

Irradiation of Poly(vinyl Chloride) with H₂ Plasma. I

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Synopsis

A system has been designed to serve as a plasma source and has the advantage of producing plasma of known energy and controlled intensity. Poly(vinyl chloride) films were irradiated with hydrogen plasma for different intervals of time. The effect of irradiation time and storing on the extent of crosslinking was investigated. The viscosity of the soluble part decreased at the initial stage of irradiation, then increased. The crosslinking extent was observed by measuring the swelling ratio of the irradiated samples. Spectral analysis indicated the formation of carbonyl groups and polyene structure in the irradiated PVC. The mechanisms of dehydrochlorination and crosslinking are discussed.

INTRODUCTION

At present plasma radiation is attracting an ever-increasing attention among polymer chemists. Recently a symposium was held in Philadelphia¹ that dealt with the relation of plasma to polymers and polymerization reactions. The effect of α and β particles on a number of polymers has been investigated by Kagiya.² Both degradation and monomer release were observed. Bezruk³ and Yasuda⁴ reported degradation in polymers especially in the presence of O₂. Mayoux⁵ also studied the degradation of polyethylene by O⁺, Ar⁺, Ne⁺, and He⁺ ions of energies of 200–2000 eV and found that the degradation increases in the presence of O₂ by using oxygen ions for bombardment. Colebrook⁶ studied the damage occurring in polyethylene, poly(methyl methacrylate), and polystyrene by an electron beam. He observed that the main damage was chain scission followed by decomposition. These results were confirmed by Ditchfield⁷ and were attributed to energy losses of the interacting particles.

Many workers^{8–13} reported that the electron beam, like other charged particles, causes crosslinking in polymers. The effect of the electron beam on polymer crosslinking was used by Tsutomo,¹⁴ Renate,¹⁵ and Donnell¹⁶ to harden unsaturated polyester resins for coating purposes. Changes in the surface due to plasma interaction was the aim of many workers^{17–19} in order to increase the hardness of polymer surface.

Tsuji²⁰ carried out ESR studies on polyethylene irradiated by an electron beam both under vacuum and in the presence of oxygen and established a mechanism for the formation of double bonds. Coryachev²¹ studied the effect of a proton beam of different density on polyethylene. The reaction forming *trans*-vinyl double bonds reaches a maximum at a depth of 34–35 mg/cm² and then decreases.

Outgassing from polymer surfaces as a result of interaction of protons with

poly(vinyl chloride) and poly(tetrafluoroethylene) was reported by Barashov.²² The outgassing products were CH_4 and HCl from the former and H_2 , CH_4 , C_3F_5 , and CF_3 from the latter. Bamford²³ also detected H_2 , CH_4 , C_2H_4 , and C_2H_6 from polyethylene as a result of high-frequency electric discharge.

The adhesion property of polymers was improved by ionized gases as reported by Westerdahe²⁴ and Kamada.¹⁰

The mechanical properties of polymers were found^{25,26} to decrease upon treatment with heavy ions at low irradiation doses. The effect of charged-particle bombardment on the electrical properties of polymers was also investigated by many workers.²⁷⁻²⁹ This paper describes a device for producing a plasma beam with known density and variable energy and the effect of the plasma on the chemical properties of poly(vinyl chloride) (PVC).

EXPERIMENTAL

The experimental setup under discussion is presented schematically in Figure 1. The plasma source is of the discharge type with an aluminum field emission cathode³⁰ the mechanism of which depends entirely upon the barrier at the surface; it has the advantage of both current homogeneity and stability as compared with those emitted thermoionically. The cathode forms the first electrode of a three-electrode "univoltage lens" and is at the same potential as the third electrode, while the control electrode is connected to the target which is earthed and is therefore considered as an anode.

The system in its entirety was a compromise between being a lens and a plasma source to control the intensity of the charged particles impinging into the specimen at the focus. Hence, the lens apertures had to be larger than the Debye length L_D ,³¹ which is a function of the particle's density n and temperature T [$L_D = 6.9(T/n)^{1/2}$].

Therefore, the electrodes were designed to be equally spaced a distance of 3 cm between each pair, the last two of which were apertured with a diameter of 4 cm. The target is 5 cm from the last electrode and is water cooled. It has a rectangular groove of 1.5 cm in depth and 1.5 cm in width at the front in the focal plane of the lens where the specimen can be fixed by two spring holders. All the parts were installed in a quartz glass tube 30 cm long and 8 cm in diameter. One end was rubber tight to a stainless steel disc with a central two-way tube: one was connected to an oil diffusion pump; and the other was connected to a hydrogen gas source through a needle valve. The other end of the vacuum tube was closed by another disc containing an outlet and an inlet of the circulating water together with all electric connections and an L-shaped tube that could be

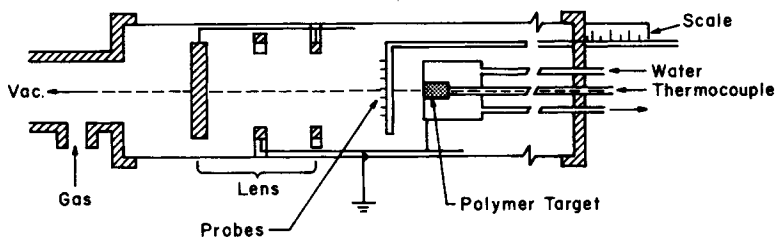


Fig. 1. The plasma source.

moved along a scale. The horizontal portion of this tube contained nine double probes arranged symmetrically along the cross section of the plasma. Such design facilitated simultaneous measurements of the particles energy and density distribution across the beam along the axis at the working conditions.

