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Distribution of Polymer Deposition in Glow Discharge Polymerization in a Capacitively Coupled System

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Synopsis

The manner by which polymers created by plasma uniformly deposit onto substrates was sought. By rotating the substrate placed midway between electrodes, completely uniform distribution of polymer deposition was accomplished, and the deviation of the polymer deposition in a radius direction of the rotating substrate was within experimental errors. Materials of the substrate on which the polymer deposited had no influence on uniformity of polymer deposition, but the electrical circuit of power source, i.e., grounding an electrode, markedly disturbed the uniformity. Thickness of polymers deposited on the substrate was linearly proportional to reaction time. Surface energies of deposited polymers prepared from methane, ethylene, and acetylene by plasma were independent of reaction time and were rather higher than those for conventionally polymerized polyolefines.

INTRODUCTION

In the practical application of glow discharge polymerization, of course, information concerning physical and chemical properties of polymers formed by plasma as well as the reaction mechanism for polymerization is indispensable, but how uniformly polymers deposit onto substrates or in what way polymers uniformly deposit onto substrates is also a technically important subject. The distribution of polymers deposited onto substrates is strongly influenced by system parameters such as the location of an energy source, a monomer inlet, and substrates as well as operational factors involving flow rate of monomer and discharge power.¹⁻⁸ This dependency of polymer deposition on these system parameters was explained as the balance among the diffusion transport of active species created by electric discharge and of polymer-forming species, and the flow of monomer and carrier gas.⁷

A system of capacitively coupled discharge rather than inductive discharge as a device of energy input to initiate plasma is considered to be favorable to get uniform polymer deposition because of simplification of system parameters. Morosoff et al.⁹ have already reported the deposition rate and the distribution of polymer deposition at the electrode and at a stationary substrate placed midway between electrodes in a capacitively coupled system as a function of operational factors such as flow rate of monomer gas, discharge power, and frequency. Their results are worthy of consideration in the application of glow discharge polymerization.

With reference to their results, in this study, the distribution of polymers deposited on moving substrate, which is placed midway between electrodes and is rotating around the axis placed on the top of the electrodes during glow dis-

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charge polymerization, was investigated to seek a coating procedure by which polymers deposited uniformly onto substrates.

EXPERIMENTAL

Plasma polymerization was carried out by an apparatus which utilized capacitive coupling of a 10 kHz audio frequency (af) source and a magnetic enhancement. The basic plasma polymerization system and the experimental procedure are essentially the same as those reported elsewhere.⁹ An aluminum plate [12 in. (30.5 cm) diameter] capable of rotating around an axis placed on the top of electrodes, as shown in Figure 1, is positioned midway between aluminum electrodes [6 in. (15.2 cm) square] the separation of which was 6 in., and then kept rotating at approximately 60 rpm by the inductive force of a magnet placed out of the bell jar during glow discharge polymerization.

Monomer gases used in this study were methane, ethylene, and acetylene which were commercially provided from Ideal Gas Products and Matheson, and their purities were above 99.5%. For all polymerization, unless otherwise noted, the

