Plasma Dissociation Reaction Kinetics. I. Methyl Methacrylate

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ABSTRACT: Fourier transform infrared spectroscopy (FTIR) was utilized to study the plasma gas-phase reaction kinetics and reaction mechanisms in capacitively coupled glow discharges of methyl methacrylate (MMA) under zero monomer flow rate conditions. The gas-phase study shows two major electron-impact-induced dissociation pathways in MMA plasmas: the C—O bond cleavage reaction and decarboxylations. The C—O bond cleavage reaction accounts for approximately one-half of the MMA dissociation, and neutral formaldehyde and dimethyl ketene (DMK) are produced via intramolecular rearrangement. Decarboxylations produce CO, CO₂, and a number of radicals that subsequently stabilize to form neutrals, including propylene, allene, and methanol. These intermediate species then further dissociate in the plasma to small hydrocarbons (methane, acetylene, and ethylene), CO, CO_2 , and H_2 . Plasma power and initial monomer pressure have only minor effects on the MMA fragmentation chemistry. However, the reaction rate increases at higher-power and lower initial monomer pressure conditions. The modeling also reveals the relative reactivities of the neutrals. A time-scale transformation technique based on the MMA decomposition half-life significantly reduces the effects of the reactor condition on the kinetics. In addition, mass balance ratios are utilized to calculate the portion of plasma species that have been accounted for by the *in situ* technique. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1-16, 1999

Key words: plasma polymerization; FTIR; methyl methacrylate; gas-phase kinetics; dimethyl ketene

INTRODUCTION

Plasma polymerization is a thin-film-deposition technique that can coat a variety of surfaces in contact with a glow discharge of organic or organometallic monomers. In general, plasma-polymerized films are pinhole free; highly crosslinked; insoluble, stable, and inert; and highly coherent and adhere to the substrates. Because of these excellent properties, plasma polymers have been studied for a variety of applications, such as for selective permeation membranes, protective coatings, biomedical materials, electronic and optical devices, and adhesion promoters.¹ In addition, plasma polymers have significantly different properties and structures from their conventional counterparts, and they do not have a well-defined repeating unit. Therefore, the term "plasma poly-

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mer" is a misrepresentation for most plasmapolymerization conditions.

Hundreds of organic materials have been the subjects of plasma-polymerization studies. Methyl methacrylate (MMA) is among one of the earliest to be studied, and it was found to have a "moderate-to-slow" plasma-polymerization rate.² One of the potential applications of plasma-polymerized MMA (PPMMA) films is the dry electron-beam resist application.³ PPMMA films showed a higher sensitivity than that of spin-coated PMMA resists,⁴ and efforts to improve the PPMMA resist sensitivity continue. For example, copolymerization with styrene⁴ or tetramethyl tin⁵ and doping with S and F atoms⁶ have all been found to improve the sensitivity of PPMMA resists.

Other investigations of PPMMA film applications include self-curing bone cements,⁷ waveguides,⁸ and humidity sensor material.⁹ Li et al. reported on the photoluminescence (PL)¹⁰ and morphology¹¹ of PPMMA films, and the PL was found to be a one-photon fluorescence process with a lifetime on the order of a few nanoseconds.¹⁰

As will be shown in the next section (Background), the plasma-polymerization chemistry of MMA was investigated by different groups using different techniques, including *in situ* mass spectroscopy (MS). The MS studies provided interesting insights into the ion chemistry in MMA plasmas.^{12,13} In this study, residual gas analysis was performed with *in situ* Fourier transform infrared (FTIR) spectroscopy to provide complimentary information on the neutral chemistry in MMA plasmas. The goals of this study were to understand the following issues:

- How does MMA break down in the plasma?
- What kinds of species are produced?
- How do the plasma process parameters influence the fragmentation chemistry?

We have previously reported on the dissociation products and reaction mechanisms of MMA plasmas.^{14–17} In this and the following communication, the reaction kinetics and plasma chemistry of MMA and related precursors are discussed. This article describes the study of gas-phase reaction kinetics of MMA glow discharges. The second article describes the plasma studies of precursors related to MMA, such as methyl crotonate, methyl isobutyrate, ethyl methacrylate, vinyl acetate, isopropanol, and methanol.

BACKGROUND

Dissociation reactions in plasmas are complex and multistep in nature. In addition, monomer dissociation often occurs via more than one pathway:

• Competitive reaction

$$e + M$$
 $A + B + e$
 $C + D + e$

• Consecutive reaction

$$e + M \rightarrow X + e \rightarrow Y + e \rightarrow Z + e$$

A number of neutral reaction products have been identified in MMA plasmas by *in situ* $FTIR^{14,15}$ and by other techniques in the literature.^{13,18–20} The molecular dissociation products of MMA plasmas are summarized in Table I according to their molecular weight.

