

Radiation Protection of Polyethylene

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Synopsis

It is known that aromatic hydrocarbons are more stable to ionizing radiation than are saturated hydrocarbons. It is shown here that polyethylene can be more stable to radiation either by mixing aromatic compounds with the polyethylene or by grafting styrene onto the polyethylene. In either case, the polymer has greater radiation resistance than predicted from the law of averages. Aromatic compounds which have the greatest resonance energy protect the polymer to the greatest extent. In mixtures, polystyrene gives the least protection, and naphthalene, anthracene, and phenanthrene give the greatest protection. Polyethylene grafted with styrene has better radiation resistance than does a polyethylene-polystyrene mixture. The $G(\text{H}_2)$ was calculated for each sample, and curves are presented illustrating the effect.

INTRODUCTION

It is known that aromatic hydrocarbons are much more stable to ionizing radiation than are saturated hydrocarbons.¹ The stability of these ring structures is attributed to energy loss by fluorescence from the π electron system of the ring.² Wyatt³ reported that naphthalene and anthracene, which have more resonance energy than benzene, are more stable to radiation than benzene.

Schoepfle and Fellows⁴ reported that aromatic hydrocarbons also protect saturated hydrocarbons from radiation. Their results showed that exposure of a solution of benzene and cyclohexane to cathode rays gives a yield of hydrogen which is less than is predictable from the law of averages. According to Manion and Burton,⁵ this protection is a result of ionization transfer and excitation transfer from cyclohexane to benzene.

Polyethylene, when exposed to high energy radiation, also reacts to give gaseous products. According to Dole, Keeling, and Rose,⁶ the gas evolved is 98% hydrogen. It would be interesting to know if this hydrocarbon polymer in the solid state can be protected from radiation damage by incorporating small amounts of aromatic structures. Wyatt³ reported that corona discharge is similar to ionizing radiation in its action on polyethylene and speculated that wire coatings made from aromatic polymers would be more stable to high voltages than the polyethylene. Polyethylene protected by small amounts of suitable aromatics might also make more stable wire coatings. This work was initiated to determine the effect of aromatic structures on the radiation stability of polyethylene.

EXPERIMENTAL

Materials

Materials used (and their sources) were as follows: polyethylene pellets (The Dow Chemical Co.); polyethylene powder for grafting (USI); polystyrene (Dow, Styron 666); naphthalene (General Chemical Co.); anthracene (Eastman); phenanthrene (Eastman); styrene (Dow Chemical Co., Texas Division production).

Sample Preparation

Physical Mixtures. The physical mixtures were blended on a roll mill for 10 min., then ground to about 30 mesh for irradiation. The graft copolymers were ground similarly. Infrared spectroscopy was used to analyze the mixtures and the copolymers.

Graft Copolymers. Styrene was grafted by two methods. In one case, the polyethylene powder, which had been irradiated to a dose of 3 Mrad, was added to a flask of styrene at 60°C. The mixture was stirred under a helium atmosphere for 1 hr. Toluene was then added to cool the mixture and dissolve any homopolymer which may have been formed. The mixture was filtered, and the filtrate was evaporated to check for homopolymer. The graft copolymer was washed until all homopolymer was removed. The other method of preparation was similar, except that the preirradiated polyethylene was added to a flask of 1:1 styrene-methanol at 56°C. Toluene was used again to wash the copolymer free of homopolymer. The grafting process was more efficient with the methanol present. Similar results were reported by Odian, Rossi, and Trachtenberg⁷ in mutual radiation grafting of styrene to polyethylene film. The two grafting methods gave similar results. The second method of grafting was chosen for this work because of ease of handling.

Determination of Hydrogen Evolution

The samples were placed in a glass reactor with a 3-in. diameter titanium window 0.004 in. thick. The reactor was evacuated, then irradiated under the electron beam generator, at 1.05 M.e.v. and 1 ma. The amount of hydrogen evolved was measured by attaching the reactor to the manifold as shown in Figure 1. The manifold was then evacuated and stopcock E was closed. Stopcock B was opened, and the pressure was read on the Dubrovin Gauge. Since the total volume of the reactor and the manifold were known, the volume of hydrogen could be calculated. Charlesby and Davison⁸ reported a G value of 3.1 for hydrogen evolution from irradiated polyethylene. The results from experimental data in this laboratory give a G value of 3.0 molecules/100 e.v. The G value was checked at several doses from 20 to 75 Mrad. These average 3.0 ± 0.06 .

