. Polymeric films produced by this process show interesting and sometimes novel properties and, therefore, have received serious consideration for different industrial or technological applications. It has to be recognized, however, that despite the great amount of laboratory work on glow discharge polymerization, only limited applications have reached the stage of commercial development.

Chemical reactions occurring in electrical discharges are very complex, and the nature of the fundamental reactions leading to polymer formation still remains to be elucidated. Many of the works published in the literature are concerned with the factors controlling the rate of polymer formation. Generally, from these observations reaction mechanisms are proposed, but authors still differ in opinion on such elementary aspect of the phenomena as whether polymer chains grow in the gas phase or at the electrodes surface.<sup>1-6</sup> Some other publications have examined polymer structures and properties.<sup>7-11</sup> Nevertheless, very few investigations have been carried out to study systematically and in details the influence of discharge parameters, such as pressure and power, on polymer structures and properties. The purpose of the present study is therefore to obtain such additional information as to elucidate some aspects of glow discharge polymerization. This paper is concerned with the reaction of benzene in a

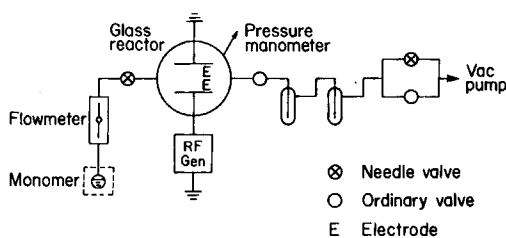


Fig. 1. Schematic representation of glow discharge reaction system.

capacitively coupled rf plasma. Benzene was chosen not only because it is a convenient system but also because it is one of the most examined monomer, which therefore allows immediate comparison with previous works.

### EXPERIMENTAL

A schematic representation of the apparatus used in this study is shown in Figure 1. The glass reactor has a 5-liter capacity. Monomer is admitted to the chamber under the desired pressure and flow rate, by means of two precision needle valves and a flowmeter. Gas pressure is measured on a McLeod tilting gauge, which provides a fairly reproducible reading. The monomer is kept in reservoir at constant room temperature to ensure a steady evaporation rate. Exact flow rate is deduced from monomer weight loss in reservoir and residence time calculated with values of flow rate and pressure. Unless otherwise stated, gap distance between electrodes was 3 cm. All feed-throughs and connection joints utilize O-ring joints or swagelok fittings. The system is evacuated down to  $10^{-3}$  torr (mm Hg) by a rotary pump before applying the discharge. Electrodes are connected to the outputs of a 13.56 MHz Tracelab RFG generator through an impedance matching unit.

The discharges were operated at a variety of pressures, power levels, and flow rates in order to investigate the effect of different variables on reaction products and their properties. Product formation occurred in all regions of the system. Deposits on reactor walls and electrodes were removed by refluxing benzene; then benzene was evaporated and the deposits weighted. Products insoluble in tetrahydrofuran solvent were removed and weighted on Micropore filters (when possible), and the solution was analyzed by gel permeation chromatography (GPC) and gas liquid chromatography (GLC). A set up of low-porosity Styragel columns (100 Å, 700 Å, 2000 Å) allowed separation by GPC of medium molecular weight compounds as well as an insight into the higher molecular weight distribution. Spectra were calibrated with compounds known to be present in reaction products, such as diphenyl; and with probably related model compounds, such as *p*-terphenyl and *m*-quinquephenyl. Several different spectra could be compared semiquantitatively by injecting corresponding samples at constant concentration and volume. Lower molecular weight compounds

(toluene, styrene, ethylbenzene, diphenyl) were detected and analyzed by GLC with Ucon Oil 550X and Carbowax 20M columns.

Additional information about the film deposited on electrodes (ATR, infrared analysis, elemental analysis, electron microscope analysis, TGA, DTA and dielectric loss) was obtained by means of an easily removable 1½-ft-diam. aluminum foil disc. All films prepared were more than 20  $\mu$ m thick. This allowed measurement of the thickness by means of a micrometer, and of the dielectric loss by applying simply a circular electrode above the film (with the aluminum foil support as counterelectrode).

