Polymerization in an Electrodeless Glow Discharge. II.   Olefinic Monomers

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Synopsis

The rates of polymer deposition from various olefinic monomers in an electrodeless glow discharge were studied.   The previously found empirical relationship (with styrene in part I) between the rate of polymer deposition R, the monomer pressure p_M, and gas pressure p_x in a steady-state flow system (i.e., $R = a(p_M)^2 [1 + b(p_x)]$, R being nearly independent of the discharge power) was also found with all monomers investigated. (The effect of gas was examined with nitrogen in this study.)   However, it was found that the polymer deposition is controlled by the monomer flow rate and R_0 (in pure monomer flow) is proportional to the flow rate of monomer F_w (based on the weight); i.e., $R_0 = kF_w$, where k is a characteristic rate constant of the polymerization.   Olefinic monomers can be generally classified into two major groups, i.e., type A monomers which predominantly polymerize, and type B monomers which decompose in a glow discharge. Type B monomers have smaller values of a and k compared to type A monomers.   The values of a and k for type A monomers both increase with increasing molecular weight of the monomer.   The values of k for all monomers investigated are within roughly an order of magnitude, indicating that the reactivity levels of monomers are very similar in a glow discharge polymerization.

INTRODUCTION

The rate of polymer deposition from styrene in an electrodeless glow discharge (part I) has recently been studied.[1]   The results of the study indicated that the mechanism of polymer deposition onto the wall of the reaction vessel in an electrodeless glow discharge is considerably different from that onto the electrode surface in glow discharge.   For instance, the deposition rate in an electrodeless glow discharge was found to be nearly independent of the discharge power, whereas the deposition rate onto electrodes was reported to be linearly proportional to the current.[2–5]   It has been postulated that the adsorption of monomer onto an electrode surface plays an important role in the deposition of polymer,[2,5,6] whereas the adsorption seems to play a small role in polymer deposition in an electrodeless glow discharge.   The rate of polymer deposition R in a flow system, in which monomer vapor pressure p_M and gas pressure p_x were maintained constants, was given by an empirical equation

$$R = a\, p_M{}^2 [1 + b\, p_x]$$

where a and b are constants characteristic to a monomer and a gas. It was postulated that the polymerization of monomer occurs in vapor phase and that a growing chain deposits as its molecular weight increases; since it cannot remain in the vapor phase. This theory was examined in this paper with various kinds of monomers, which can be generally classified as olefinic compounds. Namely, the monomers investigated have at least a double bond which can undergo polymerization by either free radical and/or ionic addition polymerization and are generally considered as "monomer" of addition polymerization. Nitrogen was used as plasma gas in this study for some monomers.

EXPERIMENTAL

The apparatus used in this study is essentially the same as the one reported previously.[1] Some minor modification was made so that pressure measurement in a closed system could be made. The system is illustrated schematically in Figure 1.
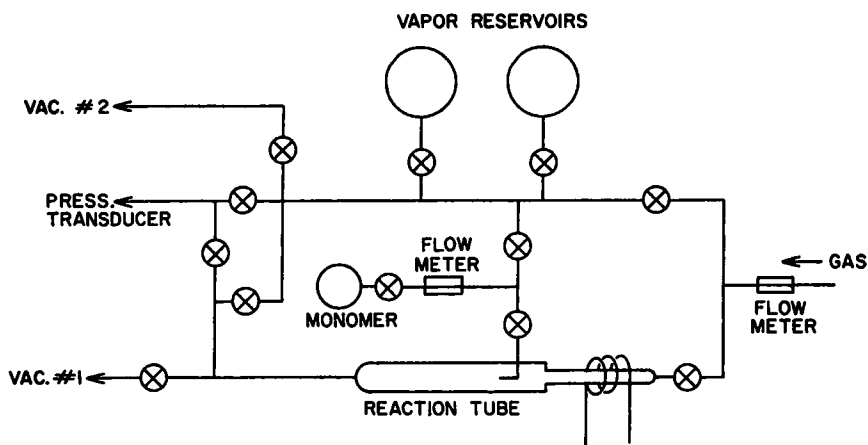

Fig. 1. Schematic representation of an electrodeless glow discharge system.

