A STUDY OF GAS PHASE PROCESSES IN RF PLASMA IN THE MIXTURE OF Ar AND METHYLMETHACRYLATE.

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Abstract

Here we use GC-IR technique (chromatographic detection using Fourier transform IR spectrometer), mass-spectrometry, and visible range spectroscopy to study the composition of stable gas products, ions and radicals produced in RF-discharges in the mixtures of Ar and methylmethacrylate for different discharge power, residence time of gas in the active zone and pressure.

Introduction

Studies of the kinetics and mechanism of the processes in rf discharges in the vapor of organic compounds are the subject of many publications [1,2]. RF discharges in methane and mixtures of methane with argon have been studied in greatest detail. However, plasma chemical processes in more complex organic system have usually found practical application up to now. Thus, a method has been proposed for obtaining uniform films of methylmethacrylate (MMA) with electron beam resist properties of these films have been studied as a function of the discharge parameters [3]. In order to obtain a fairly reliable idea of the kinetics and mechanism of the plasma chemical conversions of methylmethacrylate leading to film formation it is obviously necessary to study the processes that take place both on the surface and in the volume of the reactor.

Experimental

Two experimental setups were used in the present investigation. One reactor was intended for preparing films on different substrates, another one was specially developed for studying gas phase processes in plasma.

In first reactor discharges were driven by a 13.6 MHz rf generator using ring electrodes located 100 mm apart on the outer surface of a 22-mm-diameters quartz tube. The power of 10-100W were measured with a coaxial reflectometer after calibration with an calorimetric wattmeter. Argon and MMA were fed separately into the reactor at volume flow rates normalized to standard condition of 100-1000 cm^3/min and 1-20 cm^3/min, respectively. The pressure (60-400 Pa) was measured with a membrane probe based on mechanotron. The gas supply and pumping system made it possible to vary the residence time of the MMA in the discharges with constant pressure of Ar and MMA. The residence time vas determined under the assumption of ideal displacement.

In second reactor discharges were driven by a 5,28 MHz rf generator (the power 10-100 W) using two parallel plane electrodes (15 cm and 12cm in diameter) in the middle of the vacuum chamber (30x30x10 cm^3). The smaller electrode made of steel is connected to rf power supply. The bigger electrode made of copper is grounded. The gap between the two electrodes was fixed at 3cm. The mass-spectrometer was connected directly to the reactor and separated from plasma volume by diaphragm (diameter 0.1 mm) located on the ground electrode. Plasma irradiation spectra in visible region were registered through the quartz window. Argon (pressure 10-100 Pa) and MMA were fed into reactor through smaller electrode at volume flow rates normalized to standard condition of 50-300 cm^3/min and 0,5-8 cm^3/min, respectively.

The samples from both reactors were collected either in a liquid-nitrogen cooled trap or with the aid of a special sampling probe mounted at the outlet of reactors and consisting of a metal cylinder with a volume of 1100 cm^3 and a piston for compressing the sample by a factor of 250. The products mixture was separated in the chromatograph column (Perkin-Elmer 8500 GS) after which the flow was divided in the proportion 1:10 and delivered, respectively, to a flame ionization detector for quantitative analysis and to the gas cell of the IR Fourier spectrometer (Perkin-Elmer 1720x) for recording the IR spectrum.

Results and Discussion

30-40 substances were observed in the liquid sample taken with the nitrogen trap depending on discharge conditions. Of these 20-30 had a higher molecular weight than the MMA. The overall amount of heavy products did not exceed 1% of the amount of MMA. Gas samples taken over the surface of the liquid in the trap contained mostly substances with lower molecular weights than MMA. Product samples taken directly from the plasma chemical reactors with the aid of the sampling probe had a similar qualitative composition (Table 1). Of the 22 products listed in Table 1, ten form more 90% of the total amount of material.

With the set of detected products one can distinguish two classes of "specific" and "nonspecific" products for MMA. The nonspecific products (methane, ethane, ethylene, acetylene, hydrogen, CO) are formed in discharges with any organic substance: methane, ethane, ethyl alcohol, petroleum ether, methyl ethyl ketone, acetone, methyl alcohol. The rate at which they are produced in a plasma chemical reactor is essentially constant as the concentration of MMA falls while it undergoes plasma chemical conversion since the dissociation products of MMA are also source of these substances. When the residence time of MMA in the active zone is increased and the specific discharge power is raised the concentrations of nonspecific products saturates (Fig.1). The specific products (propene, allene, propyne, isobutene, methyl alcohol, methyl formate) are not usually major products of plasma chemical processes involving other substances. The rate of production of specific products decreases as the concentration of MMA falls during plasma chemical conversion. The yield of specific products has maxima (Fig.1) with respect to the residence time of MMA in the active zone and with respect to the specific discharge power.

