

The Initial and Terminating Stage of Glow Discharge Polymerization Investigated by Thickness Monitor

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Synopsis

An attempt to discuss the initial stage and terminating stage of glow discharge polymerization was made by selecting the monomer system of styrene and acetylene, which differ in their condensibility, and a certain polymerization procedure. Results indicate the important aspects of the initial and terminating stages of glow discharge polymerization. These aspects may not play a significant role in the study of bulk properties of plasma-polymerized polymers or in the study of polymer deposition rate. However, the initial stage effect might influence the adhesion of the polymer. The terminating stage effect might influence the surface characteristics of glow discharge-polymerized polymers. These effects are particularly important in a batch polymerization system, where the beginning and the end of process cannot be rigorously controlled with respect to the timing and sequence of the beginning and the end of monomer flow and of electric discharge. This study points to the importance of these aspects for proper utilization of glow discharge polymerization as a thin film process.

INTRODUCTION

Glow discharge polymerization may involve many modes of polymerization. According to the CAP (Competitive Ablation and Polymerization) mechanism described recently by Yasuda,¹ plasma-induced polymerization (conventional chain reaction polymerization initiated by active species created in plasma) and plasma-state polymerization (nonconventional polymerization that occurs only in plasma state) can take place simultaneously.

Although the extent of each particular mode of polymerization differs depending on many empirical factors of glow discharge polymerization, in general, plasma-state polymerization seems to be the predominant mechanism during the process of glow discharge polymerization. However, plasma-induced polymerization may play a crucial role in certain stages of glow discharge polymerization. For instance, glow discharge polymerization is generally performed by establishing a steady-state flow of a monomer (or monomers) before electric glow discharge is initiated. During this preparatory process, the adsorption of the monomer(s) on the substrate surface would inevitably occur. If adsorbed monomer molecules exist at the surface, plasma-induced polymerization of the adsorbed monomer might play an important role in the early stage of glow discharge polymerization. It has been reported that the deposition rate differs at the beginning of glow discharge polymerization,^{2,3} although linear dependence of deposition with respect to time has been established for many cases.

It is also general practice to extinguish glow discharge before the monomer

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flow is stopped, i.e., formed polymer is then exposed to the monomer flow. In this situation, polymerization of the monomer at the surface of plasma-polymerized polymer by the trapped active species, such as free radicals, might occur.

In this study, an attempt was made to examine these aspects by selecting monomer systems and a polymerization procedure whereby two monomers which can be polymerized by conventional chain reaction mechanism but differ in their condensibility are used together with nitrogen gas which does not polymerize by itself but can be copolymerized only by plasma-state polymerization (not by plasma-induced or conventional polymerization). Using these monomer combinations, the deposition rates in the initial stage and in the postdischarge period were examined by a quartz crystal monitor.

EXPERIMENTAL

The apparatus used for glow discharge polymerization in this study and experimental procedures were essentially identical to those reported elsewhere.⁴ The apparatus, which utilizes capacitive coupling of a 10 kHz audio frequency (A.F.) source and a magnetic enhancement, is a reactor of bell-jar type and is constructed with aluminum electrodes (6 in., 15.2 cm square) kept 6 in. apart, an aluminum plate (12 ft., 30.5 cm diameter) which is positioned midway between the electrodes, a thickness monitor (Veeco model QM-31), a pressure transducer (MKS Instruments Inc., 310B), and a monomer inlet. The relative orientation of these parts has been schematically presented elsewhere.⁴

The monomer and comonomer used in this study were acetylene (from Matheson Gas Products), styrene (from Eastman Kodak), and nitrogen (from Matheson Gas Products). The flow rate was calculated from the initial slope of pressure increase. Two methods in injecting the monomer and comonomer into the reactor were employed to compare the influence of the substrate surface where the polymer was deposited. In method A, before turning on the discharge, completely mixed gas of monomer and a comonomer was injected into the reactor. The surface of the substrate was exposed to the atmosphere of the mixed gas approximately 5 min to ensure adsorption of the gas on the substrate surfaces, and then the glow discharge was initiated. In method B, a comonomer gas (nitrogen) alone was first injected into the reactor, and glow discharge of the comonomer was initiated. After a few minute, monomer gas was introduced into the glow discharge, and immediately glow discharge polymerization was initiated. In this manner, adsorption of the monomer gas on the substrate surface is avoided.

