

# Plasma-Deposited Polymer Films. III. The Effects of Gamma Irradiation

W. F. OBERBECK, JR., K. G. MAYHAN,\* and W. J. JAMES, *Departments of Chemical Engineering and Chemistry, University of Missouri, Rolla, Missouri 65401*

## Synopsis

The results of a study of irradiated and unirradiated samples of polymers prepared by plasma polymerization in an inductively coupled radiofrequency (rf) reactor using infrared, elemental, thermogravimetric, and ESR analyses and density and refractive index measurements are presented. The plasma-formed polymers studied include polypropylene, poly(ethylbenzene), poly(methyl methacrylate), poly(tetrafluoroethylene), poly(chlorotrifluoroethylene), and poly(trimethylchlorosilane).

## INTRODUCTION

The chemical residual activity often found in plasma-formed polymer films is of interest because its presence may be employed as a means of grafting new polymer coatings to the existing films. In those instances where chemical inertness is essential for plasma-formed protective coatings, this residual activity must be stabilized or "quenched."

It is well known that plasma-formed polymers exhibit this residual activity in terms of oxygen affinity after removal from the plasma. It is believed that trapped free radicals react with oxygen to form peroxy radicals. These and other radicals are believed to be capable of a whole range of additional reactions, the assorted products of which result in broadened IR bands. Prior studies in our laboratories suggest that irradiation of plasma-formed polymer films may provide one technique, among several, for quenching such residual activity.

Accordingly, a broad spectrum of monomer systems was chosen for this preliminary investigation, including propylene, ethylbenzene, methyl methacrylate, tetrafluoroethylene, chlorotrifluoroethylene, and trimethylchlorosilane.

Characterization of both irradiated and unirradiated plasma-formed polymer films was carried out to determine chemical and/or physical property changes occurring as a consequence of radiation. Analysis of these data suggests that irradiation may provide a means of quenching free-radical sites.

\* Present address: Corporate Technology Center, American Hospital Supply Corp., Santa Ana, California 92715.

## EXPERIMENTAL

### Materials

The monomers used in this study were obtained from the following sources: Aldrich Chemical Co., Inc. (trimethylchlorosilane); Matheson Coleman and Bell (ethylbenzene); Matheson Gas Products (tetrafluoroethylene, chlorotrifluoroethylene, and propylene); Rohm and Haas (methyl methacrylate).

### Rf Reactor

The reactor used has been described previously.<sup>1</sup> It is a steady-state system employing in sequence two liquid nitrogen traps, an oil diffusion pump, and a roughing pump. The reactor body is 80-mm-O.D. glass of 90-cm length with a 102/75 O-ring joint. The inlet end of the reactor is fitted with an O-ring on glass leak valve and a 35/25 O-ring joint which is attached to a Granville-Phillips Series 203 variable-leak valve.

### Coating Procedure

The reactor was lined with glass sleeves within which the sodium chloride crystals were positioned. The reactor was sealed and pumped down to 1-3 microns. It was purged three times with the monomer gas through the variable-leak valve, and then the pressure was adjusted to 50 microns. The inductively coupled rf power supply was tuned to a power level of 5 W at a frequency of 3.9 MHz, at which time, if needed, a Tesla coil was used to initiate the plasma. After 24 hr of coating, the rf power supply was turned off, the variable-leak valve closed, and the reactor pumped down to 10 microns. The diffusion pump was closed off and the reactor opened to the atmosphere through the variable-leak valve. When the monomer was in liquid form, it was introduced into the reactor through a microcapillary valve for leak rate control. The microcapillary valve was in turn connected to the O-ring on glass valve at the reactor inlet so as not to contaminate the variable-leak valve.

### Irradiation Procedure

Samples of free plasma-formed film and coated sodium chloride crystals were irradiated in the University of Missouri-Rolla nuclear reactor. A cadmium-coated rabbit tube system was used to irradiate samples for 72 min at a gamma dose rate of  $8.25 \times 10^7$  rads/hr (total dose  $10^8$  rads) and neutron dose rate of  $1.11 \times 10^7$  rads/hr. During irradiation and cool-down, samples were encapsulated in 5-ml polyethylene screw-top vials. Free film samples did not require a cool-down period after irradiation, whereas coated sodium chloride crystals required a cool-down period of five days before they could be removed from the reactor for further testing.