The C—O Bond Cleavage Reaction

A large percentage of 69 amu ions was observed as a result of *the C—O bond cleavage reaction* in MS studies of MMA. The structure of this 69-amu ion was confirmed as an CH_2 — $C(CH_3)$ — C^+ —O ion which was also observed in the mass spectrum of dimethyl ketene [DMK, $(CH_3)_2C$ —C—O].²¹ Tatsumi et al. proposed that neutral DMK is generated in MMA plasmas via this C—O bond fragmentation reaction based on their *ex situ* NMR analysis of trapped effluent gas from MMA plasmas¹⁹:



The C—O bond cleavage reaction of MMA (MW = 100) into DMK (MW = 70) and COH_2 (MW = 30) involves the formation of a five-member ring and an intramolecular rearrangement.¹⁹ The DMK/COH₂ pair was found to have very similar trends in the FTIR study of flowing MMA plasmas: Both are strongly positively correlated to MMA concentration levels (0.96 for DMK and 0.94 for COH₂), and both have a similar depen-

Species	Formula	MW	Diagnostic Technique
Hydrogen	${\rm H_2}$	2	In situ MS ¹³
Methane	CH_4	16	In situ FTIR In situ MS ¹³
Carbon Monoxide	СО	28	In situ FTIR In situ MS ^{13,18}
Ethylene	C_2H_4	28	In situ FTIR In situ MS ¹⁸
Ethane	C_2H_6	30	In situ MS^{13}
Formaldehyde	COH_2	30	In situ FTIR Ex situ NMR ¹⁹
Methanol	$\rm CH_3OH$	32	In situ FTIR
Allene	C_3H_4	40	In situ FTIR
Propylene	C_3H_6	42	In situ FTIR Ex situ NMR ¹⁹
Propane	C_3H_8	44	In situ MS^{13}
Carbon	CO_2	44	In situ FTIR
dioxide			In situ MS ¹⁸ Ex situ NMR ¹⁹
Butylene	C_4H_8	56	Ex situ NMR ¹⁹
isomers			Ex situ GC/MS ²⁰
Butane	$\rm C_4H_{10}$	58	Ex situ GC/MS ²⁰
Dimethyl	C_4H_6O	70	In situ FTIR
ketene (DMK)			Ex situ NMR ¹⁹

Table INeutral Dissociation ProductsDetected in MMA Plasmas Using In Situ FTIR15(Emphasized in Bold) and Other TechniquesReported in the Literature13,18-20

dence on the process parameters (pressure, power, and flow rate).¹⁵ This further supports the C—O bond cleavage reaction as the predominant production mechanism of $\rm COH_2$ and DMK in MMA plasmas.

Decarboxylation Reactions

Decarboxylations are important dissociation processes of carboxylic acids and esters in plasmas.²² For example, benzoic acid decarboxylates to benzene, and the methyl ester of benzoic acid forms toluene and benzene as major products.²² Decarboxylations were considered by Denes et al. as the major MMA fragmentation reaction in the plasma, and propyl radicals were considered as the predominant radical species.²⁰ Decarboxylations of MMA yield CO_2 , CO, and a number of radicals:



Both disproportionation products of propyl radicals—propylene and allene—have been observed with the *in situ* FTIR measurements of MMA plasmas.¹⁵ Other radicals produced in the decarboxylation reactions can also recombine to produce new molecular species. For example, methyl radicals can produce small hydrocarbons such as methane, and methoxy radicals (OCH₃) can give rise to methanol molecules. However, methoxy radicals are less likely to produce COH₂. In a separate experiment involving plasmas initiated in pure methanol vapor, COH₂ was not observed by FTIR in CH₃OH plasmas.²³ Thus, it is unlikely that methoxy fragments produce formaldehyde in MMA plasmas.

EXPERIMENTAL

Plasma-Polymerization Reactor

The parallel-plate plasma-polymerization (P4) reactor used in this study is a 13.56-MHz capacitively coupled system. A block diagram of P4 is shown in Figure 1. The reactor includes the following components: reactor chamber, electrodes, r.f. power supply, pumping system, pressure-control system, pressure gauge, monomer, and gasdelivery systems. The reactor chamber consists of an 18-in.-high stainless-steel cylinder with an 18in. outer diameter, and the cylinder volume is about 4580 cubic in. (75 L). The parallel-plate electrodes are 6-in.-diameter aluminum disks with an adjustable vertical gap set at 3.75 in. The top electrode is connected to the power supply; the bottom electrode and the reactor chamber are grounded. The plasma glow is confined to the area between the electrodes, and the plasma/reactor volume ratio is about 2%.

Gases from pressurized cylinders are delivered and regulated by thermal mass flow controllers



Figure 1 Block diagram of the parallel-plate plasma-polymerization reactor.

(MFCs). The liquid monomers are delivered in vapor form via an MKS 1150B vapor source MFC calibrated specifically for MMA in a range from 1 to 100 sccm (standard cubic centimeter per minute). The chamber is pumped by a mechanical pump attached to the base plate on the chamber. A throttle valve is used to control chamber pressure, and a capacitance manometer (Baratron) is used to measure the pressure. A liquid-N₂-cooled cold trap is used to condense the organic vapor before it enters the vacuum pump and exhaust system.