Values of voltage corresponding to the rf generator wattmeter readings for the various conditions used were measured by means of an oscilloscope. Temperature of electrodes and plasma gas was measured with a thermocouple. The temperature readings were taken immediately after turning off the discharge, to avoid interference with the radio frequency.

## RESULTS

At low electrical field strength and pressure, molecular ionization in an electrical discharge depends mainly on pressure in the reactor system,  $P$ , and on the discharge power input,  $W$ .<sup>12</sup> Therefore, it is usual in plasma chemistry to interpret experimental data as a function of these two physical parameters. On the other hand, at a given pressure, a uniform glow discharge cannot be sustained unless a minimum power  $W_0$  is applied. With the reactor setup used in this study,  $W_0$  was observed to be proportional with pressure (Fig. 2). Thus, in order to get a parameter for power somehow independent of reaction pressure and discharge vessel geometry, it was found convenient to use the ratio  $W/W_0$  instead of  $W$ . This ratio may be considered as a measure of the effective power transferred to the discharge for chemical processing.

After each experiment, samples of reaction products were collected from electrodes surface, reactor walls, and cold traps. Their molecular weight distribution, as obtained by GPC, is given in Figures 3, 4, and 5. From these spectra, it is observed that a greater percentage of high molecular

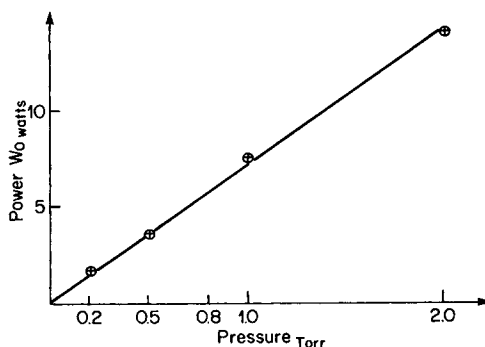


Fig. 2. Minimum power necessary to sustain plasma as function of pressure.

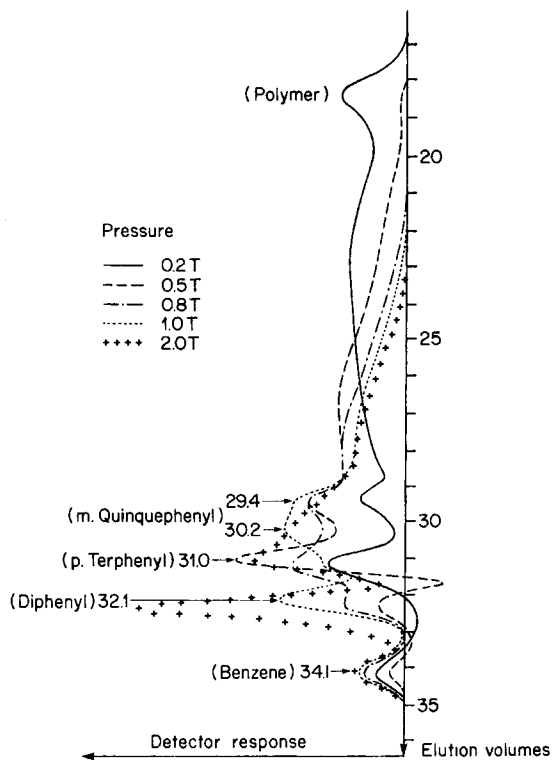


Fig. 3. GPC spectra of soluble compounds deposited on reactor walls at constant power ( $W/W_0 = 1.5$ ) as function of pressure.

weight products is formed at the electrodes, while low molecular weight compounds characterize products found in the traps; samples from reactor walls are intermediate. On the other hand, the variation of the molecular weight distributions with pressure is the same in these three cases: when pressure is reduced, polymers with higher molecular weights are formed, at the expense of medium molecular weight compounds, especially diphenyl, and, to a lower extent, compounds of size related to terphenyl and quinquephenyl. This variation of diphenyl concentration was checked by GLC. Toluene, styrene, and ethylbenzene are also present in products from GLC analysis, but their variation with pressure is not so clear, perhaps because of their very low concentration ( $\sim 0.1\%$ ).

