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Free Radicals Resulting from Plasma Polymerization and Plasma Treatment

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ABSTRACT

A glass tube is subjected to plasma treatment (nonpolymerizable plasma) or plasma coating (polymerizable plasma). Unpaired spins generated in the glass substrate alone, and in both substrate and coating for the second case, are detected by ESR. It is shown that for both polymerizable and nonpolymerizable plasmas the substrate's unpaired spins (glass radicals) are caused, in large part, by UV radiation from the plasma. In the case of plasma coating, the glass radicals are formed at the outset of the polymerization because the coating increasingly absorbs the UV radiation as deposition continues. High concentrations of free radicals in the coating appear to be correlated with a high tendency to polymerize, while high values of substrate radical surface concentration are related to high levels of UV intensity in the plasma.

Free radicals have been detected in films deposited from a plasma onto a substrate [1-7] and are attributed, at least in part, to the high population of free radicals in the plasma [1, 8-15], the precursors of the polymeric coating. These plasma free radicals are believed to react in large part by recombination, i.e., termination [8], as contrasted to the propagation reaction through double bonds in a conventional free radical polymerization. Considerable scission of carbon-hydrogen bonds occurs in the plasma, leading to considerable branching in the polymer. The combination of high free-radical concentration in the plasma and a high degree of cross-linking in the resultant polymer would be expected to be favorable to the formation of trapped free radicals in the polymer matrix.

Unpaired spins have also been observed on surfaces treated with glow discharges which form no deposit [16]. Their formation has been ascribed to the impingement of energetic particles on the surface [1, 16] and to UV radiation from the plasma [1, 17-19]. Such mechanisms could contribute to free-radical formation both in a substrate subjected to a plasma containing either polymerizable or nonpolymerizable species as well as in a polymer coating formed on the substrate.

In this work we detect the presence of trapped free-radicals in a glass (Pyrex) substrate, as well as in the polymer coating, when one is formed by the use of electron spin resonance (ESR). The choice of a glass substrate was made as glass radicals yield a complicated ESR spectrum easily distinguishable from the singlet obtained for trapped radicals in a polymer coating.

EXPERIMENTAL

The glow discharge was generated in an apparatus which utilizes inductive coupling of 13.5 MHz rf previously described [20]. Briefly, a gas (or combination of gases) is continuously introduced into a glass tube being evacuated by a pump. The rf discharge coil is wrapped around a section of the tube while samples are coated or plasma treated in an adjacent part of the tube in the "tail-flame" of the plasma. For ESR measurements, a glass tube of 4 mm OD is placed on the monomer inlet using a glass joint into which the glass tube fits snugly. Ten centimeters of the glass tube are exposed to plasma. The monomer is fed into the reaction tube through this glass tube, and the polymer deposition per unit area is measured either by weighing the tube or by placing a small cover glass below the glass tube for weight increase determination. The ESR signal is obtained by placing the tube into the cavity 5 to 30 min after the plasma-treated or plasma-coated glass tube is taken out from the plasma reactor and exposed to air. The number of spins in the ESR spectrometer cavity are estimated by comparison with the signal from a standard pitch sample of known spin concentration. In the case of a composite signal, i.e., a polymer free-radical signal superimposed on a glass radical signal, the composite signal was recorded first. The polymer coating was then wiped off the glass tube and the remaining glass radical signal obtained.

In the case of polymerizing systems, a method of subjecting the glass probe to UV radiation from the plasma without forming a coating on the glass tube was desired. This was accomplished by modifying the apparatus as shown in Fig. 1. The glass probe was placed in a "sidearm" tube connected to the main body of the apparatus by a short tube of 1.0 cm ID. The plasma could not penetrate into the sidearm although the UV radiation could.

RESULTS AND DISCUSSION

Unpaired Spins Generated in a Pyrex Tube by Nonpolymerizable Species

Treatment of a glass tube with glow discharges from nitrogen or hydrogen gas yielded the ESR spectrum shown in Fig. 2. We will discuss the intensity of this signal as a function of time of treatment, power, and pressure in N_2 plasma treatment. It may be noted that the glass radical signal, induced by N_2 plasma treatment, decays very slowly in air at the rate of 25%in 6 days.