Univoltage Lens

The lens used in our system consisted of three equally spaced operated electrodes, the outer two of which are maintained at the beam potential without disturbing adjacent potential relations and the inner of which may be at either higher or lower potential. When the inner electrode is at zero potential, i.e., only one voltage is applied, it is referred to as "univoltage lens." This type of lens is of practical importance for its simplicity and stability. This is explained by the fact that since only one voltage is applied, as a result of which the ratio $V(\text{outer electrode})/V(\text{inner electrode})$ is always infinite, the focal length does not depend on the voltage and hence fluctuations of voltage are not disturbing. Here, the focal length depends largely on electrode spacing, thickness, and aperture radii.

Further description of the design and characteristics of the lens and the system can be found elsewhere.^{31,32}

Plasma Characteristics and Procedure

After a base pressure of 10^{-5} torr was attained, the suitable electric fields were applied to the system electrodes. The ions produced along the tube where the length of each aperture exceeds the Debye length were accelerated toward the target, with the electrons by the charge separation's electric field generated by the accelerated electrons.

In a preliminary investigation, the optimum operating pressure and potential were determined and were subsequently used throughout the study. The radial density profile at different distances from the lens is given in Figure 2. At 1 cm from the lens, the profile is quite broad and indicates a lower density. However, as the distance increased, the profile tends to be exceedingly contracted with an increase in density. At a distance of 2 cm, the profile becomes approximately constant with a focused cross section of about 1.5 cm in diameter. Maximum density value is obtained at a distance of 5 cm. The plasma beam energy and density were found to depend on the voltage according to the data in Table I. After the irradiation period, the sample was removed from the target and the exposed area was separated and examined.

TABLE I
Energy and Density of Plasma Beam as a Function of Voltage

Acceleration voltage, kV	Electron density, (no. of electrons/cm ³) × 10 ¹⁰	Electron energy, eV
4	2.38	7.5
3.2	2.4	6.0
1.6	2.0	4.0
0.6	1.4	2.0

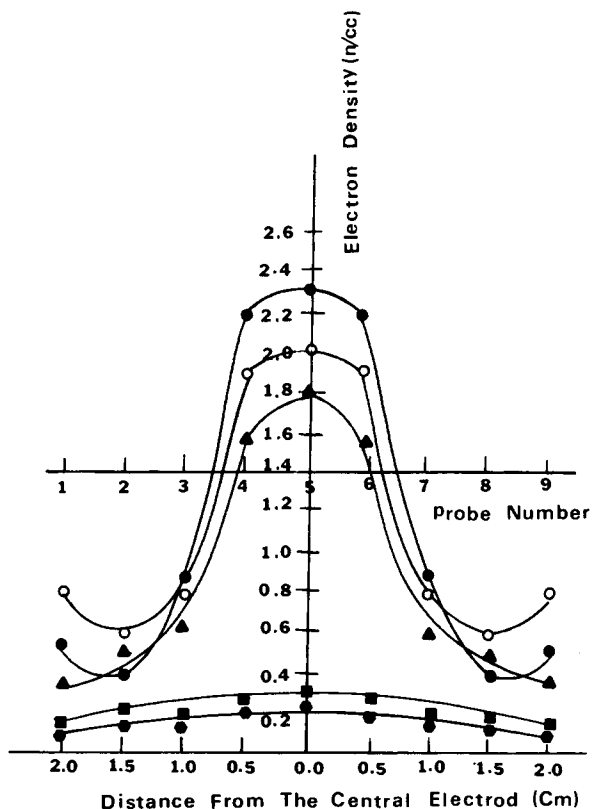


Fig. 2. Beam "electron density" profile; $P = 2 \times 10^{-2}$ mm Hg: (■) 1 cm from the lens; (▲) 2 cm from the lens; (○) 3 cm from the lens; (●) 5 cm from the lens; (●) 7 cm from the lens.

Materials

All solvents used were purified by conventional procedures. Pure-grade poly(vinyl chloride) was supplied from the Plastic National Co. in Egypt. The polymer was further purified by reprecipitation from cyclohexanone solution in methanol, filtered and dried under vacuum at room temperature.

The PVC films were prepared by casting 15% PVC in cyclohexanone over a glass plate at 50°C. The films were then cut into strips of approximately 2×1 cm and a thickness of 1 mm and were kept in brown bottles in a dry desiccator.

Determination of Solubility

The exposed area of the irradiated sample was extracted by hot cyclohexanone in a sintered glass crucible. The insoluble swelled mass was washed several times with pure cyclohexanone and dried in a vacuum oven at 50°C to constant weight. Extraction and drying was repeated several times until no further change in weight occurred.

Viscosity Determination

An Ubbelohde viscometer was used to measure the viscosities of the dilute polymer solutions. No kinetic energy corrections were made. The time of flow of the solvent in the viscometer was 120 sec.

Swelling Measurements

A swellometer was designed (Fig. 3) and used for the determination of the swelling percentage. The swellometer was calibrated as follows. The reservoir A and the two capillaries were filled with cyclohexanone to zero reading, and the sample holder was placed in its position. The swellometer was then turned upside down and immersed vertically in a water bath at 25°C for 24 hr. The swellometer was readjusted again so that the reservoir A was down and B was up, and the solvent was allowed to drop until it reached a constant height in the capillaries. The decrease in the reading from zero was considered the apparatus error and was always taken into consideration.

The weighed sample was then placed in the sample holder and the above procedure was repeated. The decrease in the solvent volume can be directly determined from the capillary reading. The sample volume is determined from its weight and density. The swelling percentage is expressed by the ratio $V_2/V_1 \times 100$, where V_2 is the corrected volume of the swelled solvent and V_1 is the sample volume.