The apparatus could be evacuated to less than 10^{-5} mm Hg by a mercury diffusion pump backed by a rotary pump; however, for most experiments the diffusion pump was bypassed, and the system was pumped down to a level of less than 10^{-3} mm Hg before the monomer vapor and plasma gas were introduced. The reference vacuum for the pressure transducer was always connected to the diffusion pump and kept at a level of less than 10^{-5} mm Hg.

The predistilled monomer was placed in a reservoir system (essentially a flask with needle valve and flowmeter) that could be connected to the plasma apparatus by means of ground-glass joints. The monomer was degassed in the reservoir and always kept in vacuum. The monomers studied are summarized in Tables I and II.

TABLE I
Polymerization Data of Olefinic Monomers—Type A

Monomer	Molecular weight	α_w, g/min·torr²	$a \times 10^4$, g/cm²·min·torr²	$b \times 10^{-1}$, for N_2, torr⁻¹	$k \times 10^4$, cm⁻²	Wattage	$p_0/p_M = \delta$
4-Vinylpyridine	105	2.16	16.4	4.5	7.59	30	3/30	.10
α-Methylstyrene	118	2.59	13.8	2.4	5.33	30	8/30	.26
1-Phenylbutene-2	162	1.95	12.8	—	6.56	60	8/50	.16
Styrene	104	2.14	12.1	8.0	5.65	30	5/50	.10
Vinyltoluene	118	1.85	11.4	6.6	6.16	30	3/38	.08
2-Vinylpyridine	105	2.16	10.4	5.0	4.81	30	3/40	.08
N-vinyl-2-pyrrolidinone	111	1.25	9.7	2.2	7.76	60	22/36	.61
Acrylonitrile	53	1.26	7.2	9.9	5.71	30	5/30	.16
Vinylidene chloride	97	1.06	5.8	—	5.47	60	33/47	.70
Butene-1	56	0.951	4.7	—	4.94	60	10/30	.33
Butadiene	54	0.991	4.4	5.0	4.44	60	12/40	.30
Allylamine	57	1.12	3.2	5.9	2.86	30	30/45	.66
trans-Butene-2	56	1.28	2.7	—	2.11	60	30/40	.75
Isobutylene	56	1.03	2.7	—	2.62	60	42/60	.70
3-Methylbutene-1	70	1.50	2.2	—	1.47	60	18/37	.49
Propylene	42	0.714	1.6	—	2.24	60	26/40	.65
Vinyl chloride	63	0.955	.97	1.4	1.02	100	28/40	.70
Ethylene	28	0.893	.32	—	0.36	100	75/90	.83

TABLE II
Polymerization Data of Olefinic Monomers—Type B

Monomer	Molecular weight	α_w, g/min·torr²	$a \times 10^4$, g/cm²·min·torr²	$b \times 10^{-1}$ for N_2, torr⁻¹	$k \times 10^4$, cm⁻²	Wattage	$p_0/p_M = \delta$
Glycidyl methacrylate	142	2.09	4.0	—	1.91	30	45/22	2.05
2-Methylbutene-2	70	1.53	3.4	—	2.22	60	43/41	1.05
Methyl methacrylate	100	1.83	2.6	4.7	1.41	150	105/40	2.62
2-Methylbutene-1	70	1.67	2.0	—	1.20	100	62/60	1.03
Methacrylic acid	86	1.23	1.9	4.7	1.54	100	100/45	2.22
Methyl acrylate	86	1.51	1.5	2.2	0.99	150	150/50	3.00
Butyl vinyl ether	100	1.91	1.5	—	0.79	150	160/60	2.67
Vinyl acetate	86	1.64	1.3	2.7	0.79	100	61/50	1.22
Vinylene carbonate	86	1.51	1.2	3.4	0.80	150	80/40	2.00
Acrylic acid	72	0.964	.73	4.7	0.76	150	140/50	2.80

The deposition of polymer was measured by determining the weight increase of a 75 mm × 25 mm glass slide placed in the sample tube. The distance of the slide from the monomer injection tube and the discharge coil was carefully controlled (30 mm and 200 mm, respectively) when the discharge vessel was connected to the vacuum manifold by a ball-socket ground-glass joint.