The mechanism of free-spin formation in the glass is of interest. Hansen and Schonhorn [16] have observed free radicals (by ESR) and cross-linking in polyethylene subjected to inert gas, hydrogen,

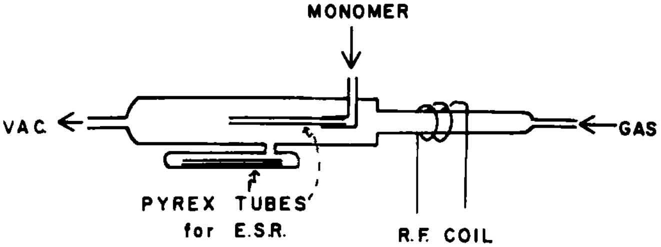

FIG. 1. Reaction tube of plasma apparatus with sidearm for exposure of Pyrex tube to UV radiation only. Pyrex tubes are shown in the sidearm as well as in the normal position, i.e., in direct contact with the plasma.

FIG. 2. ESR spectrum of radicals formed by treatment of a glass tube with N_2 plasma at a pressure of 12 mTorr N_2, 30 W power for 5 min with subsequent exposure of the tube to air.

or nitrogen plasma. Hudis [17-19] has shown that the cross-linking that occurs in polyethylene exposed to a hydrogen plasma is caused by UV radiation from the plasma. We wished to see if UV radiation from the nitrogen plasma was the cause of the free spins generated in the Pyrex tube. A thin walled (0.5 mm) quartz tube was placed in the position usually occupied by a glass tube for ESR measurements and was evacuated. A glass rod was contained within the quartz tube and the arrangement was subjected to a N_2 glow discharge. The ESR signal from the glass rod was compared to that obtained on an identical glass rod directly exposed to a N_2 glow discharge. The data obtained are shown in Table 1 and demonstrate that at least 50% of the radicals generated in a glass rod exposed to N_2 plasma are caused by UV radiation. The run, made with only 2 mm of N_2, was intended to show that the radicals would not form if a highly visible glow discharge was not generated in the apparatus. Further experiments were made with a glass tube placed inside another sealed tube which was quartz for half its length and glass for the other half, the two connected by a graded seal with the wall thickness for both halves being 1 mm. Two such graded seals were placed on the floor of the plasma chamber—one with the quartz end facing the rf induction coil, one with the glass end facing the coil. The data given in Table 2 were obtained from that end of the glass sample closest to the coil. It is seen that a glass envelope prevents free spin formation, oxygen inhibits it, while a vacuum and nitrogen do not. Oxygen absorbs UV radiation at 2000 Å and below,

TABLE 1. Generation of Spins on a Glass Rod Enclosed within a Quartz Tube and Subjected to an N_2 Plasma

Sample	Pressure (mTorr)	Power (W)	Time (min)	Spins/cm^2 × 10^{-15}
Control, no quartz barrier	50	30	67.5	4.4
Inside quartz tube	50	30	33.3	1.1
Inside quartz tube	51	30	67.5	2.4
Inside quartz tube	50	30	120	3.3
Inside quartz tube	2	30	67.5	0

TABLE 2. Generation of Spins on a Glass Tube Enclosed within a Graded Seal, Closed at Both Ends, and Subjected to an N_2 Plasma

End of graded seal	Gas and pressure inside graded seal	Time of plasma treatment (hr)	Signal intensity (a.u.)[a]
Quartz	Vacuum, 5×10^{-6} Torr	3	4.4 ± 1
Glass	Vacuum, 10^{-6} Torr	3	0
Quartz	Air, 1 atm	3	1.0
Glass	Air, 1 atm	3	0
Quartz	N_2, 664 Torr	3	5.2
Quartz	O_2, 678 Torr	3	1.3
Control, bare glass tube exposed directly to plasma		1	8.7

[a] Arbitrary units.

leading to some ozone formation. The latter absorbs strongly in the 2000 to 3000 Å range. Nitrogen gas is transparent to UV radiation of wavelength greater than 1250 Å. The data presented in Tables 1 and 2 demonstrate that radiation of wavelength between 1650 Å, the short wavelength cut off for quartz, and 3000 Å is responsible for at least half of the free spins generated in a glass rod by an N_2 glow discharge.