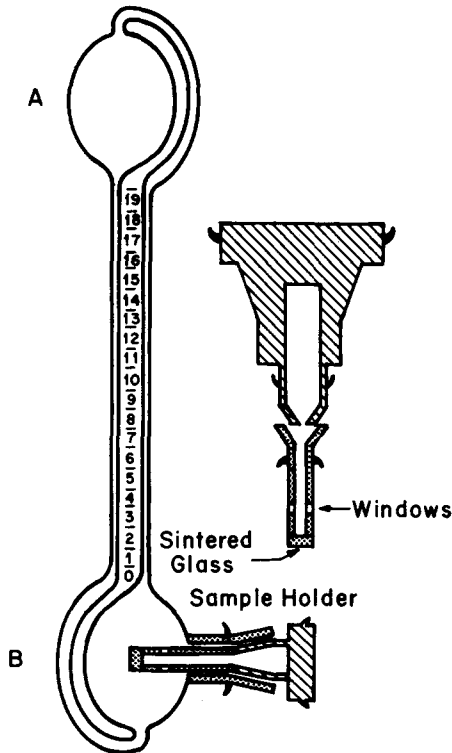


Fig. 3. Swellometer.

Spectral Measurements

The UV spectra were recorded on a double-beam Py-Unicam SP-700 spectrophotometer. A 0.2% solution of PVC in cyclohexanone was prepared and filtered prior to taking the measurements. The IR spectra were recorded on a Py-Unicam SP-200 spectrophotometer. Thin films (≈ 0.05 mm) of PVC were used for the measurements.

RESULTS

After irradiation of PVC it was found that the polymer became partially insoluble in cyclohexanone. Figure 4 illustrates the relationship between the time of irradiation of the sample and the percentage of the insoluble portion. The figure also indicates that the storing time is an important factor affecting the rate of crosslinking. The plasma particles falling on the surface of the polymer form free radicals and trapped ions. Their concentration is determined by the energy of the particles and the area of the exposed polymer film. On standing, these free radicals and ions migrate into the depth of the sample, causing an increase in the percentage of crosslinking.

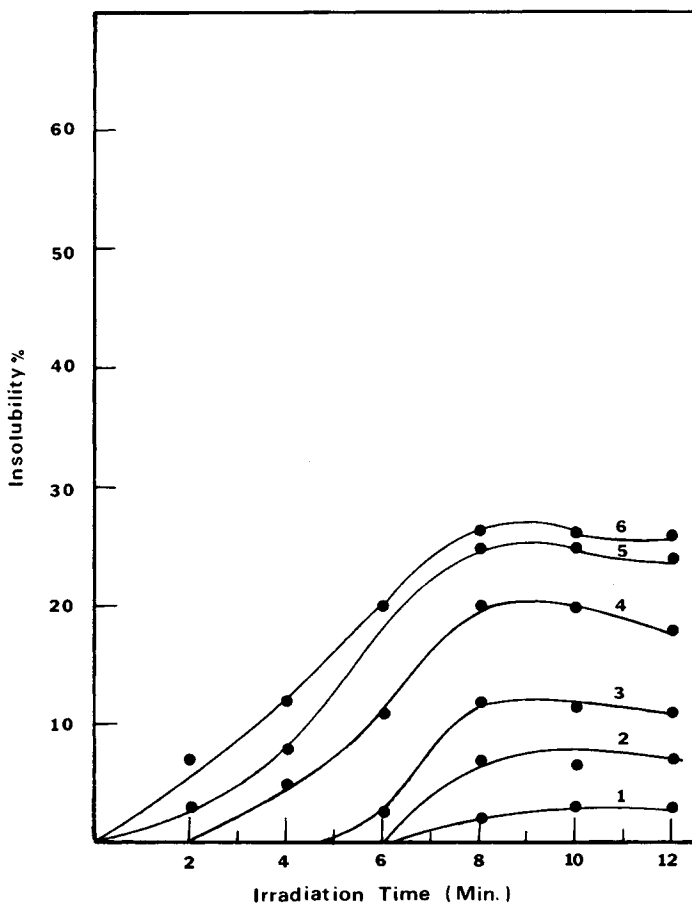


Fig. 4. Effect of irradiation time and storing period on insolubility of PVC. Storing time: (1) 10 min; (2) 1 day; (3) 3 days; (4) 7 days; (5) 30 days; (6) 45 days.

The soluble part of the polymer was isolated and the intrinsic viscosity $[\eta]$ of each sample was measured. Figure 5 shows the effect of irradiation and storage time on $[\eta]$. The viscosity was found to decrease initially with irradiation and then increase upon further exposure. A decrease in $[\eta]$ possibly indicates some degradation of the main chain. However, as a polydisperse polymer progressively crosslinks, some molecular weight separation will occur because the higher molecular weight molecules have a higher probability of becoming insoluble than the lower molecular weight molecules. Accordingly, on the average, one would expect the soluble portion to contain shorter molecules. On increasing the time of irradiation, the number of free radicals as well as the probability of their interactions increase, thus leading to branching and slight crosslinking. The viscosity increased, reaching a steady value after 8 min of irradiation. On standing, the viscosity increased markedly, even at low doses of irradiation, reaching a limiting value after seven to eight days and remained unchanged for the following 45 days.