The apparatus was then pumped down to less than 10^{-3} mm Hg before the monomer was introduced into the system; then the entire system including the slide was subjected to glow discharge (in vacuum) for 3 min in order to minimize the effect of gas and vapors adsorbed on the walls of the system. The gas and vapor were introduced by controlling the opening of needle valves, while the downstream side of the vessel was kept pumping. When both gas and vapor were used, the plasma gas was first introduced into the vessel and the pressure was measured by the pressure transducer. A steady pressure was ensured by observing the pressure for at least 5 min before the monomer was admitted into the vessel. The increase of pressure was taken as the pressure of the monomer vapor and it was controlled by the opening of a needle valve connected to the monomer reservoir. Since over 20 psi gas pressure was used for the gas head pressure, the introduction of monomer vapor (usually less than 100 μ Hg) does not alter the flow of plasma gas nor consequently the gas pressure in the vessel.

The pressure reading of the pressure transducer is independent of the type of gas or vapor, and no calibration was necessary for various gases and vapors. The flowmeters on the gas and vapor inlets were used to control the opening of the needle valves, but the actual amounts of gas and vapor were measured by the pressure. The flow rates of monomer and gases of various pressures were calculated from the initial rate of the pressure increase when the pump was disconnected from the discharge vessel.

After the steady pressure of gas–monomer mixture was confirmed, the glow discharge was initiated and allowed to operate for a given time at a fixed power. The radio frequency power supply used to produce the glow discharge is a radio frequency transmitter, Heathkit Model DX60B. The output is fed into a linear amplifier, Heathkit SB-200, having a 500-watt capacity. The amplifier output is connected to the rf coil through a network of tunable capacitors. A Bendix coupler Model 262, 0.5-225 mc/S, was used to measure the rf power. The rf power supply operates at 13.56 MHz and delivers continuously variable output power from 0 to 200 watts. A tuning circuit, located between the generator coil and the coupler, is used to match the impedance of the discharge vessel and the impedance of the amplifier output. The tuning circuit is adjusted so that the reflected power is maintained at the minimum.

The breakdown energy required to initiate plasma by the electrodeless rf discharge is dependent upon (1) the pressure, consequently the mean free path of electrons and the frequency with which they hit gas molecules, (2) the frequency of the a.c., and (3) the dimensions of the vessel, i.e.,

length and radius of a tube. With a fixed rf frequency and a discharge vessel, the breakdown energy depends mainly on the pressure and the nature of gas–vapor mixture.

It is often necessary to increase the wattage of the generator above the planned wattage of the experiment to initiate glow discharge. As soon as glow discharge is initiated, the wattage is reduced to the predetermined wattage of the experiment, still maintaining the glow discharge. The wattage selected for each vapor was the lowest wattage of the arbitrarily chosen series 30, 60, 100, 150 watts which maintained a glow discharge in the entire reaction vessel within the pressure range investigated for that compound. A previous study of styrene and investigation of some of the monomers included here have shown only a negligible dependence of polymer deposition on the wattage.

During the discharge, the pressure of the system was recorded. Although some degree of interference was observed in nearly all cases, this disturbance could be minimized by proper grounding and shielding of the coil and the pressure transducer meter. The pressure of the system during the run could be determined with quite reasonable accuracy.

For each monomer, the amount of deposition onto a slide for a given time and wattage was determined for at least three different monomer steady-state pressures, p_M. The a value listed in Tables I and II for each monomer is the slope obtained by plotting the deposition weight versus $p_M{}^2$, and has the units g/cm$^2 \cdot$ min $\cdot$ torr^2.