Table 1. Fraction of various substances in the combined conversion products of methylmethacrylate from rf discharges (power of 1W/cm^3, an Ar pressure of 170 Pa, and MMA pressure 7 Pa). Detection: FTIR - with the detector of the IR Fourier spectrometer; + good, 0 satisfactory, - not detected, ? proposed structure of the product.

Products	FTIR	GC	%	Products	FTIR	GC	%
$C_3H_6COOCH_3$	+	+	19	iso-C_3H_7COH	+	+	2
C_3H_6	+	+	18	C_4H_6 (butyne) ?	0	0	<1
CH_4	+	+	11	C_5H_{12} ?	0	0	<1
CH_3OH	+	+	9	C_4H_2 ?	0	0	<1
C_2H_2	+	+	8	C_5H_{10} ?	0	0	<1
C_3H_4 (propyne)	+	+	8	CH_3COCH_3	+	0	<1
C_2H_4	+	+	6	$CH_3COC_2H_5$	+	+	<1
iso-C_4H_8	+	+	5	C_4H_6 (bivinyl)	0	0	<1
C_2H_6	0	+	4	C_6H_{12} ?	0	0	<1
C_3H_4 (allene)	0	+	3	CO	+	-	-
$HCOOCH_3$	+	+	2	HCOH	+	-	-
iso-C_4H_{10}	+	+	2	H_2	-	-	-

The mass-spectrum of ionic component of pure argon RF discharge plasma consist of four basic peaks: Ar^+ (m/e=40), ArH^+ (m/e=41), Ar^{++} (m/e=20), Ar_2^+ (m/e=80) (Fig. 2-a). The mass-spectra of positive ions for RF discharge in pure MMA and in the mixture of MMA with argon are represented in Fig. 2 (b and c respectively). Let us note that the ionic composition of plasma in the mixture of MMA with Ar and that in pure MMA differ by the presence of Ar characteristic peaks, Ar^+ (m/e=40) peaks remaining one of the main peaks in mass-spectra of mixtures with MMA part less than 10%. The interpretation of basic peaks of the MMA+Ar mixture Rf discharge plasma mass-spectrum is represented in Table 2.

There are Ar^{++} ions in amounts comparable to those of Ar^+ ions in the plasma of Ar and the mixtures of Ar with MMA, that testifies about a significant part of high energy electrons (more than 50eV), ionizing heavy particles in discharge. It is possible for electrons to acquire such energy in thin near-electrode layers (~1mm), where main drop of voltage (100-400V), exciting the discharge, occurs. The ions formed under electron impact are involved in ion-molecular processes. The rate constants of interactions of Ar^+ with molecules are several greater then those of similar processes involving Ar^{++} ion [4], that results in increase in Ar^{++} portion compared to Ar^+.

Table 2. The interpretation of basic peaks of the MMA and Ar mixture plasma mass-spectrum.

m/e		m/e		m/e		m/e	
1	H^+	28	$C_2H_4^+$, CO^+	44	CO_2^+	71	$C_3H_7CO^+$
2	H_2^+	29	$C_2H_5^+$, HCO^+	45	HCO_2^+	73	$CH_3COC_2H_6^+$
3	H_3^+	30	H_2CO^+	50	$C_4H_2^+$	79	$C_6H_7^+$
14	CH_2^+	31	H_3CO^+	51	$C_4H_3^+$	80	Ar_2^+
15	CH_3^+	33	$CH_3OH_2^+$	53	$C_4H_5^+$	81	$C_6H_9^+$
18	H_2O^+	38	$C_3H_2^+$	55	$C_4H_7^+$, $C_2H_3CO^+$	83	$C_6H_{11}^+$
19	H_3O^+	39	$C_3H_3^+$	57	$C_4H_9^+$, $CH_3COCH_2^+$	85	$C_2H_2COOCH_3^+$
20	Ar^{++}	40	$C_3H_4^+$, Ar^+	59	$COOCH_3^+$	99	$C_3H_4COOCH_3^+$
26	$C_2H_2^+$	41	$C_3H_5^+$, ArH^+	67	$C_5H_7^+$	100	$C_3H_5COOCH_3^+$
27	$C_2H_3^+$	43	CH_3CO^+	69	$C_3H_5CO^+$	101	$C_3H_6COOCH_3^+$

The presence of peaks H_3^+ (m/e=3), ArH^+ (m/e=41), H_3O^+ (m/e=19) $MMAH^+$ (m/e=101) in the mass-spectrum testifies about proceeding the processes of proton attachment to molecular and atomic ions as a result of ion-molecular reactions. Hydrocarbon ions react with hydrocarbon molecules effectively to form ions with higher molecular mass and radicals [5,6]. In these reaction the ions with odd number of hydrogen atoms are mainly formed, in addition they have more than two times less reactivity than the corresponding molecular ions [5,6], therefore the majority of ions having odd mass number is detected in investigated Ar+MMA mixture plasma. As ion mass increases, the ion-molecular reaction rate decreases and the probability of monomolecular decay increases. So, the $MMAH^+$ ion formed effectively in a given system decays in the following way[7]:

$$
\begin{aligned}
C_3H_6COOCH_3^+ = \quad & C_3H_6CO^+ + CH_3O \\
& C_3H_5CO^+ + CH_3OH \\
& COOCH_3^+ + C_3H_6 \\
& CH_3COCH_3CH_3^+ + CO \\
& C_3H_5^+ + HCOOCH_3
\end{aligned}
$$

A kinetic scheme of gas phase reactions, including the molecular ionization and dissociation under electron impact, radical recombination and ion-molecular reaction were proposed. This scheme was computer optimized to attain maximum agreement with the experimental results on gas product formation depending on discharge conditions and with taking into account the observed plasma ionic composition.

