

Polymerization of Styrene in an Electrodeless Glow Discharge

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Synopsis

The polymerization (polymer deposition) rate of styrene in an electrodeless glow discharge from styrene vapor and a mixture of styrene vapor and gas (H_2 , He, A, and N_2) was investigated. The rate of polymerization, R , was found to be independent of the discharge power. The rate of polymerization of the pure monomer was found to be proportional to the square of monomer pressure p_M . The addition of gas increased the rate of polymerization depending upon the partial pressure of the gas, p_x , and R can be generally expressed by $R = a[p_M]^2\{1 + b[p_x]\}$. The value of b is dependent on the type of gas and follows the order of $N_2 > A > He > H_2$. The distribution of polymer deposition was found to be nearly independent of the partial pressure of the gas and of the discharge power with N_2 and H_2 as plasma gas; however, with He and A, the distribution is highly dependent on the partial pressure of the gas and on the discharge power. The study strongly suggests that polymerization occurs in the vapor phase and that the growing polymer radicals deposit on the surface of the discharge vessel, yielding highly crosslinked polymer deposition.

INTRODUCTION

The deposition of polymers in thin film form from organic vapor subjected to a glow discharge has been known for many years,¹⁻⁶ and the method has been utilized in many fields of application. The glow discharge of vapors or gases can be obtained with electrodes (a.c. and d.c.) or without electrodes (a.c.). Perhaps due to the practical interest of electrical properties of deposited polymer film, most of the studies appearing in the literature are concerned with polymer deposition onto the electrode.

Detailed studies of the deposition rate onto electrodes in a.c. glow discharge as functions of a number of externally controllable variables have been reported in the literature.⁷⁻¹¹ However, little is known about the details of deposition of polymers in electrodeless glow discharge, though properties of polymers formed by electrodeless glow discharge have been reported.¹²

The present study was undertaken to investigate the deposition of very thin layers of polymers on membrane substrates. The deposition of a flawless, homogeneous polymer layer of thickness less than a micron onto appropriate substrates that have high permeability would provide a means of preparing functional membranes suitable for a number of membrane

processes such as ultrafiltration and reverse osmosis. For this purpose, polymerization by electrodeless discharge seemed best since deposition of polymer is not limited to the electrode surface.

For such an application, it is necessary to understand the mechanism of deposition, at least as manifested by dependence upon many externally controllable variables of the glow discharge. For this purpose, styrene was taken as a model compound to study the kinetics of polymer deposition, since it is one of the most intensively investigated monomers in polymerization by a glow discharge.

The deposition of polymers in electrodeless discharge was found, in this study, to be quite different from that onto electrodes insofar as the dependence of deposition rate upon externally controllable variables such as monomer pressure, types of plasma gas and their pressure, and discharge wattage is concerned.

The electrodeless discharge used in this study was carried out in a flow system, i.e., pure monomer vapor or monomer vapor and a plasma gas are continuously fed into the system. Therefore, the deposition rate described in this study is not directly related to the conversion rate of polymerization but merely related to how fast the deposition layer increases. In this sense, it must be distinguished from results obtained with closed static systems, where the deposition rate may be directly proportional to the conversion rate of polymerization.

EXPERIMENTAL

The apparatus used in this study is illustrated schematically in Figure 1. The discharge vessel consists of glass tubes with standard tapered joints. The sample-holding unit has an inner diameter of 40 mm, and the discharge unit is tapered from 50 mm to a 22-mm section which is inserted into the discharge coil. The discharge unit has a monomer inlet placed in the center of the tube. Kovar-to-glass seals were used to connect metal parts to glass tubes, so that the system could operate at a high vacuum level. The discharge vessel is connected to a McLeod gauge and to a differential pressure transducer (the MKS Baratron Pressure Meter). The McLeod gauge was

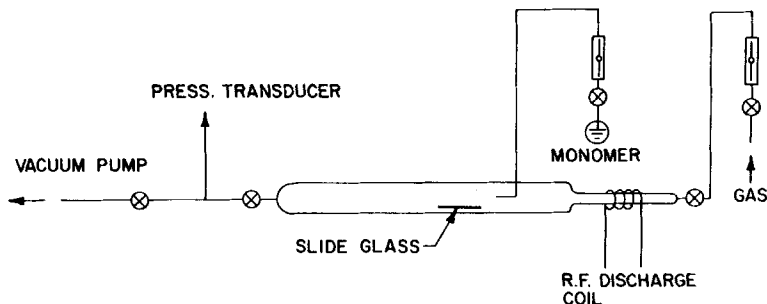


Fig. 1. Schematic representation of the electrodeless glow discharge apparatus.

used to check the reference vacuum for the differential pressure transducer (less than 10^{-5} mm Hg) and also to calibrate the pressure gauge. Since the pressure of monomer vapor cannot be measured by a McLeod gauge due to condensation of vapors during the compression process of the measurement, all pressure readings for the plasma gas and monomer vapor were taken with the pressure transducer.