In Situ FTIR Plasma Gas-Phase Diagnostics

FTIR spectroscopy is a useful and nonintrusive diagnostic tool to study the molecular species in the plasma. *In situ* FTIR has been used to study the plasma gas-phase chemistry and reaction products, such as:

- Monitoring of the reaction products of Si etching in Cl₂, Cl₂/O₂, and HBr/O₂ electron cyclotron resonance (ECR) plasmas^{24,25}; Si etching in CF₄ ECR plasmas^{26,27};
- Si etching in an r.f. Cl_2 discharge²⁸;
- Decomposition chemistry and rotational temperature in a N_2O r.f. discharge^{29,30};
- Plasma deposition of amorphous hydrogenated silicon³¹;
- Chemical vapor deposition (CVD) of SiC³²; and

 Plasma-assisted chemical vapor deposition (PACVD) of copper.³³

Other gas-phase diagnostics employed for *in situ* plasma studies include mass spectrometry, optical emission spectroscopy, optical absorption spectroscopy, IR laser diode spectroscopy, microwave absorption spectroscopy, laser-induced fluorescence spectroscopy, and Raman spectroscopy.³⁴

The *in situ* FTIR setup used in this study is shown in Figure 2. The FTIR spectrometer is a Mattson Research Series Model RS-20. The IR beam transmitted from the Mattson RS-20 spectrometer is focused by a beam condenser (consisting of a larger 90° off-axis parabolic reflector and a smaller parabolic reflector). It is then passed through a 2-in. KBr window and into the plasma



Figure 2 A schematic diagram of the *in situ* FTIR residual gas analysis setup and the reactor.

Gas	Purity	Gas	Purity
Acetylene	$\sim 98\%$	Methane	99.0%
Propylene	99.0%	Ethylene	99.5%
CO ₂	99.99%	CO	99.3%
Formaldehyde	$\sim 91-98\%$	Methanol	\sim 99\%

Table IIGases Used in the FTIR CalibrationExperiment

reactor. The electrode spacing is approximately 3.75 in. and the IR beam passes once through the center of the gap. Then, the beam is passed through another KBr window on the other side of the chamber to be collected and analyzed by a liquid N_2 -cooled HgCdTe (MCT) detector. Some other details of the experiment include the following:

- The experiments were performed at a resolution of 0.5 cm^{-1} and 370 scans.
- The entire IR optical path, except the plasma reactor chamber, is purged with N_2 gas to reduce the spectral interference from CO_2 and H_2O in the atmosphere.
- The IR optical path inside the reactor includes 6 in. in the tube between the entrance KBr window and the chamber cylinder, 18 in. inside the chamber cylinder (6 in. between the electrodes), and 6 in. in the tube between the chamber cylinder and the exit KBr window. Therefore, the total optical path inside the reactor is 30 in. (76.2 cm).
- No film deposition is observed on the KBr windows.

The FTIR responses of MMA and certain gases detected in MMA plasmas as listed in Table II were calibrated against the reactor pressure. All the gases, except formaldehyde and methanol, were delivered from pressurized gas cylinders to the reactor chamber. Methanol vapor was delivered through the vapor source MFC. Formaldehyde vapor was generated by thermally decomposing paraformaldehyde [95%, $(CH_2O)_n$, mp 163–165°], which is known to decompose to COH_2 .³⁵ These calibration experiments were carried out in the absence of plasmas.

RESULTS AND DISCUSSION

The gas-phase reactions in MMA plasmas are best described as competing consecutive reac-

tions. Two of the competing MMA dissociation reactions are identified as the C-O bond cleavage reaction and decarboxylation reactions. The reaction kinetics and reaction efficiencies of these two reactions are further investigated in the following experiment using closed (zero flow rate) plasma systems. Although closed systems are not typically employed for film deposition, they have the "mass balance" relationship among the species in the system—an advantage that greatly simplifies the kinetics treatment of plasma reactions. Therefore, a closed-system approach was chosen to study the gas-phase kinetics of CF₄ plasmas,³⁶ CH₄ plasmas,³⁷ and MMA (C₅H₈O₂) plasmas in this case. Eventually, the knowledge gained from the closed-system study must be applied to flowing systems in order to obtain kinetics information in real film-deposition situations.

During an experiment, the reaction chamber is first pumped down to establish a base pressure of less than 1 mT before it is isolated from the vacuum-pump system. Then, the monomer vapor is delivered to the chamber to fill it to the desired pressure level of 300 or 500 mT. The monomer delivery is stopped and an FTIR spectrum of pure monomer vapor is recorded (370 scans at 0.5 cm^{-1} resolution). The FTIR data acquisition process takes 4 min, and the chamber pressure typically increases at a rate of 2.5 mT/min during the acquisition.