The flow rates of monomers were calculated from the initial rate of pressure increase in the discharge vessel when disconnected from the pump. The pressure rise is automatically recorded as a function of time. With this mm Hg/min value, and the temperature and volume of the system, the flow rate in cc(S.T.P.)/min can be calculated and then plotted as a function of the square of the monomer partial pressure. The slope of this plot is denoted as α_v and has the units cc(S.T.P.)/min $\cdot$ torr.^{2} The value α_w is α_v multiplied by the gram molecular weight of the monomer/molar volume cc(S.T.P.). The value of k is a/α_w.

For many of the monomers the effect of a plasma gas on the rate of deposition was investigated. With a constant monomer pressure, the rate of polymer deposition R_0 (without a gas) and R (with various pressures p_x a plasma gas) were measured. The plot of R/R_0 versus p_x yields a straight line which intercepts at the value $R/R_0 = 1$ at $p_x = 0$. The slope of this straight line is taken as the constant b, which has the units 1/torr.

RESULTS AND DISCUSSION

The dependence of the polymer deposition rate on experimental factors found with styrene was also found with monomers investigated in this study, e.g., (1) polymer deposition is a linear function of time, (2) the deposition rate is nearly independent of the discharge power, and (3) the

deposition rate can be expressed by the monomer vapor pressure p_M and gas pressure p_x as

$$\text{rate} = a \, [p_M]^2 \, [1 + b \, (p_x)].\qquad(1)$$

In previous studies, it was assumed that only a small portion of monomer in a flow system participates in the polymerization reaction, and an attempt was made to correlate eq. (1) to possible kinetics of radical polymerization. From direct measurements of pressure of both closed and flow systems in glow discharge carried out in this study, it was determined that the absolute rate of monomer consumption is very high and the assumption made in the previous study cannot be applied in most cases.

When the pressure of a monomer reservoir which is connected to a reaction tube (glow region does not extend beyond the reaction tube) was measured as a function of time, the monomer consumption was found to be nearly first order in respect to the monomer pressure in the initial stage of the reaction. This is in contradiction to the kinetic scheme which requires the second-order reaction in respect to the monomer vapor pressure.

Another striking observation obtained by the pressure measurement of a closed system was that nitrogen introduced in a glow discharge system with a monomer is consumed as the monomer polymerizes. Examples of pressure decay in a closed system, in which styrene alone and styrene/nitrogen mixture are contained, during an electrodeless glow discharge are shown in Figure 2 as plots of log p versus time. In all cases, the pressure decrease in the initial stage is in first order. If nitrogen is not consumed, the pressure of the system should not decrease below the initial nitrogen pressure, e.g., 100 μ Hg for curve 2 and 200 μ Hg for curve 3.

When the pressure of a styrene flow system was measured during glow discharge, it was also found that the pressure of the flow system decreased very quickly to a value which is considerably lower than the steady-state flow pressure observed before the glow discharge was initiated.

These observations, i.e., pressure of a closed system and the change of pressure in a flow system, indicated that the monomer (styrene) is consumed as soon as the monomer comes into the glow discharge vessel and the deposition rate of polymer is controlled by the rate of monomer feed-in into the system. The relationship between the rate of polymer deposition and the flow rate of monomer is shown in Figure 3 as a plot of the rate of polymer deposition versus the monomer flow rate for 4-vinylpyridine.

The relationship given by eq. (1) is still valid in the case where the flow rate becomes the rate-determining step because the flow rate of monomer was found to be proportional to the square of monomer pressure in a flow system used in these experiments. In other words, the polymer deposition rate in flow rate-controlled plasma polymerization should be proportional to the square of monomer pressure (observed in a steady-state flow before the discharge is initiated).