This method was verified by the weight loss of the polymer and by analyzing the gas evolved by gas chromatography. Only traces of gases

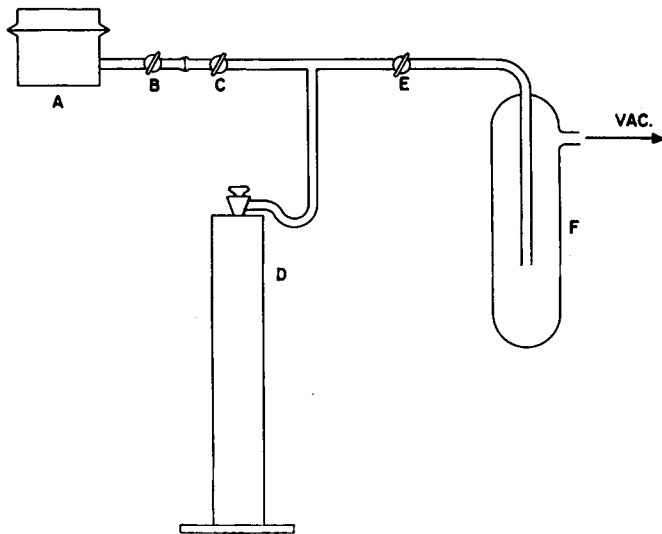


Fig. 1. Apparatus for determining hydrogen evolution from irradiated polyethylene.

other than hydrogen were detected in the evolved gas. The weight-loss method is not satisfactory for polystyrene and other aromatics because of their extremely low hydrogen evolution.⁹

Dosimetry

The total dose given the polymer during the hydrogen evolution studies was determined by electron beam tube characteristics and by blue cellophane dosimetry. DuPont 300 MSC light-blue cellophane was cut in strips $1\frac{1}{2} \times 2$ in. One piece was taped over a Beckman DU spectrophotometer sample holder. The sample holder was placed in the spectrophotometer and the initial transmission at 6550 Å. was read. The sample holder was placed inside the reactor and irradiated under the same conditions as were used in the irradiation of the polymer. The transmission was determined again, and the change in transmission was noted. This change in transmission was converted into megarads by reference to a plot of change in transmission (ΔT) versus dose. This plot of ΔT versus dose was prepared from data of Henley and Richman.¹⁰

RESULTS AND DISCUSSION

Physical Mixtures

Four solid aromatic compounds were chosen for study. These are polystyrene, naphthalene, anthracene, and phenanthrene. These were chosen because of their varying resonance energies and availability. Their structure and resonance energies¹¹ are shown in Table I.

TABLE I
Compounds Used in Physical Mixtures with Polyethylene

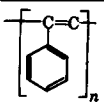

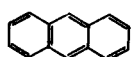
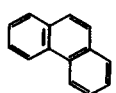
Aromatic compound	Structure	Resonance energy, Kcal./mole
Polystyrene		38
Naphthalene		61
Anthracene		83
Phenanthrene		92

TABLE II
Hydrogen Evolved from Polyethylene Mixtures

Compound	Electron fraction in polyethylene	$G(H_2)$, molecules/100 e.v.
Polystyrene	0	3.0
	0.085	2.5
	0.143	2.2
	0.177	2.2
	1.0	0.02 ^a
Naphthalene	0.056	2.1
	0.150	1.6
	0.165	1.6
	0.198	1.5
	1.0	0.012 ^a
Anthracene	0.035	2.4
	0.101	1.85
	0.252	1.6
	1.0	0.012 ^a
Phenanthrene	0.082	1.5
	0.167	1.2
	1.0	0.012 ^a

^a Data of Swallow.⁹

The materials listed in Table I were mixed in varying proportions with polyethylene, and each mixture irradiated as described in the experimental section. Table II and Figure 2 show the results of these experiments.