Following the completion of monomer data acquisition, a plasma is initiated for a certain reaction time (ranging from 1 s to 10 min) before the power is turned off. An FTIR spectrum of the reacted gas mixture is recorded *after* the power has been turned off to measure the species concentrations and reaction mixture composition. The chamber is then evacuated and brought to atmospheric pressure, and film-deposition substrates are removed. The film-deposition kinetics will be presented in another manuscript in the future. This cycle is repeated for a series of different reaction times to obtain kinetic data at the four different pressure/power combinations in a 2^2 full factorial designed experiment as shown below:

	\Rightarrow Pressure Le	vel Increase \Rightarrow
↑ Power	300mT 100 W	$500 \mathrm{mT}$ 100 W
Level Increase	$\begin{array}{c} 300 \mathrm{mT} \\ 75 \mathrm{~W} \end{array}$	$500 \mathrm{mT}$ 75 W



Figure 3 In situ FTIR spectra of (a) pure MMA vapor in the reactor chamber (500 mT), (b) gas mixture after 45 s at 100 W, and (c) the difference spectrum between (a) and (b). Each number corresponds to one MMA dissociation product (see text for assignment). Resolution is 0.5 cm^{-1} .

Figure 3(a) shows the FTIR spectrum of an MMA vapor (500 mT) before the discharge, and Figure 3(b) shows the spectrum of a reacted gas mixture at 100 W for 45 s. The reacted mixture spectrum shows the absorption signature of MMA and the dissociation products. Figure 3(c) shows the difference spectrum of Figure 3(a,b). All the species were identified in flowing MMA plasmas by FTIR,¹⁵ including **1**—*acetylene* (C₂H₂), **2**—*allene* (C₃H₄), **3**—*propylene* (C₃H₆), **4**—*ethylene* (CH₄), **7**—*formaldehyde* (COH₂), **8**—*dimethyl ketene* [DMK, (CH₃)₂C=C=O], **9**—CO, and **10**—CO₂.

Kinetics of MMA Consumption

MMA consumption mechanisms in plasmas include both dissociation and deposition processes. Dissociation reactions increase the number of particles in the gas phase and the total pressure while deposition reactions reduce the pressure. The reaction chamber pressure was found to increase after plasma discharges. Figure 4 shows the total chamber pressure monitored by a Baratron that can measure up to 1100 mT as a function of plasma reaction time for the four experimental conditions. The significant system pressure increase suggests that dissociation events occur more frequently than do deposition events in the system.

The overall MMA consumption, on the simplest level, can be regarded as MMA + $e^- \rightarrow$ products, and plasma products exist as either gases or solids (such as plasma polymer film and plasma dust). Generally, the rate of a chemical reaction in a closed system is defined as the change of any reactant or product concentration with time:

$$aA + bB \rightarrow cC + dD$$
, and Rate $= -\frac{1}{a}\frac{dB}{dt}$
 $= \frac{1}{c}\frac{dC}{dt} = \frac{1}{d}\frac{dD}{dt}$

Therefore, the rate of MMA consumption in the closed plasma is expressed as

Rate =
$$-\frac{d[\text{MMA}]}{dt} = \text{k}[\text{MMA}][e^{-}]$$
 (1)

The electron density, [e⁻], refers to the electron population that contributes to the MMA consumption processes, and k is the reaction rate constant. The rate constant, k, is known to have a general expression of

$$\mathbf{k} = \int \sigma(\boldsymbol{v}, \boldsymbol{\varepsilon}_i) \, \boldsymbol{v} \, f(\boldsymbol{v}, \boldsymbol{\varepsilon}_i) d\boldsymbol{v} d\boldsymbol{\varepsilon}_i \tag{2}$$



Figure 4 Kinetics of total chamber pressure in different process conditions as a function of reaction time.



Figure 5 A schematic of competing MMA consumption reactions in the plasma.

where $\sigma(\nu, \varepsilon_i)$ is the reaction cross section; ν , the velocity of colliding molecules; and $f(\nu, \varepsilon_i)$, the distribution of colliding molecules with respect to velocities and internal degrees of freedom as defined by a set of ε_i parameters.³⁸ The cross section typically has a value of zero until some threshold, and only those electrons with energies above the threshold contribute to that process. Conditions favoring a higher average electron temperature, such as high-power and low-pressure conditions, have a more significant overlap between $f(\nu, \varepsilon_i)$ and $\sigma(\nu, \varepsilon_i)$, which results in a higher k.³⁹ In addition, these conditions are usually associated with higher electron densities which also results in a higher k.³⁹

Both k and $[e^-]$ in eq. (1) are difficult to determine experimentally, and they are simplified into a *reaction rate coefficient* (k), and $k = k [e^-]$. Equation (1) is then reduced to a first-order rate equation, and k can be determined experimentally via the kinetic relationship

$$Rate = k[MMA]$$
(3)

A number of authors have found that monomers, particularly hydrocarbons, typically follow an overall first-order consumption kinetics in plasmas.^{36-38,40}

Since MMA consumption occurs simultaneously via competing reactions as illustrated in Figure 5, k is the sum of the individual k's of all the competing reactions: $k = (x_ik = x_1k + x_2k + x_3k \text{ and } x_1 + x_2 + x_3 = 1$. Because x_i is the fraction of MMA that decomposed via that particular reaction pathway, it is also the *reaction pathway efficiency*.

