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Mechanism and Kinetics of Polymerization of Propylene in a Microwave Plasma[1]

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Flowing microwave plasma of propylene and propylene with argon was studied by mass spectrometry. Plasma composition was investigated as a function of external parameters such as pressure, argon/propylene ratio, and microwave-induced power. It was found that the propylene broke down to C_2H_2 and CH_4, or reacted further with propylene. Two main products, leading to the determination of three main-chain reactions for the polymerization of propylene by ion–molecule interactions, were observed, namely, C_2H_2 and CH_4. These were the propylene, acetylene, and ethylene chain reactions. It was also found that the propylene disappeared in a pseudo-first-order reaction. Consequently an overall rate constant for the polymerization was determined (50 sec^{-1} at 1 torr pressure for propylene plasma). This constant is found to be linearly dependent upon the propylene percent concentration, and nonlinearly dependent upon plasma pressure.

KEY WORDS: Plasma; kinetics; polymerization; propylene.

1. INTRODUCTION

When low-molecular-weight hydrocarbons such as methane, acetylene, or propylene are introduced into a microwave plasma, an irreversible reaction takes place, the product of which is a carbonlike solid, named pyrocarbon.(1–4) The addition of an inert gas such as argon increases the polymerization reaction rate to a large extent.(1–6)

In order to investigate the mechanism and kinetics of the reactions taking place in the plasma, a mass spectrometric study was carried out, in which plasma was examined at various stages of its propagation.

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Two general approaches to the study of the chemical mechanism of hydrocarbon pyrolysis and polymerization can be found in the literature, namely:

(i) The positive ion–molecule type reaction(4,7) for the polymerization of high-molecular-weight hydrocarbons; and
(ii) The radical molecule type reaction.(8,9)

In a previous paper,(10) the diagnostics of methane (or propylene)–argon mixtures in a microwave discharge was considered and the pattern of positive ion–molecule reactions was indicated. Also, Melton,(7) studying methane–argon mixtures in the ionization chamber of a mass spectrometer, concluded that the pyrolytic pattern is governed by the ion–molecule reactions.

Davis and Libby,(4) working on the polymerization of methane by radiolysis with and without NO as a free-radical scavenger, obtained no effect of the NO in the polymerization products. Vasile and Smolinsky(11–13) extracted positive ions from plasmas and in later works(14,15) on C_2H_4 and C_2H_2 RF plasmas concluded that the polymerization is propagated by positive ion species. Westwood(16) and Thompson and Mayhan,(17) and recently Khait *et al.*,(18) showed that the deposition rate on a biased electrode in the plasma is nearly linearly proportional to be biasing voltage, indicating that the nature of the deposition by polymerization is dependent upon charge carriers.

2. THEORETICAL CONSIDERATIONS

The mean electron energy in the microwave plasma is 3–4 eV.(5,6) With a Druyvesteyn energy distribution(19) a rough estimation shows that over 20% of the electrons have energy above the ionization threshold of Ar. Previous works(5,6) show the electron concentration to be in the range 10^{11}–10^{12}/cm^3, so that there are enough ionizing electrons to make the ionization process play an important role.

In the plasma, atom or molecule may be ionized in one of several processes(19–21): atom–atom collision accompanied by energy transfer with low cross section $<10^{-20}$ cm^2; electron–atom impact, cross section $\sim 10^{-16}$ cm^2; electron-transfer collision, cross section $<10^{-20}$ cm^2; charge-transfer reaction, cross section $\simeq 10^{-14}$ cm^2; and chemi-ionization, which involves chemical change. The cross sections show that the electron–atom impact and the charge-transfer reactions are dominant in the plasma.

Thus, the first ionization stage of propylene is expressed as follows:

$$\begin{aligned}
\mathrm{Ar}+e &\rightarrow \mathrm{Ar}^{+}+2e\\
\mathrm{Ar}^{+}+\mathrm{C_3H_6} &\rightarrow \mathrm{Ar}+\mathrm{C_3H_6^{+}}\\
&\rightarrow \mathrm{Ar}+\mathrm{C_3H_5^{+}}+\mathrm{H^{\cdot}}\\
\mathrm{C_3H_6}+e &\rightarrow \mathrm{C_3H_6^{+}}+2e\\
&\ \mathrm{C_3H_5^{+}}+\mathrm{H^{\cdot}}+2e
\end{aligned}$$

This is the initiation stage for many ion–molecule reactions taking place in the plasma. Field and Munson(22) and Chen *et al.*(23) have shown that the concentrations of the species behave in a pseudo-first-order kinetic manner.