The intensity of the glass radical signal obtained where a glass tube is directly exposed to an N_2 glow discharge is shown in Fig. 3 as a function of time. There is an initial region of rapid free spin formation followed by one where free spins are generated at a reduced rate. The data presented in Figs. 4 to 6 was obtained from samples exposed to the N_2 glow discharge for 5 min periods. A plot of ESR signal intensity vs power input to the glow discharge is shown in Fig. 4. At a given pressure there is an initial rapid rise in rate of free-spin generation followed by a plateau where additional increments of power result in very little increase in the rate of free-spin generation. One possibility that must be

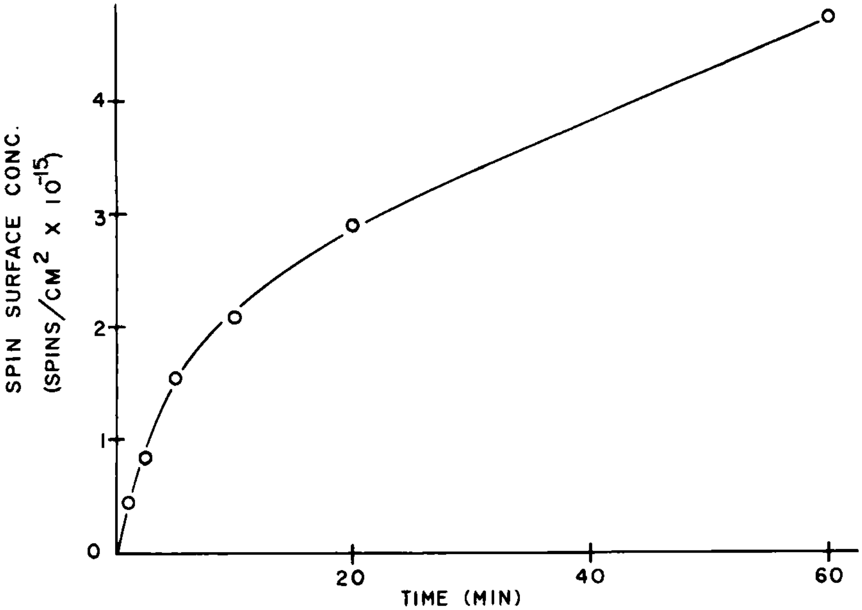

FIG. 3. Spin surface concentration of the glass spins plotted against time of glow discharge treatment. Conditions of treatment are an initial N_2 pressure of 50 mTorr and power of 30 W.

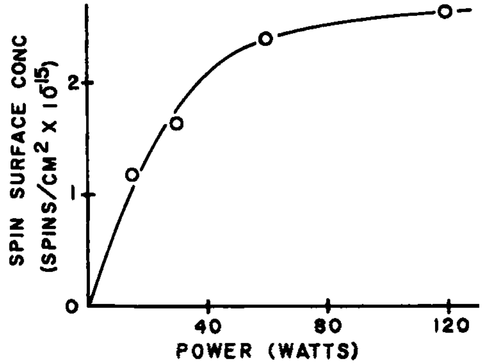

FIG. 4. Spin surface concentration of the glass spins plotted against power used in the glow discharge treatment. The initial pressure of N_2 was kept constant at 50 mTorr; the time of treatment was 5 min.

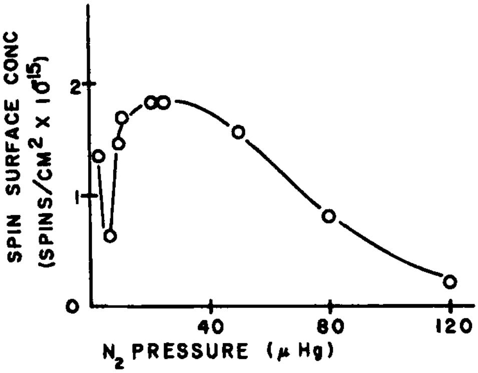

FIG. 5. Spin surface concentration of the glass spins plotted against initial pressure of N_2 used in the glow discharge treatment. The power was kept constant at 30 W, and the time of treatment was 5 min.