The first two reactions in Figure 5 are homogeneous gas-phase dissociation reactions (C—O bond cleavage reaction and a fraction of decarboxylation reactions that yields propylene), and the third term represents all the other possible MMA consumption reactions, including other gas-phase reactions and heterogeneous reactions. The rate eq. (3) of MMA is as follows when considering the multipath nature of the consumption reactions:

Rate =
$$-\frac{d[\text{MMA}]}{dt} = k[\text{MMA}]$$

= $(x_1k + x_2k + x_3k) [\text{MMA}]$ (4)

and the integrated rate equation is

$$[MMA] = [MMA]_0 \exp(-kt) = [MMA]_0 \exp\{-(x_1k + x_2k + x_3k)t\}$$
(5)

where $[\text{MMA}]_0$ is the original MMA concentration when, time, t = 0. The starting monomer pressures of the data points in each experimental condition are averaged and used as the original MMA concentration, $[\text{MMA}]_0$, when solving eq. (5) for k.

To find the best solution to eq. (5), the method of *least-square fitting for the nonlinear model* is used to statistically fit the MMA kinetic data obtained by *in situ* FTIR measurements. The bestfit solutions of the overall consumption rate coefficient, k, for the four experimental conditions are shown in Table III. Figure 6 shows the model goodness of fit and measured MMA concentrations as a function of reaction time under different experimental conditions. The measured species concentration is represented by the data point, and the model output is represented by the curve in the figure.

However, the observed rate coefficients, k, in Table III are volume-averaged quantities since the reaction is restricted to the plasma zone which has a volume ratio of approximately 2% with respect to the reactor chamber volume. The large reactor and wide-gap electrode configuration allows fast diffusion and material exchange between the small plasma zone and the much larger reactor chamber; thus, the reaction time is

Table IIIVolume-Averaged MMA ConsumptionRate Coefficients (s⁻¹) at DifferentExperimental Conditions

		\Rightarrow Press	ure Level Incre	ase \Rightarrow
↑ Power Level Increase	300 mT 100 W	k = 0.025 $R^2 = 120$	k = 0.015 $R^2 = 850$	500 mT 100 W
	300 mT 75 W	k = 0.021 $R^2 = 160$	k = 0.009 $R^2 = 2000$	500 mT 75 W

 R^2 is the multiple correlation coefficient.



Figure 6 Kinetic modeling results of overall MMA consumption rates in closed plasmas under different conditions of initial monomer pressure and reactor power. The symbols represent the experimental data points and the lines represent the modeling output.

lengthened and the *k*'s must be divided by this volume ratio to reflect the true *k* values of the plasma.³⁶

Kinetics of MMA Plasma Dissociation Products

Among the dissociation products, kinetic modeling of the intermediate species revealed interesting information regarding the monomer dissociation rates and efficiencies in the plasma. However, the kinetics of small hydrocarbons and oxygenated species (CO and CO_2) are much more difficult to model because they can be produced from a number of species other than MMA. Therefore, only the kinetics of the intermediate species are modeled in this study, and the kinetics of the small hydrocarbons and oxygenated species are not.

The kinetics of intermediate species are modeled using the rate equation for intermediate species in first-order multistep consecutive reactions that have been modified for competing reactions:

$$\mathrm{MMA} \xrightarrow{x_i k} B_i \xrightarrow{k_i} Z_i$$

where x_i is the reaction pathway efficiency (i.e., the fraction of MMA consumed by this dissociation reaction); k, the overall MMA decomposition rate; k_i , the decomposition reaction rate coefficient of the intermediate species—B; and Z, the stable final product.

When $[MMA] = [MMA]_0$, $[B_i] = 0$, and $[Z_j] = 0$ at t = 0, the kinetics of the intermediate species, B, is described as follows:

Rate =
$$\frac{d[B_j]}{dt} = x_i k [\text{MMA}] - k_i [B_i]$$
 (6)

and

$$[B_i] = \frac{x_i k [\text{MMA}]_0}{k_i - k} \times \{\exp(-kt) - \exp(-k_i t)\} \quad (7)$$

The method of least-square fitting for nonlinear model is once again utilized to solve eq. (7) for a number of intermediate species in MMA plasmas, such as COH_2 , DMK, propylene, and methanol. Since k (overall MMA consumption rate coefficient) is determined by the relationship in eq. (5), the other two parameters in eq. (7) are determined using the fitting procedure—namely, the production term (x_i) and the consumption term (k_i) of the intermediate species.

Formaldehyde and DMK

The method of least-square fitting for a nonlinear model was used on the formaldehyde kinetic data to obtain x_{COH2} and k_{COH2} . The same procedure was performed on DMK data, but only the DMK consumption rate coefficient, k_{DMK} , could be determined since DMK data were not calibrated. However, the production rate of DMK and COH₂ should be very close if not identical. As discussed earlier, COH₂ and DMK are the direct dissociation products of the C-O bond cleavage reaction of MMA. They are either deposited in PPMMA or further dissociated in the plasma to form other species as they are produced in the gas phase. This production/consumption dynamic is reflected in the species concentration kinetics as shown in Figures 7 and 8 for COH₂ and DMK, respectively. Both COH_2 and DMK show a rapid increase of concentrations at short reaction times and a gradual decay at longer times.