The type of reaction encountered in the plasma is

$$\mathrm{A}^{+}+\mathrm{B} \rightarrow \mathrm{C}^{+}(+\mathrm{D})$$

which calls for second-order behavior. Here, B designates a molecule that is the reactant (propylene) and that is present in great excess, so that the concentrations of the species behave in a pseudo-first-order reaction.

The kinetic model and the kinetic calculations for such species have been described elsewhere,(6,22,23) and a similar approach may be adopted here.

As the propylene molecule participates in all stages of the reaction, its concentration is indicative of the rate of reaction propagation. By assuming a plug flow through the reactor, the length of the reactor may be correlated to the duration of the flow. For a first-order reaction for the propylene we have $-d[\mathrm{C}]/dt = k[\mathrm{C}]$ where [C] is the propylene concentration which may be replaced by a property proportional to this concentration. For the mass-spectrometric data, we may replace [C] by $I_{\mathrm{C_3H_6}}/\Sigma I$, where $I_{\mathrm{C_3H_6}}$ is the peak intensity of propylene and ΣI is sum of all peak intensities. k is the rate constant times the propylene pressure. Rewriting and integrating the rate equation, we get

$$-\int_{c_1}^{c_2} \frac{1}{[\mathrm{C}]}\, d[\mathrm{C}] = \int_{t_1}^{t_2} k\, dt$$

$$\ln \frac{I_{\mathrm{C_3H_6}}}{\Sigma I} = -k\Delta t$$

From the plug-flow assumption, we draw

$$\ln \frac{I_{\mathrm{C_3H_6}}}{\Sigma I} = -k\Delta x/u$$

where Δx is the distance between the sampling points, and u is the gas velocity in the reactor. A plot of the left-hand side of the previous equation versus propylene pressure yields a straight line. The value of $k\Delta t$ is obtained from the slope of the line, and k (the overall rate constant) is found by calculating the plug-flow velocity, so that Δt is known. (Different sets of reaction conditions such as total pressure in the reactor, and argon/propylene ratios, are expected to yield different values of k, for it is an experimental fact that these factors alter the reaction rate.) The kinetic model is discussed in Section 4 of this study.

3. EXPERIMENTAL

Figure 1 shows the experimental setup. Pre-mixed gases (R) are controlled (C) so as to flow at a steady rate of 7.5 SCCM[4] of propylene and argon through a quartz tube reactor (T). The reactor is fitted with a sampling port which is connected via a 20-μm sampling orifice to the differential pumping system (D_i) and then through a second 20-μm orifice to the ionization chamber (E) of a quadrupole mass spectrometer (Q).

The system is pumped down by a rotary pump R_p and by two high-vacuum pumps D_p and I_p. Plasma is induced inside the reactor by a $1/4\lambda$ Evenson cavity (A) operated by a 2.45-GHz microwave generator at 150 W. Various regions of the plasma may be sampled by simply moving the cavity along the reactor tube. Three main positions were studied, namely an upstream position (at the beginning of the plasma reactions), the center of the plasma, and a downstream position, labeled H, G, and F respectively.

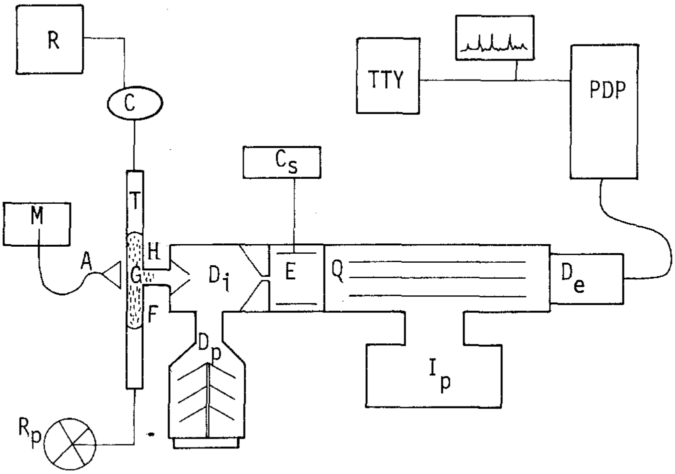


Fig. 1. System setup. For explanation of symbols, see text.