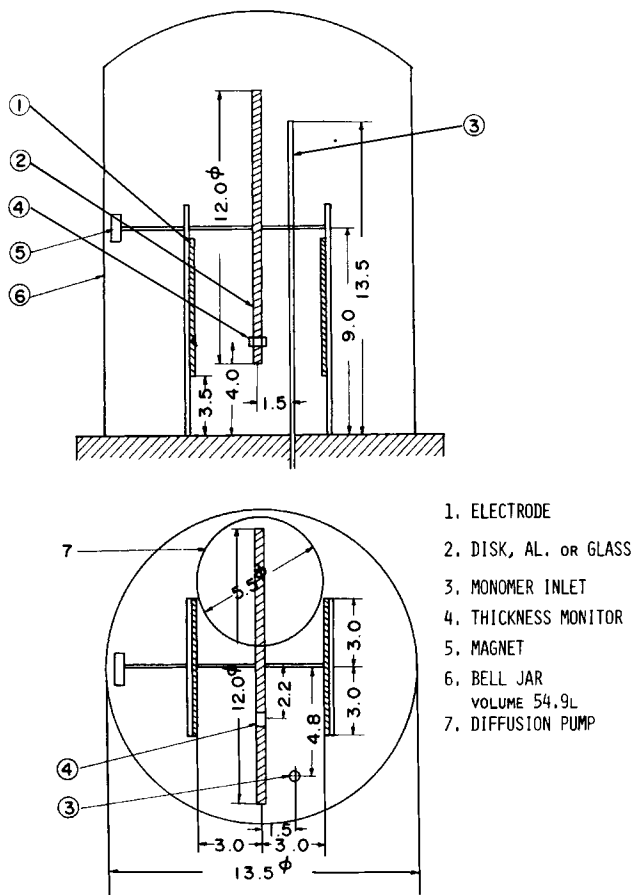


Fig. 1. Schematic representation of the apparatus used for glow discharge polymerization; unit: inch.

monomer flow rate of approximately 2.1 cm^3 (STP)/min, calculated from the pressure volume relationship by closing the outlet valve, the total pressure before glow discharge of 30 mtorr, and the constant current of a power of 250 mA were employed. These conditions maintained the most stable flow discharge without arcing. The pressure changes in the system and the voltage level between electrodes were continuously recorded during polymerization with a MKS Baratron pressuremeter and a Hewlett Packard digital multimeter 3435A, respectively.

The deposition rates were measured from weight increase of aluminum foils [0.001 in. (0.0254 mm) thickness, 6.35 mm (0.25 in.) \times 22 mm] placed on the aluminum plate at 30 mm, 50 mm, 70 mm, 100 mm, 120 mm, and 150 mm from the center of the plate to determine the distribution of the deposition rate. In addition, with a thickness monitor (Veeco model QM-31), the deposition rate was continuously followed during polymerization. The relative orientation of the thickness monitor positioned between electrodes is shown schematically in Figure 1. The relationship between a thickness monitor reading, R in $\text{k}\text{\AA}$, and deposition rate, r in mg/cm^2 , onto aluminum foils placed on the aluminum plate was analyzed according to the least squares method, and presented as the following empirical equation, based on the density of polymers as unit:

$$r = 0.434 \times 10^{-2}R - 0.243 \times 10^{-2}$$

Contact angle of water, glycerol, formamide, diiodomethane, and tricresyl phosphate were measured by a drop-on plate method using a cathetometer with a goniometer eyepiece. The contact angle data were analyzed according to Kaelble's method,¹⁰ and the dispersion contribution, γ_s^d , and the polar contribution, γ_s^p , were calculated.

RESULTS

Pressure Change

The pressure changes observed in the glow discharge polymerization of methane, ethylene, and acetylene are shown in Figure 2. The pressure change

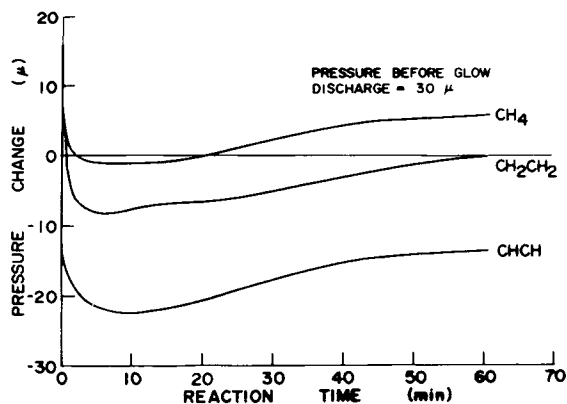


Fig. 2. Pressure changes in glow discharge polymerization as a function of used gas and reaction time.