Table IV summarizes the kinetic parameters $(x_i \text{ and } k_i)$ for the different species, including COH₂ and DMK, and the fitting result is shown graphically in Figures 7 and 8. The kinetic modeling shows that the C—O bond cleavage reaction has an efficiency (x_{COH2}) of 41–54% in the experimental regime. Hence, a significant portion of MMA decomposes by the C—O bond cleavage reaction, and COH₂ and DMK are significant intermediate species.

Propylene and Methanol

The same fitting procedure was applied to the propylene and methanol kinetics data to obtain



Figure 7 Kinetic modeling results of COH_2 in closed MMA plasmas. The symbols represent the experimental data points and the lines represent the modeling output.

their kinetic parameters. Since both propylene and methanol are products of the decarboxylation reactions, there is a potential overlap between $x_{\rm C3H6}$ and $x_{\rm CH3OH}$; therefore, $x_{\rm CH3OH}$ should be excluded from the summation of $\Sigma x_i = 1$ mentioned previously. It should be noted that the unsaturated propyl radicals produced from the decarboxylation reactions yield both propylene and allene molecules. Therefore, $x_{\rm C3H6}$ can only account for part of the total decarboxylation efficiency.

The experimental data and model goodness of fit is shown in Figure 9 for propylene and in Figure 10 for methanol. The fit quality of the propylene data (Fig. 9) indicates that propylene is a direct product of MMA fragmentation instead of other intermediates, such as DMK. Although



Figure 8 Kinetic modeling results of DMK (normalized to 1) in closed MMA plasmas. The symbols represent the experimental data points and the lines represent the modeling output.



Figure 9 Kinetic modeling results of propylene in closed MMA plasmas. The symbols represent the experimental data points and the lines represent the modeling output.

methanol was previously classified as an oxygenated species in the flowing plasma experiment,¹⁵ Figure 10 shows that it is better described as an intermediate species. The kinetic parameters for the different species are summarized in Table IV. Among these reactions, 17–22% of MMA yields propylene and 7–8% yields methanol through decarboxylations in our experimental regime.

The kinetic modeling of the intermediate species shows that (1) the C—O bond cleavage reaction is an efficient mechanism of MMA dissociation, and the magnitude of x_{COH2} and x_{C3H6} shown in Table IV suggests that it is at least as efficient as decarboxylations in the experimental regime used in the study; and (2) the consumption rates of the different species reveal the relative reactivity of the different neutral species: $k_{\text{DMK}} > k$ $\approx k_{\rm COH2} > k_{\rm C3H6} > k_{\rm CH3OH}.$ MMA and ${\rm COH_2}$ have roughly the same consumption rates, but DMK has a consumption rate almost twice as much as that of MMA and COH₂ in all four experimental conditions. Therefore, the intermediate species, DMK, is the most reactive neutral molecule in MMA plasmas, even more reactive than the monomer itself.

Ethylene

One of the small hydrocarbons in MMA plasmas, ethylene, is subjected to the same modeling procedure to demonstrate the consequences of fitting eq. (7) to a nonintermediate species. Figure 11 clearly shows a lack of fit which excludes ethylene as an intermediate species. This shows that only an intermediate species can be successfully modeled by eq. (7).

Pressure (mT)	Power (W)	$x_{ m COH2}$	$x_{\rm C3H6}$	x _{CH3OH}	k	$k_{ m COH2}$	$k_{ m DMK}$	$k_{ m C3H6}$	$k_{ m CH3OH}$
500	100	0.54	0.22	0.07	0.015	0.014	0.027	0.005	0.003
500	75	0.50	0.18	0.07	0.009	0.009	0.015	0.003	0.001
300	100	0.41	0.17	0.08	0.025	0.024	0.053	0.009	0.007
300	75	0.45	0.17	0.08	0.021	0.016	0.037	0.006	0.004

Table IV Summaries of Reaction Pathway Efficiencies (x_i) and Volume-Averaged Consumption Rate Coefficients of MMA (k) and Intermediate Species (k_i)

Effects of Pressure and Power on Reaction Kinetics

The factor effects of pressure and power on pathway efficiencies and rate coefficients were analyzed using the analysis of variance (ANOVA) technique, and the result is summarized in Table V. The details of this approach in an MMA plasma study were described previously.¹⁵

Effects on Reaction Efficiencies (x_i)

As shown in Table V, the pressure exhibits an effect of -8 to +10% and the power exhibits an even smaller effect of -4 to +6% on the reaction pathway efficiencies. This implies that a higher power hardly affects the fragmentation chemistry of MMA and product distribution of the intermediate species. However, a higher initial monomer pressure may cause a slight change in the MMA fragmentation chemistry. At low pressure, the excited monomer will achieve a higher excitation energy on average; thus, it is possible that the monomer can dissociate via pathways other than the C—O cleavage reaction and decarboxylations.



Figure 10 Kinetic modeling results of methanol in closed MMA plasmas. The symbols represent the experimental data points and the lines represent the modeling output.

Effects on Reaction Rates (k and k_i)

When pressure increases from 300 to 500 mT (a 67% increase), the k's in Table V decrease anywhere from 26 to 44%. When power increases from 75 to 100 W (a 33% increase), the k's increase over the range of 15–25%. These effects can be explained in terms of the influence of the process parameters on the electron energy distribution and electron density.