For all polymerizations, a total flow of 2.0 cm³ (STP)/min, a total pressure (before discharge) of 30 mtorr, and a constant current of 250 mA were employed. The pressure change and the voltage level between electrodes during polymerization were recorded with an MKS Baratron pressure meter and a Hewlett-Packard digital multimeter 3435A, respectively. The polymer deposition rate was continuously recorded with a thickness monitor (Veeco model QM-31) positioned midway between the electrodes during polymerization. The surface of the sensor of the thickness monitor, which is made of quartz (10 mm diameter), was kept at 20 ± 0.5°C by circulating temperature-controlled water.

Contact angles of water, glycerol, formamide, diiodomethane, and tricresyl

phosphate against polymers deposited on cover glasses which were mounted on the aluminum plate with double Scotch tape were measured by the drop-on-plate method using a cathetometer with a goniometer eyepiece. The contact angle data were analyzed according to Kaelble's method,⁵ and the dispersive component γ_s^d and the polar component γ_s^p were calculated.

RESULTS AND DISCUSSION

The effects of the manner of injecting a monomer and a comonomer into the reactor on the polymer deposition rate can be seen in Figure 1 and 2 as a function of the combination of monomer and comonomer and the reaction time. In the styrene–nitrogen system, the initial deposition rate, when a discharge is initiated in the atmosphere of the mixed gas introduced in method A, is as high as 27.3 Å/min. The polymer deposition rate gradually decreases and then, after approximately 20 min from the initiation of the discharge, reaches the steady-state rate of 6.9 Å/min. In method B, the polymer deposition, when monomer (sty-

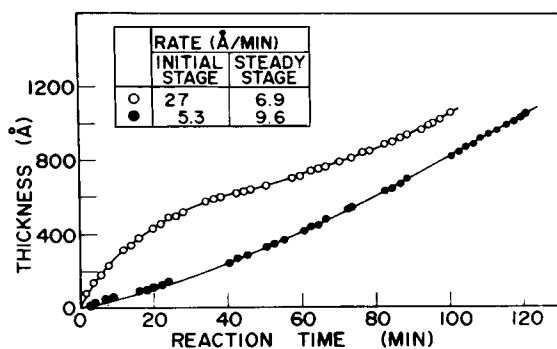


Fig. 1. Polymer deposition in the styrene–nitrogen system as function of mixing method of gases and time exposed to plasma: (O) method A; (●) method B.

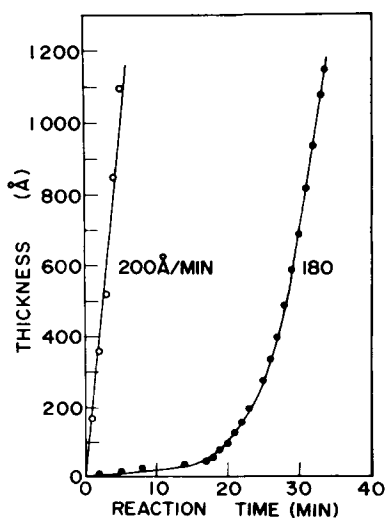


Fig. 2. Polymer deposition in the acetylene–nitrogen system as function of mixing method of gases and time exposed to plasma: (O) method A; (●) method B.

rene) is introduced into nitrogen plasma, is initially slow and then gradually increases. Finally, after approximately 60 min, the polymer deposition reaches the constant rate of 9.6 Å/min. A similar effect of the manner of injecting a monomer and a comonomer gas on the polymer deposition rate can be also seen in the system of acetylene and nitrogen, as shown in Figure 2. The effect in this system is more clear than that in the styrene–nitrogen system. Acetylene, which is introduced into the reactor in method A, shows a constant polymer deposition rate of 200 Å/min, even at the beginning of the reaction, and the rate is kept constant over all the employed reaction times. However, acetylene injected into the reactor in method B deposits at a polymer deposition rate as low as 2.3 Å/min for the initial 15-min period. Thereafter, the polymer deposition gradually rises and finally reaches 180 Å/min, which is comparable to that observed in method A.