The pressure measurement of a flow system with various monomers in the glow discharge revealed that organic compounds with olefinic double bond
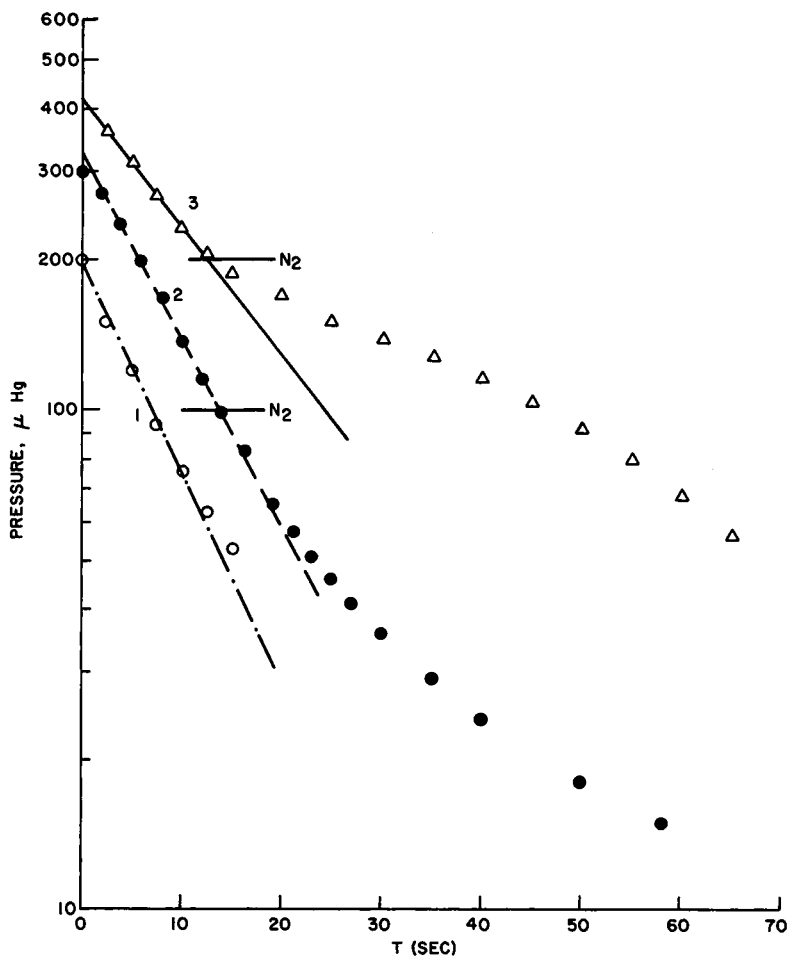
Fig. 2. Pressure change of a closed system, which contains 1:200 μ styrene, 2:200 μ styrene, and 100 μ N_2, and 3:200 μ styrene and 200 μ N_2 with time of glow discharge at 60 watts.

could be classified into two major groups.   One is the monomers (type A) of which pressure decreased when the glow discharge was initiated (closed and flow systems), and the other is the monomers (type B) of which pressure increased when the glow discharge was initiated.

The straightforward polymerization of monomers in vapor phase should yield a decrease of pressure, as was the case observed with type A monomers.   On the other hand, if a monomer undergoes simultaneous decomposition of the monomer and polymerization of both original monomer and decomposed fragments of the monomer, a decrease of pressure cannot always be expected.   Whether total pressure would decrease or increase is dependent on the relative rates of polymerization and of decomposition. Consequently, the grouping of monomers by pressure change alone will not
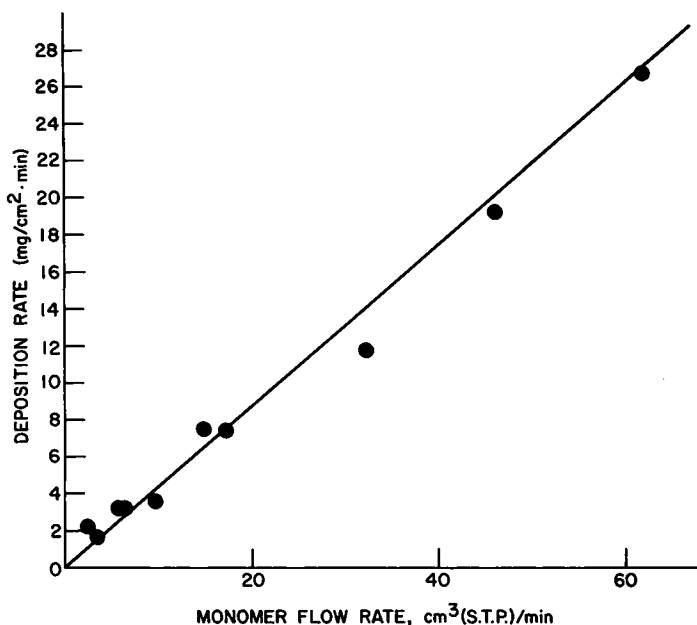
Fig. 3. Dependence of polymer deposition rate on monomer (4-vinylpyridine) flow rate.