Manion and Burton⁵ assumed that the amount of energy absorbed in each compound in a mixture is proportional to the total number of electrons present in each compound (e.g., the combined atomic number of a compound times its mole fraction in the mixture). Figure 2 is a plot of electron fraction of the components in an irradiated mixture versus the G value for the hydrogen evolved. The broken line shows what we would

expect if each component were contributing in proportion to its electron concentration. The fact that in each case the data points fall below this line indicates that energy is in some way being transferred from the polyethylene to the aromatic structures. The energy is then apparently dissipated, resulting in less degradation. It also appears from this curve that the amount of protection, is at least in part, related to the resonance energy of the aromatic additive. The possibility that hydrogen is scavenged by

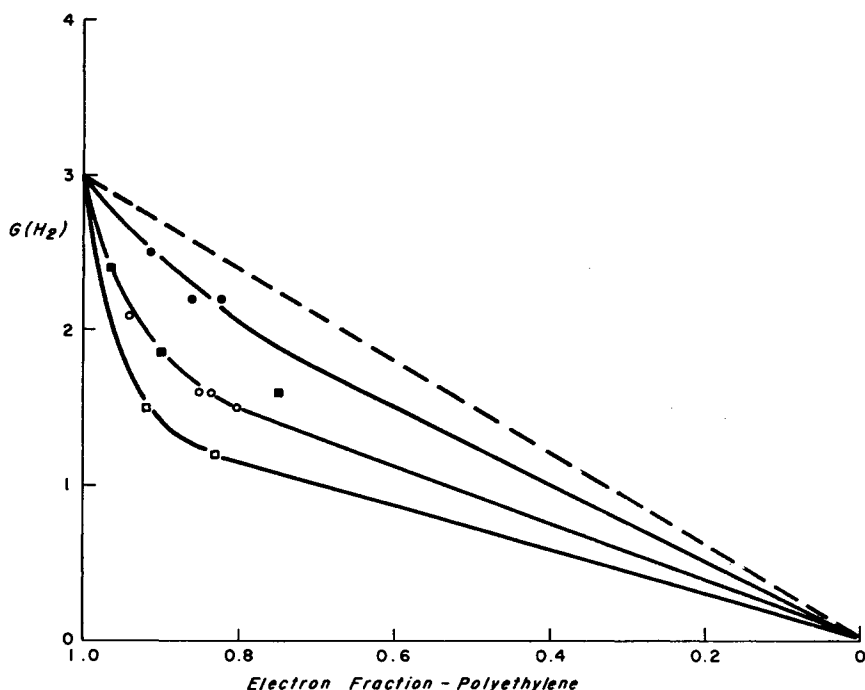


Fig. 2. G values for hydrogen evolved from physical mixtures of polyethylene: (●) polyethylene-polystyrene; (○) polyethylene-naphthalene; (■) polyethylene-anthracene; (□) polyethylene-phenanthrene.

the aromatic ring and accounts for some of this decrease of course cannot be ruled out. Looking at the resonance energies, one would expect the anthracene curve to fall between the naphthalene and phenanthrene curves (Fig. 2). Possibly one reason that it does not is that anthracene has a melting point (217°C.) higher than the operating temperature of the roll mill (160°C.). This would tend to hinder intimate mixing on the roll mill.

Graft Copolymers

Styrene was grafted to polyethylene powder from a styrene methanol mixture as described above. The amount of styrene grafted at various radiation doses is shown in Table III. The G value for hydrogen evolution for each of these samples was then determined and is shown in Table IV

TABLE III
Styrene Grafted at Various Doses

Dose, Mrad	Methanol, %	Temp., °C.	Styrene grafted, %
3	0	60	7.4
0.9	50	56	19
4.7	50	56	25

TABLE IV
Hydrogen Evolved from Polyethylene Graft Copolymers

Electron fraction, % Styrene	$G(H_2)$, molecules/100 e.v.
0	3.0
0.014	2.7
0.075	2.1
0.180	1.7
0.238	1.6
0.375	1.3
1.0	0.02

and in Figure 3. These data show that grafted styrene also protects polyethylene from radiation damage. If Figure 3 is compared to the polystyrene curve in Figure 2, it is apparent that styrene polymer grafted to the poly-