The deposition of polymer was measured by determining the weight increase of a 75-mm \times 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 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 the level of less than 10^{-5} mm Hg.

The monomer was placed in the reservoir which was attached to a flowmeter and to the apparatus by ground glass joints. The predistilled styrene was degassed in the reservoir and kept always under vacuum. After degassing the monomer, the apparatus was pumped down to less than 10^{-3} mm Hg, and then 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 amount of gas and vapor was measured by the pressure.

The flow rates of monomer and gases of various pressure were calculated from the rate of pressure increase when the pump was disconnected from the discharge vessel. The flow rate of the monomer at the partial pressure of 0.02 mm Hg is approximately 6.0×10^{-2} cm³ (STP)/min; and the flow rate of gas at the partial pressure of 0.06 mm Hg is approximately 17.5×10^{-2} cm³ (STP)/min for N₂ and He, 20×10^{-2} cm³ (STP)/min for H₂, and 15.0×10^{-2} cm³ (STP)/min for A.

After the steady pressure of gas-monomer mixture was confirmed, the discharge was allowed to operate for a given time at a fixed power. During the discharge, the pressure meter was turned off, since the radio frequency interferes with the meter. After the discharge was stopped, the pressure of each component was checked by reading the total pressure and gas pressure in order to make sure that no change occurred during the run, and the residual gases were pumped out before air was admitted to the vessel.

The rf power supply 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 coupled to the generator coil through a Bendix coupler Model 262, 0.5-225 mc/S. The r.f. power supply operates at 13.56 MHz and delivers continuously variable output power from 0 to 500 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 to initiate plasma by the electrodeless r.f. discharge is dependent upon (1) the pressure and 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 dimension of the vessel, e.g., length and radius of a tube. With a fixed r.f. frequency and a discharge vessel, the breakdown energy depends mainly on the pressure and the nature of the gas-vapor mixture. Consequently, 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 pre-determined wattage of the experiment, still maintaining the glow discharge.

RESULTS AND DISCUSSION

Under conditions used in this study, the deposition of polymer was found to be linear with time, as shown in Figure 2. Therefore, the deposition of polymer in a fixed time (e.g., 20 min) was used to calculate the deposition rate in the following investigation. In contrast to the findings observed in discharge with electrodes,⁷⁻¹⁰ the discharge power was found to have no effect on the deposition rate, as seen in Figure 3, though the apparent intensity of the glow discharge is greatly dependent on the discharge power. The degradation of certain polymers by He plasma (glow discharge with He) manifested by the weight loss was found to be greatly dependent upon the discharge power, and details will be presented elsewhere. Apparently different species in the gas plasma and mechanism are responsible for polymerization of styrene and for degradation of polymers.

Since styrene monomer alone also yields deposition of polymer by glow discharge, the pressure dependence should be investigated as a function of the partial pressures of gas and monomer vapor. The dependence of polymer deposition on the monomer pressure was examined by injection of pure monomer (without gas). It was found that the deposition rate

increases proportionally to the square of monomer pressure, as seen in Figure 4 where deposition rate is plotted against the square of monomer pressure. This square dependence on monomer pressure is again in strong contrast to the dependence found for deposition of polystyrene onto electrodes in glow discharge. Although the monomer pressure ranges reported in the literature^{7,9} are much higher than the monomer pressure used in this

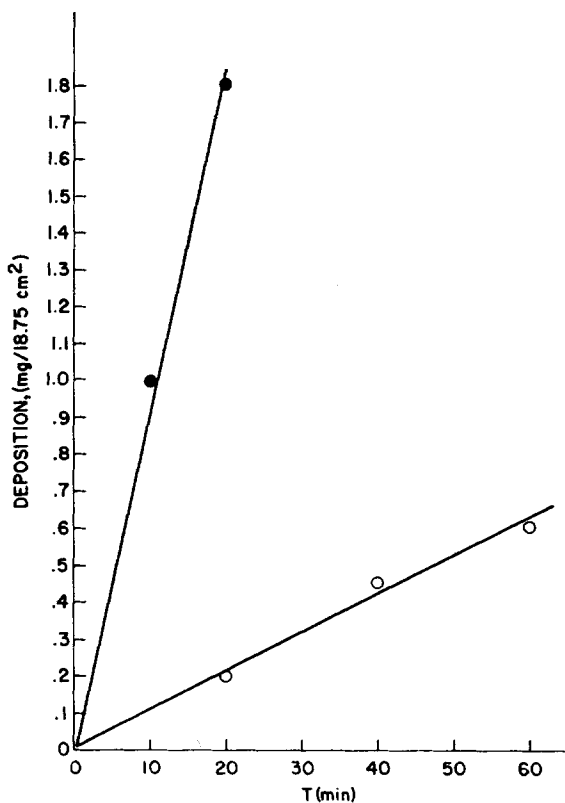


Fig. 2. Time dependence of polymer deposition; mg per 18.75 cm² glass slide vs. time: (a) 20 μ Hg styrene and 100 μ Hg N₂; (b) 20 μ Hg styrene, both at 30 watts discharge power.

study, the deposition rate of polystyrene onto electrodes was found nearly independent of monomer pressure above a certain minimum, and the shapes of the curves do not suggest square dependence on the monomer pressure in the low pressure range.