as a function of the time exposing to plasma, was a similar profile, although the extent of the change depended on the monomer gas used. The pressure in the system rose up as soon as glow discharge was initiated, after a few seconds went down rapidly, and then gradually increased through the minimum, finally reaching a steady-state pressure. The initial pressure rose immediately after turning on the glow discharge and the minimum pressures expressed in mtorr were (16, 29), (15, 22), and (3, 8) for methane, ethylene, and acetylene, respectively. The steady-state pressure was 35.5, 30, and 16 mtorr for methane, ethylene, and acetylene, respectively. A pressure change in the system is controlled by a balance of the consumption of monomer gas to polymerize, fragmentation of the monomer gas to ionize, and evolution of small molecules such as hydrogen, and the pressure indicates a number of molecules residing in the system. The initial pressure rise, as shown in Figure 2, seems to result from the degassing from the surfaces exposed to plasma and also from the fragmentation of monomer gas that are caused by ionization to start glow discharge. Molecules that are excited by plasma polymerize stepwise, and a number of molecules in the system decreases. This consumption of monomer gas to form polymers seems to reflect the consecutive, rapid decrease in pressure. The level of the pressure drop at the minimum, therefore, is considered to be proportional to the rate of polymer formation; i.e., the faster the polymer formation, the lower the system pressure. The deposition rate under exactly the same conditions, as presented in the latter section, is the same order (acetylene > ethylene > methane) as that expected from the pressure drop, and the extent of the initial pressure rise was approximately 8 mtorr independently of the monomer gases used, which indicates that the initial pressure increase is not related to the polymer formation reactions. The gradual increase of the system pressure during plasma polymerization may be due to the increase of temperature, particularly of the electrodes. Since the properties of polymers formed at different reaction times are not appreciably affected, as shown in a later section, it is speculated that no drastic changes in chemical reactions are involved.

Distribution of Deposited Polymers

The distribution of polymer deposition onto a rotating aluminum plate placed midway between electrodes is shown in Figure 3. Results indicate that the distribution of deposited polymers is remarkably uniform without slight maximum deposition in a radius direction of the aluminum plate. An average amount of the deposited polymer and relative deviations that were calculated by the least squares method are presented in a parenthesis in the figure. The relative deviation of the distribution tends to increase with increasing the rate of polymer deposition, but the deviation which is within experimental error is indeed acceptable. From these results polymers deposited onto the rotating aluminum plate are surely more uniform than those deposited onto the stationary aluminum plate, as reported previously,⁹ which have a small maximum at around 6 cm from the center of the plate.

If the aluminum plate is placed on a geometrically symmetrical position against the electrodes, polymers deposited onto the aluminum plate from the right and left sides would be the exactly same amount because of using alternating current of a 10-kHz frequency source as a discharge power. Results shown in Figure 3

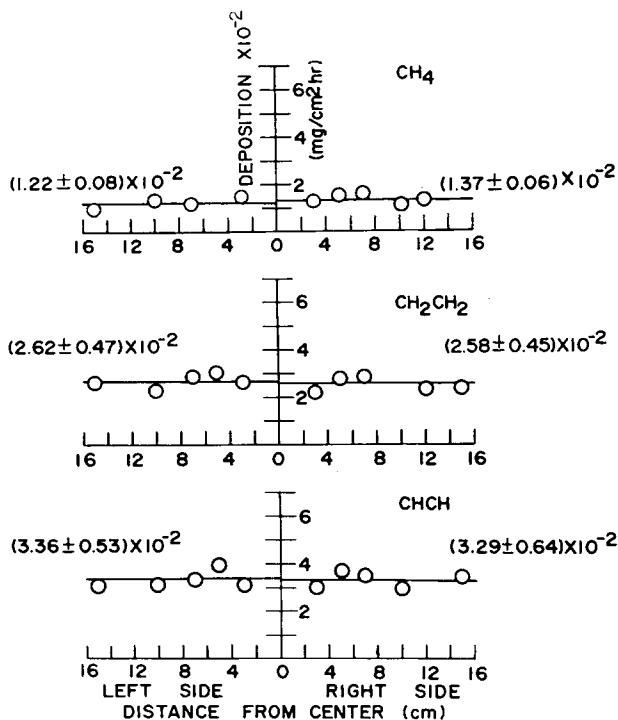


Fig. 3. Distribution of polymer deposition in a radius direction as a function of used gas.