Plasma was sampled on-line by the QMS 301 Blazers quadrupole fitted with a cross-beam ion source and a 90° off-axis ion-deflection unit. The mass spectrometer was operated at low, 16–10 eV, electron energy in order to minimize the fragmentation(23,24) of the sampled species and yet have enough energy to ionize them. Table I shows the spectra obtained for a propylene–argon mixture with and without plasma. Without plasma, except for a single fragment at mass number 27 (corresponding to $C_2H_3^+$) with a relative intensity of 5.8% and little hydrogen (0.5%), only C_3 carbon ions are observed.

The other parameters of the mass spectrometer (C_s) were set so as to produce a sufficient signal for the secondary electron multiplier (D_e).

The plasmas were sampled as a function of total gas pressure (1–10 torr), argon/propylene feed ratio, position of the plasma (H, G, F), and microwave incident power. Each mass spectrum was sampled by 100 scans, which were multichanneled by an on-line PDP 11/10 computer operating on the Sparta Program. The mass spectra were recorded on a floppy disc and later decoded, background subtracted, and normalized.

Before each set of experiments, the instrumental background was recorded and stored in the computer. Each gas mixture was sampled first

Table I. Normalized Spectra of Both Propylene–Argon Mixture at $R = 5$, under 5 torr Pressure, with and Without a Plasma (150 W), and Propylene Flow Rate 7.5 SCCM

No.	Mass (m/e)	Ion	$I/\Sigma I$(%) No plasma	$I/\Sigma I$(%) Plasma	No.	Mass (m/e)	Ion	$I/\Sigma I$(%) No plasma	$I/\Sigma I$(%) Plasma
1	2	H_2^+	0.5	4.33	20	53	$C_4H_5^+$	—	0.59
2	12	C^+	—	0.40	21	54	$C_4H_6^+$	—	1.03
3	15	CH_3^+	—	2.80	22	55	$C_4H_7^+$	—	1.03
4	16	CH_4^+	—	4.39	23	56	$C_4H_8^+$	—	1.03
5	26	$C_2H_2^+$	—	20.50	24	57	$C_4H_9^+$	—	0.44
6	27	$C_2H_3^+$	5.8	3.83	25	65	$C_5H_5^+$	—	0.44
7	28	$C_2H_4^+$	—	12.86	26	66	$C_5H_6^+$	—	0.71
8	29	$C_2H_5^+$	—	1.78	27	67	$C_5H_7^+$	—	0.44
9	30	$C_2H_6^+$	—	1.10	28	68	$C_5H_8^+$	—	0.31
10	39	$C_3H_3^+$	6.5	3.84	29	69	$C_5H_9^+$	—	0.25
11	40	$C_3H_4^+$	7.6	6.45	30	74	$C_4H_{14}^+$	—	0.44
12	41	$C_3H_5^+$	29.4	9.04		74	$C_6H_2^+$	—	0.44
13	42	$C_3H_6^+$	48.2	10.89	31	78	$C_6H_6^-$	—	1.20
14	43	$C_3H_7^+$	2.3	1.56	32	79	$C_6H_7^+$	—	0.48
15	44	$C_3H_8^+$	—	0.54	33	80	$C_6H_8^+$	—	0.36
16	49	C_4H^+	—	0.21	34	81	$C_6H_9^+$	—	0.32
17	50	$C_4H_2^+$	—	3.24	35	91	$C_7H_7^+$	—	0.74
18	51	$C_4H_3^+$	—	0.59	36	92	$C_7H_8^+$	—	0.45
19	52	$C_4H_4^+$	—	1.39					

without and then with microwave power. This enabled clearing the plasma spectrum of masses such as argon, nitrogen, and water, which would appear as impurities or additives, and calculating $I/\Sigma I$ for each peak. The results obtained were tabulated and drawn by the computer.