considered is that the plateau represents an upper limit to the number of spins that the Pyrex tube will yield when subjected to the UV radiation emitted by plasma above about 60 W power. However, a free-spin concentration of 6.3×10^{15} spins/cm^2 was observed for a glass tube exposed to a 50 mTorr, 120 W plasma for

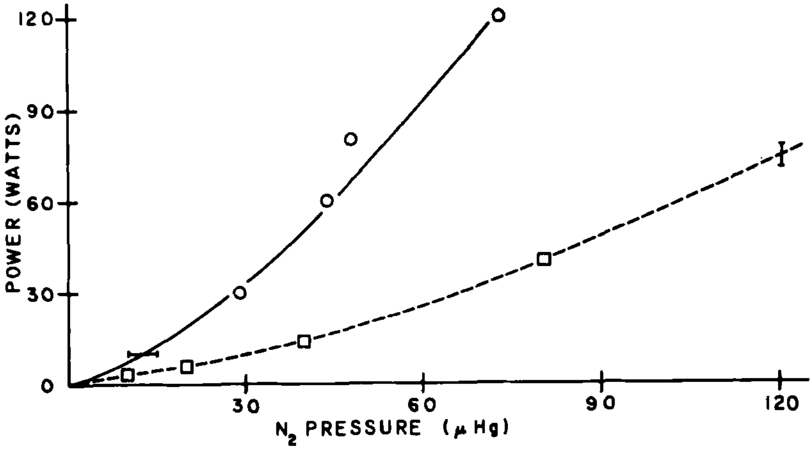

FIG. 6. Plot of the reaction conditions required to fill the reaction chamber (dotted line), as ascertained visually, and (full line) to attain the maximum ESR signal intensity in a Fig. 5-type plot as applied to the data in Table 3.

10 min as opposed to the value of 2.5×10^{15} spins/cm^2 when the time of exposure is 5 min. We are thus assured that the plateau in Fig. 3 reflects a property of the plasma rather than of the glass tube.

The effect of changing nitrogen pressure on the rate of free spin generation by the plasma is given in Fig. 5. The ESR signal intensity is seen to increase with pressure initially, peak, and then decrease at higher pressures. Figures 4 and 5-type plots can be obtained for a wide range of constant pressure and powers, respectively, as seen in Table 3. These are ESR signal intensities obtained after 5 min treatments of Pyrex tubes at a variety of N_2 pressure, power conditions. An explanation of these results is obtained by comparison of the data in Table 3 with the power-pressure parameters needed to just fill the reaction chamber as ascertained visually. The power-pressure combinations that are required for the latter are given by the dotted line in Fig. 6. The solid line was obtained from Table 3 by estimating the position of the maximum in a Fig. 5-type plot at various constant power levels. It also delineates the approximate beginning of the plateau region in a Fig. 4-type plot at various constant N_2 pressures. The plots are similar in shape although the solid line is at higher power inputs than the dotted line. The behavior outlined above is consistent with a "tail-flame" of constant UV intensity issuing from the region encircled by the rf

TABLE 3. ESR Signal Intensity (of Pyrex Glass) as a Function of N_2 Pressure and rf Power (spins/cm^2 × 10^{-15})

Pressure (mTorr)	rf power (W) 5	10	30	60	80	120
10	0.70	0.81	1.4	1.6	1.8	1.5
25	0.54	0.78	1.6	2.0	1.8	2.3
50		0.14	1.4	2.2	2.2	2.5
80			0.81	1.8	1.7	2.6
120			0.32	1.4	1.5	1.9

coil followed by a "tip" of diminishing UV intensity at greater distances from the coil. Figure 4 is then explained as a movement of the "tip" of the "tail-flame" past the glass tube until the region of constant UV intensity reaches the Pyrex tube at high power levels. Figure 5 shows that the UV intensity increases in the constant intensity region of the tail flame as the pressure is initially increased. Further increases of pressure lead to a contraction of the "tail-flame" to the point that the glass tube is moved once again into the "tip." Thus, at the powers and pressures utilized in this study, the main effect of increasing the power-pressure parameter is to increase the volume in which UV radiation is emanated, rather than to increase the intensity or energy of this UV radiation at a given point in the "tail-flame."