The infrared spectra exhibit the same main absorption bands, as previously reported.<sup>1,8,10</sup> These were generally related to a polystyrene-type backbone, with some additional double- and triple-bond structures. In our case it was possible, in addition, to detect an increase, with pressure and power, of the ratio of the aromatic  $-\text{CH}$  band (at  $3015\text{ cm}^{-1}$ ) to the aliphatic methylene band ( $2920\text{ cm}^{-1}$ ). The observation from elemental analysis that the hydrogen-to-carbon ratio decreases with pressure (Fig. 6)

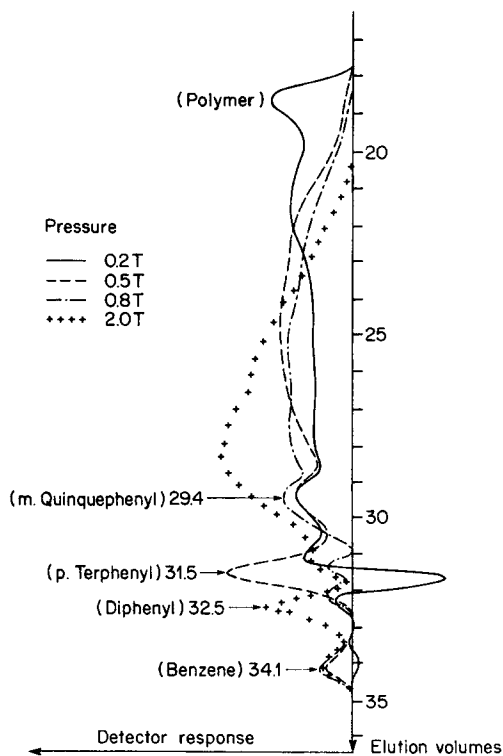


Fig. 4. GPC spectra of soluble compounds deposited on electrodes at constant power ( $W/W_0 = 1.5$ ) as function of pressure.

brings further evidence of the higher degree of unsaturation of polymers formed at more elevated pressure.

It was found possible to make a rough classification of the mechanical resistance to deformation of polymer films: in the case of low-pressure films for a given film thickness, deformation may be quite important without cracking or peeling. With increasing pressure, this resistance falls rapidly; adhesion and flexibility of higher-pressure films are very poor. Altogether, the overall film mechanical resistance decreases with pressure, power, and film thickness.

The effects of the parameters on polymer film solubility, temperature stability, and dielectric properties are summarized in Figures 7, 8, and 9.

## DISCUSSION

### Structure and Properties of Films

Many of these experimental data are interconnected, and these relationships will be discussed in the following three cases: high-, low-, and intermediate-pressure films:

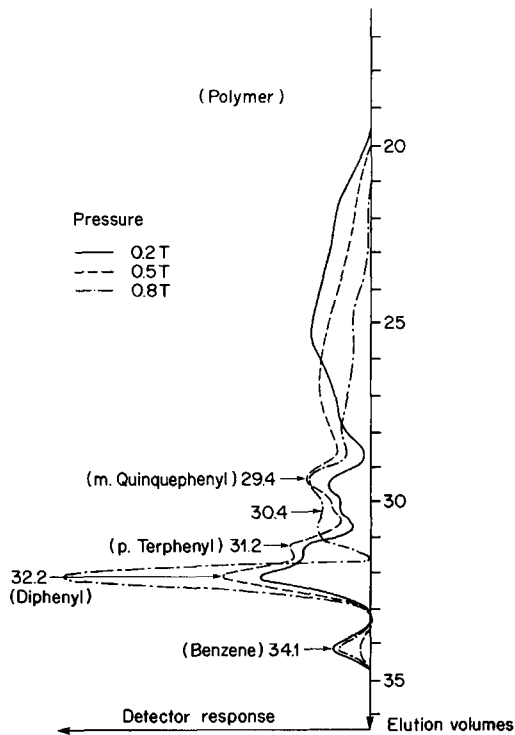


Fig. 5. GPC spectra of soluble compounds in traps at constant power ( $W/W_0 = 1.5$ ) as function of pressure.