4. RESULTS AND DISCUSSIONS

Mixtures of pre-mixed gases were sampled at different pressures and positions. Table I is a typical example of the mass spectrum obtained from the gaseous phase of the plasma at 5 torr. Figure 2 is a graphical representation of the data obtained from sampling the plasma at different pressures at the points H, G, and F. At this pressure range (1–10 torr) the spectrum obtained is rather different than the spectrum obtained[(25)] at lower pressures (5 μm). The results show high relative concentrations of m/e 26, 28, 42, and 50–57, i.e., acetylene, ethylene, propylene and the C_4 species, respectively.

It may also be noted that when the plasma pressure increases, the "concentration" of the intermediate species decrease whereas that of the propylene increases. This is due to the fact that at higher pressures the mean free path of charged particles decrease, and the rate of recombination increases, thus inhibiting the rates of propagation and initiation. From the linear part of the slopes of Fig. 2 the rate constants for the formation

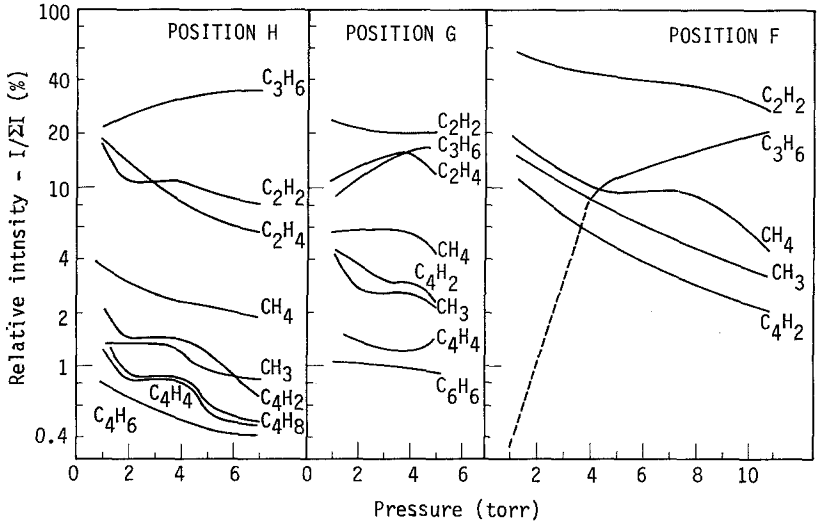


Fig. 2. Relative intensity of ionized species as a function of pressure at different sampling positions and at 7.5 SCCM flow.

of the intermediates may be obtained in the manner described by Field and Munson.(22)

4.1. Plasma Reaction Mechanism

Most species may be accounted for by a mechanism similar to that presented by Smolinsky and Vasile(14) for the ethylene plasma.

From the results shown in Fig. 2 for the propylene plasma, three main parallel chain reactions are presented, namely:

(i) propylene chain,
(ii) the acetylene chain, and
(iii) the ethylene chain.

The main type of reaction considered is the ion–molecule reaction, where propylene is always the molecule because of its presence in great excess. All chain reactions are initiated by the following ionizations of the propylene molecule by either electrons, argon ions, or metastable argon:

$$C_3H_6 \xrightarrow{e,\ Ar^+,\ Ar^*} C_3H_6^+ \ (+e, \text{ or } +2e)$$

The propylene ion formed may now continue to react in one of the three chains.

(i) *Propylene chain.* This is a straightforward reaction of the propylene ion with the excess propylene, producing a C_6 hydrocarbon ion which reacts with propylene similarly to give a C_9 hydrocarbon ion.

$$C_3H_6^+ \xrightarrow{C_3H_6} C_6H_{10-6}^+ \xrightarrow{C_3H_6} C_9H_r \xrightarrow{C_3H_6} \cdots C_pH_q^+ \qquad p>q$$

As the chain propagates, the hydrocarbon ion becomes less saturated and p exceeds q. The product is a highly unsaturated hydrocarbon (pyrocarbon) and is deposited on the walls of the reactor.

