Polymerization of Hexamethyldisiloxane by Plasma on Activated Charcoal: Investigation of Parameters

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Synopsis

The polymerization of hexamethyldisiloxane by plasma (glow discharge) on activated charcoal was investigated. The effects of discharge power, discharge duration, and monomer flow rate on polymer deposition were examined. Maximum deposition was observed when the applied power, monomer flow rate, and discharge duration were 20 W, 50 cm^3/min, and 1 h, respectively. The deposited film was investigated by IR, SEM, and ESCA. The same tests were also carried out for plasma-induced polymer deposits.

INTRODUCTION

Gas plasma generated by glow discharge usually initiate polymerizations of monomers and leads to deposition on substrates.[1] By this technique, it is possible to modify surface properties of a substrate without altering the bulk properties. In a comparative study of plasma polymerization of different monomers, the most difficult problem is the generalization of the conditions. It is often experienced that a set of experimental parameters (e.g., flow rate of monomer, discharge power, pressure, etc.) found to be optimal for a few monomers may not be suitable for the others. Geometrical factors of the reactor (e.g., the shape of the reactor, dimensions of electrodes, distance between them, etc.) also affect the result.[2,3] In addition, since no simple method to describe the plasma kinetics is available at present, it is not possible to predict the nature of the product as well as that of intermediates and the yield for a specific reaction, even for a fixed geometry. Every reaction and system, therefore, must be considered as unique and a series of experiments for optimization of the conditions are necessary.[4]

In this work, plasma polymer hexamethyldisiloxane (ppHMDS) coated on activated charcoal was employed, which was shown as a potent system for hemoperfusion of blood.[5] During discharge, the operational parameters (applied power, monomer flow rate, and discharge duration) were changed whereas the geometrical factors were not, and the effects of these parameters were followed by measuring weight increase of substrate. In addition to these, plasma-induced polymer deposits (pipHMDS) were also prepared. Being different from plasma and plasma-initiated polymerizations,[6] in the plasma-induced case, a certain period of monomer flow in the absence of discharge followed by an initial discharge application without monomer was employed. The deposited polymers were analyzed by IR, ESCA, and SEM.
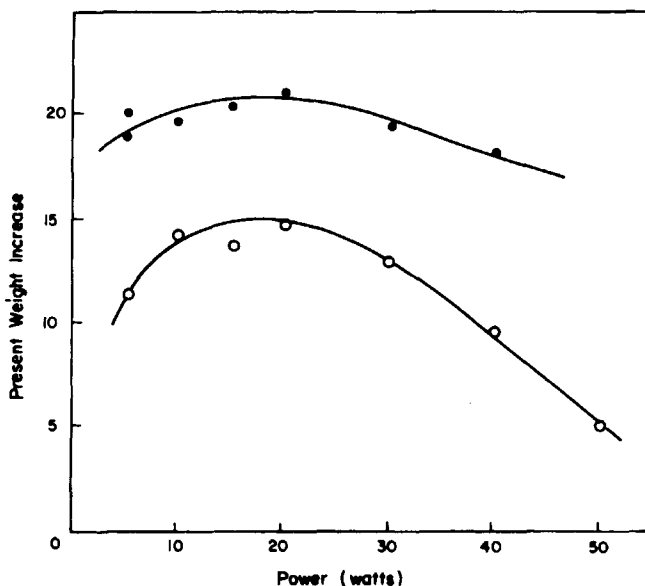
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Fig. 1. Effect of RF power on weight increase. F: ($\bullet$) 50 cm^3/min; ($\circ$) 40 cm^3/min. Discharge duration: 15 min for both.

EXPERIMENTAL

Plasma Polymerization. Plasma polymerization was carried out with the use of a 13.57 MHz radiofrequency source in a capacitively coupled system described previously.[7] Activated charcoal Nuchar WV-G(12 × 40) (kindly supplied by Westvaco), which was previously washed and dried and brought to constant weight by application of vacuum (0.5 mm Hg) for 1 h was placed on the lower electrode in a copper container and used as the substrate on which coating would take place. The amount of activated charcoal was about 3.5 g for each experiment, and it was spread in the copper boat as a monolayer. Then the system was degassed until the inner pressure was reduced to 0.5 mm Hg. The monomer flow rate was adjusted and a steady flow has maintained for 0.5 h. The reaction was initiated by the application of electrical discharge. During this process, only one of the three operational parameter has varied at a time. After the completion of discharge period, the monomer flow was stopped and the system was degassed for 1 h at 0.5 mm Hg.