### Characterization

Infrared spectra were obtained using a Beckman IR-12 infrared spectrophotometer. A study of the influence of radiation on the spectral quality of sodium chloride showed no detectable effect.<sup>2</sup>

Polymer density was determined in a gradient column.<sup>3</sup>

A Mettler thermoanalyzer was used to obtain simultaneous thermogravimetric and differential thermal analyses. Irradiated and unirradiated films were run back to back in sequence. Two-milligram samples of plasma polymer were run in 10-mm platinum crucibles against 7 mg aluminum oxide for reference. The atmosphere was flowing air at 10 l./hr with a heating rate of 6°C/min.

Refractive index measurements were taken employing the Becke line technique using the Cargille index of refraction liquids.

A Perkin-Elmer Model 240 elemental analyzer was used to determine the carbon, hydrogen, and nitrogen content. Two oxygen analyses were carried out by Intelcom Rab Tech using activation analysis. The remainder of the elemental analyses was done by Galbraith Laboratories, Inc.

ESR data were taken at room temperature on a Varian Associates Model V-4502 EPR spectrometer operated in the high-power mode. A Varian Associates Model V-4531 multipurpose EPR cavity was used in conjunction with an X-band microwave frequency of about 9.5 GHz and a 100-kHz modulation field. A standard ESR technique was used to maximize detector sensitivity; i.e., the crystal detector was biased by reflecting part of the input microwave power directly off a tuning stub and directly to the detector (via a hybrid tee).

### RESULTS AND DISCUSSION

Most plasma-formed polymer films are insoluble and cannot be characterized by the dilute solution techniques used with many conventional polymers. This is the primary reason for selecting the modes of characterization set forth above. Where applicable, comparisons will be made to conventional polymers. However, it should be pointed out that due to structural differences such comparisons are not completely valid.

The following abbreviations will be used for simplification: irradiated samples will be designated (I) and, unirradiated samples will be designated (U). In this section each monomer system will be discussed individually, followed by an overall examination.

#### Propylene

Infrared spectra of the propylene (U) sample were characterized by CH<sub>2</sub> and CH<sub>3</sub> absorption peaks at 2870 (s), 2930 (s), and 2960 (s) cm<sup>-1</sup> and also at 1460 (m) and 1380 (m) cm<sup>-1</sup>. The (I) spectra showed these same absorption frequencies in addition to a weak carbonyl group at 1720 cm<sup>-1</sup>. Since five days were required for cooldown, the (I) sample could have reacted with atmospheric gases during this period or the carbonyl group could have been formed from absorbed gases during the radiation exposure. The former is more likely since previous work with propylene has shown that plasma-formed polymers from this monomer react with atmospheric gases slowly due to low gas diffusion rates.<sup>4</sup>

Two C, H, N analyses were obtained on (U) and (I), because when the oxygen analysis was carried out six months after the initial C, H, N analysis, (U) had a

TABLE I  
Elemental Analyses for Plasma Polypropylene

Propylene	Weight percent				Total
	C	H	N	O	
First C, H, N analysis for (U)	79.51	9.43	2.39	8.67 <sup>a</sup>	100.00
Second C, H, N, and O analysis for (U) after 6 months	73.31	8.72	2.42	15.70	100.15
Estimated second C, H, N, and O analysis for (U)	73.39	8.70	2.21	15.70	100.00
First C, H, N analysis for (I)	79.32	9.27	2.46	8.95 <sup>a</sup>	100.00
Second C, H, N, and O analysis for (I) after 6 months	76.46	9.34	2.58	10.45	98.83
Estimated second C, H, N, and O analysis for (I)	78.01	9.12	2.42	10.45	100.00

<sup>a</sup> Estimated value for oxygen.

50% greater weight percent oxygen than (I) (Table II). A second C, H, N analysis made shortly thereafter is presented in Table I. The predicted values for the second C, H, N analysis in Table I were calculated as follows. Assuming the unknown weight percent in the first C, H, N analysis to be oxygen and that only the addition of oxygen takes place with no change in carbon, hydrogen, or nitrogen during the time between the two C, H, N analyses, predicted values for the second C, H, N analysis were calculated using a dilution factor calculated from the change in oxygen weight percent. The predicted C, H, N values for (U) were close to the experimental values, whereas for (I) they showed a pronounced difference. This might be due to the low permeability of plasma-formed films and delayed gas evolution products created by irradiation. These results could be reproduced with greater accuracy from experimental procedures designed to look specifically at elemental changes in plasma-formed polymer films.