(ii) *Acetylene chain.* This starts with fragmentation of the propylene ion:

$$\begin{aligned} C_3H_6^+ &\rightarrow C_2H_2^+ + CH_4 \qquad \Delta H = 70\ \text{kcal} \\ &\rightarrow C_2H_2 + CH_4^+ \qquad \Delta H = 99\ \text{kcal} \end{aligned}$$

Thermodynamic(26) and mass spectrometric(27) data make the first of the above two reactions more probable. The acetylene ion then continues reacting with excess propylene molecule as follows:

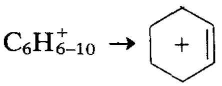
$$C_2H_2^+ \xrightarrow{C_3H_6} C_5H_{4-6}^+ \xrightarrow{C_3H_6} \cdots C_rH_s^+ \qquad r>s$$

This reaction accounts for the presence of the C_5 hydrocarbon species in the plasma.

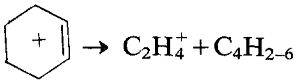
(iii) *Ethylene chain.* Mass spectra of propylene without plasma and at 70 eV show(26) no ethylene fragment. When submitted to microwave radiation, propylene plasma produces ethylene in high concentrations. Therefore ethylene must be a product of a different mechanism. Considering the first stage in the propylene chain, we get the C_6 hydrocarbon species:

$$C_3H_6 + C_3H_6^+ \rightarrow C_6H_{8-10}^+$$

The stability of the C_6 ion increases when it transforms into a nonsaturated six-membered ion ring(27,28):



By undergoing a Mclafferty rearrangement (retro Diels–Alder), this ion produces ethylene and C_4 species:



Thus, the ethylene and the C_4 species which appear in the spectrum are accounted for. The ethylene formed continues to react with excess propylene according to the patterns of acetylene and propylene chains:

$$C_2H_4^+ \xrightarrow{C_3H_6} C_5H_{5-8}^+ \xrightarrow{C_3H_6} \cdots C_uH_r \qquad u > r$$

These three chains end in a solid highly unsaturated hydrocarbon—the pyrocarbon which deposits on the walls of the reactor as a black solid. Because of the nature of the pyrocarbon, all stages of polymerization evolve hydrogen whose presence is noted in Table I.

4.2. Kinetics in the Plasma

The term "kinetics in the plasma" is used here in the sense of the rate of the chemical reaction of the reactant gas, i.e., propylene, which reacts in various parallel chain reactions. Figure 3 shows for the propylene, on a logarithmic scale, a nearly linear decrease in concentration along the reactor, from which a first-order kinetics for the propylene is deduced ($\delta \ln I/\delta t$ is a constant). By sampling the plasmas at different pressures for several argon/propylene ratios, various slopes for the propylene concentration are obtained. Figure 4 shows some slopes for the propylene under different working conditions.

Because the x-ordinate is proportional to the time that propylene traveled in the plasma, the kinetic rate constant for the decrease in the