Plasma-Induced Polymerization. Two types of polymerizations were carried out under the same experimental conditions of discharge duration, monomer flow rate, and RF power of 5 min, 50 cm^3/min, and 20 W, respectively. In the first case, the discharge was applied to charcoal in the absence of monomer in the hope of creating active centers on charcoal. After the discharge was shut off, the monomer was let into the system for different lengths of time. In the second case, the monomer flow and discharge were applied simultaneously, and therefore active centers were created both on the substrate and the monomer. After the discharge was stopped, the monomer flow was maintained for different lengths of time.
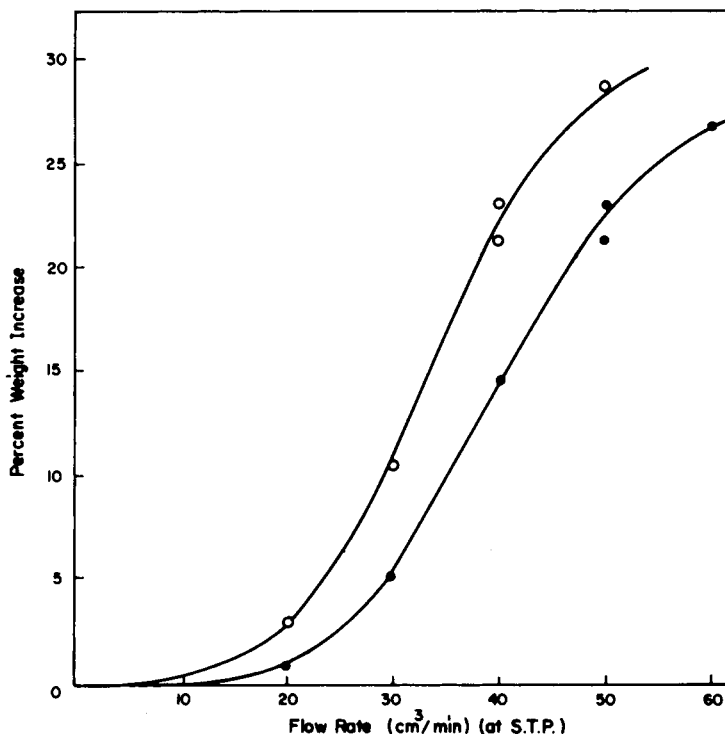
Fig. 2. Effect of monomer flow rate on weight increase: (O) Discharge duration 60 min; (●) Discharge duration 15 min.   Power is 20 W for both.

In order to analyze the polymer with IR, deposition was carried out on a NaCl crystal.   In other cases, deposition was on charcoal.

ESCA analysis of coated and uncoated samples were done using MgK_α source with $h\nu$ = 1253.6 eV at 10^{-6} mm Hg.

Scanning electron micrographs of the samples were obtained by using Cambridge-Stereoscan S4-10 Instrument at 10^{-4}–10^{-5} mm Hg.

RESULTS AND DISCUSSION

In the experiments, the amount of polymer deposited on activated charcoal samples under plasma conditions were investigated as percent weight increase.

The effect of RF power is represented in Figure 1.   In the curve for flow rate 40 cm^3/min, a maximum, at about 20 W is observed.   When the flow rate was increased to 50 cm^3/min, a broader maximum at around 20 W is observed.   In the literature, similar curves for vinyl compounds[8] and for tetrafluoroethylene[9] were reported with maxima at low flow rates and almost no dependency of deposition rate to power at higher flow rates.   In order to explain these observations, the CAP (competitive ablation and polymerization)[10] scheme may be recalled.   The electrical discharge has a dual function, it both creates active centers on monomers for the initiation of polymerization and leads to the degeneration of
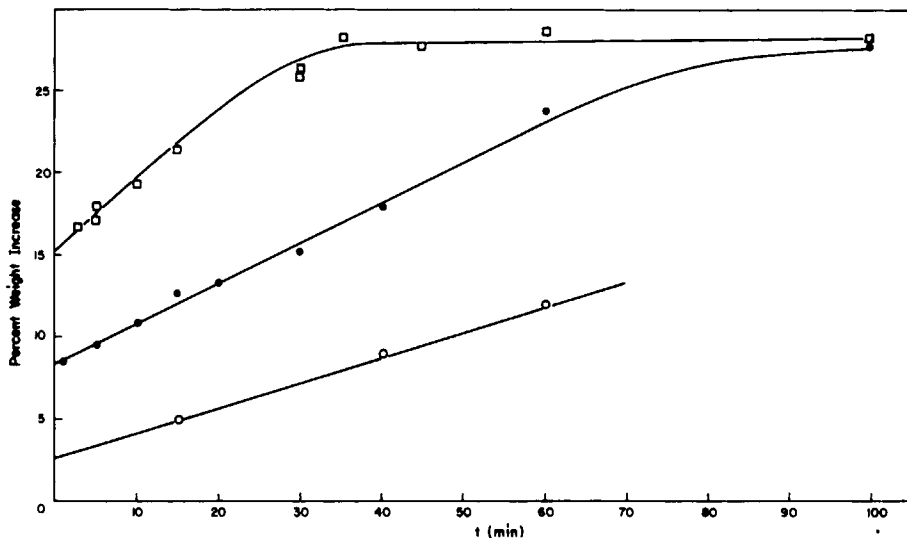
Fig. 3. Effect of discharge duration on weight increase. F: (□) 50 cm/min; (●) 40 cm/min; (O) 30 cm/min. Power is 20 W for all.