As shown in eq. (2), the reaction rate constant, k, has a strong dependence on the population of hot electrons with energies above the cross-section threshold. It is known that higher pressure results in a lower average electron energy and a lower electron density; hence, pressure has negative effects on k.³⁹ In contrast, higher power is accompanied by an increase in the average electron energy and electron density; thus, power has a positive effect on k. Since increasing power does not significantly affect the fragmentation chemistry of MMA (similar x_i at 75 and 100 W), a higher power can be used in a film-deposition process to increase the reaction rate and shorten the pro-



Figure 11 Kinetic modeling results of a nonintermediate species, ethylene, in closed MMA plasmas. The symbols represent the experimental data points and the lines represent the modeling output.

Table V	Reactor Parameter (Pressure and
Power) E	Iffects on Reaction Pathway
Efficienc	ies (x_i) and Reaction
Rate Coe	efficients (k_i)

	Means	Pressure Effect (%)	Power Effect (%)	Interaction (%)
x _{COH2}	0.47	+10	-4	+4
x _{C3H6}	0.18	+8	+6	+5
x _{CH3OH}	0.08	-8	-1	+2
k	0.018	-30	+15	+2
$k_{\rm COH2}$	0.016	-26	+20	$^{-5}$
k _{DMK}	0.033	-37	+21	+3
k _{C3H6}	0.006	-28	+23	-4
k _{CH3OH}	0.004	-44	+25	$^{-6}$

Effects are shown in % of the corresponding means.

cessing time. A lower pressure also speeds up the reaction, but the gas-phase reaction becomes more complex and may affect the film quality undesirably.

Regularities in MMA Plasma Gas-Phase Kinetics

When the time scale of the kinetics data is transformed from seconds to MMA decomposition halflives $(t_{\frac{1}{2}} = \ln \frac{2}{\hbar})$, an interesting regularity is observed. For the monomer, let $t = xt_{\frac{1}{2}}$, and apply this relationship to eq. (5); then, MMA decomposition kinetics follows the expected exponential decay as shown in Figure 12:

$$[MMA] = [MMA]_0 exp(-x \ln 2)$$

and the kinetics data are differentiated only by the starting monomer pressures, $[MMA]_0$, at any *x*.

The same time-scale transformation is performed on the dissociation products. Figure 13(a) shows the normalized DMK absorbance under different conditions as a function of the MMA decomposition half-life $(t_{1/2})$, and Figure 13(b–d) shows the kinetics data of the other intermediate species (COH₂, propylene, and methanol). These plots show a consistent dependence of the intermediate species on the MMA $t_{1/2}$. For the four different conditions, the relative concentrations of DMK reach the maximum around 1 MMA $t_{1/2}$, formaldehyde around 1.5 $t_{1/2}$, propylene around 2 $t_{1/2}$, and methanol around 3 $t_{1/2}$.

Figure 14(a,b) shows the dependence of the oxygenated species (CO and CO_2) on the MMA

decomposition $t_{1/2}$. The CO data show the least consistent measurement result due to the complication of spectral overlap between CO and DMK. The real CO concentrations in the plasma most likely will have similar trends as shown by CO₂ in Figure 14(b).

As shown in Figure 14, the concentrations of CO and CO_2 increase rapidly immediately after the initiation of the discharge as they are produced from MMA and later on from COH₂ and other species. Their concentrations remain relatively stable without a significant decrease at long reaction times, which indicates that CO and CO_2 are not deposited in the film and they do not react to yield other species. Thus, CO and CO_2 are stable final products of the MMA plasma. Roughly one-third of the total chamber pressure corresponds to CO at 300 mT of the initial monomer pressure. The other oxygenated species, CO_2 , is present in much lower concentrations. The ratio of $CO:CO_2$ at long reaction times is about 3:1for the four runs.

The kinetics of small hydrocarbons are shown in Figure 15(a–d). The ethylene concentration reaches a maximum around 4.5 $t_{1/2}$ [Fig. 15(a)], and methane [Fig. 15(b)] and acetylene [Fig. 15(c)] have maxima around 7 $t_{1/2}$. Acetylene is the most abundant species among the three, followed by methane and ethylene. The C₂H₂ : CH₄ : C₂H₄ ratio is about 2 : 1 : 0.6 for the four runs. However, the small hydrocarbon yield at 500 mT and 75 W is more similar to that at 300 mT. The explanation for this is not clear, but it might be related to the fact that it is more difficult to achieve a good power match for the high-pressure and low-power condition.

A brief S-shaped induction period can be observed in acetylene for the first 1.5 $t_{1/2}$ as shown



Figure 12 MMA consumption kinetics shows the expected relationship with respect to the decomposition half-lives $(t_{1/2})$.





Figure 14 Dependence of oxygenated species concentrations on the monomer decomposition half-lives $(t_{1/2})$ at different process conditions: (a) CO; (b) CO₂.

in Figure 15(d), which suggests that it is a decomposition product of intermediate species instead of MMA. Because these are fast reactions compared with the diagnostic time resolution, the induction period can be seen only to some degree. However, a time lag is observed in the initial concentration increase of all the small hydrocarbons when compared to the intermediate and oxygenated species. At long reaction times, all the small hydrocarbons show decreasing concentrations, which suggests that they are being dissociated by the plasma to other species in the gas phase and/or they are being incorporated in the film.