1. High-pressure films ( $P > 1.5$  torr) exhibit a low hydrogen-to-carbon ratio (Fig. 6); and even at high values of  $W/W_0$ , carbonization occurs. Consequently, it is not surprising to find high dielectric loss values (Fig. 9) due either to unsaturation (Fig. 6) or to the presence of carbon in the film. Carbonization could be related to the temperature of gas in the plasma, which increases rapidly with pressure, as can be seen in Figure 10. At high pressures, this temperature is close to or above the temperature of

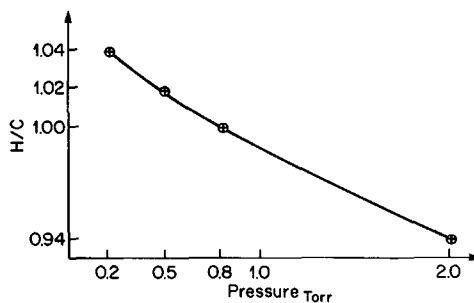


Fig. 6 Variation of hydrogen-to-carbon ratio with pressure ( $W/W_0 = 1.5$ ).

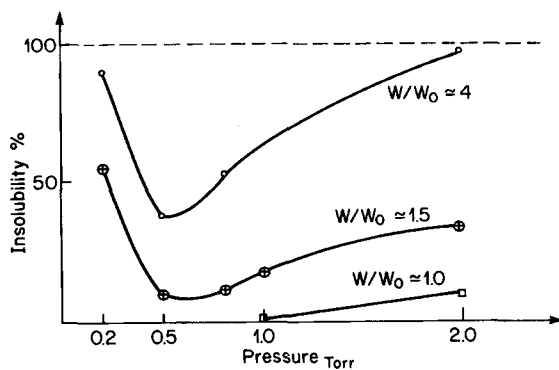


Fig. 7. Variation of percentage of insolubility of polymer films with pressure and power.

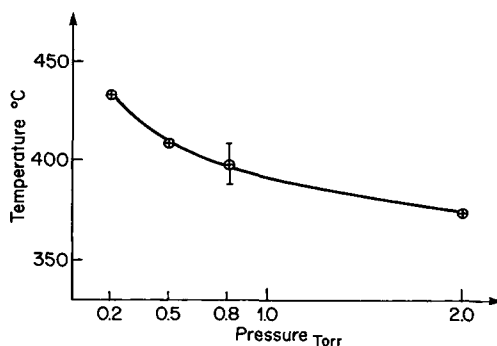


Fig. 8. Variation of maximum degradation temperature of polymer films with pressure ( $W/W_0 = 1.5$ ).

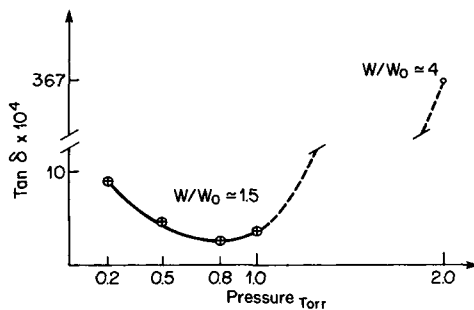


Fig. 9. Variation of dielectric loss of polymer films with pressure (frequency = 1 kHz; thickness: 40 to 100  $\mu\text{m}$ ).

maximal degradation of formed polymers (Fig. 8), involving at least partial pyrolysis of films and thus reducing their solubility (Fig. 7).