the formed polymer by scission of the bonds producing volatile gas, a highly crosslinked liquid, or solid products. Assuming that, at low flow rates in the low power region, the rate of polymerization is higher than that of degradation, the net effect would be an increase in the amount of polymer deposited. After a certain RF value, however, the rate of degradation might become dominant, leading to a decrease in the yield with further increase of power. Thus, one would obtain a bell-shaped deposition vs. power curve for low flow rates. At much higher flow rates, in the high power region, the ratio of the two rates may stay almost constant and the yield becomes independent of power variation.

In the examination of effect of monomer flow rate on deposition rate, both the applied power and the discharge duration were kept constant. After the monomer flow was stabilized, the resultant pressure in the system was observed to be dependent on the capacity of the vacuum pump used, and it had a different value for each flow rate. Upon application of discharge, the pressure at first increased followed by a slow decrease, and it was finally stabilized. The effect of monomer flow rate on the yield gave an S-shaped curve as shown in Figure 2. In the literature, similar curves were abundant.[11-13,9] Bell-shaped curves, however, are also frequently reported.[8,14-16] It can be suggested that, for at least some of the S-shaped curves, if the flow rate had been increased further, bell-shaped curves have resulted. However, since the major phenomenon in the present case is adsorption and possibly the creation of active centers takes place after adsorption, a reduction in polymer deposition after a certain flow rate leading to a bell-shaped curve is not expected.

The effect of discharge duration upon polymer deposition, while the flow rate and RF power were kept constant, is given in Figure 3. It is observed that there is a linear relation that is followed by a plateau region at quite long discharge durations. In the literature mostly a linear increase had been reported.[13,17,18]
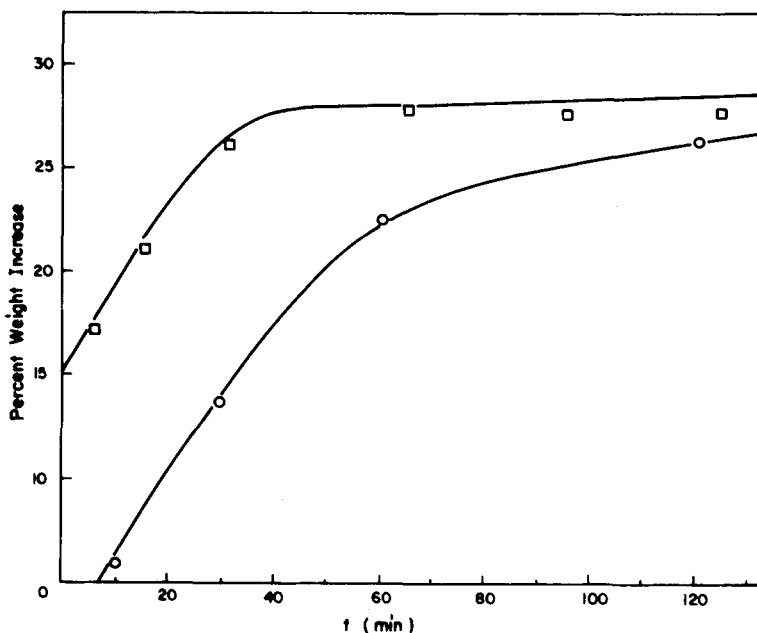
Fig. 4. Effect of monomer flow time in plasma-induced polymerization on weight increase: (□) 5 min discharge to charcoal and monomer; (○) 5 min discharge to charcoal; $F = 50$ cm/min and $P = 20$ W in both.