The effect of dose rate upon $[\eta]$ is shown in Figure 6. Separate PVC samples were irradiated with a beam of plasma of 2 eV for 30 min, 4 eV for 15 min, 6 eV for 10 min, and 7.5 eV for 8 min. The beam density was almost constant and

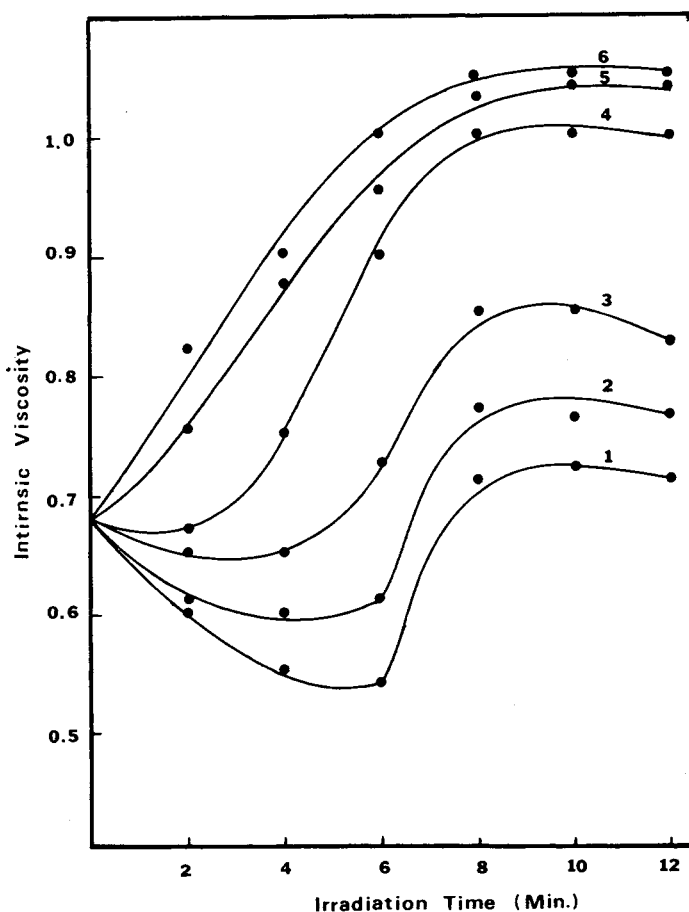


Fig. 5. Effect of irradiation time and storing periods on intrinsic viscosity of PVC (plasma energy 7.5 eV). Storing time: (1) 10 min; (2) 1 day; (3) 3 days; (4) 7 days; (5) 30 days; (6) 45 days.

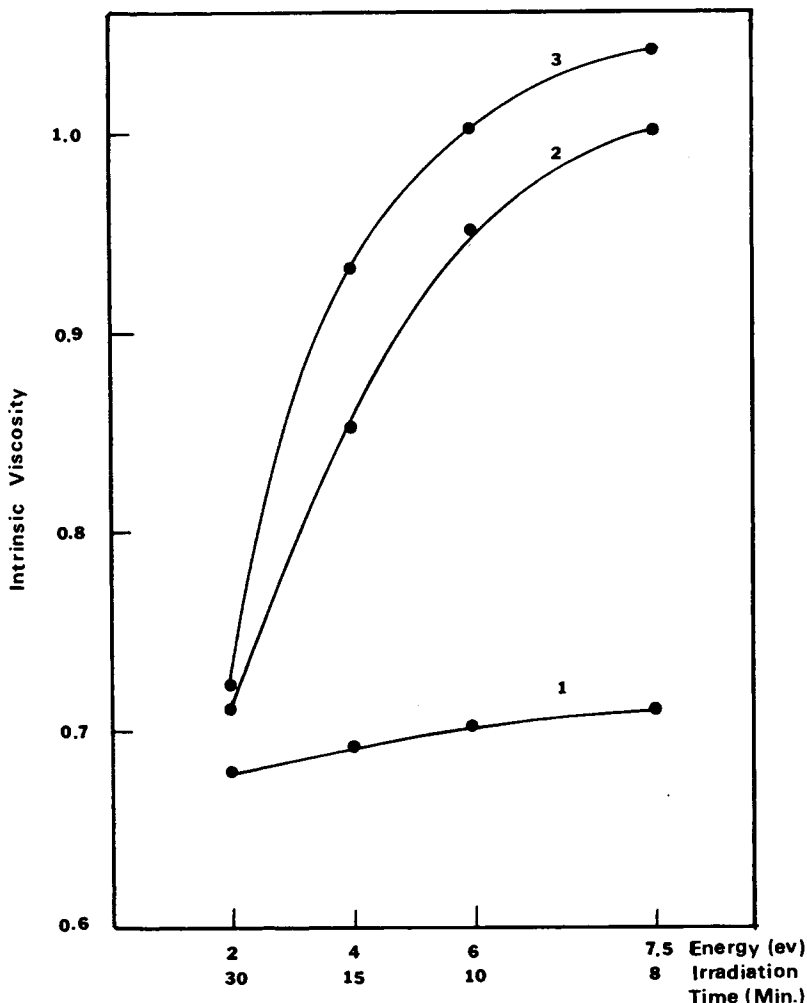


Fig. 6. Effect of dose rate and storing periods on intrinsic viscosity of PVC. Storing period: (1) 10 min; (2) 7 days; (3) 45 days.

equaled 1.8×10^{10} electrons/cm²-sec. The curve shows that $[\eta]$ increased with the dose rate and that the effect is very pronounced on standing.

The elemental analysis of the irradiated samples was followed and is given in Table II. It is apparent from the table that the percent of chlorine decreases from 55.8 in the original PVC to 40.8 after irradiation for 12 min and storing for 45 days. This decrease is a consequence of dehydrochlorination; moreover, the extent of dehydrochlorination increases progressively on standing.