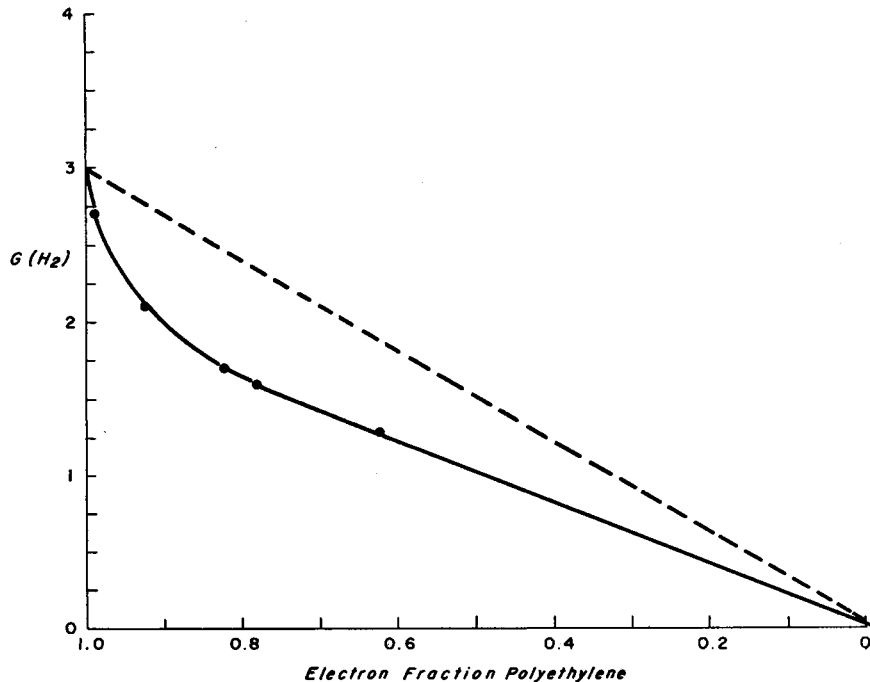


Fig. 3. G values for hydrogen evolved from styrene-grafted polyethylene.

ethylene chain is more effective in reducing radiation damage than is polystyrene that is physically mixed with polyethylene. In fact the results with grafted polystyrene are similar to that obtained with physical mixtures of polyethylene with anthracene, which has more than twice the resonance energy of polystyrene. These results indicate that energy is transferred more readily to attached polymer chains than to adjacent polymer chains and suggests that if aromatic molecules with higher resonance energy could be vinylated and grafted, even more efficient protection would be imparted than has been experienced with styrene grafts.

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Résumé

On sait que les hydrocarbures aromatiques sont plus stables vis-à-vis des radiations ionisantes que les hydrocarbures saturés. On montre que l'on peut rendre le polyéthylène plus stable vis-à-vis des radiations soit en le mélangeant avec des composés aromatiques soit par greffage de styrène sur le polyéthylène. Dans chaque cas le polymère présente une résistance à la radiation plus grande que celle prévue à partir de la loi des moyennes. Les composés aromatiques qui possèdent la plus grande énergie de résonance protègent le plus le polymère. Dans des mélanges, le polystyrène offre la protection la plus faible, et le naphthalène, l'anthracène et le phénanthrène donnent la protection la plus grande. Le polyéthylène greffé avec du styrène possède une meilleure résistance à la radiation que le mélange polyéthylène-polystyrène. Le $G(\text{H}_2)$ a été calculé pour chaque échantillon et on présente des courbes qui illustrent cet effet.

Zusammenfassung

Est ist bekannt, dass aromatische Kohlenwasserstoffe gegen ionisierende Strahlung beständiger sind als gesättigte Kohlenwasserstoffe. Hier wird gezeigt, dass Polyäthylen gegen Strahlung entweder durch Mischung aromatischer Verbindungen mit dem Polyäthylen oder durch Aufpfropfung von Styrol auf Polyäthylen beständiger gemacht werden kann. In jedem Falle besitzt das Polymere eine grössere Strahlungsbeständigkeit als dem zu erwartenden Mittelwert entspricht. Aromatische Verbindungen mit der grössten Resonanzenergie liefern den grössten Schutz des Polymeren. Bei den Mischungen ergibt Polystyrol den geringsten Schutz und Naphthalin und Anthrazen und Phenanthren den grössten. Polyäthylen mit aufgepfropftem Styrol besitzt eine bessere Strahlungsbeständigkeit als eine Polyäthylen-Polystyrolmischung. Der $G(\text{H}_2)$ -Wert wurde für jede Probe berechnet und Kurven zur Veranschaulichung des Effekts werden vorgelegt.

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