TABLE II  
Elemental Analyses for Plasma Polymers

Monomer	Elemental weight percent <sup>a</sup>							Total detected
	C	H	N	O	F	Cl	Si	
Propylene								
(U)	79.51	9.43	2.39	15.70				107.03
(I)	79.32	9.27	2.46	10.45				101.5
Ethylbenzene								
(U)	82.55	7.56	3.04	9.22				102.37
(I)	81.68	7.44	2.96	8.50				100.58
Methyl methacrylate								
(U)	59.36	6.86	10.21	25.17				101.6
(I)	58.73	6.90	9.96	22.35				97.94
TFE								
(U)	29.05	0 <sup>b</sup>	2.14	6.67 <sup>a</sup>	62.14			93.33
(I)	28.07	0 <sup>b</sup>	2.31	3.21 <sup>c</sup>	66.41			96.79
Chlorotrifluoroethylene								
(U)	25.78	0 <sup>b</sup>	0.58	3.14 <sup>c</sup>	44.20	26.30		96.86
(I)	26.72	0 <sup>b</sup>	0.59	0.53 <sup>c</sup>	46.77	25.39		99.47
Trimethylchlorosilane								
(U)	21.48	6.07	0.17	16.7 <sup>d</sup>		2.77	3.35	50.54
(I)	23.49	6.21	0.21	15.6 <sup>d</sup>		2.92	5.16	53.59

<sup>a</sup> Standard deviation  $\pm$  3%.

<sup>b</sup> Not distinguishable from instrument error.

<sup>c</sup> Oxygen by difference.

<sup>d</sup> Oxygen by activation analysis.

Table III shows the C/H ratios for propylene, (U), and (I) as 5.14, 8.43, and 8.56, respectively. This shows that hydrogen is lost during polymerization and additionally during and/or shortly after irradiation. The hydrogen loss due to irradiation probably results in free-radical crosslinking and the creation of the carbonyl groups observed in the infrared spectra, although unsaturation was not detected in the infrared spectra.

The thermograms for the (U) and (I) samples showed little or no difference. Both samples were characterized by two major oxidative exotherms which appeared as independent events. Table IV gives the major details of the patterns. It should be noted that the (U) sample showed a slight weight increase (3%), during decomposition, in the range of 40°–240°C. This weight increase was not noted in the thermogram for the (I) sample. The activation energies reported are based upon an Arrhenius plot, and the values appear to be the same if experimental and computational errors are taken into account.

Refractive index and density ranges reported in Table V showed no significant differences. The 1.56+ refractive index reported for this polymer is higher than the 1.49 reported for the conventional linear polymer. This value for the plasma-formed polymer is consistent with the corresponding increase in density, as shown in Table V.

ESR measurements of plasma-formed polypropylene gave  $5 \times 10^{16}$  spins/g before irradiation. After irradiation and a period of one week, ESR measurements of (U) and (I) exhibited a significant difference of  $2 \times 10^{16}$  and  $6 \times 10^{16}$  spins/g, respectively. This indicates that during irradiation the number of spins/g increased to above that noted shortly after polymer formation. Thus, the threshold concentration of spins/g was not reached during film formation and possibly not upon irradiation.

### Ethylbenzene

Infrared spectra of the (U) sample were characteristically identical to ethylbenzene in peak positions and intensities. After irradiation, (I) showed the same absorption peaks with the addition of peaks at 880 (*w*), 1020 (*w*), 1270 (*m*), 1680

TABLE III  
Elemental Ratios for Plasma-Formed Polymers and Monomer

Monomer	C/H	C/O	C/F	C/Cl
Propylene	5.14			
(U)	8.43			
(I)	8.56			
Ethylbenzene	9.6			
(U)	10.92			
(I)	10.98			
Methyl methacrylate	7.5	1.88		
(U)	8.65	2.36		
(I)	8.51	2.63		
TFE			0.32	
(U)			0.47	
(I)			0.32	
Chlorotrifluoroethylene			0.42	0.68
(U)			0.58	0.98
(I)			0.57	1.05