In order to compare the results shown in Figures 1 and 2, it may be worth comparing all possible factors. These factors are tabulated in Table I. Results shown in Figures 1 and 2 indicate that after a steady state of polymerization is established, there is no difference between polymer deposition rate of method A and that of method B for both styrene–N₂ and acetylene–N₂ systems. Method B shows a time lag before establishing a linear increase of polymer deposition with respect to time of glow discharge. This time lag is due to the time necessary to establish a new steady flow of the mixture, or the time necessary to establish complete mixing of the monomer and nitrogen. It is worth noting here that the time lags observed in both cases are approximately 25 min. Because the bell-jar system used has a rather large volume compared to the flow rate of the monomer, the mixing by diffusion of gases plays a predominant role. The slightly lower deposition rate observed for method B of the acetylene–N₂ system may be due to the fact that the time of observation was not long enough to establish complete mixing. It takes three times the time lag (extrapolated intercept of a linear portion) to reach a steady state; i.e., in this case, 25 × 3 = 75 min. The styrene–N₂ system confirms this situation. Therefore, observation made for acetylene–N₂ (method B) represents pseudo-steady state, and consequently a slightly smaller slope than that for a steady state.

The important difference between styrene–N₂ and acetylene–N₂ is that the initial rate of polymer deposition from the styrene–N₂ system in method A is significantly larger than the steady-state deposition rate, but the initial depo-

TABLE I
Comparison of Characteristics of Monomers

	Monomer		
	Nitrogen	Styrene	Acetylene
Adsorption	None at the temperature of experiment	High	Very low
Plasma-state polymerization	No polymerization, but copolymerize with styrene or acetylene	High	Very high
Plasma-induced polymerization of adsorbed monomer	None	Possible	Possible
Postplasma polymerization by plasma polymer	None	Possible	Possible

sition rate in the acetylene–N₂ system in Method A is virtually identical to the steady-state deposition rate. The higher polymer deposition rate in the initial stage of styrene–N₂, method A, would be very likely due to the absorbed styrene since styrene is an easily condensable vapor, whereas acetylene is a gas at the temperature of the experiment (~25°C) up to very high pressures. Whether condensed monomer (or adsorbed monomer) polymerized in a condensed phase during the plasma-induced polymerization or reevaporized under the influence of plasma cannot be determined by this experiment. However, the higher deposition rate persists for a considerable length of time (i.e., approximately 5 min), and the time which establishes the steady-state deposition rate roughly coincides with the value of three times the time lag observed in method B (i.e., 75 min). This suggests that the styrene adsorbed on the surface (not only of the substrate or thickness monitor sensor, but also of the electrodes and all walls of the reactor) is released as vapor as soon as glow discharge is initiated and increases the vapor pressure of styrene, and consequently increases the deposition rate.

The surface energy data shown in Table II also support this concept of plasma-state polymerization of desorbed monomer. If styrene polymerizes by plasma-induced polymerization of adsorbed monomer, the polar contribution of the surface energy should be lower than that for plasma-polymerized styrene. The data indicate that there is no significant difference; i.e., a value slightly higher rather than lower is observed for the sample with thin polymer deposit. However, this argument does not eliminate the possibility of plasma-induced polymerization of adsorbed styrene at the surface of the substrate. Such a polymerization may well be taking place, but the experimental data are not adequate to detect it. Plasma-induced polymerization of adsorbed monomer may influence the adhesion characteristics of the glow discharge polymers.