It is clear that the UV radiation that induces free spins in the glass will also do so in a polymer substrate. This is indicated by the already quoted work of Hansen and Schonhorn [16] and of Hudis [17-19]. It is also supported by our own observations on a glass tube coated with polysulfone and then exposed to an N_2 plasma at 120 mTorr of N_2 and 150 W for 1 hr. An ESR signal was observed indicating the presence of free radicals in the polysulfone film exposed to air. The decay of these free radicals was that characteristic of a second-order reaction. A linear plot of the reciprocal of the free-radical concentration against time was obtained with a half-life of 9.6 hr.

The presence of free radicals in polysulfone films (of approximately 85 cm^2 surface area) exposed to an N_2 plasma at 50 mTorr of N_2 and 30 W power was also indicated by exposing such films to 5 ml of 8×10^{-5} $\underline{M}$ solutions of diphenylpicrylhydrazyl (DPPH). The polysulfone film was degraded by the plasma treatment as indicated by a yellow cast to the film. Treatment of such a film with a solution of DPPH in CCl_4 indicated that free radicals were present in the degraded portion of the film at a surface concentration of $2 \times 10^{15}/cm^2$ of film surface. Treatment of an identical film with a solution of DPPH in benzene indicated that there were also free radicals in the undegraded portion of the film, not accessible at the surface, and that the total number of free radicals in the film (both degraded and undegraded) was in excess of $3 \times 10^{16}/cm^2$ of film surface. Thus free radicals are formed below the immediate surface of the film by the plasma treatment.

Unpaired Spins Generated on a Pyrex Tube by Polymerizable Species and Trapped Free Radicals in the Polymer Coating

Polymerizable species were utilized in a glow discharge to form coatings on Pyrex tubes. Such species were used both alone and in combination with the nonpolymerizable gases, N_2 and H_2O. Results obtained for plasma exposures of 20 min to 1 hr are given in Table 4. The change of the steady-state flow pressure due to a glow discharge is expressed in the table 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 (or monomer-gas mixture) before a glow discharge is initiated. Plasma precursors include various combinations of 4-picoline with N_2 and H_2O and the N_2-ethylene oxide and N_2-acetylene-H_2O systems.

The system 4-picoline with various gases has been studied at a variety of pressures, times, and combinations of components. These are seen to have very little effect on the concentration of radicals in the polymer coating with all data falling in the range 1.0 to 2.5×10^{18} spins/g. The width of the ESR peak also changes very little from sample to sample, and the value observed, 15 G, is in the range quoted by Ingram [21] for radicals trapped in a hydrocarbon glass. The yield is affected, as expected, by the flow rate of the components [20, 22, 23].

The data in Table 4 reveal the factors that determine the extent of free-spin formation in the Pyrex substrate. It may be noted that in no system studied does the glass free-spin signal increase with time. The spins are apparently generated in the first few minutes (i.e., in a time period smaller than 20 min), and further alteration of the substrate is prevented by absorption of the UV radiation by the deposited polymer film. Support for this interpretation is found for the N_2-acetylene-H_2O system given in Table 4 by results obtained using a sidearm tube on the plasma chamber. There was no physical barrier between the glass tube in the sidearm and the plasma, but the plasma did not penetrate into the sidearm as indicated by the absence of glow therein and by the fact that no film was deposited