TABLE IV  
 Thermal Analyses Data<sup>a</sup>

Monomer	$T_{I.D.}, ^\circ\text{C}$	mg/min $\left(\frac{dw}{dt}\right)_{I.D.}$	$E_a$ , kcal/mole	$k, \text{min}^{-1}$	$T, ^\circ\text{C}^b$								
					20% WL	40% WL	60% WL	80% WL	100% WL	Exo. 1	Exo. 2	Exo. 3	Exo. 4
Propylene (U)	220	0.088	15.7	0.028	320	370	445	495	580	340	500		
	(I)	0.073	16.1	0.028	320	370	445	495	570	350	500		
Ethylbenzene (U)	70	0.078	—	0.036	285	360	470	515	580	180	305	360	510
	(I)	0.095	—	0.036	285	360	470	515	580	150	310	360	520
Methyl methacrylate (U)	70	0.046	—	0.030	260	320	390	480	590	130 <sup>c</sup>	330		
	(I)	0.063	—	0.029	205	300	360	480	580	110 <sup>c</sup>	330		
TFE (U)	85	0.281	—	0.051	225	265	295	315	380	125 <sup>c</sup>			
	(I)	0.335	—	0.054	230	270	300	320	380	125 <sup>c</sup>			
Chlorotrifluoro- ethylene (U)	90	0.060	—	0.043	210	250	280	305	385	135 <sup>c</sup>			
	(I)	0.140	—	0.049	230	265	290	315	385	120 <sup>c</sup>			
Trimethylchloro- silane (U)	100	0.013	—	0.027	320	370	425	510	650 <sup>d</sup>	335 <sup>c</sup>			
	(I)	0.018	—	0.028	325	370	430	505	650 <sup>d</sup>	340 <sup>c</sup>			

<sup>a</sup>  $I.D.$  = Initial decomposition;  $E_a$  = activation energy of initial decomposition;  $k$  = first-order decomposition rate constant; Exo. = exotherm.

<sup>b</sup> Maximum error of  $\pm 10^\circ\text{C}$ .

<sup>c</sup> Most distinguishable exotherm.

<sup>d</sup> Maximum weight loss at that temperature.

TABLE V  
 Refractive Index and Density Data

Monomer	Refractive index range <sup>a</sup>	Density range, <sup>b</sup> g/cm <sup>3</sup>
Propylene		
(U)	1.562-1.564	1.082-1.090
(I)	1.560-1.562	1.088-1.100
Ethylbenzene		
(U)	1.606-1.608	1.191-1.194
(I)	1.608-1.610	1.196-1.200
Methyl methacrylate		
(U)	1.568-1.570	1.269-1.271
(I)	1.566-1.568	1.268
TFE		
(U)	1.380-1.385	1.87-2.01
(I)	1.380-1.385	1.87-2.01
Chlorotrifluoroethylene		
(U)	1.456-1.460	
(I)	1.456-1.460	
Trimethylchlorosilane		
(U)	1.518-1.520	1.210-1.229
(I)	1.514-1.516	1.203-1.222

<sup>a</sup>  $n_D$  at ambient temperature using sodium light.

<sup>b</sup> Gradient density technique at 25.0°C.

(*m*) and 1720 (*w-m*)  $\text{cm}^{-1}$  and greater absorption from 3200 to 3600  $\text{cm}^{-1}$ . The peaks at 1020 and 1270  $\text{cm}^{-1}$  are possibly from aromatic ether linkages, and the 1720  $\text{cm}^{-1}$  peak arises from carbonyl groups. The 880  $\text{cm}^{-1}$  adsorption is most likely due to single hydrogen substitution on the benzene ring. The increased absorption from 3200 to 3600  $\text{cm}^{-1}$  is primarily due to OH and NH stretching frequencies.

The elemental analysis (Tables II and III) yielded C/H ratio values of 10.92, 10.98, and 9.6 for (U), (I), and ethylbenzene, respectively, thus showing the loss of hydrogen during polymerization. The infrared spectra indicate incorporation of oxygen and nitrogen into the polymeric structure as the apparent addition products to free radicals created by the possible hydrogen loss during irradiation.

The TG-DTA of (U) and (I) were characteristically the same, with both having a complicated set of oxidative exotherms of which four were distinguishable. These are noted in Table IV along with other details. The first noted exotherms exhibit (I) to be undergoing a specific series of thermal breakdowns sooner than (U), yet the temperature of the weight percent loss was the same for (U) and (I) over the entire decompositional temperature range. Previous mass spectrometer studies of the thermal breakdown of plasma-formed polymer films show very complicated fragmentation patterns.<sup>5</sup> This might involve benzene fragments where scissions help to facilitate the initiation of this series of thermal breakdowns. Complete decomposition of (U) and (I) occurred between 70°-580°C with a maximum first-order decomposition rate constant *k* of 0.036  $\text{min}^{-1}$ . (U) showed an initial weight gain of 7% from 45° to 150°C.