The effect of gas pressure can be examined by maintaining the monomer pressure constant and varying the gas pressure. The results are presented in Table I, where the effects of gas pressure as well as monomer pressure were examined.

TABLE I
Deposition of Polystyrene on a Glass Slide (25 × 75 mm)

Composition of plasma	Partial press		Power, watts	Time, min	Deposited weight, mg	Number of red bands	Position of red bands*	
	Gas, μ Hg	Monomer, μ Hg						
Styrene	0	20	30	20	0.20	0	—	
	0	24	30	20	0.35	1	75	
	0	30	30	20	0.50	1	75	
	0	40	30	20	0.70	1	68	
	0	40	10	20	0.70	2	7, 75	
	0	40	65	20	0.70	1	73	
	0	40	80	20	0.80	1	73	
	0	40	150	20	0.80	1	75	
	0	51	30	20	1.20	2	17, 75	
	0	60	30	20	1.30	2	27, 75	
	Styrene-Helium	11	20	30	20	0.35	1	47
		22	20	30	20	0.50	1	75
		30	20	30	20	0.80	1	38
32		20	30	20	0.50	3	10, 26, 78	
42		20	30	20	0.70	3	7, 26, 56	
50		20	30	20	0.40	3	6, 18, 42	
52		20	30	20	0.70	4	5, 13, 29, 75	
61		20	30	20	0.65	5	3, 10, 21, 40, 75	
70		20	30	20	0.70	5	3, 11, 22, 37, 75	
80		20	30	20	1.00	6	3, 9, 17, 35, 50, 70	
112		20	30	20	1.20	8	3, 6, 12, 21, 33, 45, 61, 75	
15		40	30	20	0.80	2	17, 48	
25		40	30	20	1.30	3	10, 31, 75	
42	40	30	20	1.40	6	3, 8, 14, 23, 42, 73		
42	40	10	20	1.50	3	4, 13, 74		
42	40	55	20	1.50	7	4, 8, 15, 24, 36, 54, 75		
40	40	80	20	1.50	7	5, 11, 17, 25, 32, 49, 75		

	42	40	80	20	1.80	7	5, 8, 13, 31, 42, 58, 74
	42	40	150	20	1.60	9	3, 8, 12, 16, 22, 30, 40, 54
	60	40	30	20	1.60	6	6, 11, 20, 32, 50, 75
	100	40	30	20	3.40	7	3, 5, 15, 40, 52, 64, 75
	42	48	30	20	1.90	6	3, 6, 14, 25, 48, 75
Styrene-Nitrogen	20	20	30	20	0.60	1	75
	40	20	30	20	0.90	1	48
	40	20	10	20	0.90	2	5, 56
	40	20	80	20	1.00	1	54
	40	20	150	20	0.90	1	58
	60	20	30	20	1.30	1	30
	60	20	30	20	1.40	1	32
	80	20	30	20	1.65	2	17, 75
	98	20	30	20	1.80	3	5, 22, 75
	100	20	30	10	1.00	1	19
Styrene-Hydrogen	20	20	30	20	0.30	b	—
	30	20	30	20	0.40	—	—
	40	20	30	20	0.30	—	—
	45	20	30	20	0.50	—	—
	50	20	30	20	0.40	—	—
	60	20	30	20	0.55	—	—
	70	20	30	20	0.60	—	—
	80	20	30	20	0.60	—	—
	87	20	30	20	0.50	—	—
	100	20	30	20	0.45	—	—
	110	20	30	20	0.45	—	—
Styrene-Argon	40	20	30	20	0.80	5	4, 10, 23, 42, 61
	60	20	30	20	1.25	6	6, 17, 27, 38, 55, 75

^a Distance (in mm.) from the slide edge adjacent to the monomer injection port.

^b The polymer deposited as a clear film, and no rainbow pattern was observed.

Considering that monomer alone would initiate polymerization under a glow discharge and also that gas plasma would initiate polymerization of styrene, the result can be best represented by the expression

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

where a and b are constants, and p_M and p_x are monomer pressure and gas pressure, respectively.