The observed difference might be due to the substrate being the highly adsorptive activated charcoal in the present case. In this process polymerization initially takes place on charcoal and then on the polymer layer that had formed on the charcoal. Since the interaction between charcoal and monomer is much greater than that between polymer and monomer, in the low time regions charcoal–monomer interaction leads to linear increase followed by a negligible increase (plateau region) at longer periods caused by polymer–monomer interaction.

In the case of both plasma-induced polymers, the maximum weight increase was obtained at about 28%, and further increase of flow duration did not cause any increase beyond this value, as shown in Figure 4. Here, the question whether the weigh increase is solely due to polymer or partially due to absorbed monomer might have arisen. In order to help to investigate this, the plasma-induced polymer deposit on NaCl crystal was prepared by the second procedure described, and the IR spectra of the product were obtained just after polymerization and after 10 days storage in vacuum (Fig. 5). Both spectra were exactly superimposable, indicating that there was no detectable monomer residues on the NaCl crystal. In addition, the comparison of the IR spectra of plasma polymer and plasma-induced polymer showed some differences in the intensity of some of the peaks (Fig. 6). The shape of the peak at 1050 cm^{-1} (Si—O—Si stretching) is quite similar to that of the plasma-induced polymer, indicating that in this case the monomer structure is kept more intact in comparison to that obtained in plasma polymerization. This is understandable, because the application of extra discharge in plasma polymerization could lead to more changes in the monomer structure than in plasma-induced polymerization.
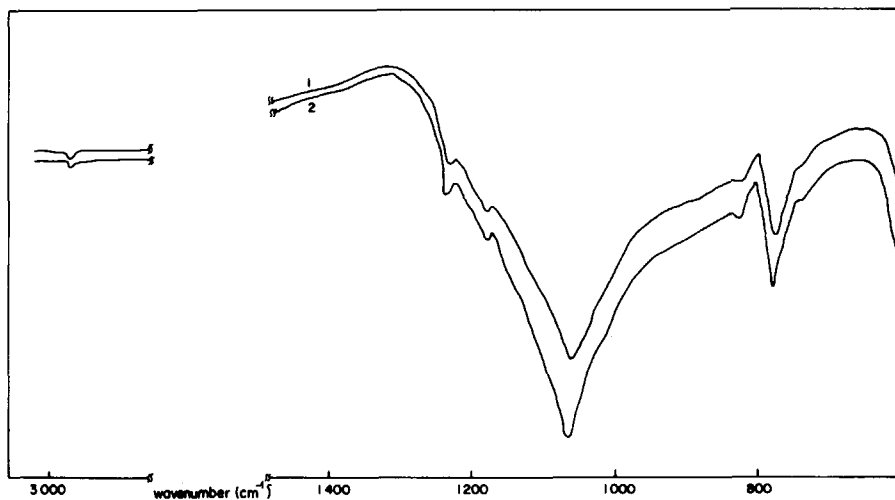
Fig. 5. IR spectra of plasma-induced polymer: (1) fresh; (2) after 10 days in vacuum.