distinguish whether a monomer simply polymerizes or whether decomposition and polymerization of the monomer occur simultaneously in the glow discharge. However, the comparison of chemical structure of monomers in both groups and of the rates of polymer deposition from those monomers tends to indicate that polymerization predominates with type A monomers, whereas decomposition of the monomers predominates with type B monomers, though this kind of classification is arbitrary and a gradual transition of typical A to typical B is observed.

The rate of polymer deposition from monomer plasma R_0 is given by eq. (1) as

$$R_0 = ap_M{}^2 \tag{2}$$

where a is a constant in units of $g/cm^2 \cdot min \cdot torr^2$.

The flow characteristic of monomer vapor is also given by a similar expression,

$$F_v \equiv [\text{flow rate in cc(S.T.P.)/min}] = \alpha_v p_M{}^2 \tag{3}$$

where α_v is a constant in units of $cc(S.T.P.)/min \cdot torr^2$.

The flow rate F_w based on the weight of monomer is given by

$$F_w \equiv [\text{flow rate in g/min}] = \frac{\alpha_v M p_M{}^2}{2.24 \times 10^4} = \alpha_w p_M{}^2 \tag{4}$$

where M is the molecular weight of a monomer and α_w is a constant in units of $g/min \cdot torr^2$.

The pressure of a vapor is dependent on the number of molecules. The rate of polymer deposition, on the other hand, is dependent on the weight of polymer (and weight of the vapor molecules). Therefore, the characteristic rate constant of vapor phase polymerization should be given by

$$R_0 = kF_w. \tag{5}$$

From eqs. (2), (4), and (5), the characteristic rate constant k is given by

$$k = \frac{a}{\alpha_w}. \tag{6}$$

The rate constant k is not a rate constant of the chemical reaction in a strict sense, since the polymer deposition rate by plasma polymerization is dependent on certain geometric factors of a reaction vessel such as the ratio of surface area to volume, shape of the vessel, the distance from rf antenna, etc. The constant k has the unit of cm^{-2}.

The polymer deposition rate is measured only at a portion of the reaction vessel, and it was found that considerable distribution of polymer deposition exists along the direction of the tube. On the other hand, the pressure measurement reflects the total pressure of the entire system. Consequently, a quantitative estimate of polymer deposition and decomposition of a monomer based on the experimental data is not possible; therefore, the data can be dealt with only in a semiquantitative sense.

Values of constants a, b, k, and α_w are summarized in Tables I and II. The change of the steady-state flow pressure due to a glow discharge is expressed by $\delta = p_g/p_M$, where p_g is the steady-state flow pressure in a glow discharge and p_M is the steady-state flow pressure of the monomer before a glow discharge is initiated. The value of δ for a monomer is dependent on the value of p_M; however, since the sign of $(\delta-1)$ does not usually change with the value of p_M, the value of δ can be used as an indication of the behavior of the monomer in a glow discharge. The values of δ listed in Tables I and II are selected from the nearest value of p_M to a common value of 40 μ Hg.

Plots of the constant a versus molecular weight are shown in Figure 4 for type A and B monomers. The value of a is apparently dependent on $M^{2.5}$. This dependence is not unreasonable from a view based on the vapor-phase polymerization; namely, the excitation of a molecule by an electron and collision of excited molecules to polymerize both should be proportional to $M^{1/2}$. The weight of depositing polymer should be proportional to M. Hence, a power higher than 2 of the molecular weight is expected for the dependence of polymer deposition.