From eq. (1),

$$R/R_0 = 1 + b[p_x] \quad (2)$$

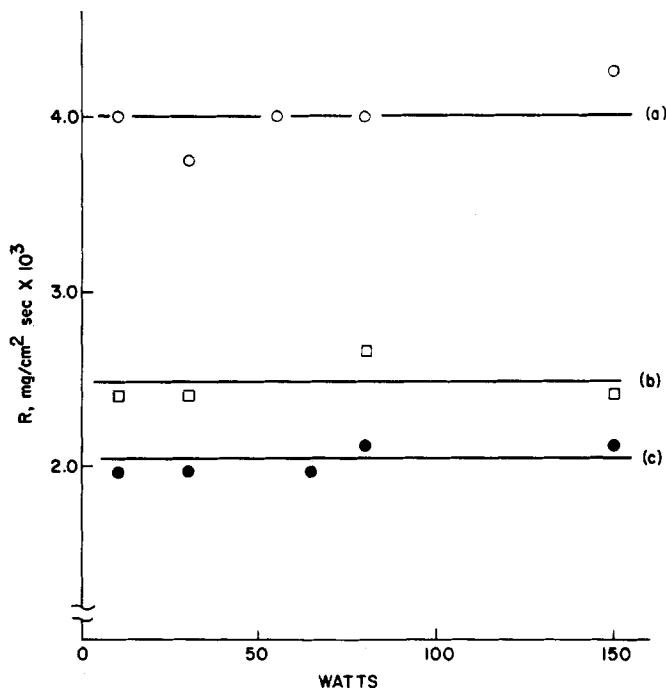


Fig. 3. Dependence of polymer deposition rate on the discharge power (watts): (a) 40 μ Hg styrene and 40 μ Hg N₂; (b) 20 μ Hg styrene and 40 μ Hg N₂; (c) 40 μ Hg styrene.

where R_0 is the deposition rate of pure monomer at a given pressure, R is the deposition rate with the mixture of monomer (at the same pressure) and a gas, and p_x is the pressure of the gas. This expression is indeed observed with experimental data, as shown in Figure 5.

Although the detailed mechanism of polymer deposition by a glow discharge is no doubt complex, it is tempting to speculate on it by polymerization kinetics. Since the observed results were surprisingly simple, a simplified approach may be well justified, at least as a first approximation. In the polymerization of styrene with electrodes, it was postulated that the

polymerization occurs at the surface of the electrode. The dependence of the polymerization rate on the wattage and the monomer pressure supported the mechanism of polymerization of adsorbed monomer on the electrode surface.

In electrodeless discharge, however, the deposition of polymer occurs on the wall of the discharge vessel, and not all mechanisms postulated for deposition of polymer onto electrodes seem to apply, since the dependence of the polymerization rate on wattage and monomer pressure is completely

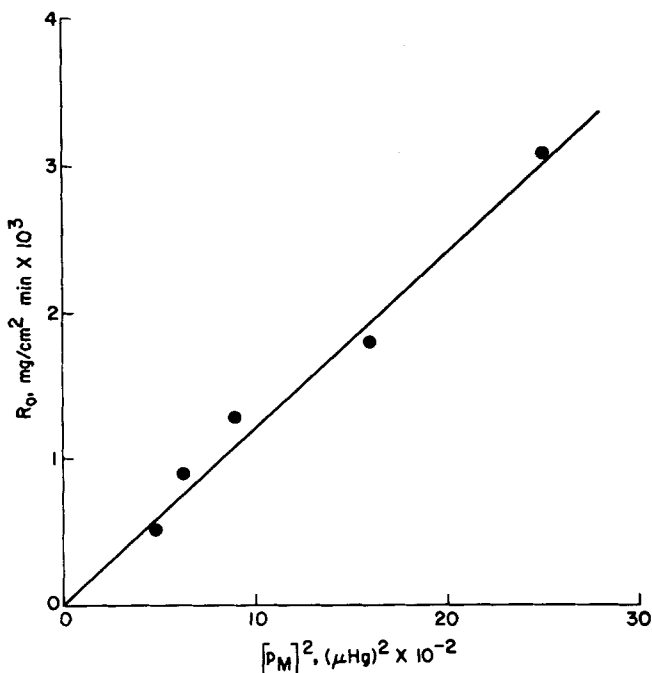


Fig. 4. Dependence of polymer deposition rate on the square of monomer vapor pressure.

different. Therefore, it seems more likely that, under the conditions used in this study, most polymerization occurs in the vapor phase.

As mentioned in the introduction, the polymer deposition rate in a steady-flow system does not correspond to the conversion rate of monomer existing in the system at a given time. Consequently, it may be assumed that polymerization is initiated and propagates in the vapor phase, and as propagation proceeds, the growing polymer deposits on the wall of the discharge vessel, since it cannot remain in the vapor phase. Under this assumption, the termination of the polymer chain occurs on the wall, and the deposition rate is directly proportional to the propagation rate of growing polymer in the gas phase. The following kinetic scheme may be written for such conditions.