show that the polymers deposited onto the aluminum plate from both sides in the same amount. The symmetry of polymer deposition, however, is strongly influenced by an electrical circuit of the power source, i.e., the electrode is either floating or grounded. Under the same operational conditions, glow discharge polymerization of ethylene was carried out, and the polymer deposition onto both sides of the surface of the aluminum plate was measured. In the case of using a grounded electrode, independently of monomer flow rate and af power, the symmetry of polymer deposition is lost, and polymer deposition onto the aluminum surface facing to the grounded electrode is lighter by 20–30% as compared to polymer deposition onto the other surface. This disparity in polymer deposition, as shown in Table I, still remains even when a glass plate is employed instead of the aluminum plate. In the case of employing a grounded electrode, the stainless steel base plate which supports the bell jar and which is positioned below the electrodes seems to operate as the third electrode. Evidently, the visual event of the discharging glow being expanded toward the stainless steel base plate was observed. By this expansion of glow the symmetrical balance of a concentration of excited molecules and monomer gas present between the electrodes may be disturbed to cause the disparate polymer deposition. A main factor causing this disparity in polymer deposition is not yet clear at present, but an electrostatic effect also seems to relate this irregularity of polymer deposition.

Finally, the influences of the materials of the rotating plate and the substrate onto which the polymers deposited were investigated, and results are presented in Figure 4. Ethylene as a monomer gas and aluminum and glass as a rotating

TABLE I
Symmetry of Polymer Deposition Prepared from Ethylene onto Both Left and Right Surfaces of a Rotating Disc

Gas flow rate [cm ³ (STP)/min]	af power		Material of substrate	Deposition rate × 10 ² (mg/cm ² · h)			
	Current (mA)	Power (W)		Floating electrodes		Grounded electrode ^a	
				Left surface	Right surface	Left surface	Right surface
0.40	250	70	aluminum	2.1 ₁	1.8 ₉	1.9 ₃	1.5 ₃
2.0	250	80	aluminum	2.4 ₈	2.5 ₃	2.5 ₆	1.7 ₆
2.0	250	80	aluminum	2.5 ₈	2.6 ₂	2.2 ₉	1.6 ₅
2.0	400	150	aluminum	3.5 ₈	—	3.7 ₉	—
0.40	250	70	glass	1.7 ₆	1.7 ₆	1.6 ₀	1.3 ₉
2.0	250	80	glass	2.7 ₈	2.9 ₂	2.3 ₄	1.7 ₈
2.0	400	150	glass	—	—	3.0 ₈	2.0 ₈

^a The electrode at right side was grounded.

plate and a substrate were employed, and polymer deposition onto substrates placed in four different environments, i.e., on glass mounted on a glass plate, on aluminum placed on a glass plate, on glass mounted on an aluminum plate, and on aluminum placed on an aluminum plate, was measured. Results indicate that the materials of the plate and the substrate have little influence on polymer deposition.

Surface Energy of Deposited Polymers

Surface energies of deposited polymers as a function of reaction times are summarized in Figure 5 to characterize surface properties of deposited polymers. Results indicate that surface energies are almost constant within experimental error, independently of reaction times. A polymer produced from acetylene shows the highest surface energy, and polymers from ethylene and methane have almost similar energies. These polymers, however, have fairly high surface energies compared with polyolefines conventionally polymerized, the surface energy of which is about 30 dyn/cm. This high surface energy of polymers prepared by glow discharge polymerization seems to be due to polar groups such

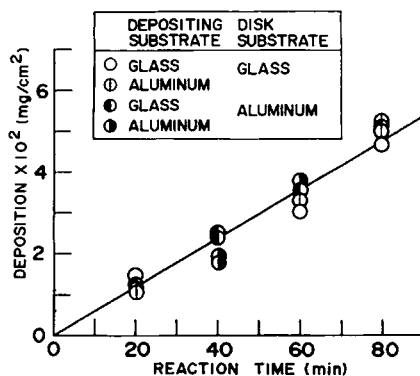


Fig. 4. Effects of materials of substrate on which polymers deposit as a function of reaction time.