The change obtained in the composition of charcoal upon coating was investigated by ESCA. Figure 7 is the ESCA spectra of uncoated and coated charcoal, respectively, and the coating conditions were as follows: power = 20 W, monomer flow rate = 50 cm³/min, and discharge duration = 1 h. It can be seen from O_{1s} and C_{1s} peaks that binding energies are 531 and 284 eV respectively for both samples indicating the equivalence of binding energies for these samples. There are, however, differences in relative concentrations of elements. In Si_{2p} peaks, there are differences both in binding energies and in peak areas. The maximum has shifted 1.5 eV towards lower binding energies. The area of the Si_{2p} peak was nearly three times larger in coated charcoal than in uncoated charcoal. Uncoated charcoal was found to contain 4.8% Si (as determined by X-ray fluorescence).
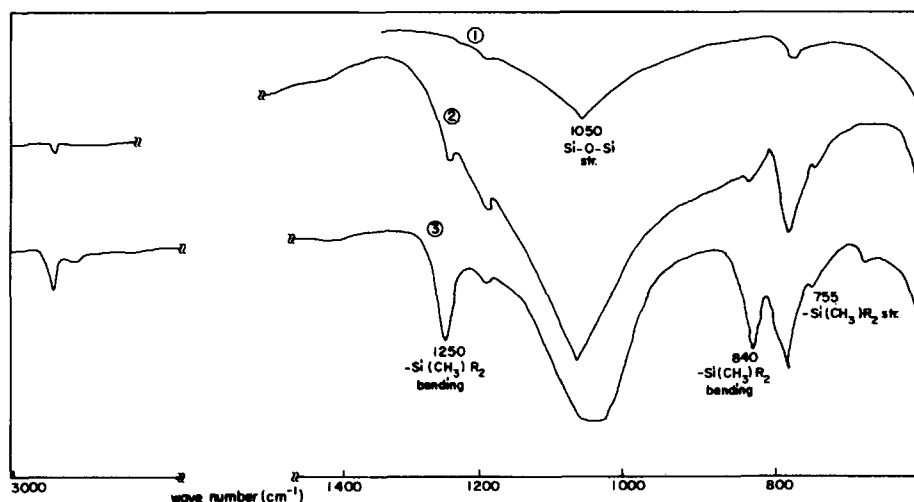

Fig. 6. IR spectra: (1) HMDS monomer; (2) plasma-induced HMDS polymer; (3) plasma polymer HMDS.
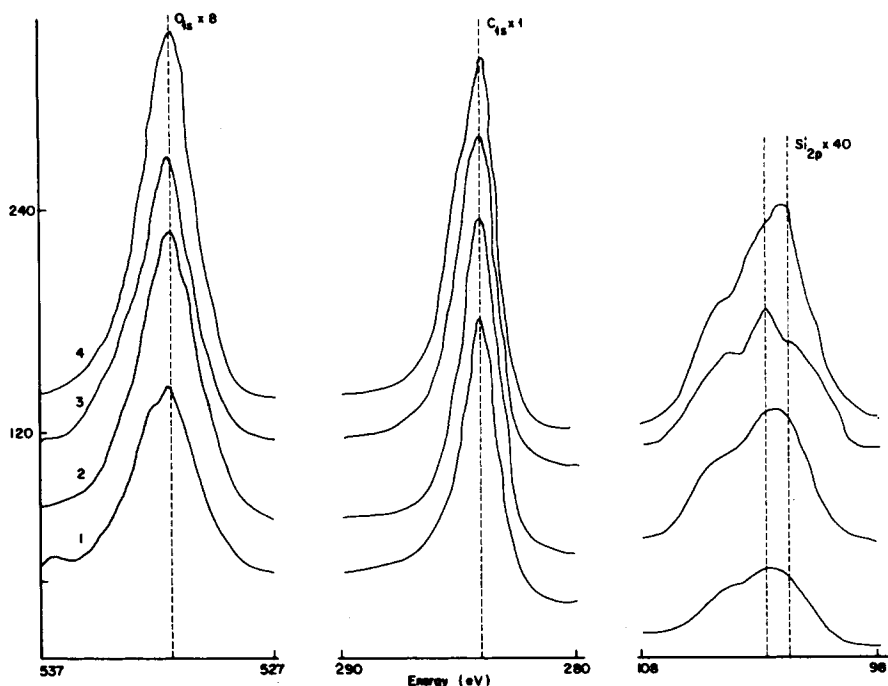
Fig. 7. ESCA spectra of: (1) uncoated charcoal; (2) plasma-induced (discharge only on charcoal) coated charcoal; (3) plasma-induced (discharge on monomer and charcoal simultaneously) coated charcoal 4-coated (by ppHMDS) charcoal.

Thus coated charcoal had to contain $2 \times 4.8\% = 9.6\%$ more Si than uncoated charcoal. On the other hand, the weight increase for the coated sample is 28%. Assuming that there is no structural change upon polymerization, 9.7% of this weight increase would be due to Si ($28 \times 56/162 = 9.7\%$). Both these values are in a very good agreement. As a result, it can be concluded that, since in ESCA studies only the contribution from polymer (not monomer) is expected and observed, the monomer that had initially been adsorbed on the charcoal is completely polymerized.