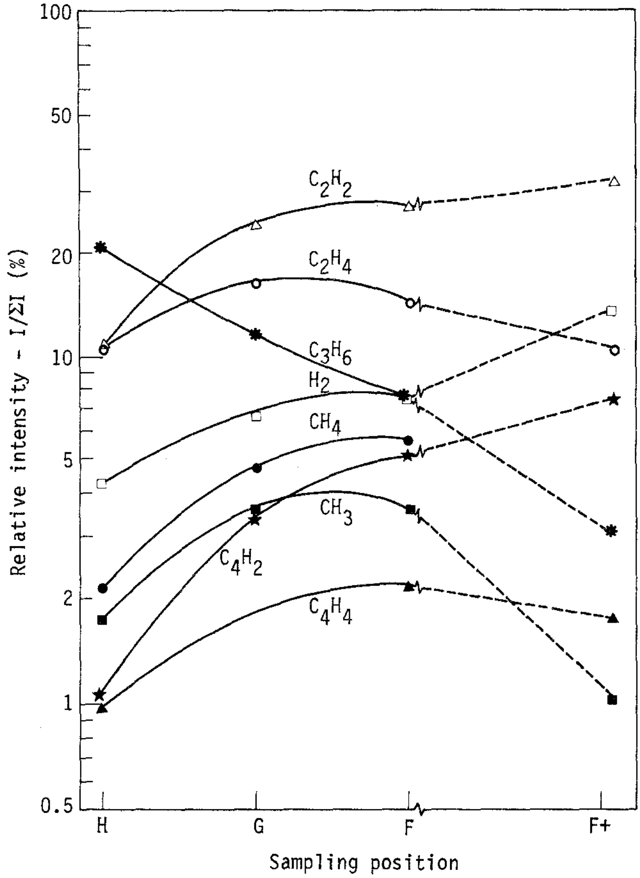


Fig. 3. Relative intensity of species along the plasma reactor at 3 torr total pressure and argon/propylene ratio 5; microwave power 150 W, propylene flow rate 7.5 SCCM.

propylene concentration may be calculated from

$$k = -d \ln I/dt$$

The rate at which the propylene concentration decreases is the overall reaction rate and is identified with the term "kinetics in the plasma."

The calculated values of the reaction constant k, plotted against propylene (or argon) percentage concentration, show a linear behavior as shown in Fig. 5. It is seen that:

(i) k is linearly proportional to the argon concentration, and
(ii) k decreases in a nonlinear way with increasing plasma pressure.

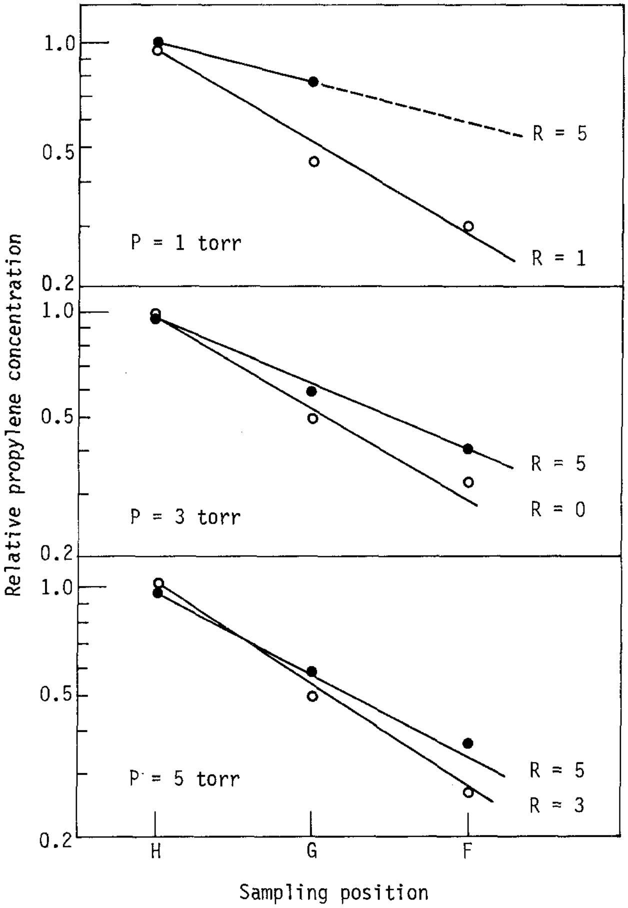


Fig. 4. Relative propylene concentration along the reactor at different argon/propylene ratios *R* and at various pressures; microwave power 150 W, propylene flow rate 7.5 SCCM.

The dependence of *k* on argon concentration is in accordance with the phenomenological observation that addition of argon increases the rate of pyrocarbon formation. In other words, argon affects the overall rate by increasing initiation rates through an increase in the propylene ionization rate. Without argon, the sole mechanism for the ionization of propylene is via electron impact. The addition of argon increases the ionization of propylene by both charge transfer and Penning effect reactions. The addition of argon increases the mean electron energy(6) as well, and thereby the ionization cross section of propylene and argon becomes more favorable.