The refractive index and density range shown in Table V for (U) and (I) revealed no experimentally significant differences. The same trends of refractive index and density as compared to conventional polymers are evident.

### Methyl Methacrylate

Infrared spectra of (U) were characterized by  $\text{CH}_2$  and  $\text{CH}_3$  absorption peaks at 1380 (*w*), 1460 (*w*), 2870 (2), 2930 (*w*), and 2960 (*w*)  $\text{cm}^{-1}$ . Also present was a compound carbonyl group at 1720 (*m*) and 1680 (*s*)  $\text{cm}^{-1}$ , peaks of the normal ester and possibly of acrylic acid. A broad 3100–3600  $\text{cm}^{-1}$  absorption from NH and OH stretches due to possible acrylic acid was also present.

After irradiation, (I) showed increased absorption in the 3100–3600 (*m*–*B*)  $\text{cm}^{-1}$  region and a new absorption peak at 1250  $\text{cm}^{-1}$  (*w*–*B*). The 3100–3600  $\text{cm}^{-1}$  absorption shows an increase in bound nitrogen within the polymeric structure. The 1250  $\text{cm}^{-1}$  absorption may be related to the carbonyl formation.

Ratios of C/H and C/O are given in Table III, showing a decrease of hydrogen and oxygen upon formation of the plasma film, then an increase of hydrogen and a decrease of oxygen due to irradiation. However, the changes due to irradiation might have come about by CO and/or  $\text{CO}_2$  being major constituents of evolved gaseous products. The infrared spectra showed an increase in nitrogen compounds, but also an increase in carbonyl groups. The six months lag time between the oxygen and C, H, N analysis plus infrared spectral analysis is probably the reason for the discrepancy.

The TG–DTA of (U) and (I) each had two major oxidative exotherms between which was a set of complicated smaller exotherms. The initial exotherm for (I) occurred at 110°C and for (U), at 130°C. Also notable from the major details of decomposition given in Table IV was the difference in the temperature of the percent weight loss at lower temperatures than (U). As with the previous carbon–hydrogen systems, (U) underwent a weight gain, this time of 8%, from 130° to 170°C.

The refractive index and density ranges for (U) and (I) shown in Table V reveal no notable differences.

### Tetrafluoroethylene

The infrared spectra for (U) and (I) were similar, with major absorption bands at 1100–1300 (*s*), 1740 (*s*), 980 (*m*), and 740 (*m*)  $\text{cm}^{-1}$ . The 1100–1300 band is characteristic of CF and  $\text{CF}_2$  bonds. The band at 1740  $\text{cm}^{-1}$  is attributed to C–F groups in the polymer. An appreciable amount of the initial double bonds is not reacted under the conditions of this polymerization. Some carbonyl characteristics may be included in this band, however, they do not predominate. The band at 740  $\text{cm}^{-1}$  is characteristic of a CF– $\text{CF}_3$  linkage and is not readily explainable. No interpretation has been assigned to the band at 980  $\text{cm}^{-1}$ . A structure corresponding to C–F is a possibility.

Both the (I) and (U) spectra show evidence of the polymer reacting with atmospheric gases. Small absorption bands at 1880 (*w*), 2360 (*w*), 2500 (*w*), and 3250 (*w*)  $\text{cm}^{-1}$  would indicate the formation of  $\text{CF}_2\text{COF}$ ,  $-\text{CF}_2\text{CN}$ , and some cyclics involving oxygen or the formation of  $\text{CF}_2\text{H}$ .

The elemental analysis gave C/F ratio values of 0.47, 0.42, and 0.32 for (U), (I) and tetrafluoroethylene, respectively, as shown in Table III.

These values show that a large amount of fluorine was stripped from the polymer during plasma polymerization, leading to increased crosslinking and possible residual unsaturation as suggested by the IR spectra. However, the unsaturation observed in the IR spectra might also arise from unreacted



monomer. Further, the increase in the weight percent fluorine after irradiation shows a higher degree of fragmental loss containing carbon as the result of scissioning of the C-C bond rather than the evolution of F<sub>2</sub> leading to crosslinking of chains.