The visible absorption spectra of PVC samples, plasma irradiated for different doses and stored for various intervals of time, are presented in Figure 7. This figure consists of a series of absorption maxima in the range of 350–625 nm. The maxima shift to longer wavelengths and are intensified on standing. The presence of a deep broad absorption band at 490 nm and a series of small maxima in the region of 350–500 nm in the spectra of gamma-irradiated PVC was also noted by Chapiro.³³ He suggested that the color in the visible region is due to

TABLE II
Effect of Irradiation Time and Storing Periods on Element Percentage of PVC
(Plasma Energy 7.5 eV)

Irradiation time, min	Storing period	Carbon, %	Hydrogen, %	Chlorine, %
6	10 min	38.9	4.1	56
8	10 min	40.2	4.1	55.7
10	10 min	40.1	4.2	55.6
12	10 min	40.4	4.2	54.9
10	1 day	41	4.1	54.5
12	1 day	41.4	4.3	53.9
10	3 days	43.1	4.2	52.2
12	3 days	42.2	4.3	52.6
10	7 days	46.7	4.4	47.7
12	7 days	46.6	4.4	47.8
8	30 days	49.7	4.6	43.9
10	30 days	50.3	5.0	42.9
12	30 days	49.6	4.6	44.1
6	45 days	47.9	4.0	47.2
8	45 days	51.7	6.0	39.9
10	45 days	51.2	6.1	41.0
12	45 days	51.0	6.2	40.8
Blank	—	39.8	4.3	55.8

both frozen free radicals and conjugated double bonds. Similar bonded structures in the absorption spectra of the irradiated PVC have been observed by Atchison.³⁴ An excellent review covering the mechanism of degradation and the UV and visible spectra of PVC has been written by Geddes.³⁵

The infrared spectra of PVC samples are shown in Figure 8. The samples were subjected to plasma irradiation for different periods of time under vacuum and stored in air. The spectra illustrate the formation of a carbonyl group as evident from the characteristic band in the 1700 cm^{-1} region. The spectrum of the unirradiated sample shows a very weak band in this region which may be due to a residual carbonyl group formed in the polymer during the process of polymerization or storing of the polymer in air. The presence of a very weak band at 320 nm in the visible spectrum of the original sample is consistent with the above finding.

The extent of crosslinking was also followed by measuring the swelling of the PVC gel formed after irradiation. Table III compiles the result of swelling measurements for PVC irradiated with different doses and stored for different periods of time. It appears that the swelling ratio is nearly inversely proportional to the extent of crosslinking. Again it can be seen that crosslinking increases with irradiation time and storage.

DISCUSSION

As a result of irradiation of PVC films with a beam of hydrogen plasma, the polymer changed color gradually to red, brown, and finally black. Analysis of the solubility, intrinsic viscosity, and swelling data, in addition to the spectra, shows that the free radicals are formed at the beginning of irradiation. The postirradiation effect indicates firmly that the free radicals formed on the surface

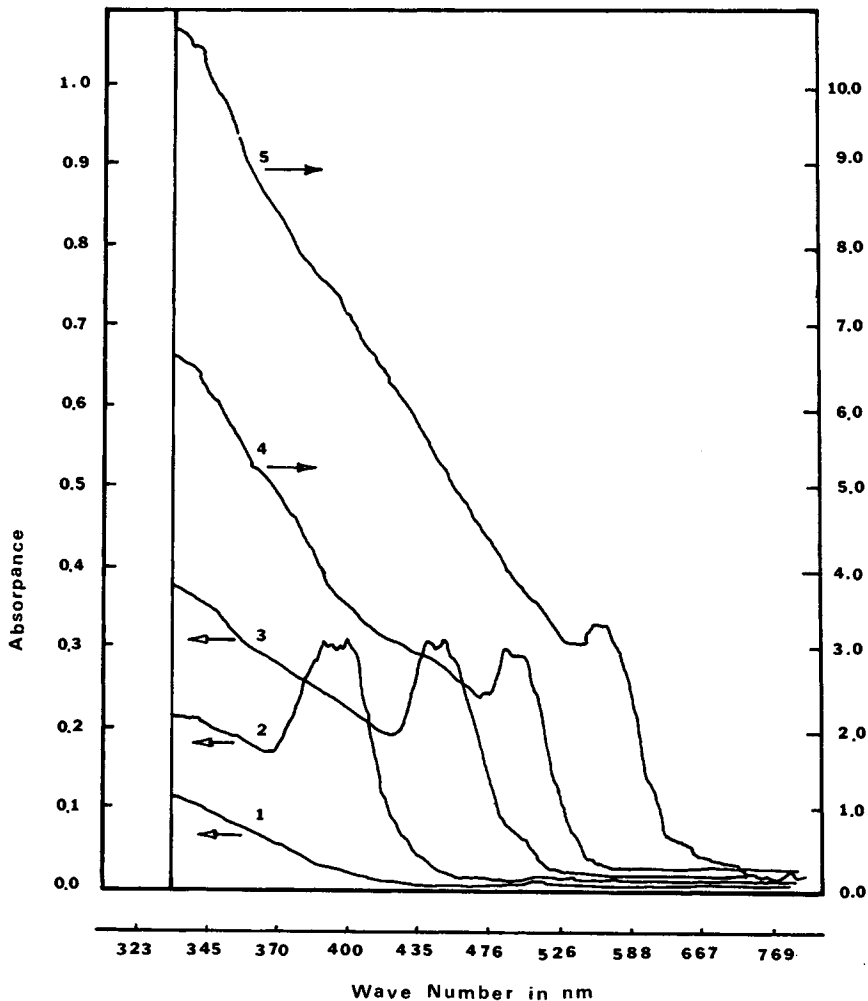
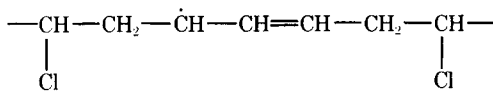


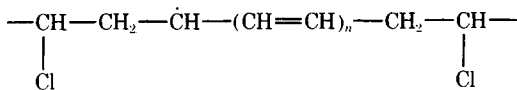
Fig. 7. Effect of storing period on absorption spectra (visible and UV) of PVC (irradiation time 8 min; plasma energy 7.5 eV): (1) blank; (2) 10 min; (3) 3 days; (4) 7 days; (5) 45 days.

plus the trapped ions migrate into the interior of the sample. The elemental analysis indicates a decrease in Cl_2 content, which should result from dehydrochlorination reaction.