TABLE 4. Unpaired Spins Detected in Deposited Film and Substrate after

Components and P_M of components in mTorr	Total P_M (mTorr)	Duration of glow discharge treatment (min)	Yield of polymer film (mg/cm^2)	Spin concentration in polymer film (spins/g × 10^{-19})
4-picoline, N_2				
(30) (30)	60	20	0.05	0.23
		40	0.11	0.20
		60	0.18	0.18
N_2, 4-picoline	50	20	0.03	0.20
(30) (20)		40	0.06	0.14
		60	0.09	0.11
4-picoline, N_2	32	60	0.03	0.17
(16) (16)				
4-picoline (50)	50	60	0.10	0.20
4-picoline, N_2	98	20	0.16	0.21
(49) (49)				
4-picoline, N_2, H_2O	60	20	0.05	0.19
(25) (25) (10)		40	0.06	0.21
		60	0.14	0.24
N_2, ethylene oxide	60	20	0.008	
(30) (30)		40	0.016	
		60	0.05	0.41
N_2, acetylene, H_2O	60	20	0.03	
(20) (30) (10)		40	0.06	
		60	0.07	0.18

[a] Rate of film deposition per hour obtained from 20 min value.

Glow-Discharge Treatments for Times ≤ 1 hr at 30 W Power

Line width of ESR first deriv. signal (G)	Spins near surface of glass substrate (spins/cm^2 × 10^{-15})	$\delta = P_g/P_M$	P_g (mTorr)	Code on Fig. 7
16				
17				
16	0.4	0.15	9	B
17	0.5	0.14	7	
15	0.5	0.11	6	
15	0.5	0.11	6	A
17	0.75	0.12	3.8	C
16	0.4	0.16	8	D
15	0.1	0.61	60	E[a]
14	0.7	0.33	20	
16	0.7	0.33	20	
19	0.8	0.33	20	F
	2.5	1.0	60	
	2.5	1.0	60	
17	2.8	1.0	60	
	3.1	0.32	19	
	3.0	0.32	19	
16	3.3	0.32	19	

in the sidearm even after 5 hr of operation which left a heavy brown film on the walls of the rest of the apparatus. The glass radical signal was observed to increase with time of exposure in a manner similar to that shown in Fig. 3 for N_2 plasma. Furthermore, the highest mean free-spin surface concentration obtained is 5×10^{15} spins/cm^2, well above the 3×10^{15} spins/cm^2 given in Table 4. Once again, the latter value reflects a property of the plasma and polymer coating, not an upper limit to the free-spin surface concentration which may be induced in the Pyrex substrate when exposed to UV. Decreasing the total pressure as in the case of [16 mTorr 4-picoline, 16 mTorr N_2] leads to a slower rate of polymer deposition and increasing glass free-spin signal; increasing the total pressure [49 mTorr 4-picoline, 49 mTorr N_2] has the opposite effect.

A quantitative expression for these results may be developed as follows.

If it is assumed that UV radiation is the sole cause for the radicals formed in the glass substrate, then the UV intensity for monochromatic light penetrating through the polymer coating is expressed by Beer's law, and the number of spins S_t generated after time t can be given by the expression

$$S_t = \frac{kI_0}{ar} (1 - e^{art}) \tag{1}$$

where k is a constant relating the rate of free-spin generation to the intensity impinging on the surface, r is the rate of polymer deposition on the surface, and a is the absorption coefficient. When art is very large, Expression (1) reduces to

$$S_\infty = kI_0/ar \tag{2}$$

indicating that after a certain thickness of coating is built up, no radiation reaches the substrate. In the case of a polychromatic radiation source of constant spectral composition, it would be expected that the quantity S_t would be expressed by a relationship somewhat more complex than Eq. (1), but it can be shown that S_∞ can be simply expressed as

$$S_\infty = \frac{I_0}{r} C \tag{3}$$

where I_0 is the total intensity of the UV radiation emitted by the plasma and C is a constant. To relate Eq. (3) to measured quantities, we may refer to Fig. 5 which implies that I_0 increases with pressure at low values of p_g. Assuming that I_0 is directly proportional to p_g, we may write

$$S = C' \frac{p_g}{r} \tag{4}$$

Clearly the quantity S is that given in Table 4 as none of the glass free-spin concentrations change as a function of time. A plot of the number of free spins induced in the glass tube against the quantity p_g/r is given in Fig. 7 for all 4-picoline systems described in Table 4. In the cases of systems in which 4-picoline and N_2 gas are present in approximately 1:1 concentration ratio and p_g is less than about 10 mTorr, Eq. (4) appears to describe the generation of