Acetylene, being a gas (not an easily condensable vapor), does not show an increased polymer deposition rate at the initial stage of plasma polymerization. Figure 3 presents the polymer deposition rate in the system of acetylene and nitrogen where audio frequency (A.F.) power and/or flow of acetylene are interrupted for some interval. The areas marked crosshatched and double crosshatched in Figure 3 represent the intervals which the flow of acetylene was stopped and the A.F. power was switched off, respectively. At a reaction time within 30 min from triggering the glow discharge, the polymer deposition is stopped as soon as the A.F. power is turned off, and is initiated again at the same rate, 200 Å/min, immediately when the A.F. power is turned on. On the other

TABLE II
Surface Energy of Polymers from Styrene and Nitrogen and Acetylene and Nitrogen

Composition of gas mixture	Mixing method ^b	Plasma film thickness, Å	Surface energy, dyn/cm		
			γ_s	γ_s^d	γ_s^p
Styrene–nitrogen (2:1) ^a	A	60	46.4	34.8	11.6
		217	39.1	30.0	9.1
	B	60	45.0	36.5	8.5
Acetylene–nitrogen (1:1)	A	213	38.9	27.4	11.5
	B	256	51.8	33.8	18.0
		269	48.2	35.1	13.1

^a Molar ratio.

^b The mixing methods are described in the experimental section.

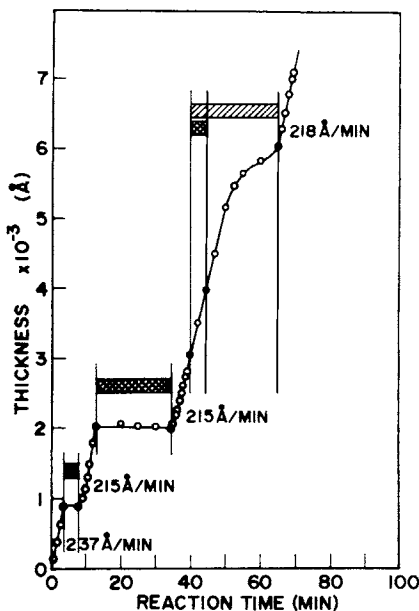


Fig. 3. Polymer deposition in the acetylene-nitrogen system: (□) glow discharge stopped; (▨) flow of CH_2CH_2 stopped.

hand, at any time after 40 min, polymers continue to deposit even when the A.F. power and the flow of acetylene are interrupted, and this polymer deposition is kept at least for approximately 10 min without extremely decreasing the polymer deposition rate. Thereafter, the polymer deposition rate, as seen in Figure 3, markedly decreases. This indicates that after a certain amount of polymer is deposited on a substrate, plasma-polymerized polymer can initiate (postplasma) polymerization of acetylene, perhaps initiating polymerization by trapped free radicals. It has been reported that plasma-polymerized acetylene has extremely high concentration of trapped free radicals.^{6,7} The prolonged polymer deposition after the monomer supply was stopped is probably due to the large reactor volume compared to the glow discharge volume; i.e., ample monomer exists in the total bell-jar system.

It is surprising that the rate of deposition did not change abruptly. It is also surprising that the same did not happen in the earlier steps. These questions must be answered by further studies of these phenomena. Nevertheless, this result (shown in Fig. 3) indicates the possible influence of postplasma polymerization depending on how the glow discharge polymerization process was terminated.

CONCLUSIONS

Results shown in this report indicate the important aspects of the initial stage and of the terminating stage of glow discharge polymerization. These aspects may not play a significant role in the study of bulk properties of plasma-polymerized polymers or in the study of polymer deposition rate. However, the initial-stage effect might influence the adhesion of the polymer. The terminating-stage effect might influence the surface characteristics of glow discharge-polymerized polymers.

These effects are particularly important in a batch polymerization system, where the beginning and the end of the process cannot be rigorously controlled with respect to the timing and sequence of the beginning and the end of monomer flow and of electric discharge. This study points out the importance of these aspects for proper utilization of glow discharge polymerization as a thin film-forming process.

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