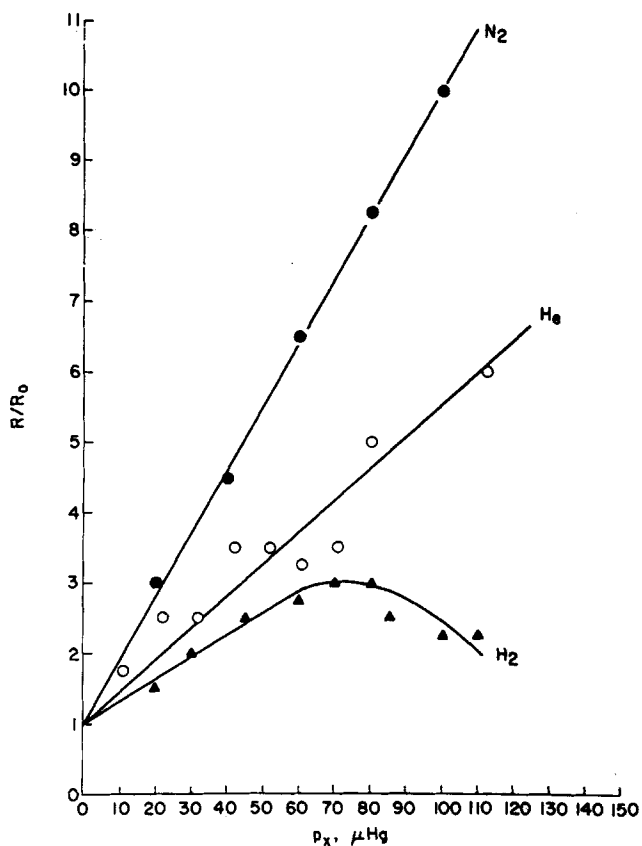
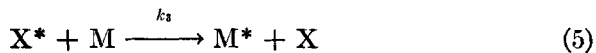


Fig. 5. Dependence of polymer deposition rate on the partial pressure of gas. The relative deposition rate R/R_0 is according to eq. (2).

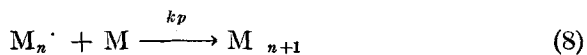
Excitation Step:



Initiation Step:



Propagation Step:



where M is monomer, M^* is excited monomer, X is plasma gas, and X^* is excited plasma gas. Then the rate of propagation can be given by $[M]$ and $[X]$ as follows:

$$\begin{aligned} \text{rate of propagation} &= k_i k_p k_1 [M]^2 + k_i k_p k_2 k_3 [M]^2 [X] \\ &= k_i k_p k_1 [M]^2 \left\{ 1 + \frac{k_2 k_3}{k_1} [X] \right\}. \end{aligned} \quad (9)$$

Equation (9) is of exactly the same form as eq. (1), and the experimental data seems to support the reaction mechanism.

In spite of the fact that the monomer is injected into the plasma gas stream, the deposition of polymer onto the glass wall of the discharge vessel occurs even at the backstream side of the monomer injection port. Uneven and exceptionally heavy deposition occurs on the tube wall under the generator coil. Ignoring this heavy deposition under the coil, polymer deposition seems to have a certain distribution having the peak in the vicinity of the injection point. Further away from the injection point and from the discharge coil, the deposition of polymer decreases; however, the distribution of polymer deposition is greatly dependent on monomer pressure, type

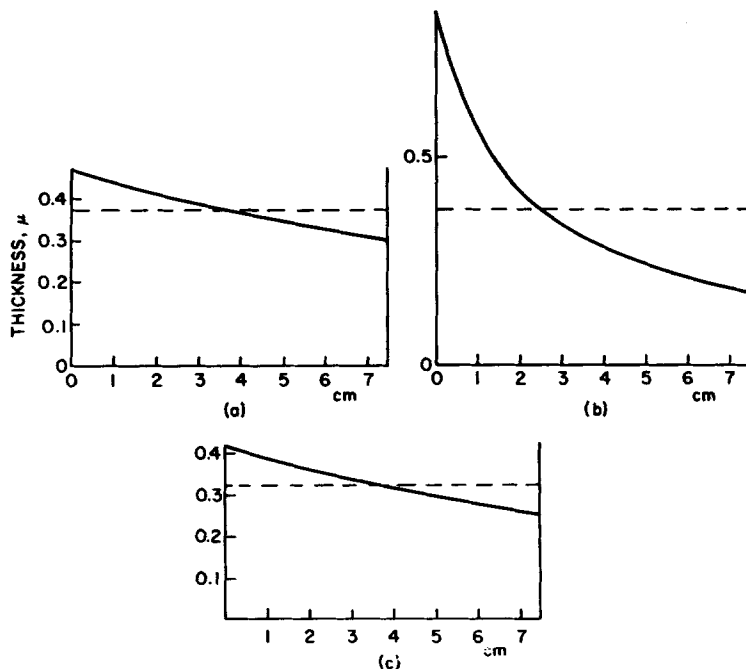


Fig. 6. Distribution of polymer deposited on a glass slide, thickness (μ) vs. distance (cm) from the slide edge next to the injection point. The role of the gas-monomer mixture is compared using slides which have approximately the same amount of polymer deposited by the discharge at 30 watts for 20 min: (a) 40 μ Hg styrene; (b) 50 μ Hg He and 20 μ Hg styrene; (c) 20 μ Hg N_2 and 20 μ Hg styrene.