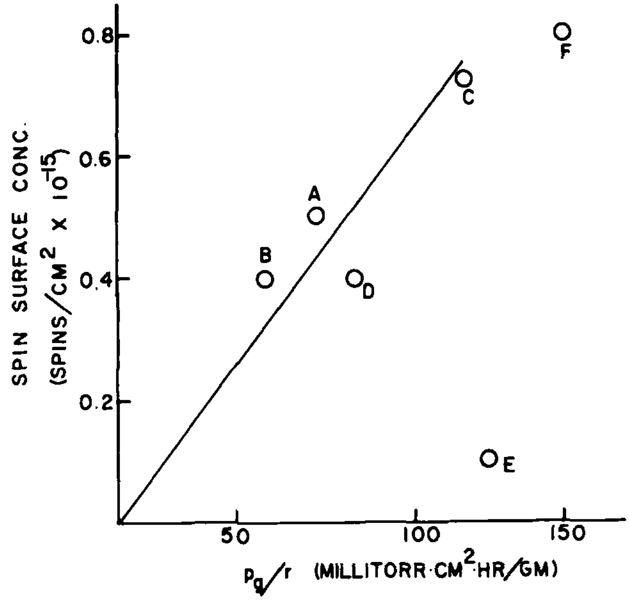

FIG. 7. Spin surface concentration of glass spins obtained after plasma treatment with all 4-picoline systems given in Table 4 plotted against p_g/r. p_g is the total pressure during plasma treatment and r is the rate of film deposition.

free spins in the substrate fairly well. The point for 49 mTorr 4-picoline, 49 mTorr N_2 (E) is well off the line, but p_g is so high in this case that we may expect that intensity is no longer proportional to p_g for this case. It is surprising that points D and F lie so close to the line drawn through A, B, C, and the origin, but at least for point F this may be caused by two compensating deviations from the assumptions leading to Eq. (4).

Data obtained for glow discharges of a variety of monomers used to coat a Pyrex tube for a period of 1 hr, at 30 W power, are given in Table 5. The bulk of the data is for the monomers acetylene and allene with the gases N_2, H_2O, and CO either singly or in various combinations. Data on various substituted disiloxanes and other monomers are also included. All investigations were carried out with P_M in the range 65 to 40. The highest concentration of radicals in the polymer film is found for acetylene. Introduction of CO or N_2 as a gas together with the acetylene monomer leads to a decrease in polymer spin concentration and an increase in the Pyrex free-spin signal. Introduction of water vapor with acetylene leads to an increase in p_g and in the rate of free-spin production in the substrate and a decrease in the trapped radical concentration to a level below the limit of detectability if the only gas added to the monomer is water. The above comments are also generally applicable to the monomer allene—alone and in conjunction with other gases.

As a general rule, the data in Table 5 indicate that low values of δ are associated with high trapped free-radical concentrations in the coatings and vice versa. This is consistent with the idea that low values of δ are associated with an elevated tendency to polymerize [22] which, in turn, is associated with an elevated population of free radicals in the plasma leading to a large trapped radical population in the polymer coating. Generally, systems with $\delta \leq 0.2$ are associated with a trapped free-radical concentration of 2×10^{19} spins/g or greater. Lesser free radical concentrations are observed if δ is greater than 0.2. However, the N_2-allene system does not follow this rule and neither do the 4-picoline + gas systems. In the latter case the trapped free-radical concentration appears to be remarkably insensitive to the addition of various gases and to the value of δ.

It may be noted that the ESR signal observed for the substituted disiloxanes is about 1/2 the width of the coatings obtained from the plasmas of carbon-based monomers.

Inasmuch as all samples were placed in the ESR spectrometer cavity after exposure to air, it would be expected that all free radicals accessible at the surface would have reacted with oxygen before the ESR signal is obtained. An indication that the concentration of such undetected free radicals is not large was obtained from an experiment in which a glass rod was subjected to an acetylene plasma. After turning off the power, the apparatus was evacuated and the polymeric coating formed was exposed to styrene vapor for 17 hr. There was no detectable difference in weight gain or free-radical concentration between this sample and one prepared in identical fashion but exposed to vacuum instead of styrene vapor for 17 hr.