As the molecular weight increases, the vapor pressure at ambient temperature decreases; hence, there is a practical limit of the molecular weight of monomers usable in plasma polymerization. Accordingly, there also should be a certain range for the values of a and k. The dependence of k on the molecular weight should be one power less than that for a.
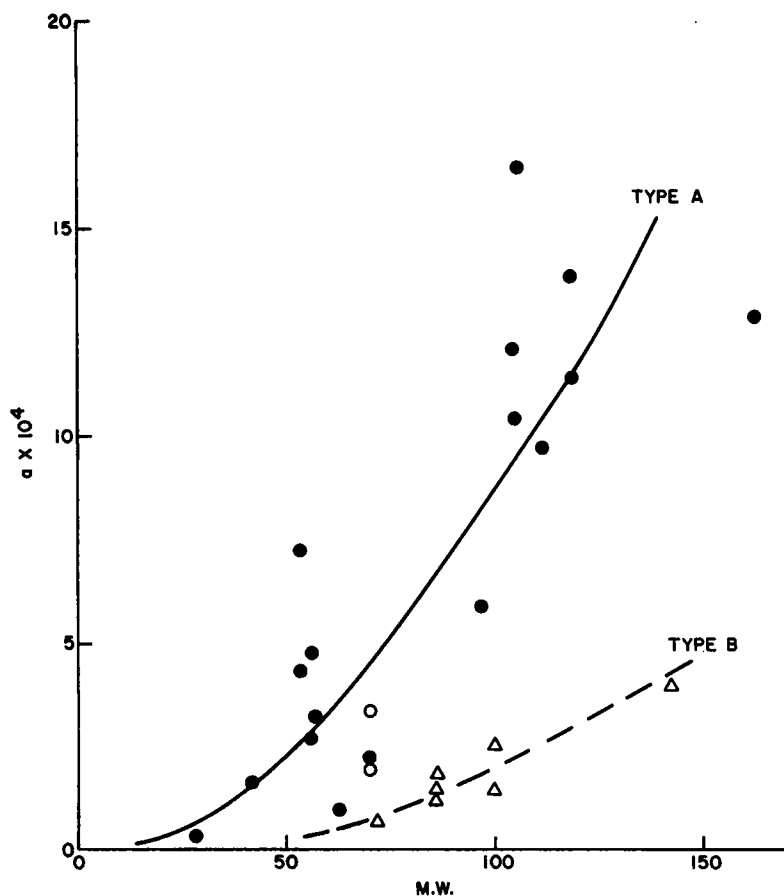
Fig. 4. Dependence of polymer deposition rate constant a on molecular weight (M.W.) of monomers. The polymer deposition rate R_0 g/cm²· min is given by $R_0 = a\,p_M{}^2$, where p_M is monomer vapor pressure of a flow system; a in units of g/cm²· min· torr².

It is interesting to note that the highest and lowest values of k for these monomers are only roughly tenfold (reflecting that the range of molecular weights is roughly tenfold). In other words, all monomers behave more or less similarly in plasma polymerization; no great difference due to chemical nature of monomers such as the ones observed in free-radical and ionic addition polymerization of various monomers is found in a glow discharge polymerization.

All monomers which are classified as type B have relatively low values of a and k. Together with the increase of pressure, it seems quite reasonable to assume that decomposition of monomer in glow discharge predominates with type B monomers.

Some of the chemical structures of the monomers can be attributed to the plasma decomposition susceptibility of type B monomers, e.g., (a) carboxylic acid, (b) ester, (c) ether.

The high plasma susceptibility of monomers that contain these groups is also reflected in their high breakdown wattage as seen from run wattage necessary to keep a uniform glow. In other words, it seems more difficult to ionize these monomers without knocking off the above-mentioned substituents. Although run wattages listed in Tables I and II are not true breakdown wattage of monomers, a definite correlation seems to exist between the rate of polymer deposition (at a given monomer pressure or at a given flow rate) and the breakdown wattage of a monomer; i.e., the higher the breakdown wattage, the lower the deposition rate. This correlation may be explained by the assumption of an equilibrium between polymer deposition from monomer vapor and decomposition of formed polymer.