of gas, and total pressure. The polymer layer deposited onto the glass slide generally shows a rainbow pattern owing to the interference of reflected light by the varying thickness of the polymer deposition. Since the position of the glass slide in the discharge vessel is carefully controlled, the

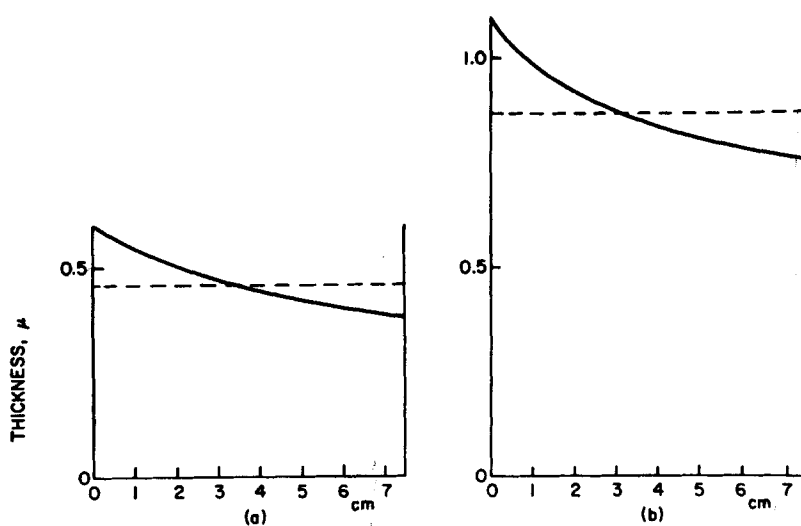


Fig. 7. Effect of N_2 partial pressure on the distribution of polymer deposition: (a) 40μ Hg N_2 and 20μ Hg styrene; (b) 80μ Hg N_2 and 20μ Hg styrene, both at 30 watts for 20 min.

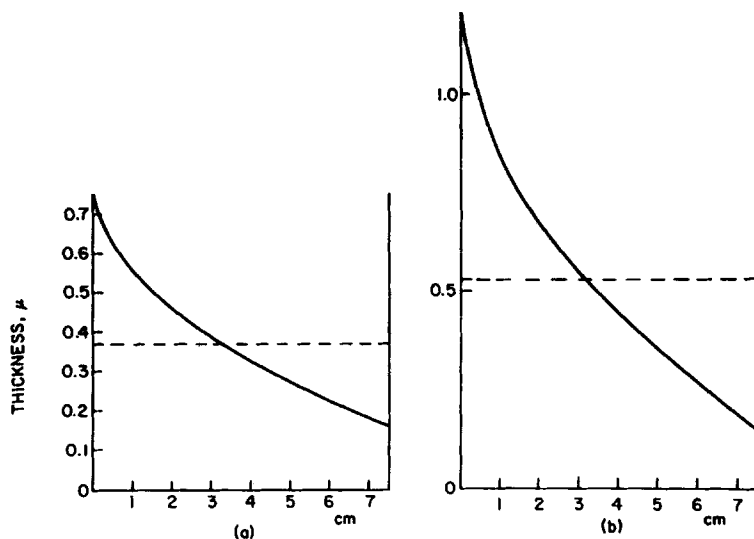


Fig. 8. Effect of He partial pressure on the distribution of polymer deposition: (a) 40μ Hg He and 20μ Hg styrene; (b) 80μ Hg He and 20μ Hg styrene, both at 30 watts for 20 min.