Figure 13 Dependence of intermediate species concentrations on monomer decomposition half-lives $(t_{1/2})$ at different process conditions: (a) DMK has a maximum around 1 $t_{1/2}$; (b) COH₂ has a maximum around 1.5 $t_{1/2}$; (c) propylene has a maximum around 2 $t_{1/2}$; (d) methanol has a maximum around 3 $t_{1/2}$.



It is noteworthy that the chemical regularities of the monomer and dissociation products can be expressed using $t_{1/2}$ as the time unit regardless of the conditions. Hence, effects of the reactor conditions on the reaction kinetics are mitigated by this time-scale transformation technique. This technique, thus, might be able to alleviate the strong system dependence encountered in the analysis of plasma chemistry studies from different reactors.

Mass Balance Ratios

In situ FTIR has been used to simultaneously monitor 11 different neutral species in the plasma gas phase, including MMA and 10 dissociation products in this study. However, FTIR cannot detect all the plasma species. For example, H_2 and other homonuclear diatomic molecules are IR-inactive even though dehydrogenation is a significant reaction in hydrocarbon plasmas.^{41,42} Besides the IR-inactive species, there are other gasphase species that were not identified due to spectral overlap. In addition, plasma polymers and other heterogeneous products will not be detected by this or other gas-phase diagnostic techniques.

To determine the proportion of detected versus undetected plasma products in the closed MMA plasmas, *mass balance ratios* (MBRs) are calculated for the three elements present in the MMA molecule, namely, carbon, hydrogen, and oxygen. The MBR of carbon is shown here as an example:

$$C_{\rm MBR} = \frac{\sum_{x} x \times [C_x H_y O_z]}{5 \times [C_5 H_8 O_2]_{\rm initial}}$$

(

MBRs of hydrogen and oxygen can be calculated in a similar fashion. Uncalibrated species, such as allene and DMK, are not included in the calculations.

Figure 16 displays the MBRs for the four runs. All these four plots show that FTIR was successful at monitoring oxygen-containing species, but less so for the carbon and hydrogen-containing species. After about 100–200 s, only about onehalf of the total carbon and one-third of hydrogen in the plasma system have been accounted for

Figure 15 Dependence of small hydrocarbon concentrations on the monomer decomposition half-lives $(t_{1/2})$ at different process conditions: (a) ethylene, (b) methane, (c) acetylene, and (d) acetylene in the first 1.5 $t_{1/2}$.



Figure 16 MBRs of oxygen, carbon, and hydrogen in MMA plasmas as a function of reaction time.

using this diagnostic technique. Film deposition and dehydrogenation reactions are considered as the main factors for the low values of carbon and hydrogen MBRs.

CONCLUSIONS

This article demonstrates the importance of gasphase diagnostics to the study of plasma chemistry. *In situ* FTIR data have facilitated the identification and kinetic monitoring of neutral byproducts of MMA plasmas, and a methodology was established to study the reaction chemistry of a relatively large organic monomer. The gasphase reaction kinetics of MMA plasmas were modeled as competing multistep reactions. Monomer decomposition rate coefficients, dissociation pathway efficiencies, and intermediate species consumption rate coefficients were experimentally determined in closed plasmas with a zero monomer flow rate.

The C—O bond cleavage reaction is found to be an efficient MMA dissociation pathway in glow discharges, responsible for about one-half of the monomer depletion in the gas phase. Dimethyl ketene (DMK) and COH2 molecules are the dissociation products of this intramolecular rearrangement reaction. In addition, decarboxylations are also significant dissociation pathways in MMA plasmas. The neutral molecules produced from decarboxylations include CO, CO₂, propylene, allene, and methanol. These species, besides CO and CO_2 , are either incorporated into the film or they are further dissociated in the plasma to other species. Different reactivities were observed for the plasma neutrals: DMK is the most reactive among all neutrals, followed by COH_2 and the monomer, propylene, methanol, ethylene, methane, and acetylene. CO and CO_2 are the most stable species.

The process conditions (power and initial monomer pressure) were found to have minor effects on the MMA dissociation chemistry. However, the process condition has much more significant effects on the speed of the reactions. All the gas-phase reactions proceed faster at high-power and low-pressure conditions.

A time-scale transformation based on the monomer decomposition half-life $(t_{1/2})$ was demonstrated to reduce the effects of the process condition on the reaction kinetics. Kinetics regularities of the monomer and dissociation products can be expressed using $t_{1/2}$ regardless of the conditions. Thus, this might be a method to compare studies of plasma chemistry in different reactors by alleviating the strong system dependence of plasma conditions.

MBRs were used to evaluate the overall monitoring capability of the *in situ* FTIR diagnostic tool. FTIR was found to be successful at monitoring O-containing species, but less so at monitoring C- and H-containing species. Film deposition and dehydrogenation reactions are the main factors for the lower counts of total carbon and hydrogen observed by this technique.

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