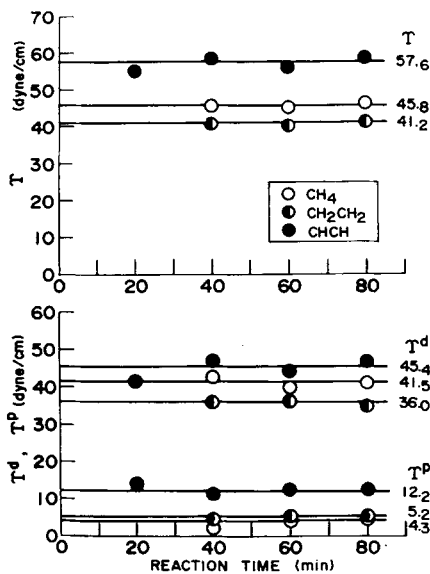


Fig. 5. Surface energies for polymers prepared from methane, ethylene, and acetylene as a function of reaction time.

as the carbonyl groups which are formed by reaction between the remaining radicals and oxygen when the polymers are exposed in air.

DISCUSSION

The distribution of polymers deposited onto stationary and rotating aluminum plates placed between electrodes was compared. The distribution of polymers onto the stationary aluminum plate, as reported previously,⁹ is somewhat uniform, but there is a small maximum at around 6 cm from the center of the plate, while, polymer deposition onto the rotating aluminum plate is completely uniform, indicating that by moving a substrate in the flow discharge very uniform deposition of the polymer can be obtained from a magnetron discharge polymerization system.

A amount of polymers deposited onto the rotating plate, as shown in Figure 6,

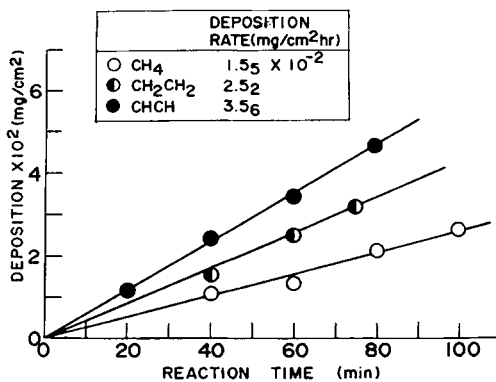


Fig. 6. Deposition rate as a function of used gas.

TABLE II
Conversion of Gas to Polymer Deposited onto Substrate

Monomer Gas	Flow rate [cm ³ (STP)/min]	af Current (mA)	Conversion to polymer (%)	
			0–8 cm	0–15.2 cm
CH ₄	2.1 ₂	250	2.9 ^a	10.3 ^a
CH ₂ =CH ₂	2.1 ₄	250	3.3 ^a	11.8 ^a
CH≡CH	2.1 ₆	250	4.4 ^a	16.1 ^a
CH ₂ =CH ₂	6.1 ₄	60	3.7 ^b	
		115	5.6 ^b	
		200	8.9 ^b	

^a Deposited onto a rotating substrate.

^b Deposited onto a stationary substrate.

is linear to a reaction time up to about 80 min, and the deposition rate which is calculated from the slope of these straight lines is $1.5_5 \times 10^{-2}$, $2.5_2 \times 10^{-2}$, and $3.5_6 \times 10^{-2}$ mg/cm²·h for methane, ethylene, and acetylene, respectively. From these deposition rates the conversion of monomer gas to polymers deposited onto the rotating plate can be estimated, and the result is listed in Table II together with that reported previously in the system where the stationary aluminum plate was used.⁹ The conversion to polymer deposited onto the rotating plate is as much as 10–15% of the monomer gas injected in the system. This level of conversion seems to be rather higher than that deposited on the stationary plate, taking into account that only approximately $\frac{1}{6}$ of the plate is always exposed to plasma.

CONCLUSION

Results presented in this paper point out the following important aspects of the distribution of polymer deposition in the glow discharge polymerization in a capacitively coupled system.

(1) By rotating substrates placed midway between electrodes at approximately 60 rpm completely uniform polymer deposition onto the substrates is accomplished.

(2) Materials of the substrates onto which the polymers deposit have no influence on the uniformity of polymer deposition.

(3) An electrical circuit of power source, i.e., a grounded electrode, markedly disturbs the uniformity of polymer deposition.

(4) A thickness of deposited polymers is linearly proportional to a reaction time and is, therefore, able to controlled by the exposure time.

(5) Surface energies of deposited polymers prepared from methane, ethylene, and acetylene by plasma are almost constant, regardless of reaction time.

(6) Surface energies of those glow discharge polymers are considerably higher than those for conventional polyolefines.

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