It is expected that oxygen reacts rapidly with radicals at the surface of the polymeric film immediately after removal from the glow discharge apparatus. The trapped radicals that remain are very long lived. When a Pyrex tube is exposed to an acetylene glow discharge for 60 min at 30 W power and P_M = 60 mTorr and then placed in the ESR cavity, the decay is linear with log (time) for the period 1 to 340 hr with a half-life of 45 hr. Even after 9300 hr (15 months), 13% of the original free-radical concentration remains. By contrast, the decay rate for a polysulfone film exposed to an N_2 glow discharge is more rapid, as mentioned above.

SUMMARY

1. Unpaired spins are generated on substrates exposed to the plasma of a nonpolymerizable gas such as N_2 and are formed below the immediate surface of the substrate by UV emission from the plasma.

2. ESR signals obtained from a plasma polymer (deposited onto a substrate) are generally obtained from unpaired spins in both the polymer deposit and in the substrate. The spin signal in the substrate, S_1, is related to the UV emission intensity of the polymer-forming plasma, I_0, and the rate of polymer deposition, r, by

$$S_1 = \frac{kI_0}{ar}(1 - e^{art})$$

when k is a constant relating the rate of free spin generation to the intensity impinging on the surface, and a is the absorption coefficient of the polymer deposit. It is generally observed that S_1 reaches a plateau value and becomes independent of the deposition time as predicted by the above equation.

There is an apparent correlation between S_1 and the spin concentration in the polymer deposit S_2; i.e., the higher the S_1 the lower is the S_2 and vice versa.

TABLE 5. Unpaired Spins Detected in Polymer Films and Substrates after Glow-Discharge Treatments for 1 hr at 30 W Power

Components and P_M of components in mTorr	Total P_M (mTorr)	Rate of polymer deposition (mg/cm^2 hr)	Spin concentration in polymer film (spins/g × 10^{-19})	Line width of ESR first deriv. signal (G)	Spins near surface of glass substrate (spins/cm^2 × 10^{-15})	$\delta = P_g/P_M$	P_g (mTorr)
Acetylene (81)	81	0.09	4.8	16		0.10	8
Acetylene (60)	60	0.04	7.4	18		0.12	7
Acetylene (40)	40	0.02	6.5	16	0.6	0.10	4
N_2 (30), acetylene (30)	60	0.02	3.3	16	0.3	0.08	5
Acetylene (30), H_2O (20)	50	0.05	-	-	3.8	0.79	40
N_2 (20), acetylene (30), H_2O (10)	60	0.07	0.18	16	2.7	0.37	22
CO (20), acetylene (30)	50	0.19[a]	4.1	16		0.10	5
CO (20), acetylene (30), H_2O (15)	65	0.14[a]	0.29	12	2.1	1.3	84
Allene (40)	40	0.05	2.0	20	1.1	0.20	8
N_2 (30), allene (30)	60	0.09	0.18	19	0.8	0.12	7

Allene, H_2O (30) (20)	50	0.04	-	-	3.6	0.90	45
N_2, allene, H_2O (20) (30) (15)	65	0.03	1.1	18	2.0	0.50	32
N_2, allene, H_2O (20) (30) (10)	60	0.08	0.21	18	1.3	0.25	15
Ethylene (40)	40	0.025	0.7	21	3.7	0.55	22
Benzene (40)	40	0.066	2.2	19	0.6	0.10	4
Tetrafluoroethylene (40)	40	0.011	-	-	8.7	0.90	36
Propionic acid (40)	40	0.013	-	-	6.9	2.30	92
Ethylene oxide (40)	40	0.089	-	-	7.2	1.5	60
N_2, hexamethyl (30) disiloxane (30)	60	0.22	0.04	6	-	1.1	66
Tetramethyl disiloxane (40)	40	0.12	0.07	7	-	1.15	46
Divinyl tetramethyl disiloxane (40)	40	0.38	0.06	6	-	0.70	28

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[a] The abnormally high polymer deposition rate observed for this sample is not a characteristic of monomer and gas used but caused by the fact that this sample was run on a slightly different apparatus.

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