2. The good mechanical properties of low-pressure film ( $P < 0.5$  torr) can be easily attributed to the presence of higher molecular weight compounds (Fig. 4), which are known to increase the general flexibility of polymers. On the other hand, the insolubility of low-pressure films (Fig. 7)

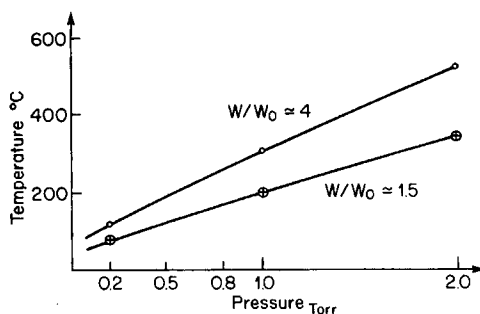


Fig. 10. Variation of plasma gas temperature with pressure and power.

could be due, with the low temperatures encountered in that case (Fig. 10), to crosslinking via electron or ion bombardment. If so, crosslinking should increase with the kinetic energy of bombarding species. This kinetic energy is proportional to the mean free path and voltage drop in the dark space between plasma and electrode surface, i.e., to the  $V/P$  ratio. Figure 11 shows clearly that the  $V/P$  ratio increases when pressure is reduced. Furthermore, under any condition, insolubility is greater on the non-grounded electrode and greater on both electrodes than elsewhere in the system. This is consistent too with general sputtering effects.<sup>13</sup> Dependence of sputtering upon voltage drop  $V$  rather than electric field  $E$  was checked by varying the electrode gap. Sputtering has little if any effect on dielectric loss. No sputtered films consist of spherical polymer particles of regular sizes (about 2000 Å); particles are smaller and display heterogeneous sizes (between 100 Å and 600 Å) in sputtered films.

3. In the case of intermediate-pressure films ( $0.5 < P < 1.5$  torr), values of hydrogen-to-carbon ratio ( $H/C \simeq 1$ ), dielectric loss ( $\tan \delta \simeq 2 \times 10^{-4}$ ), degradation temperature ( $\sim 400^\circ\text{C}$ ), aromatic-to-aliphatic group ratio ( $\text{CH}/\text{CH}_2 \simeq 1$ ) are nearest those of conventional polystyrene (respectively, 1,  $0.5 \times 10^{-4}$ ,  $400^\circ\text{C}$ , and 1). Films are optically transparent and are probably more regular and stoichiometric.

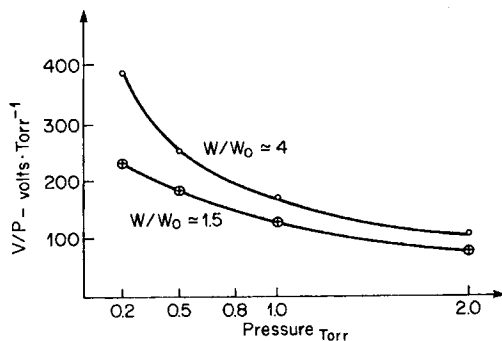


Fig. 11. Variation of the  $V/P$  ratio with pressure and power.



### Reaction Mechanisms

One of the first problems pointed out by all workers who tried to propose a mechanism of polymer formation is whether reaction occurs in the gas phase or at the surface of substrates. Our own observed variations of the degree of polymerization agree with a mechanism involving both possibilities.

For instance, carbonization of polymers should be restricted to the plasma volume, as the temperature is not high enough on the electrodes, walls, or outside the plasma (about half on the electrodes than inside the plasma itself). Consequently, carbonized polymers collected on reactor walls must have formed actually in the gas phase. Strong analogies can be found between glow discharge carbonization and carbon black formation: values of sizes of particules formed are in the same range, and carbon black particules are supposed to build up through aromatic polymer rearrangement.<sup>14</sup> Values of temperature of pyrolysis are much lower in the case of glow discharge carbonization (450°C instead of 800°C), perhaps because the molecules are already in an excited state.

Now, such initiated chains formed in the gas phase discharge cannot stay in the gas phase and deposit on surfaces. Monomer molecules are adsorbed on these surfaces according to pressure. If pressure is high enough (above 1 torr, according to Denaro<sup>2</sup>) there is enough monomer present to dissolve the migrating chain, and the polymerization degree is found to be limited (Figs. 3 and 4). At lower pressures, the surfaces are not covered with even a monomolecular layer of monomer, and the chain is found to go on growing (Figs. 3 and 4). Both cases are consistent with a mechanism related to emulsion polymerization<sup>15</sup> that would occur in the incompletely adsorbed layer of monomer on the electrode, with vacuum as the nonsolvent phase.