It has been reported³⁶⁻⁴⁰ that the allyl radical formed in either electron- or gamma-irradiated PVC has the following structure:



I



II

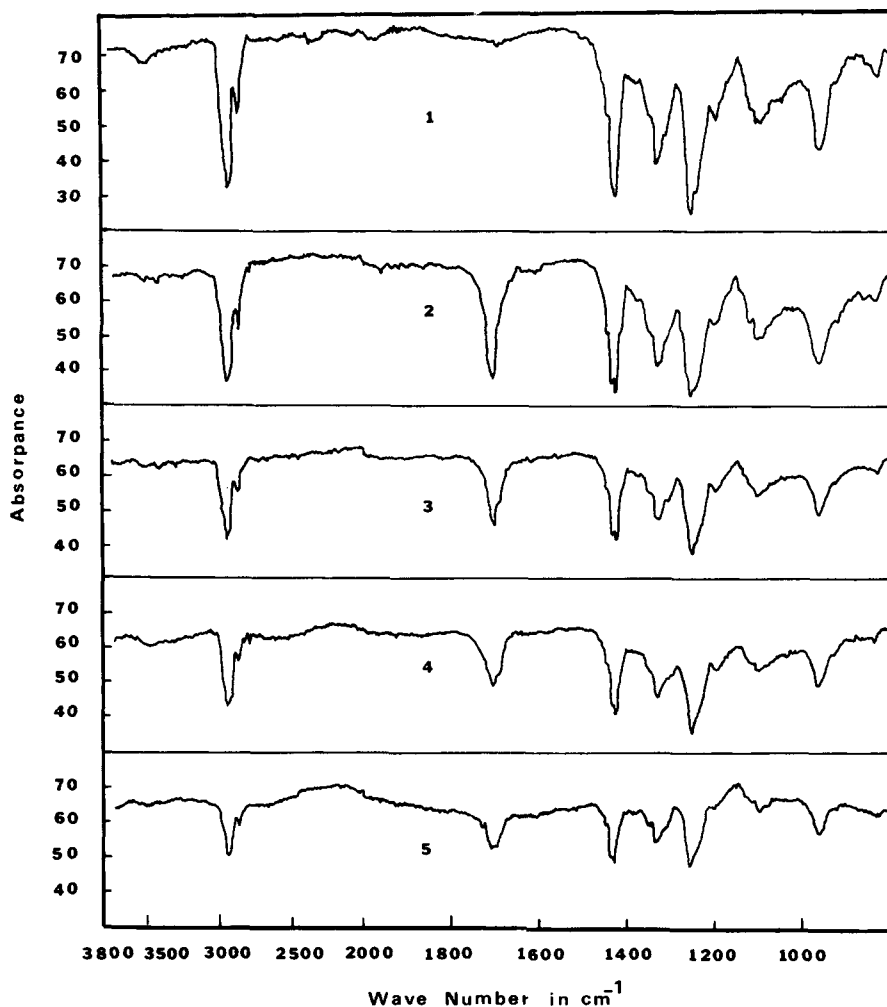


Fig. 8. Effect of storing period on absorption spectra (IR) of PVC (irradiation time 8 min; plasma energy 7.5 eV): (1) blank; (2) 10 min; (3) 1 day; (4) 7 days; (5) 45 days.

Other authors^{41,42} using ESR techniques also have reported that under gamma irradiation in vacuo at room temperature a conjugated polyene structure will be formed. When the plasma-irradiated samples were kept in air, molecular oxygen abstraction took place and carbonyl groups were formed, as indicated by the sharp peak at 1700 cm^{-1} in the early stage of irradiation. This sharp peak broadened on standing, and a shoulder appeared which may be attributed to polyene structure formation.

The energetic plasma ions fall on the polymer surface, eliminating a hydrogen atom and forming the following structure:

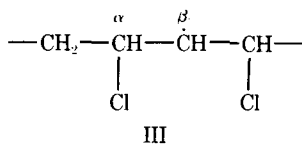
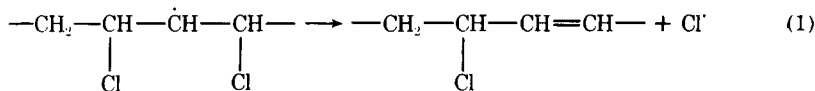


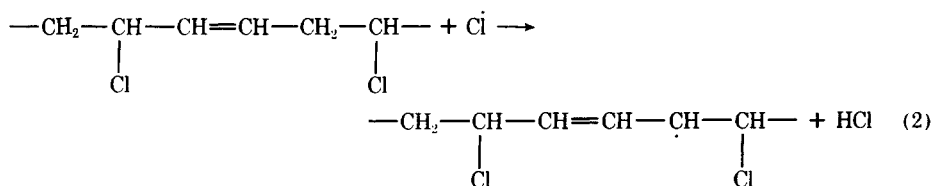
TABLE III
Swelling Percentage of PVC Gel

Storing period, days	Irradiation time, min	Swelling, %
7	6	45
7	8	34
7	10	40
7	12	48
30	6	36
30	8	32
30	10	34
30	12	34
45	6	34
45	8	30
45	10	32
45	12	32

When an unpaired electron is formed in the β position to the halogen atom, a halogen radical is expelled and double bond is formed⁴³:

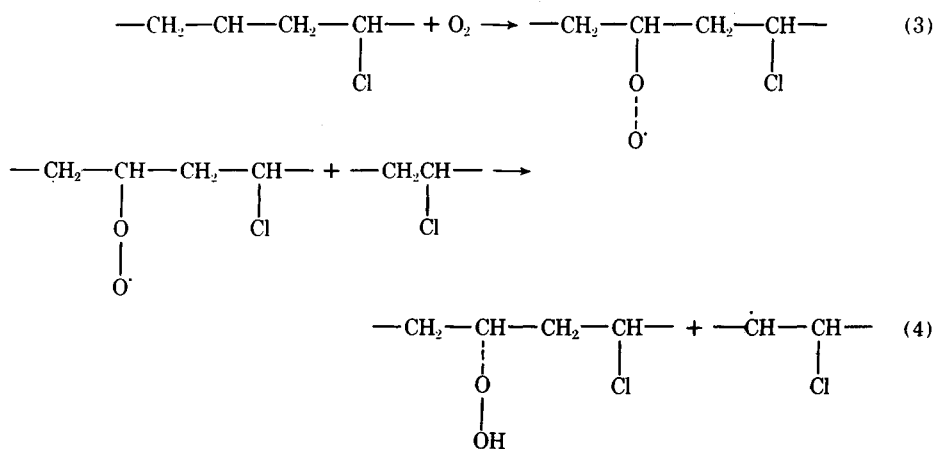


Hydrogen abstraction from ethane by chlorine free radical occurs much more easily than from chlorinated methane. Therefore, the chlorine radicals may abstract hydrogen atom from methylene groups preferentially:

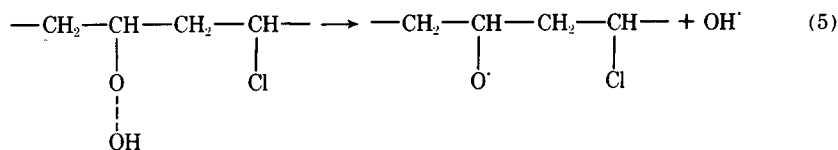


Further reactions are analogous and mean a repetition of reactions (1) and (2). This mechanism explains the formation of polyene configuration.

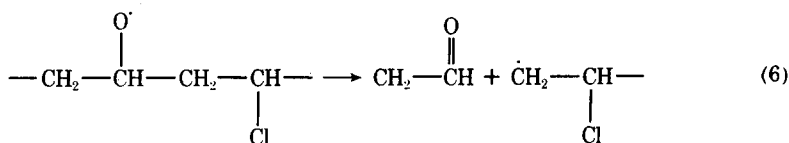
In the presence of oxygen, peroxy radicals are formed rapidly:



The hydroperoxide bonds dissociate easily in the presence of energetic plasma particles:

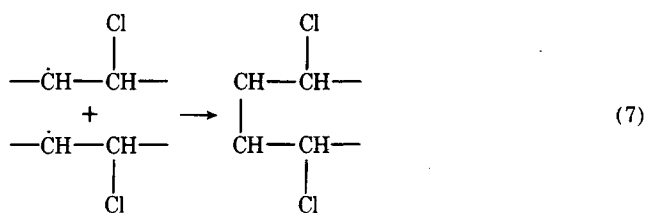


The oxy radicals are reactive and readily dissociate to form carbonyl groups:

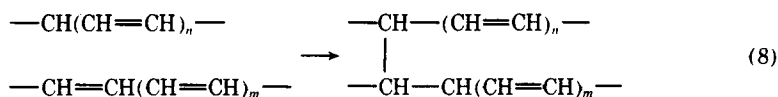


Reaction (6) also may account for the slight decrease in molecular weight in the early stage of irradiation.

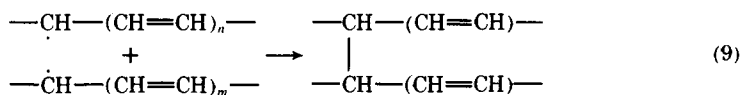
It has been found that backbone scission and crosslinking could occur simultaneously in the same polymer sample. It is generally assumed⁴⁴ that crosslinking under vacuum occurs by the termination of two radicals:



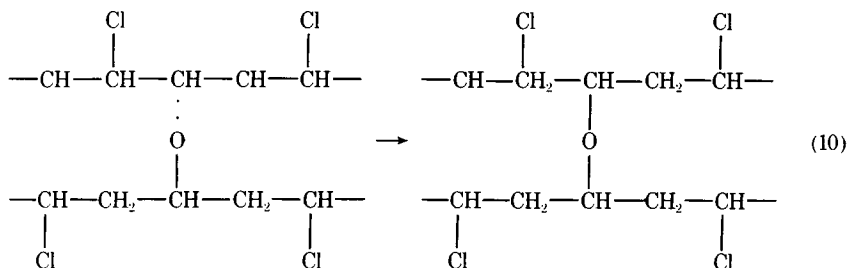
Rabek et al.⁴⁵ have proposed a mechanism of unpaired electron transfer from one polyenyl radical to a double bond in another conjugated system:



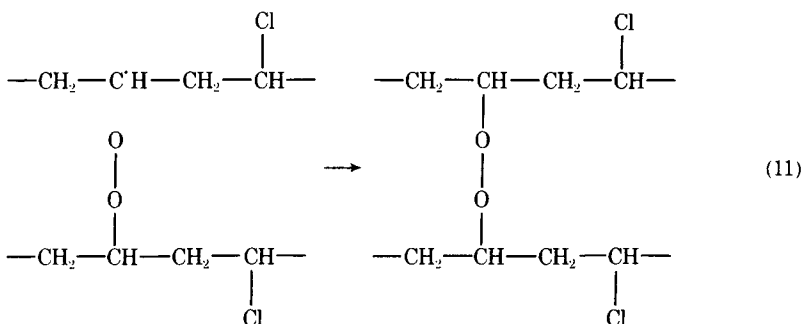
It seems likely that two delocalized polyene radicals may combine:



When samples are kept in air, alkoxy and peroxy radicals participate in crosslinking reaction by termination:



or



CONCLUSIONS

The irradiation of PVC films with hydrogen plasma results in the formation of crosslinked structure. A free-radical mechanism may be responsible for the formation of the polyene structure. The effect of oxygen atmosphere shows that macroradicals form peroxy and carbonyl groups by addition of oxygen. The effect of different plasticizers, stabilizers, and fillers on the interaction of plasma with PVC will be discussed in a coming communications.