Conclusion

According to simulation results one can draw a conclusion that the following mechanism of gas phase processes is probable: MMA molecules dissociate under electron impact (50% - hydrogen atom detachment, 30% - CH_3OCO group detachment, 10% - methyl radical detachment), radical interact between themselves to form "specific" products, which are in turn and in the same way transformed into simpler "nonspecific" products. The ionization mainly occurs in thin near-electrode layers and does not play an important role for MMA primary transformation. Ion-molecular processes do also not contribute in formation of basic gas product, however they are responsible for the formation of hydrocarbons C_4-C_6, ketons and water molecules. Thus, the processes in near-electrode layers involving high energy electrons and ions accelerated in near-electrode potential drop do not affect the gas phase chemical transformations significantly.

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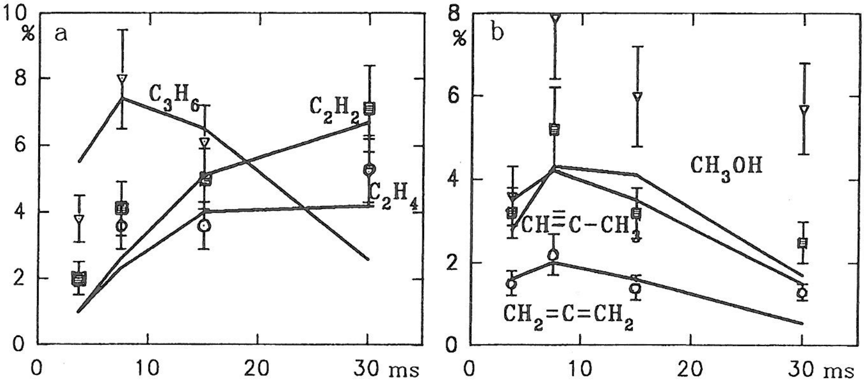

Fig.1. Molar fraction of various products relative to the initial amount of MMA as functions of the residence time of MMA in the discharge zone. Points are experimental data and curves, calculations according to the proposed kinetic scheme. The pressure of argon is 170 Pa and MMA 3 Pa. The specific discharge power is 0.4 W/cm^3.

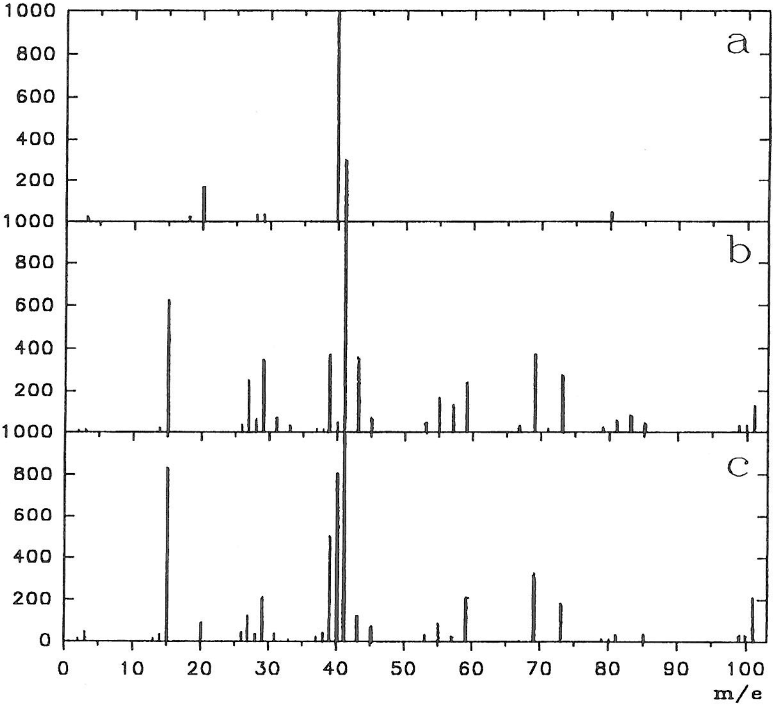

Fig. 2. The mass-spectrum of positive ions for RF discharge (30 W) in pure Ar (a), in pure MMA (b) and in mixture of MMA (3%) with Ar (c). The pressure of Ar is 100 Pa.