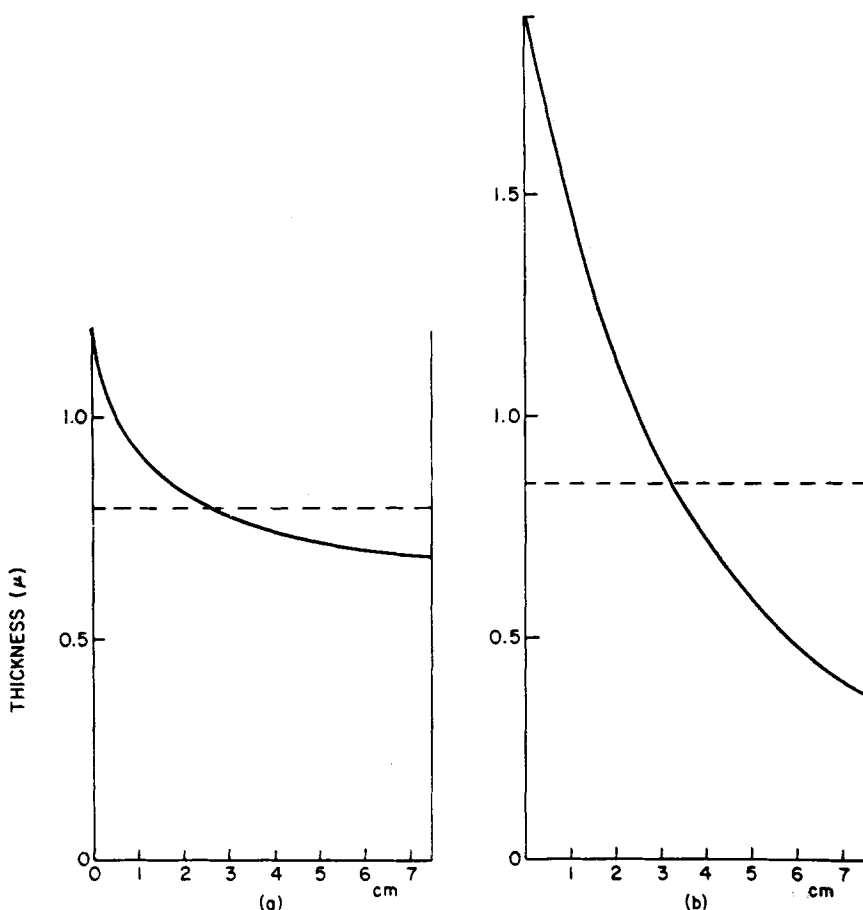


Fig. 9. Effect of discharge power on the distribution of polymer deposited from the mixture of 20 μ Hg styrene and 40 μ Hg He in discharge of 20 min: (a) at 10 watts; (b) at 150 watts.

distribution of the polymer deposition observed on the slide can be utilized to judge the uniformity of deposition by a glow discharge.

Since the interference of light occurs owing to the thickness d , which is related to the wavelength λ and the refractive index n of the medium as $d = \lambda/2n$, the red band spacing observed on the glass slide should correspond approximately to 0.17 μ of thickness variation; i.e., $n = 1.5$, $\lambda = 0.5 \mu$. The variation of thickness observed can be plotted against the position of the red bands observed. The number of red bands and approximate positions are listed in Table I. By this means, it is possible to show semischematically the distribution of deposition as a function of distance along the flow direction. From the weight increase, on the other hand, it is possible to estimate the expected thickness if the deposition occurred uniformly. Consequently, it is possible to reconstruct the distribution of

thickness of the deposition graphically. These reconstructed thickness distribution patterns for some typical cases are shown in Figures 6 to 9.

The lateral distribution of polymer deposition is greatly dependent upon the type of plasma gas. In Figure 6, the distributions of three slides which have approximately the same amount of deposition (in 20 min) are compared. The depositions from 40 μ Hg 100% styrene (Fig. 6a) and from the mixture of 50 μ Hg N₂ and 20 μ Hg styrene (Fig. 6c) have very uniform distributions; however, the deposition from the mixture of 50 μ Hg He and 20 μ Hg styrene (Fig. 6b) yielded uneven distribution.

With N₂ as the plasma gas, the distribution of polymer deposition is virtually independent of the partial pressure of the gas and of the discharge power. However, with He and A as the plasma gas, the distribution of polymer deposition is greatly dependent upon partial pressure of the gas and also upon the discharge power.

The effects of the partial pressures of N₂ and He are shown in Figures 7 and 8, respectively. The effect of discharge power on the distribution of the polymer deposition (in 20 min) by He-styrene mixture ($p_x = 40 \mu$ Hg, $p_M = 40 \mu$ Hg) is shown in Figure 9 for discharge powers of 10 and 150 watts.

The distribution of polymer deposition may be considered as the lateral distribution of excited species that have high enough energy to initiate the polymerization of styrene. Discussion of the exact species which initiate styrene polymerization is beyond the scope of this study. For instance, the chemical reactions of active hydrogen in H₂ plasma could be due to one or more of the following species: hydrogen atom H, excited hydrogen atoms H*, H₂⁺ ions, excited hydrogen molecules H₂^{*}, protons H⁺, or unstable complex H_k^{*}. The energy required for excitation of the H₂ to the repulsive ³ Σ_u triplet state which results in dissociation to two normal H atoms is about 9 eV (207 kcal/mole), and the ionization potential for formation of H₂⁺ ions is about 15.4 eV.

The uneven distribution of deposition observed with He and A makes the kinetic results obtained with those gases somewhat ambiguous; i.e., the deposition rate should depend on the relative position of the slide in the discharge tube, and the deposition rate which is apparently independent of discharge power is a consequence of a fortuitous position selected in this study. However, trends such as the relative deposition rate which is linearly dependent upon the gas pressure and independent of the discharge power are also observed with N₂. Since the distribution of polymer deposition with N₂ does not depend much on the partial pressure of the gas or on discharge power, the trends found do not seem to be mere coincidence.