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References

1. *J. Macromol. Sci. Chem.*, **A10**(3), (1976) (entire issue).
2. T. Kagiya, *Kagaku No Ryoiki* **26**(8), 617 (1972).
3. L. T. Bezruk and E. V. Lebedev, *Vysokomol. Soedin.*, **A15**(7), 1674 (1973).
4. H. Yasuda, C. E. Lamaze, and K. Sakaoku, *J. Appl. Polym. Sci.*, **17**, 137 (1973).
5. C. Mayoux, A. Antoniou, Bui AI, and R. Lacoste, *Eur. Polym. J.* **9**, 1069 (1973).
6. A. Colebrook and A. H. Windle, *Proc. Conf. Scanning Electron Microsc. Syst., Appl.*, London (1973), p. 132-135.
7. R. W. Ditchfield, D. T. Grubb, and M. J. Whelan, *Phil. Mag.*, **27**(9), 1267 (1973).
8. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.*, **16**, 2317 (1972).
9. J. C. Bray and E. W. Merrill, *J. Appl. Polym. Sci.*, **17**, 3779 (1973).
10. K. Kamada and T. Nakajma, *Kogyo Zairyo*, **21**(9), 33 (1973).
11. W. Knappe and A. Zyball, *Kunststoffe*, **62**(9), 580 (1972).
12. P. R. Hall, U.S. Pat. 3,644,161 (Feb. 1972).
13. K. H. Morganstern, *ACS Div. Org. Coat. Plast. Chem. Paper*, **33**(1), 256 (1973).
14. M. Tsutomo and M. Koichiro, *Ger. Pat.* 2,227,984 (CL, C. 08f) (Jan. 1973).

15. K. Renate, Z. Guenter, Z. Gisela, D. Guenter, L. Walter, and W. Roland, Ger. Pat. (East) 92,320 (CL.C. 089) (Sept. 1972).
16. J. H. Donnell, *Proc. Aust. Inst.*, **41**(3), 68 (1974).
17. F. Y. Chang, M. Shen, and A. T. Bell, *J. Appl. Polym. Sci.*, **17**, 2915 (1973).
18. V. A. Vonsyatskii, E. P. Mamunya, and Yu. S. Lipatove, *Proc. Third Tihany Symp. Radiat. Chem.*, Budapest, Hungary (1971), vol. 1, p. 963-974.
19. D. F. Kolicky and R. F. Hall, Can. Pat. 914,606 (1972).
20. K. Tsuji, *J. Polym. Sci.*, **11**, 467 (1973).
21. H. M. Coryachev and L. N. Pankratova, *High Energy Chem. USSR*, **7**(6), 488 (1973).
22. E. A. Barhashov, V. A. Bogalov, and B. A. Banchin. *Fiz. Khim. Math. Moler.*, **8**(6), 66 (1972).
23. C. H. Bamford and J. C. Ward, *Polymer*, **2**, 277 (1961).
24. A. L. Westerdahi, J. R. Hall, N. J. Bodnar, and D. W. Levi (Picatinny Arsenal, Dover, N.J.) U.S. Nat. Tech. Inform. Serv. AD. Rep. No. 749253, 1972.
25. M. A. Bagirov, S. A. Abasov, U. P. Malin, and T. F. Abbasov, *J. Polym. Sci. C*, **33**, 153 (1971).
26. Takahashi, Yuzo, *Chuo Deigaku Rikogakubu Kiyo, Japan*, **15**, 155 (1972).
27. V. A. Cheryshov and O. G. Kazakov, *Izv. Vysh. Ucheb. Zaved. Fiz.*, **No. 9**, 136 (1972).
28. J. R. Liyan and S. A. Liyan, *Rev. Mex. Fiz.*, **4046**, **157**, 71 (1967).
29. C. Mayoux, *Proc. 2nd Int. Conf. on Gass Discharge*, London, 1972.
30. M. Venugapalan, *Reaction Under Plasma Conditions*, Vol. 1, Wiley-Interscience, New York, 1971.
31. L. Spitzer, *Physics of Fully Ionized Gases*, Interscience, New York, 1956.
32. E. E. Nofal, Ph.D. Thesis, Cairo University, 1977.
33. A. Chapiro, *J. Chim. Phys.*, **53**, 895 (1956).
34. G. J. Atchison, *J. Polym. Soc.*, **49**, 385 (1961); *J. Appl. Polym. Sci.*, **7**, 1471 (1963).
35. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).
36. R. E. Michel, *J. Polym. Sci. A2*, **10**, 1841 (1972).
37. E. J. Lawton and J. S. Balwit, *J. Phys. Chem.*, **65**, 815 (1961).
38. S. Ohnishi, Y. Nakajima, and I. Nitta, *J. Appl. Polym. Sci.*, **6**, 629 (1962).
39. J. N. Hay, *J. Polym. Sci. A1*, **8**, 1201 (1970).
40. B. R. Loy, *J. Polym. Sci.*, **50**, 245 (1961).
41. R. Salovey, J. P. Luongo, and W. A. Yager, *Macromolecules*, **2**, 198 (1969).
42. T. Nakagawa, H. B. Hopfenberg, and V. T. Stannett, *J. Appl. Polym. Sci.*, **15**, 747 (1971).
43. R. Kh. Friedlina, in *Advances in Free-Radical Chemistry*, Vol. 1, G. H. Williams, Ed., Logos, London, 1971, Chap. 6.
44. J. M. Tedder, *Quart. Rev.*, **14**, 336 (1960).
45. J. F. Rabek, G. Chanback, J. Lucky, and B. Ranby, *J. Polym. Sci., Chem. Ed.*, **14**, 1447 (1976).

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