TG-DTA data in Table IV show the similarity of (U) and (I) with both totally decomposing from 85° to 380°C with a complicated set of exotherms characterizing both. The first exotherm at 125°C for both (U) and (I) further attests to their similarity. This was the largest exotherm for each sample and therefore distinguishable, even though they did not appear as singular events.

The refractive index and density ranges for (U) and (I) were the same within experimental limits, as shown in Table V. The values reported for the density of the plasma-formed polymers do not show an increase as has been reported with the other plasma-formed polymers. This could be an indication that these polymers are not as highly crosslinked or that the morphology of the polymer is such as to preclude a close packing arrangement.

### Chlorotrifluoroethylene

The infrared spectra for the unirradiated (U) and the irradiated (I) samples were the same. There was no direct evidence that this polymer had reacted with atmospheric or absorbed gases during the radiation. These spectra were characterized by an intense doublet at 1230 and 1175 cm<sup>-1</sup>, reflecting the C-F and C-Cl stretches. A broad band at 800-1000 (*m*) cm<sup>-1</sup> most probably reflects the formation of various alicyclic structures formed as the result of plasma reactions. Weak bands at 1600-1650 and 740 cm<sup>-1</sup> indicate that a small amount of the unsaturated groups did not react. Also present is a 1720 (*w*) cm<sup>-1</sup> absorption peak due to carbonyl groups. ESR measurements ( $4 \times 10^{17}$  spins/g) indicate an appreciable residual free-radical activity from which one would expect the film to react with atmospheric gases.

The elemental analysis results in Table II and III gave C/F ratio values of 0.58 and 0.57 for (U) and (I), respectively. The C/Cl ratio values were 0.98 and 1.05 for (U) and (I), respectively. Compared to the C/F and C/Cl values of 0.42 and 0.68, respectively, for chlorotrifluoroethylene, a loss of fluorine and chlorine in the plasma-formed film is evident. This probably yields unsaturation due to the low crosslinking of this film as shown by its ready solubility in a variety of solvents. The similar C/F ratio for (U) and (I) and yet the different C/Cl ratios indicate (I) to have undergone a loss of chlorine during irradiation. This might be expected due to C-Cl having a lower bond energy than C-F, but the transfer of excitation energy to chlorine is required along the polymeric structure. The loss of chlorine did not increase detected unsaturation in the IR spectra, though the loss may not have been sufficient to be detectable by our infrared spectrophotometer. Crosslinking might have occurred if two chlorine atoms left active sites on carbon backbones close enough to crosslink.

One oxidative exotherm characterized TG-DTA for (U) and (I) showed several differences in thermal data (Table IV). The exotherms occurred at different temperatures, with (U) at a higher temperature, yet (U) showed a greater weight percent loss at lower temperatures. The temperature of the weight percent loss difference further substantiates the possibility of crosslinking when chlorine is lost during irradiation. Both samples showed a weight gain: (U) had a 4% gain at 40°-130°C and (I) gained 3% at 35°-135°C.

Only the refractive index range which is the same for (U) and (I) within experimental error is reported in Table V because the plasma-formed film dissolved in the density calibration medium.

### Trimethylchlorosilane

Infrared spectra of (U) and (I) after irradiation were diffuse. With the exception of showing the characteristic absorption bands at 800–1100  $\text{cm}^{-1}$  associated with C–Si and C–O–Si, they are not interpretable.

Due to the partial inorganic nature of this plasma-formed film and the analytical methods employed, the elemental analysis gave incomplete data (see Table II) by the total detected weight percent of the samples. Thus, only the oxygen analysis, which was done by fast neutron activation, is considered accurate and shows (I) to have a lower weight percent oxygen than (U).

The TG–DTA for (U) and (I) were characteristically the same, with both having a series of complicated oxidative exotherms of which the largest was reported in Table IV along with other thermal data.

Refractive index and density ranges for (U) and (I) shown in Table V showed no significant differences.

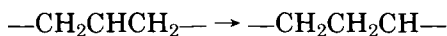
### Significance of Thermal Study

The morphological and molecular structures of plasma-formed polymers are of importance to an understanding of the data of this study. Havens, using low-angle x-ray scattering and SEM techniques, has shown that plasma-formed films of polyethylene and polystyrene are made up primarily of fairly uniform spheres bound together by a less dense amorphous phase.<sup>6</sup>

When viewed by SEM, the spheres often appear as large agglomerates; but at high magnification, the smaller subspheres are evident.<sup>5</sup> SEM photographs also confirm the spherical nature and dimensions as predicted by the low-angle x-ray scattering technique.