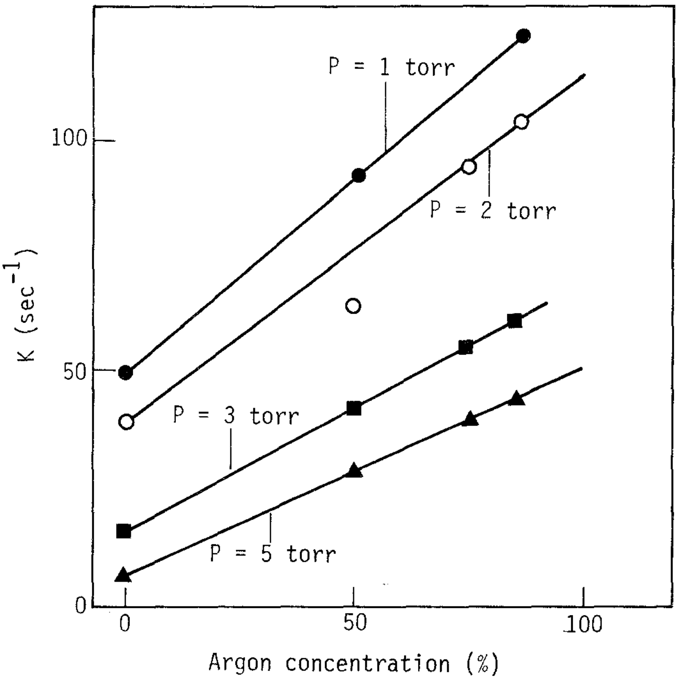


Fig. 5. The dependence of *k*, the reaction constant, upon the working variables (pressure and argon concentration); microwave power 150 W, propylene flow rate 7.5 SCCM.

During the propagation of the chain reaction, some terminations occur, including termination at the reactor's walls or recombination of ions with electrons. The product of such terminations is an uncharged low-weight gaseous particle (P). This particle may be reionized by Ar^+ and then continue its polymerization:

$$P + Ar^+ \rightarrow P^+ + Ar$$

Both process which are attributed to the presence of argon contribute to the increase in the overall reaction rate. Considering first-order kinetics, we get, for the reaction rate *R*,

$$R = -d[C]/dt = k[C]$$

where [C] is the propylene concentration. By increasing the argon concentration (1 − [C]), *k* is also increased, and [C] is decreased. From this behavior a maximum rate should be expected.

Examination of the concentration of propylene at position F as a function of $[Ar]/[C_3H_6]$ in the feed and at different pressures shows a

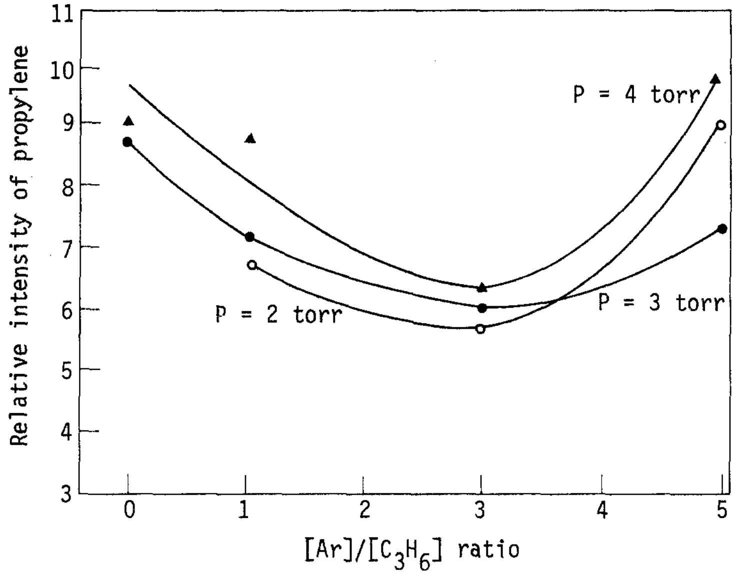


Fig. 6. Relative intensity of propylene at position F as a function of argon/propylene ratio at different total working pressures; microwave power 150 W, propylene flow rate 7.5 SCCM.

minimum, as expected (Fig. 6). This minimum, which is equivalent to the maximum reaction rate, occurs for propylene concentration at all pressures.

The dependence of k on the total pressure is not yet fully understood because the various k_i are independent of each other and have different pressure dependences; k_i is the rate constant for the ith step in the polymerization, and k is a certain combination of these k_i.

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