In support of these proposals, conventional gas-phase as well as emulsion polymerization generally lead to formation of small spherical polymer particles, with sizes similar to those encountered here. It is not surprising that still active polymer chains may stop growing, as has been often observed,<sup>2,8</sup> and that many free radicals are trapped inside the polymer films obtained. Products found in the cold traps outside the reactor are always composed of low molecular weight compounds (Fig. 5) which cannot undergo further polymerization, dissolved as they are in large quantities of unreacted monomer.

Both polymerization mechanisms are consistent with the observed reaction rates: ion molecule reactions in gas phase as well as the rate of arrival of monomer molecule to a surface are known to increase with pressure. Film deposition rate (Fig. 12), as previously observed, and global reaction rate of benzene, too (Fig. 13), are actually increasing with pressure. Figures 12 and 13 show that these rates increase with power, too, but film deposition rate is power limited (as previously observed), while global reaction rate is nearly proportional to power. This is not clearly under-

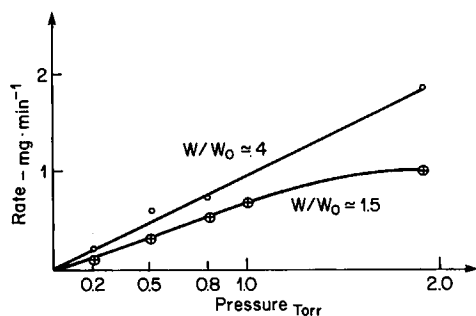


Fig. 12. Rate of film deposition as function of pressure and power.

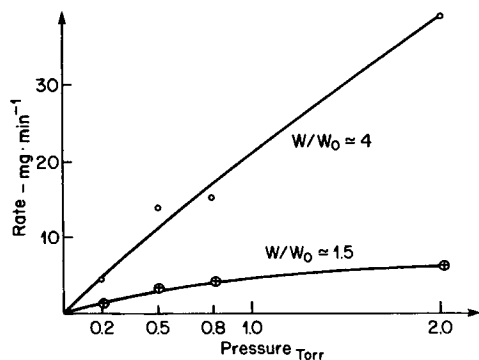


Fig. 13. Rate of global reaction of benzene as function of pressure and power.

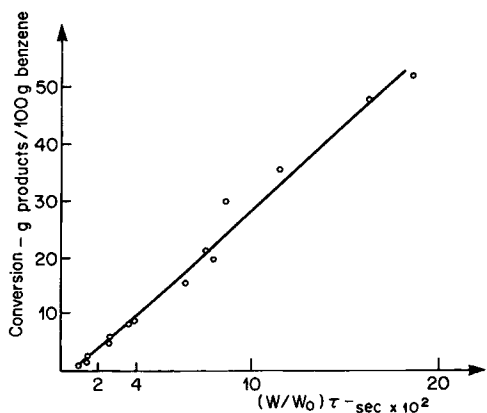


Fig. 14. Conversion with respect to benzene.

stood and could be related to the warmer surface temperature of the electrode, involving less adsorption of monomer (a slightly higher degree of polymerization is effectively observed on the electrodes).

From an industrial coating application point of view, it could be interesting at last to have an idea of conversion with respect to benzene.

Conversion data, obtained with a wide range of values of residence time ( $0.5 \times 10^{-2} < \tau < 10 \times 10^{-2}$  sec), pressure, and power ( $1 < W/W_0 < 5$ ), were found to be best fitted by means of the expression  $(W/W_0)\tau$ , as shown in Figure 14. Conversion is the only value found to be significantly dependent upon residence time.

The authors wish to thank MM. Y. Giguère and J. P. Crête for their technical assistance. The help of Dr. G. Perreault, of the Centre de Recherches pour la Défense de Valcartier (CRDV), for the GPC analysis is gratefully acknowledged.

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Received August 2, 1972