ESCA spectra of plasma-induced deposits on charcoal prepared by application of discharge only on charcoal or on monomer and charcoal simultaneously (Fig. 7) showed differences in the intensity of the Si peaks when compared to that obtained from uncoated charcoal. In both plasma induced polymers peak areas increased 1.6 times with respect to uncoated charcoal, and this much increase in Si content corresponds to 8.6% increase in polymer deposit weight. Since the percent weight increase was about 28% (as determined by weighing), one concludes that most of the weight increase is due to adsorbed monomer. One important point is that there is still some polymer deposit, and an explanation for how a saturated monomer could produce this polymer deposit is not easily found for the time being.

Electron micrographs of uncoated and coated charcoal samples are presented in Figures 8(a) and 8(b). It can be seen that the rough surface of the charcoal was completely coated by a "snowing" type of deposit by plasma polymerization,

(a)
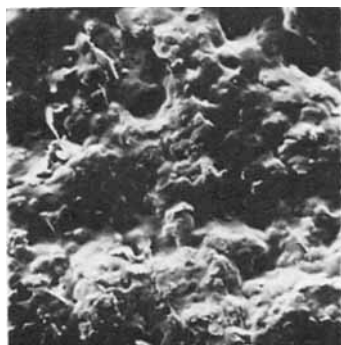
(b)

Fig. 8. SEM of (a) uncoated and (b) coated charcoal. (Magnification, × 1700.)

while such a coat was not easily identifiable in the case of plasma-induced polymerization.

CONCLUSION

The optimum parameters for coating of activated charcoal by ppHMDS in glow discharge was obtained at 20 W and 50 cm^3/min applied power and monomer flow rate, respectively. Previously different values were reported for coating on aluminum foil by using the same system.[4] The difference between the values indicates that the mechanisms in both cases are probably different. When aluminum surface is used as the substrate, according to a proposed mechanism,[19] the active species may be produced in the gas phase, and film formation occurs when these species diffuse to the substrate surface. In the present case, however, another approach seems to be more probable. Monomer adsorption on substrate surface probably takes place first and then subsequent bombardment of the monomer by active species and radiation leads to the formation of a film cost. A more detailed study to clarify the effects of nature of substrate both on mechanism and the product is currently being done in our laboratories.

In the case of plasma-induced polymer preparation, a question remains unexplained. This is whether it is possible to obtain polymer deposition from a saturated monomer by plasma induction or such a deposition is the product

of another type of reaction between the substrate and the monomer. Investigations are being concentrated on this matter as well.

References

1. H. Hiratsuka, G. Akovali, M. Shen, and A. T. Bell, *J. Appl. Polym. Sci.*, **22**, 917 (1978).
2. K. G. Müller, *Chem. Eng. Tech.*, **3**, 122 (1973).
3. H. Yasuda and T. Hirotsu, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 313 (1978).
4. G. Akovali, *Polym. Eng. Sci.*, **21**(11), 662 (1981).
5. H. Hasirci and G. Akovali, "Hemocompatibility and Hemoperfusion Studies with Plasma Polymer Hexamethyldisiloxane Coated Activated Charcoal," to appear.
6. Y. Osada, A. T. Bell, and M. Shen, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 309 (1978).
7. M. Y. Bölük and G. Akovali, *Polym. Eng. Sci.*, **21**(11), 664 (1981).
8. H. Yasuda, IUPAC Third International Congress, 1977.
9. H. Yasuda and T. Hirotsu, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 743 (1978).
10. H. Yasuda, in *Plasma Polymerization*, ACS Symposium Series 108, M. Shen and A. T. Bell, Eds. American Chemical Society, Washington, D.C., 1978, p. 37.
11. K. C. Brown, *Eur. Polym. J.*, **8**, 117 (1972).
12. K. C. Brown and M. J. Copsery, *Eur. Polym. J.*, **8**, 129 (1972).
13. M. Y. Bölük and G. Akovali, *Polym. Eng. Sci.*, **21**, 11, 658 (1981).
14. A. R. Westwood, *Eur. Polym. J.*, **7**, 368 (1971).
15. A. K. Sharma, F. Millich, and E. W. Hellmuth, *J. Appl. Polym. Sci.*, **26**(7), 2197 (1981).
16. H. Kobayashi, A. T. Bell, and M. Shen, *Macromolecules*, **7**, 277 (1974).
17. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.*, **16**, 2317 (1972).
18. H. Yasuda and C. E. Lamaye, *J. Appl. Polym. Sci.*, **15**, 2277 (1971).
19. A. R. Denaro, P. A. Owens, and A. Cranshaw, *Eur. Polym. J.*, **4**, 93 (1968).