It has been shown that the rate of decay of free radicals trapped in highly crystalline, conventional, linear polymers is slower than that found for more amorphous or less crystalline polymers.<sup>7,8</sup> A large number of free radicals can be created in films formed by plasma polymerization, e.g.,  $\sim 10^{19}$  spins/g for polyethylene. Specifically, in the case of plasma-formed polyethylene, polystyrene, etc., the rate of decay is quite slow, and this may be compared to the slow decay of free radicals in highly crystalline, conventional, linear polymers. Furthermore, the insolubility of most plasma-formed polymers can again be compared to the insolubility of conventional polymers that have been irradiated so as to become crosslinked to the point of insolubility.

Studies of the mechanism of free-radical migration by Dole, Keeling, and Rose suggested migration in conventional polyethylene by random jumps of a hydrogen atom from an adjacent site to a free-radical site, e.g.,<sup>9</sup>



This mechanism for free-radical migration has been adopted by other investigators.<sup>10–12</sup> Evidence for free-radical migration within crystalline regions from ESR<sup>13</sup> and from crosslinking and viscosity data<sup>14</sup> has shown the migration to be to the phase boundary between the crystalline and amorphous regions.

With the preceding in mind, a plasma-formed polymer model is proposed wherein the dense phase of subspheres is assumed to possess some structural order. In this model the spheres are of a higher density and have a lower permeability to diffusion of gases than the amorphous material which essentially binds the spheres together. The molecular structure of the subspheres contains the sites of the long-lived free radicals which in plasma-formed polymers decay by one or more mechanisms, one being the migration of the radical sites to the surface of the spheres (to the amorphous region) where they react with atmospheric gases. Thus, the reaction of the sites with atmospheric gases over long periods of time should be controlled by the rate of decay of free radicals through migration and the relative differences of the permeability of the two polymer phases.

This model would appear to account for the results of the thermogravimetric data reported in this study. In the case of the unirradiated samples (U) of polypropylene, poly(methyl methacrylate), and poly(ethylbenzene), the consistent gain in weight of 3%–8% in the temperature region of 40°–240°C suggests that the sites in the irradiated samples which do not exhibit this weight gain were probably close to being quenched as measured by their inertness to oxygen uptake. In the thermal techniques applied here, the samples for TG–DTA studies are crushed to a fine powder, thus decreasing delayed reaction with atmospheric gases due to low permeability. The decay of free radicals through possible migration of the sites from within the spheres to the surface is facilitated by heating.<sup>8,12,15</sup> This would, in turn, promote reaction with atmospheric gases in the amorphous or less dense region. The free-radical sites in the amorphous regions of the irradiated samples, on the other hand, react with atmospheric gases during the irradiation process which created the free-radical sites. The atmospheric gases which reacted with the free-radical sites during irradiation were probably adsorbed in the amorphous regions of the plasma-formed polymers from the time they were exposed to the atmosphere from vacuum.

Support for this conceptual model is provided by the work of Morita, Mizutani, and Ieda on plasma-formed polystyrene heated in air.<sup>16</sup> Using ESR, they measured the spin density of plasma-formed polystyrene while heating samples from 0° to 400°C in air and vacuum. The sample heated in vacuum decreased in spin density to 340°C, where it increased sharply. The sample heated in the air behaved similarly, but the transition occurred at 150°C. The transition in spin density at 150°C was attributed to the formation of oxygen radicals. Though no reason for the transition at 340°C was given, it is likely due to thermal degradation and breaking of chemical bonds. Ethylbenzene, one of the monomers used in this study, forms a polymer that is closely related to polystyrene. Upon heating unirradiated plasma-formed polyethylbenzene, a weight gain occurred between 45° and 150°C. This weight gain results from reaction with atmospheric gases of which some form of oxygen was the major reactant as evidenced from the infrared spectra of the plasma-formed polymer taken at ambient temperature. These two events, occurring at 150°C for two plasma-formed polymers with closely related monomer systems that were heated in air, might involve coincidence, but both systems did take up oxygen up to 150°C. A reasonable explanation for this might be that reaction with a form of oxygen while heating up to 150°C destroyed the free radicals faster than the oxygen radicals formed. At 150°C, thermal degradation and weight loss become major events; and thus radical formation occurs at a higher rate than radical destruction.

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