Any reactions with the monomer which do not yield the polymer are not reflected in the result according to the vapor phase reaction scheme. In this respect, the polymerization by H₂ plasma may need special attention. The plot of R/R_0 versus the partial pressure of hydrogen (Fig. 5) indicates a definite decline at higher partial pressure, which was not observed with N₂, He, and A. This decreasing deposition rate at higher partial pressure

may be due to the increased saturation of the vinyl double bond of styrene at higher partial pressure of H_2 , since the ionization potential of H_2 for the removal of a single electron is nearly the same as those for A and N_2 . It may be worth noting here that the polymer deposited by H_2 plasma is completely clear and colorless, whereas all other polymers deposited by the discharge are light amber. Therefore, the hydrogenation of both polymer and monomer most likely occur during the discharge of H_2 plasma. The hydrogenation of polymer would hardly affect the deposition rate since the weight increase is very small, but hydrogenation of monomer would decrease the rate of polymer formation.

If we take the initial slope of the plot shown in Figure 5 as the value of b in eq (2), values of b for different gases can be summarized in Table II. The values for He and A may include some error due to the distribution of deposition, as discussed earlier. It is interesting to note that the parameter b given by eq. (2) is proportional to k_2k_3/k_1 , which is the relative efficiency of energy transfer of the plasma gas to initiate polymerization of styrene. As the plasma gases, N_2 and A are more effective for polymerization of styrene than He and H_2 ; however, no reasonable correlation between the value of b and properties such as ionization potential is found, though b is apparently proportional to the cube root of the molecular weight of the gas.

TABLE II
The Constant b for Various Gases^a

Gas	$b \times 10^2, (\mu \text{ Hg})^{-1}$
H_2	3.3
He	(4.5)
A	(8.5)
N_2	9.0

^a Reaction conditions: $p_M = 20 \mu \text{ Hg}$, discharge power = 30 watts. $R/R_0 = 1 + b[p_x]$, where R is the polymerization rate with partial pressure p_x of gas, and R_0 is the polymerization rate of pure monomer at a given pressure.

All polymers formed by the plasma are apparently highly crosslinked, because they are not soluble in any solvent. If the deposition mechanism, which involves the initiation and the propagation in vapor phase, and the termination (at least a part of it) on the wall surface are correct, it is highly probable to have highly crosslinked polymers.

The temperature dependence of polymerization has not been carefully examined owing to the limitation of monomer vapor pressure and the difficulty of controlling the temperature of the entire discharge vessel; however, no change in the deposition rate is observed when the ambient temperature is reduced from 25°C to 10°C . The deposition onto electrodes in which the reaction occurs at the surface is reported to be a function of the temperature of the electrode, and the deposition rate increased with a decreasing temperature.¹¹ This observation also supports the idea that the poly-

merization occurs in the vapor phase, since the temperature of the plasma is independent of ambient temperature in the temperature range under consideration.

The kinetic study does not provide proof of the reaction scheme by itself. Nevertheless, the deposition of polystyrene under conditions used in this study is quite well represented by the expression given by eq. (9), and it offers at least a reference for comparative study of the polymerization of various monomers under similar conditions.

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References

1. C. S. Schoepfle and L. H. Connell, *Ind. Eng. Chem.*, **21**, 529 (1929).
2. W. D. Harkins and D. M. Gans, *J. Amer. Chem. Soc.*, **52**, 5165 (1930).
3. E. G. Linder and A. P. Davis, *J. Phys. Chem.*, **35**, 3649 (1931).
4. J. Goodman, *J. Polym. Sci.*, **44**, 551 (1960).
5. A. Bradley and J. P. Hammes, *J. Electrochem. Soc.*, **110**, 15, 543 (1963).
6. R. Brick and J. R. Knox, *Modern Packaging*, **38**, 123 (1965).
7. T. Williams and M. W. Hayes, *Nature*, **209**, 769 (1966).
8. T. Hirai and O. Nakada, *Japan. J. Appl. Phys.*, **7**, (2), 112 (1968).
9. A. R. Denaro, P. A. Owens, and A. Crawshaw, *Eur. Polym. J.*, **4**, 93 (1968).
10. A. R. Denaro, P. A. Owens, and A. Crawshaw, *Eur. Polym. J.*, **5**, 471 (1969).
11. A. R. Westwood, Paper presented at the 157th American Chemical Society Meeting, Minneapolis, Minn., April 1969; *Polymer Preprints*, **10** (1), 433 (1969).
12. G. Smolinsky and J. H. Heiss, Paper presented at the 155th American Chemical Society Meeting, San Francisco, California, April 1968; *Division of Organic Coating and Plastic Chemistry Preprints*, **28**, (1) 537 (1968).

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