A separate study[7] has indicated that polymers degrade and weight losses are observed when they are exposed to a glow discharge. The rate of weight loss is highly dependent on the wattage of discharge, whereas the rate of polymer deposition is nearly independent of the wattage. Consequently, the equilibrium for type B monomers which requires high wattage to initiate plasma will be shifted in favor of degradation of polymer, yielding low overall polymer deposition rates. According to this hypothesis, wattage dependence of type B monomer should be negative; however, due to the already too high wattage required for the minimum discharge power, it has not been possible to investigate this point.

The infrared spectra of polymer deposited from acrylic acid by prolonged treatment showed very small absorption of OH and carbonyl bands, indicating that the carboxylic group was knocked off from the plasma-polymerized polymer. At the level of deposition used in this study, the accurate measurement of the IR spectrum was not obtainable. If it is assumed that ester and ether substituents of vinyl and acrylic monomers will be knocked off in a glow discharge, the values of the deposition rate constant k for these monomers should be close to those for propylene and ethylene. As seen in Tables I and II, the value for k for acrylic ester, acrylic acid, vinylacetate, vinylether, and vinylene carbonate are close to the value for ethylene. Therefore, the above assumption seems reasonable.

A nondiscriminatory pattern of plasma polymerization is reflected also in the polymerization of some monomers which do not polymerize by radical polymerization, e.g., ethylene, propylene, butenes, and α-methylstyrene. The polymerization rate of α-methylstyrene was nearly as fast as that of styrene, and its polymerization is not affected by the presence of water. Therefore, this suggests that plasma polymerization proceeds neither by radical nor by ionic addition polymerization of olefinic double bond.

The increased polymer deposition rate with plasma gas, such as nitrogen and helium, may be explained as a trapping of gas molecules similar to the phenomenon observed in pumping action in deposition of metal vapors. Whether nitrogen is chemically incorporated in plasma-polymerized polymer or physically occluded in the polymer has not been elucidated in this study. The drying of slides, with polymer deposition obtained in the presence of nitrogen, in a vacuum oven (80°C, 10^{-3} mm Hg for 4 days) did

not cause any weight change, indicating that incorporation of nitrogen is not mere trapping of gaseous nitrogen. The values of the constant b listed in Table I may include variation due to change of distribution of polymer deposition; however, the increase of polymer deposition rate, which can be described by eq. (1), has been observed with all monomers investigated in the presence of nitrogen.

It may be concluded that the empirical expression, eq. (1), found with styrene in the previous study was also found with various olefinic compounds; however, the reaction mechanism of polymerization does not seem to be by addition polymerization (either by free radical or by ions) of olefinic double bond. If a monomer contains a plasma-susceptible structure of substituents, the decomposition of monomer occurs and the chemical structure of plasma-polymerized polymer may differ considerably from what is expected from the chemical structure of the monomer. In all cases investigated in this study, plasma-polymerized polymers are highly crosslinked and are insoluble in solvents. The dependence of polymer deposition rate on the flow rate and on the molecular weight of monomers strongly suggests that polymers are formed in the vapor phase and that the growing species deposit on the wall of the discharge vessel.

References

1. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **15**, 2277 (1971).
2. T. Williams and M. W. Hayes, *Nature*, **209**, 769 (1966).
3. T. Hirai and O. Nakada, *Japan J. Appl. Phys.*, **7**, (2), 112 (1968).
4. A. R. Denaro, P. A. Owens, and A. Crawshaw, *Eur. Polym. J.*, **4**, 93 (1968).
5. A. R. Westwood, *Eur. Polym. J.* **7**, 363 (1971).
6. A. R. Denaro, P. A. Owens, and A. Crawshaw, *Eur. Polym. J.*, **6**, 487 (1970).
7. H. Yasuda, C. E. Lamaze, and K. Sakaoku, *J. Appl. Polym. Sci.*, "Effect of Electrodeless Glow Discharge on Polymers" **17**, 137 (1973).